Abstract

The garnet group of minerals is of geological importance, forming 13-15% of the Earth's upper mantle, with Al-deficient majorite garnet forming 40-60% of the transition zone. Thus, it is important to understand the properties of this group. The thermodynamic properties of crystals are governed by the motions of their constituent atoms and the processes operating at the atomistic level may be described within the framework of lattice dynamics. We have performed lattice dynamical simulations of pyrope garnet, Mg$_3$Al$_2$Si$_3$O$_{12}$, using the PARAPOLCS code (Parker and Price, 1989); although the simulated structural and thermodynamic properties of pyrope show good agreement with the experimental values, the elastic moduli are overestimated by 15-30%.

By performing symmetry analysis of the calculated eigenvectors of pyrope, we have determined the infrared- and Raman-activity of the 240 vibrational frequencies of this phase. These show excellent agreement with modes observed using infrared and Raman spectroscopies. Analysis of the eigenvectors and the frequency shifts associated with simulated $^{26}$Mg and $^{30}$Si substitution, has enabled assignment of the vibrational modes of pyrope to specific site or atomic motions. Our assignments show that the high-frequency modes are attributable to the $v_1$-$v_4$ motions of the SiO$_4$ tetrahedra, whereas the low-frequency vibrations show substantial mode-mixing.

Using inelastic neutron scattering, we have measured the vibrational density of states of pyrope and grossular garnet, Ca$_3$Al$_2$Si$_3$O$_{12}$, with the experimental spectra successfully interpreted using lattice dynamical simulations. Using Raman spectroscopy, we have studied the intrinsic anharmonic behaviour of a germanate analogue for tetragonal majorite, CaGeO$_3$, from the observed pressure- and temperature-induced shifts of the Raman-active modes. By comparison with the anharmonic behaviour observed for grossular and pyrope (Gillet et al., 1992), we suggest that MgSiO$_3$ tetragonal majorite will display greater anharmonicity than our germanate analogue. This has important implications for modelling of the Earth's interior which must take into account this anharmonic behaviour.
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To Mum, Dad and Paul - Thank you

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CHAPTER 1: Introduction

1.1 Internal Structure of the Earth and Composition of the Mantle

The Earth has a layered internal structure (Fig. 1.1), consisting of a series of approximately radially symmetric shells whose density increases towards the centre. Thus, the Earth's interior is subdivided into an outer crustal layer (0-50 km depth), the upper mantle (10-400 km), the transition zone (400-670 km), the lower mantle (670-2890 km), a liquid outer core (2890-5150 km) and a solid inner core (5150-6370 km). These subdivisions have been determined from the observed seismic discontinuities in the velocity-depth profile of the Earth's interior defined by the Preliminary Reference Earth Model (PREM - Dziewonski and Anderson, 1981) and derived from the inverted travel time data for seismic waves propagating through the Earth following an earthquake event. Although analysis of seismic velocities provides insights into the structural, density and elastic variations within the Earth, the mineralogical assemblages associated with these variations are more difficult to determine. Only the uppermost part of the crust is accessible for direct sampling, either from outcrop or borehole excavation, and mantle materials are only rarely brought to the surface in ophiolite complexes, kimberlite pipes and xenoliths. Consequently, most of our knowledge regarding the composition of the Earth's interior is derived from indirect sources and based on studies of mineral behaviour at high-pressures and temperatures, constrained by observed cosmic abundances and the parameters of the PREM model. Thus, several mineralogical models for the Earth's mantle have been proposed and these may be subdivided into two classes: the pyrolite models - those with no chemical difference between the upper and lower mantle (e.g. Ringwood (1979), who proposed a residual peridotitic upper mantle composed predominantly of olivine and orthopyroxene, with some clinopyroxene and aluminosilicate garnet); and the piclogite models - those with a more silica- and iron-enriched lower mantle, consistent with a chondritic mantle having melted and differentiated at an early stage of the Earth's history (e.g. Anderson (1984), Anderson and Bass (1986), and Duffy and Anderson (1989), who proposed a peridotitic upper mantle, a transition zone, consisting of a clinopyroxene and garnet-rich assemblage with minor amounts of olivine, and a silica-rich lower mantle of perovskite).
Figure 1.1: Schematic diagram of a cross-section of the Earth's interior, with excerpt showing the dominant mineralogy and phase changes in the upper mantle and transition zone.
Phase equilibria studies of the dominant minerals comprising the upper mantle models have demonstrated that with increasing pressure, pyroxene dissolves into the garnet structure resulting in an increase of the volume fraction of garnet with depth in the Earth's interior (Fig. 1.2). The transformation of pyroxene is considered to be complete at approximately 400 km depth (e.g. Ringwood and Major, 1966; Ringwood, 1967, 1970; Akaogi and Akimoto, 1977; Ito and Takahashi, 1987; Kanzaki, 1987; Akaogi et al., 1987; Irifune, 1987; Gasparik, 1989), thus contributing to the observed seismic discontinuity which separates the upper mantle from the transition zone, with garnet subsequently forming 40-60% of this region of the Earth (e.g. Irifune and Ringwood, 1987; Weidner and Ito, 1987; Ita and Stixrude, 1992). Similar studies have shown that at approximately 400 km, olivine transforms to wadsleyite with an associated change in density and elasticity, thus also contributing to this seismic discontinuity. With increasing depth, wadsleyite transforms to spinel (ringwoodite) within the transition zone, at pressures above approximately 22 GPa (e.g. Ringwood and Major, 1970; Akaogi et al., 1984; Yagi et al., 1987; Katsura and Ito, 1989; Madon et al., 1989), where it coexists with garnet. At pressures in excess of approximately 25-29 GPa, garnet and spinel dissociate to form perovskite and MgO, generating the seismic discontinuity separating the transition zone from the lower mantle, and constituting the dominant mineralogy of the lower mantle (e.g. Liu, 1974; Ming and Bassett, 1975; Ito and Matsui, 1978; Ito and Yamada, 1982; Poirier et al., 1986; Ito and Takahashi, 1989; Ito and Katsura, 1989; Ahmed-Zaïd and Madon, 1995; Kesson et al., 1995; Irifune et al., 1996; Serghiou et al., 1998). Thus, with the most widely accepted models of mantle mineralogy suggesting that garnet is a fundamental constituent of the Earth's interior, forming 13-15% of the uppermost mantle by volume, and with this value increasing with depth within the mantle to 40-60%, it is essential to understand fully the physical, chemical, vibrational and thermodynamic properties of this phase and their variation under mantle conditions in order to facilitate accurate geophysical interpretations of this region of the Earth. In this thesis, we propose to study the behaviour of garnet as a major phase by both computer simulation and experimental techniques in order to further our understanding of the vibrational character of this phase. In the following sections, we will describe the physical and chemical structure of garnet (section 1.2), and the techniques by which we will study the vibrational behaviour of this mineral (section 1.3).
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1.2 The Physical Structure and Properties of Garnets

1.2.1 The Cubic Aluminosilicate Garnets

The aluminosilicate garnets are orthosilicate minerals and have the general chemical formula $X_3Y_2Si_3O_{12}$, in which $X$ represents the divalent cations (commonly Mg, Fe$^{2+}$, Mn or Ca, although substitution by rare earth elements such as Y, Er, Gd, Eu, Tb or Yb is permitted), and $Y$ represents the trivalent cations (usually Al, Fe$^{3+}$, Ti or Cr, with substitution by Ga also possible). In addition to their ubiquitous presence in the upper mantle, the aluminosilicate garnets are also commonly observed at the Earth's surface as high-pressure phases in medium-grade metamorphic rocks, and their compositional flexibility has resulted in a wide range of commercial applications, including abrasive papers and cloths, crystals for lasers, wave-guide components for microwave communications, low-conductivity magnetic bubble domain devices, and as semi-precious coloured gemstones. The garnet group of minerals is subdivided according to the dominant $X$-cation chemistry, into the 6 common end-members:

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrope</td>
<td>Mg$_3$Al$_2$Si$<em>3$O$</em>{12}$</td>
</tr>
<tr>
<td>Almandine</td>
<td>Fe$_3$Al$_2$Si$<em>3$O$</em>{12}$</td>
</tr>
<tr>
<td>Spessartine</td>
<td>Mn$_3$Al$_2$Si$<em>3$O$</em>{12}$</td>
</tr>
<tr>
<td>Uvarovite</td>
<td>Ca$_3$Cr$_2$Si$<em>3$O$</em>{12}$</td>
</tr>
<tr>
<td>Grossular</td>
<td>Ca$_3$Al$_2$Si$<em>3$O$</em>{12}$</td>
</tr>
<tr>
<td>Andradite</td>
<td>Ca$_3$Fe$_2$Si$<em>3$O$</em>{12}$</td>
</tr>
</tbody>
</table>

These end-members combine to form the pyralspite and ugrandite subgroups, within which there is substantial solid-solution behaviour. However, such behaviour between the 2 subgroups is more restricted due to constraints on the relative sizes of substituting $X$-cations. The atomic structure of garnet may be described in terms of isolated SiO$_4$ tetrahedra linked by their apices to YO$_6$ octahedra (Fig.1.3). These polyhedra form the basic three-dimensional framework of the structure, with intervening dodecahedral sites containing the $X$-cations (Novak and Gibbs, 1971). The aluminosilicate garnet structure is highly symmetric, with cubic symmetry (space group $Ia3d$), and has a complex unit cell containing 20 formula units or 160 atoms.
Figure 1.3: Polyhedral model of the atomic structure of garnet projected along the x-axis, showing 4 unit cells, each consisting of independent SiO$_4$ tetrahedra (orange) linked to YO$_6$ octahedra (green) by corner-sharing; intervening dodecahedral sites contain the 8-fold coordinated X- (pink) cations (constructed using Cerius$^2$, Molecular Simulations, Inc.).
The physical characteristics of the cubic aluminosilicate garnets have been studied in detail since the beginning of the 20th century, when the relationships between garnet chemistry and density, molecular weight and refractive index were the primary properties investigated (e.g. Ford, 1915; Stockwell, 1927; Winchell, 1933; Fleischer, 1937). The attention of subsequent studies focused on the chemical structure and bonding of garnet at ambient conditions (e.g. Abrahams and Geller, 1958; Zemann and Zemann, 1961; Zemann, 1962; Gibbs and Smith, 1965; Prandl, 1966; Novak and Gibbs, 1971), and since their importance as a major planet-forming phase has been established, the more recent studies have concentrated on those properties which affect garnet stability, in order to establish the phase relations of the garnets and the depth to which they exist within the Earth's interior. Thus, investigations of the high-temperature and high-pressure structural, elastic, vibrational and thermodynamic behaviour of the end-member garnets and their solid-solutions have been reported in more than 200 publications, resulting in an extensive database of garnet properties. However, significant gaps still remain in our knowledge of the aluminosilicate garnet group, particularly in the vibrational behaviour of its members, which is the subject of this study.

1.2.2 The Majoritic Garnets

Within the upper mantle, as mentioned in section 1.1, pyroxene (MgSiO₃) dissolves into the garnet structure, forming the Si-enriched garnet majorite (e.g. Kato and Kumazawa, 1985; Kato, 1986; Sawamoto, 1987; Ito and Takahashi, 1987; Gasparik, 1989; Presnall and Gasparik, 1990; Ohtani et al., 1991; Irifune et al., 1996). This garnet phase differs from those described in the previous section because it is deficient in Al, and has both Mg- and Si-cations present on the octahedral sites. Majorite was discovered only relatively recently when it was found naturally occurring in the Coorara chondritic meteorite by Smith and Mason (1970), and since that time, its importance as a major Earth-forming phase and its solid-solution behaviour with pyrope garnet have been established (e.g. Akaogi and Akimoto, 1977; Kanzaki, 1987; Akaogi et al., 1987; Gasparik, 1990; Parise et al., 1996; Heinemann et al., 1997; Sinogeikin et al., 1997). Similarly, the observation that considerable amounts of Ca are present in the upper mantle in phases such as calcic clinopyroxene (diopside) and grossular garnet, has led to the recognition of the importance of Ca-bearing majorite, CaSiO₃, in the transition zone.
(e.g. Hazen et al., 1994; Gasparik, 1989, 1990; Canil, 1994). Thus, a full knowledge of the structural, elastic, vibrational and thermodynamic properties of pyrope and majorite end-members, their intermediate compositions and their Ca-counterparts is essential for understanding the upper mantle and transition regions of the Earth's interior.

Although natural majorite has cubic ($Ia\overline{3}d$) symmetry, majorite synthesized in the laboratory is reduced to tetragonal symmetry (space group $I4_{1}/a$), due to ordering of the Mg- and Si-cations on the octahedral sites (Angel et al., 1989; Hatch and Ghose, 1989; Parise et al., 1996). Thus, the properties of cubic majorite are poorly constrained due to the limited sample availability. Although, tetragonal majorite has been studied more extensively than its cubic polymorph, its properties are still poorly known in comparison with the aluminosilicate garnets, particularly its vibrational behaviour. Thus, it is important to gain a full understanding of the vibrational properties of majorite and the relationship they share with the aluminosilicate garnets.

1.3 Lattice Dynamics, and the Structure of this Thesis

The vibrational properties of a crystalline solid are derived from the microscopic motions of its constituent atoms about their equilibrium sites, and are dependent upon the forces exerted between the atoms. These atomic motions within the crystalline system - the lattice dynamics - are of particular importance in the study of geologically relevant phases because they govern the bulk thermodynamic properties of the system, and consequently its stability. Thus, in order to understand the thermodynamic properties of any phase, it is essential to have a full knowledge of the processes operating at the atomistic level. If these processes can be accurately simulated, it therefore follows that the thermodynamic properties may also be calculated. As the modelling of each electronic interaction in a solid (ab initio simulations) is difficult, particularly in complex systems, a more approximate approach is provided through atomistic modelling, in which only the interactions between individual atoms in the crystal structure are described. This type of lattice dynamical modelling will be applied to the magnesium aluminosilicate end-member garnet, pyrope, in order to simulate the structural, elastic and thermodynamic properties widely observed for this phase at ambient conditions, and at high-temperature and pressure (Chapter 2). The vibrational behaviour of pyrope will be examined in greater detail in Chapter 3, with simulations of the Brillouin zone centre
phonon frequencies measurable by the experimental techniques of infrared and Raman spectroscopy, which will also be discussed. In Chapter 4, we will describe the experimental technique of coherent inelastic neutron spectroscopy, its application to the measurement of phonon frequencies away from the Brillouin zone centre in both pyrope and grossular garnets, with presentation of experimental data and its interpretation using lattice dynamical simulations. In Chapter 5, we will examine the intrinsic anharmonic behaviour of a germanate analogue for Ca-bearing tetragonal majorite, using the pressure- and temperature-induced variations of its vibrational frequencies, and compare its behaviour with the cubic aluminosilicate garnets, making predictions for the anharmonic behaviour of MgSiO$_3$ majorite. Finally, in Chapter 6 we will present a summary of our lattice dynamical study of garnets, the conclusions we can draw from it and suggestions for future work which will enable us to improve our understanding of the processes occurring within the Earth's interior.
 CHAPTER 2: The Computer Simulation of Pyrope Garnet, $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$. 

2.1 Introduction

At temperatures above absolute zero, the atoms in a solid vibrate vigorously about their mean equilibrium lattice positions. The magnitude of these vibrations is dependent upon the interatomic forces, controlled by the mass and geometric arrangement of the atoms. These microscopic motions characterize the vibrational properties of the solid and govern the macroscopic thermodynamic behaviour of the system. Thus, by simulating the processes which occur at the atomistic level, the bulk thermodynamic properties of a solid may also be modelled. The properties of a solid may be determined from an explicit solution of the Schrödinger equation, thereby establishing the energy surfaces associated with the interactions of electrons and nuclei within the solid. However, this type of \textit{ab initio} approach involves large and complex calculations. Thus, a more simple and approximate method for simulating the properties of solids is provided through \textit{atomistic modelling}, which describes only the interactions between individual atoms or ions in the structure, as opposed to each electronic interaction. Such an approximation is usually based on the classical Born model of solids (Born and Huang, 1954) in which potential functions are defined to describe the net effective interatomic forces. In this approximation, only the forces associated with electron clouds are included and the masses involved are too small for gravitational forces to be significant; this level of approximation excludes strong and weak nuclear forces but may be extended to include magnetic and many-body effects.

Previous simulation studies of common aluminosilicate garnet end-members have included lattice dynamical calculations of pyrope using empirical potentials for simple oxides (Parker \textit{et al.}, 1984; Winkler \textit{et al.}, 1991; Patel \textit{et al.}, 1991), molecular dynamical calculations of pyrope and grossular using optimized potentials for phases in the CaO-MgO-Al$_2$O$_3$-SiO$_2$ system (Matsui, 1996), fully-optimized calculations of garnet end-members (Ottonello \textit{et al.}, 1996; Downs and Bukowinski, 1997) and an \textit{ab initio} study of pyrope (D’Arco \textit{et al.}, 1996). In general, these studies have reported successful simulation of the structural and thermodynamic properties of garnet at ambient conditions, and at pressure and temperature. However, the simulation studies which calculated the elastic properties of this phase have reported either a gross overestimation...
(by 20-30% - Winkler et al., 1991; Patel et al., 1991; D'Arco et al., 1996; Downs and Bukowinski, 1997) or underestimation (by 10-15% - Matsui, 1996) of the elastic moduli (except the study by Ottonello et al. (1996), in which the parameters of their model of garnet were fitted to the experimental data at each stage of the calculation). Thus, the recent unoptimized simulation studies of garnet, although incorporating a wide range of modelling techniques, have failed to reproduce all the properties of this phase with sufficient accuracy. We therefore propose to perform a lattice dynamical study of pyrope garnet, Mg$_3$Al$_2$Si$_3$O$_{12}$, in which different sampling methods of the first Brillouin zone are employed, in order to examine the effect of such sampling on the calculated properties. Thus in this chapter, we present the theoretical background to lattice dynamical calculations (section 2.2) and the application of this method using different Brillouin zone sampling techniques to the simulation of the structural, elastic and thermodynamic properties of pyrope at ambient conditions (section 2.3), and at high-temperatures (section 2.4) and pressures (section 2.5); comparison of our simulated results with experimental data is also presented in these sections. Finally in section (2.6), we provide a summary of our simulation study and the conclusions that we can draw from it.

2.2 Atomistic Modelling of a Crystalline System

2.2.1 Interatomic Pair Potential Energy Functions

In atomistic modelling of crystalline systems, only the interactions between individual atoms in the structure are considered and the net effective forces exerted between the atoms are described by potential energy functions. In order to model these atomic interactions, the nature of the potential energy functions which describe them must be understood. This is initially achieved by considering pairwise systems (many-body systems are generally too complex), although simple 3-body terms may be included. If 2 particles are separated by an infinite distance, their interaction is negligible and the total energy of the system is the sum of the individual energies of the 2 particles. However, if the 2 particles are separated by a finite distance $r$, then the total energy of the system requires an additional energy term from their interaction. This is described by the interatomic pair potential energy function which has the form:
\[ U(r) = \int_{r}^{\infty} F(r) dr \]  

(2.1)

where \( U \) is the work done in transporting the atoms from infinity to their separation distance \( r \), and \( F \) is the force acting between the atoms, described by the first derivative of the potential energy function:

\[ F(r) = -\frac{\delta U}{\delta r} \]  

(2.2)

When neutral or oppositely charged ions are separated far from their equilibrium separation distance, the interactive force \( F \) is negative; when 2 such ions are forced together beyond their equilibrium separation, \( F \) becomes positive. The graphical summation of these opposing forces yields the potential energy function (Fig.2.1) which describes the net effective force between the 2 ions. In atomistic modelling, it is assumed that an analytical form of the potential energy function such as this, is an accurate representation for the relationship between interatomic potential energy and atomic separation. The sum of the potential functions of all constituent atom pairs, \( ij \), in a crystalline solid yields the lattice energy of that solid. When no net forces are acting on the atoms, the sum of the attractive and repulsive potential energies between each pair of atoms in a crystalline solid at zero Kelvin is termed the static lattice energy, and is defined as:

\[ U_{k}(r_{ij}) = \sum_{y} e^{2} \frac{q_{i}q_{j}}{r_{ij}} + \sum_{y} q_{y} + \sum_{y} \theta_{y} \]  

(2.3)

The first term on the right hand side of this equation is the contribution from the long-range Coulombic attraction for an infinite, periodic array of atoms. The parameters \( q_{i} \) and \( q_{j} \) are the assumed point charges associated with ions \( i \) and \( j \); \( r_{ij} \) is the separation distance of ions \( i \) and \( j \), and \( e \) is the charge of the electron. In ionic or semi-ionic solids such as silicate minerals, this energy term is the major contributor to cohesive energy. Calculation of the Coulombic energy gives rise to difficulties because summation of \( q_{i}q_{j}/r_{ij} \) is very slowly convergent and thus computationally expensive. In our calculations,
Figure 2.1: Interatomic potential energy function, where \( r_e \) is the equilibrium separation distance for 2 ions. The black curve represents the anharmonic curve of the interatomic potential; the dashed curve is the harmonic approximation.

this is overcome by use of the Ewald Method in which the summation of the electrostatic interactions are split into 2 separate summations, one in real space and one in reciprocal space, which are both rapidly convergent. This is achieved by a mathematical manipulation of the \( 1/r \) term, using standard mathematical identities \((e.g.\ Ewald, 1921, 1937; \text{Catlow and Norgett, 1978})\). This approximation allows the sum of the Coulombic interactions to be performed several orders of magnitude more rapidly than direct summation, without any loss in accuracy. The second term on the right hand side of equation (2.3) accounts for the diffuse nature of the electron clouds surrounding the nucleus. It includes the short-range interactions associated with Pauli repulsion between neighbouring electron clouds, and the short- and long-range components of van der Waals attraction. Such short-range interactions may be described by pairwise potential functions such as the Lennard-Jones, Morse or Buckingham potentials. In our
simulations, we have employed the latter potential function to describe the pairwise interactions, and this has the form:

$$\varphi(r_{ij}) = \sum_{ij} A_{ij} e \left( -\frac{r_{ij}}{B_{ij}} \right) - \frac{C_{ij}}{r_{ij}^6}$$

where $A_{ij}$, $B_{ij}$ and $C_{ij}$ are constants and $r_{ij}$ is the interatomic separation. $A_{ij}$ and $B_{ij}$ represent the effective repulsive parameters, and $C_{ij}$ is the effective dispersion coefficient describing the van der Waals induced dipole-dipole attraction. These parameters must be derived for each pair of atomic species, $ij$, in the structure.

Calculation of the short-range interaction between the nucleus and electrons of an atom may also be included in atomistic modelling to provide a simple mechanical description of ionic polarizability. In such a shell model (Dick and Overhauser, 1958), the ion (usually oxygen) is described as having a massive core, surrounded by a massless charged shell, representing the outer valence electron cloud. The core and shell are coupled by a harmonic spring (Fig. 2.2), and their interaction is described by:

$$U_s = \sum_{i} k_i^s r_i^2$$

where $k_i^s$ is the shell spring constant, and $r_i$ is the core-shell separation. The resulting free-ion polarizability of an ion, $\alpha_i$, is given by:

$$\alpha_i = \sum_{i} \frac{(Y_i e)^2}{k_i^s}$$

where $Y_i$ is the shell charge and $e$ is the charge on the electron.

The third term on the right hand side of equation (2.3) accounts for explicit three-body interactions which, for severely ionic solids in which pairwise interactions are dominant, may be negligible. However, it is well established that bonding in silicate minerals is not expected to be fully ionic and a degree of directional, covalent bonding exists. This directionality may be modelled by introducing a three-body bending term, which has the form:
where \( k_{ij}^\theta \) is the derivable spring constant; \( \theta_{ijk} \) is the simulated bond angle; and \( \theta_0 \) is the equilibrium bond angle.

\[
\varphi(\theta_{ijk}) = \frac{1}{2} \sum_{ijk} k_{ij}^\theta (\theta_{ijk} - \theta_0)^2
\]  

Figure 2.2: The shell model in which a massive anion core is coupled to its surrounding massless shell by harmonic springs.

2.2.2 The Static Lattice Simulation

Static lattice simulations are used to determine the minimum energy configuration of a structure at zero Kelvin. When the cell dimensions are known, the static lattice energy is obtained via a constant volume minimization procedure, in which the initial atom coordinates are allowed to relax until the structure reaches its minimum energy configuration. The minimization technique used in our simulations is the Newton
Raphson method (Norgett and Fletcher, 1970) in which the first step is to expand the lattice energy to the second-order form about a point $r$:

$$U(r') = U(r) + g^T \cdot \delta + \frac{1}{2} \delta^T \cdot W \cdot \delta$$  \hspace{1cm} (2.8)

where $\delta = r' - r = \delta r$, the Cartesian displacement of the atomic positions (coordinate strain). The term $g$ is the first derivative of the potential energy with respect to atomic displacement, and defined as:

$$g_i = \frac{dU(r)}{d\delta r_i}$$  \hspace{1cm} (2.9)

where each $g_i$ is an element of the matrix $g$. The $W$ term in equation (2.8) represents the set of second derivatives of the lattice energy in matrix form defined by:

$$W = \begin{bmatrix}
W_{rr} & W_{er} \\
W_{er} & W_{ee}
\end{bmatrix}$$  \hspace{1cm} (2.10)

where $\varepsilon$ is the bulk strain, and $W_{rr}$ is given by:

$$W_{rr} = \frac{\delta^2 U}{\delta r_i \delta r_j}$$  \hspace{1cm} (2.11)

The remaining elements of the above matrix may be similarly defined. These calculations are made repeatedly, with the atomic coordinates adjusted slightly at each iteration until all the forces acting on the atoms, $g$, become zero so that the coordinate strain, $\delta r$, is removed, i.e:

$$\frac{dU}{d\delta r} = 0$$  \hspace{1cm} (2.12)

Thus, the minimum energy atomic configuration will occur when:
The atomic coordinates are updated by \( \delta r \) at each stage, and the revised coordinates after the \((k+1)\)th interaction, are related to the initial coordinates, \( r_k \), by the expression:

\[
\mathbf{r}_{k+1} = \mathbf{r}_k - g_k \cdot H_k
\]

(2.14)

where \( H_k = (W_{rr})_{k}^{-1} \), the initial inverse of the second derivative matrix defined by equation (2.10). The minimized coordinates are obtained via the repeated application of this expression until the forces \( g \), acting on the atoms are removed. However, the calculation of the second derivative matrix, \( W \), and its inverse \( H_k \), is complex and computationally expensive. Hence, Norgett and Fletcher (1970) developed a method which significantly reduces computer time by using an updating procedure for the inverse matrix:

\[
H_{k+1} = H_k + \frac{\delta r \cdot \delta r^T}{\delta g} - \frac{H_k \cdot \delta g \cdot \delta g^T \cdot H_k}{\delta g^T \cdot H_k \cdot \delta g}
\]

(2.16)

where \( H_{k+1} \) is known as the Hessian matrix; \( \delta r \) and \( \delta g \) are the vectors describing the differences in atomic positions and forces acting on each atom, respectively, for subsequent iterations, so that \( \delta r = r_{k+1} - r_k \), and \( \delta g = g_{k+1} - g_k \). In our calculations, the Hessian matrix is updated after 1000 iterations, and this procedure continues until equation (2.12) is satisfied and all forces acting on the atoms are zero, so that a minimum energy equilibrium structure at constant cell volume is obtained.

For a constant pressure calculation, an additional minimization of the bulk strain energy is required. This involves the relaxation of both the atoms in the unit cell and the cell dimensions themselves, corresponding to the removal of all mechanical strain acting on the unit cell. This is followed by a constant volume minimization, as described previously, until all forces acting on the atoms and the unit cell are zero. The first step in the constant pressure minimization is again the expansion of the lattice energy to the second-order form (equation 2.8) and calculation of the first and second derivatives of the lattice energy with respect to strain. In this case, \( \delta = \delta c_{ii} \), which represents the 6 independent strain elements of the symmetric strain matrix:
The first derivative of the lattice energy with respect to strain gives the mechanical pressure or stress, defined by:

$$g_i = \frac{dU(\varepsilon)}{d\varepsilon_i}$$  \hfill (2.18)

The second derivative of the lattice energy with respect to strain gives the elastic constants (assuming the equilibrium condition, $g = 0$), the matrix $C$ of which is given by:

$$\frac{\partial^2 U}{\partial \varepsilon^2} = C = \frac{1}{V}(W_{\omega} - W_{\omega} \cdot W_{\omega}^{-1} \cdot W_{\omega})$$  \hfill (2.19)

From Catlow and Mackrodt (1982), the strained coordinates are given by the relationship:

$$r' = (I + \varepsilon) \cdot r$$  \hfill (2.20)

where $\varepsilon$ is the strain on the original coordinates and lattice vectors $r$; $I$ is the identity matrix; and $r'$ represents the resultant coordinates and lattice vectors after applying the strain. The strain matrix follows Voigt notation and using equation (2.17), equation (2.20) may be written as:

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} 1 + \varepsilon_1 & \frac{1}{2} \varepsilon_6 & \frac{1}{2} \varepsilon_3 \\ \frac{1}{2} \varepsilon_6 & 1 + \varepsilon_2 & \frac{1}{2} \varepsilon_4 \\ \frac{1}{2} \varepsilon_3 & \frac{1}{2} \varepsilon_4 & 1 + \varepsilon_3 \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix}$$  \hfill (2.21)

where $x, y, z$ are components of $r$. The strains are calculated from the elastic constants and stress acting on the crystal assuming Hooke's Law, in which stress is proportional to strain, and the elastic compliance tensor (the inverse of the elastic constants) is the constant of proportionality.
The first derivative of the lattice energy with respect to strain is more easily determined by considering the square of the displacement $r'$:

$$r'^2 = r^2 + 2r^T \cdot \varepsilon \cdot r + r^T \cdot \varepsilon^2 \cdot r$$

(2.22)

Differentiation of equation (2.22) with respect to strain yields the mechanical or static pressure:

$$P_{st} = \frac{\delta U}{\delta \varepsilon_i} = \frac{\delta U}{\delta r} \cdot \frac{\delta r^2}{\delta \varepsilon_i} \cdot \frac{\delta r}{\delta \varepsilon^2}$$

(2.23)

and evaluation of the differential at zero strain yields:

$$\frac{1}{2} \frac{\delta r^2}{\delta \varepsilon_i} = r^\alpha \cdot r^\beta$$

(2.24)

where:

<table>
<thead>
<tr>
<th>$r^\alpha$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r^\beta$</td>
<td>x</td>
<td>y</td>
<td>z</td>
<td>y</td>
<td>x</td>
<td>x</td>
</tr>
</tbody>
</table>

If the Ewald Method is employed to determine the Coulombic component of the lattice energy, further strain derivatives must be considered. This is because the Ewald method sums much of the Coulombic interaction in reciprocal space and hence, the effect of strain on the reciprocal lattice vectors $G$, and cell volume $V$, must also be evaluated, following the relations:

$$\frac{1}{2} \frac{\partial G^2}{\partial \varepsilon_i} = -G^\alpha G^\beta$$

(2.24)

with $i$, $\alpha$ and $\beta$ defined above, and:

$$\frac{\partial V}{\partial \varepsilon_i} = V$$

(2.25)
where $i = 1, 2, 3$. In addition to the mechanical strain, the elastic constant matrix $C$ (equation 2.19) is required to calculate the bulk strains. Using Hooke's Law, the bulk strains are determined from:

$$
\delta \varepsilon = \frac{\partial \delta U}{\partial \delta \varepsilon} \cdot C^{-1} 
$$

(2.26)

This equation may be substituted into equation (2.20) to give the updated atomic coordinates and cell dimensions. As the above expressions are approximate, the calculations proceed iteratively until all residual strains are removed; all internal strains are removed at each iteration by performing successive constant volume minimizations described above. Hence, a minimum energy structure is obtained free of internal and bulk strain, and therefore at constant pressure.

2.2.3 Dynamic Simulation

The dynamic contribution to the energy of the crystalline system by the vibrational motions of its constituent atoms at temperatures above zero Kelvin may be calculated via molecular dynamics, for medium-to high-temperature simulations (e.g. Dove, 1988), or via lattice dynamics, for low-to medium-temperature simulations (e.g. Price et al., 1987; Dove, 1993). Lattice dynamics is a semi-classical method which uses the quasi-harmonic approximation, in which it is assumed that each atom moves in simple harmonic motion about its equilibrium position which remains fixed. The classical approach is derived from the Newtonian analysis of the dynamics of the constituent atoms or ions. The lattice dynamical method allows for the description of the unit cell in terms of independent quantised harmonic oscillators whose frequencies vary as a function of unit cell, thus allowing for thermal expansion (e.g. Born and Huang, 1954). The motions of the individual atoms are treated collectively as lattice vibrations or phonons, and the equations of motions of these vibrating species are solved to obtain their vibrational frequencies within the periodic structure. The thermodynamic properties and stabilities of crystalline solids are determined from the calculated vibrational frequencies via statistical mechanics, thus providing the quantitative link between the microscopic and macroscopic properties of a phase.
In order to calculate the vibrational frequencies of a system, the relative motions of each atomic species must first be considered. Such motions are controlled by the potential energy function, assuming an already equilibrated unit cell. The potential function describing the interactions of 2 atoms \( i \) and \( j \) at original positions \( r_i \) and \( r_j \), displaced by \( u_i \) and \( u_j \) to new positions \( R_i \) and \( R_j \), respectively, may take the following form:

\[
U = \frac{1}{2} \sum_{i \neq j} u_i D(r_i - R_j) u_j
\]  

(2.27)

The displacement of atom \( i \) by \( u_i \) from its equilibrium position, will experience a restoring force \( F_i \), where:

\[
F_i = \frac{\delta U}{\delta u_i}
\]

(2.28)

The equations of motion that must be solved for atoms \( i \) and \( j \), with mass \( m_i \) and \( m_j \) respectively, have the form:

\[
m_i \frac{\delta^2 u_i}{\delta t^2} = -\frac{\delta U}{\delta u_i} ; \quad m_j \frac{\delta^2 u_j}{\delta t^2} = -\frac{\delta U}{\delta u_j}
\]

(2.29)

From the theory of small displacements (e.g. Ziman, 1964), it may be shown that:

\[
\frac{\delta U}{\delta u_i} = \sum_j \frac{\delta^2 U}{\delta u_j \delta u_i} u_j
\]

(2.30)

which may be interpreted as meaning that the sum on the right-hand side of equation (2.30) represents the force acting on atom \( i \) due to the displacement \( u_j \) of atom \( j \). Similarly,

\[
\frac{\delta U}{\delta u_j} = \sum_i \frac{\delta^2 U}{\delta u_j \delta u_i} u_i
\]

(2.31)

However, in accordance with Block’s theorem (e.g. Ziman, 1964), equations (2.29-2.31) must be translationally invariant, so that:
\[ u_i(R_j) = e_i(q) \exp(i(q.R_i - \omega(q)t)) \] (2.32)

and,

\[ u_j(R_j) = e_j(q) \exp(i(q.R_j - \omega(q)t)) \] (2.33)

where \( q \) is the reciprocal lattice vector, \( \omega(q) \) is the frequency of the vibrational mode, and \( e(q) \) is the polarization vector which describes the atomic displacements during the vibration and thus, the direction in which the atoms move. Manipulation of equations (2.27-2.31) yields the expression:

\[ -m\omega^2 u_i(R_i) = -\sum_{R_j} D(R_i - R_j) u_j(R_j) \] (2.34)

and substitution of equations (2.32) and (2.33) into equation (2.34) gives:

\[ m\omega^2 e_i(q) \exp(i(q.R_i - \omega t)) = \sum_{R_j} D(R_i - R_j) e_j(q) \exp(i(q.R_j - \omega t)) \] (2.35)

where \( D(q) \) is the dynamical matrix:

\[ D(q) = \sum_{R,R_j} D(R_i - R_j) \exp(-i(q.R_i - q.R_j)) \] (2.36)

Substitution of equation (2.36) into equation (2.35) gives the final result:

\[ m\omega^2 e_i(q) = D(q)e_j(q) \] (2.37)

Solution of this equation for a given value of wavevector \( q \) yields \( 3n \) eigenvalues which are the squared frequencies \( (\omega^2(q)) \) of each of the normal modes of the crystal, obtained from diagonalization of the dynamical matrix, and \( 3n \) sets of eigenvectors \( (e_x(q), e_y(q), e_z(q)) \) which describe the pattern of atomic displacements for each normal mode.

Theoretical lattice dynamics (e.g. Kittel, 1971) demonstrates that the vibrational frequencies of a system vary as a function of wavevector \( q \). Thus, in order to determine the thermodynamic properties of a solid accurately, it is necessary to calculate the vibrational frequencies over all possible wavevectors. However, this is impossible due to...
the size and complexity of the calculation required. This problem is commonly overcome by using an approximation in which the phonon frequencies are calculated at selected points on an imaginary three-dimensional grid within the Brillouin zone, a procedure known as *zone sampling*. Weighting factors are applied to the selected points according to the number of times the points are generated by the symmetry of the Brillouin zone. At low-temperatures, the acoustic phonons with wavevectors close to the zone centre are the only thermally excited modes. Hence, a fine grid is required in this region in order to calculate the phonon frequencies and therefore the thermodynamic properties correctly.

Having determined the phonon frequencies for points within the irreducible Brillouin zone, it is possible to calculate the thermodynamic functions: vibrational energy ($E$), entropy ($S$), free energy ($G$), and heat capacity ($C_v$), using the following expressions based on statistical thermodynamics:

\[ E = kT \sum_i^M \frac{x}{2} + \frac{x}{e^x - 1} \]  
 \hspace{92pt} (2.38)

\[ S = k \sum_i^M \ln(1 - e^{-x}) + \frac{x}{e^x - 1} \]  
 \hspace{92pt} (2.39)

\[ G = kT \sum_i^M \frac{x}{2} + \ln(1 - e^{-x}) \]  
 \hspace{92pt} (2.40)

\[ C_v = k \sum_i^M \frac{x^2 e^x}{(e^x - 1)^2} \]  
 \hspace{92pt} (2.41)

where each function is summed over the total number of phonon frequencies, $M$, and where,

\[ x = \frac{\hbar \omega_i}{kT} \]  
 \hspace{92pt} (2.42)

and the zero point energy,

\[ E_0 = \sum_i \frac{\hbar \omega_i}{2} \]  
 \hspace{92pt} (2.43)
is included in the vibrational energy and the free energy.

According to the harmonic approximation on which equations (2.38-2.43) are based, the structure has a thermal expansion coefficient of zero. However, under the assumption of the quasi-harmonic approximation, the volume dependence of the thermodynamic and structural properties may be calculated. To minimize a structure at constant pressure above zero Kelvin, the kinetic pressure generated by the atomic vibrations must be included in the total pressure of the system. The kinetic pressure is the first derivative of the free energy, $G$, with respect to volume. Thus, for an isotropic material,

$$ P_K = \left( \frac{dG}{dV} \right)_T $$

(2.44)

By calculating $G$ at a given volume, and then recalculating after making a small adjustment to the cell volume, the kinetic pressure may be determined. The thermally equilibrated structure is then obtained from a constant pressure energy minimization, in which the total pressure is now defined as the sum of the mechanical, hydrostatic and kinetic pressures. The strain on the crystal system is then determined from the kinetic pressure and elastic constants (equation 2.26). A constant volume minimization is performed each time the cell volume is modified to ensure that the atoms remain at their potential energy minima and thus within the constraints of the harmonic approximation. As the final static pressure is likely to be non-zero, correction terms must be applied to the elastic constants. Barron and Klein (1965) have shown that the elastic constants under an isotropic initial stress should be calculated as:

$$ C_{\alpha\beta\sigma\tau} = \frac{1}{V} \left( \frac{\delta^2 U}{d\varepsilon_{\alpha\beta}d\varepsilon_{\sigma\tau}} \right) + \frac{1}{2} P_{St} \left( 2\delta_{\alpha\beta}\delta_{\sigma\tau} - \delta_{\alpha\sigma}\delta_{\beta\tau} - \delta_{\alpha\tau}\delta_{\beta\sigma} \right) $$

(2.45)

where $P_{St}$ is the static pressure, $\delta$ is the Kronecker delta, and $\alpha$, $\beta$, $\sigma$ and $\tau$ refer to the tensor notation of the strain directions.
From equation (2.45), the proposed corrections for the 21 independent elastic constants are shown in Table 2.1, and these corrections have recently been demonstrated by Wall et al. (1993) to be applicable to the elastic constants calculated from the second derivative of the lattice energy with respect to strain at non-zero pressures and temperatures.

<table>
<thead>
<tr>
<th>elastic Constants</th>
<th>Static Pressure Corrections</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}, C_{22}, C_{33},$</td>
<td>None</td>
</tr>
<tr>
<td>$C_{14}, C_{15}, C_{16},$</td>
<td></td>
</tr>
<tr>
<td>$C_{24}, C_{25}, C_{26},$</td>
<td></td>
</tr>
<tr>
<td>$C_{34}, C_{35}, C_{36},$</td>
<td></td>
</tr>
<tr>
<td>$C_{45}, C_{46}, C_{56},$</td>
<td></td>
</tr>
<tr>
<td>$C_{12}, C_{13}, C_{14},$</td>
<td>$+P_s$</td>
</tr>
<tr>
<td>$C_{44}, C_{55}, C_{66},$</td>
<td>$-\frac{1}{2}P_s$</td>
</tr>
</tbody>
</table>

Table 2.1: Pressure corrections appropriate for elastic constants at non-zero static pressures proposed by Barron and Klein (1965).

In order to determine the temperature-dependent properties of the structure obtained thus far, the relevant thermodynamic parameters must be calculated as a function of volume. For example, the thermal expansion coefficient, $\alpha$, may be evaluated from the finite difference between 2 minimized volumes at 2 finite temperatures:

$$\alpha = \frac{1}{V} \frac{dV}{dT}$$

(2.46)
The thermal expansion coefficient may also be determined from the thermodynamic
definition of the Grüneisen parameter, $\gamma$:

$$\alpha = \frac{\gamma C_v}{K_T V} = \frac{\gamma C_p}{K_S V}$$ (2.47)

where $K_T$ and $K_S$ are the isothermal and adiabatic bulk moduli respectively, and $C_V$ and $C_P$ are the heat capacities at constant volume and constant pressure, respectively. The Grüneisen parameter itself is determined using the original microscopic definition (Grüneisen, 1912) which relates $\gamma$ to the variation of vibrational frequencies with cell volume:

$$\gamma_i = -\frac{d \ln \omega_i}{d \ln V}$$ (2.48)

The mode or thermal Grüneisen parameter is determined from the average of the heat capacity weighted Grüneisen parameters via the equation:

$$\bar{\gamma} = \frac{1}{C_V} \sum_i C_i \gamma_i$$ (2.49)

where $C_i$ is the heat capacity for mode $i$.

The theory described above is given in greater detail by Parker and Price (1989) and Vočadlo (1993), and is incorporated in the lattice dynamics computer code PARAPOLCS (Parker and Price, 1989), which may be used to calculate the structural, elastic, vibrational and thermodynamic properties of a crystalline solid at a specified temperature and pressure, by minimization of both the static and dynamic components of the lattice energy at constant pressure, within the quasi-harmonic approximation (Fig.2.3), and under the assumption that the vibrational component of the elastic constants is sufficiently small so as to be neglected. However, the success of the simulations in predicting such properties is largely dependent on the reliability of the interatomic potential models employed to describe the atomic interactions rather than any of the approximations inherent in the computer code.
Initial Structure

Constant Volume Minimization

Phonons Calculated

Calculate Free Energy and Crystal Properties

Adjust Crystal Volume

Constant Volume Minimization

New Free Energy

Thermal Pressure from Change in Free Energy with Volume

Reset Crystal Structure

Calculate Total Pressure From Hydrostatic, Static and Thermal Pressure

Is Total Pressure within 0.1 kbars?

VALID FREE ENERGY MINIMIZATION

Figure 2.3: Flow diagram showing the outline of the PARAPOCS routine.
2.3 Results of Simulations of Pyrope at Ambient Conditions

2.3.1 Interatomic Potentials

Our simulations of pyrope were performed using the lattice dynamics computer code PARAPCO (Parker and Price, 1989), described in section (2.2). The Buckingham potential (equation 2.4) was employed to describe the short-range repulsive and attractive dispersive forces between each atom pair in the garnet structure; the shell model (Dick and Overhauser, 1958) was invoked to describe the polarizability of the oxygen ions (equation 2.5); and a three-body bending term was used to model the directionality of the O-Si-O bond (equation 2.7). The potential parameters used in our simulations (Table 2.2) have previously been shown to successfully reproduce the structural and thermodynamic properties of pyrope (Patel et al., 1991).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Potential Parameters</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^{2-} - O^{2-}$</td>
<td>$A$ (eV) $\rho$ (Å) $C$ (eVÅ$^6$)</td>
<td>1</td>
</tr>
<tr>
<td>Mg$^{2+}$ - $O^{2-}$</td>
<td>1428.5 0.2945 0.0</td>
<td>2</td>
</tr>
<tr>
<td>Al$^{3+}$ - $O^{2-}$</td>
<td>1114.9 0.3118 0.0</td>
<td>2</td>
</tr>
<tr>
<td>Si$^{4+}$ - $O^{2-}$</td>
<td>1283.9 0.3205 10.6616</td>
<td>3</td>
</tr>
<tr>
<td>$k$ (eV/rad$^2$)</td>
<td>2.097</td>
<td>3</td>
</tr>
<tr>
<td>O$^{2-}$ - Si$^{4+}$ - O$^{2-}$</td>
<td>$k(eV/Å^2)$</td>
<td>3</td>
</tr>
<tr>
<td>O$^{2-}$ core-shell</td>
<td>74.9204</td>
<td>3</td>
</tr>
</tbody>
</table>


Our simulations of pyrope were performed employing several different methods of Brillouin zone sampling (described in the following section) of both the primitive (80 atoms) and the full body-centred cubic unit cells (160 atoms), in order to determine the effect of these sampling procedures on the calculated properties of pyrope.
2.3.2 Brillouin Zone Sampling Techniques

The vibrational modes of a solid may be more conveniently described in terms of reciprocal space, where the propagation direction of each vibration is described by a wavevector \( \mathbf{k} \), whose magnitude is \( 2\pi/\lambda \), where \( \lambda \) is the wavelength of the lattice mode. The infinite wavelength limit of vibrational waves is described by \( \mathbf{k} = 0 \), the origin of reciprocal space. The short wavelength limit is described by \( \mathbf{k} = 2\pi/2\lambda = \pm \pi/a \), where \( a \) is the lattice repeat in real space. The vector \( \mathbf{k} = \pi/a \) is half the distance to the reciprocal lattice point (at \( 2\pi/a \)) in this direction, and lies at the boundary of a volume of reciprocal space, centred around the origin, known as the Brillouin zone. Hence, this zone defines the short wavelength limits of all wavevectors in the crystal.

The form of the Brillouin zone for any crystal lattice is defined by the planes that are perpendicular bisectors of vectors drawn from the origin of the reciprocal lattice to the nearest and next-nearest neighbour points, forming a volume of reciprocal space known as a Wigner-Seitz cell (Wigner and Seitz, 1933). The reciprocal lattice of the body-centred cubic (BCC) garnet structure is a face-centred cubic (FCC) lattice. There are 12 nearest and next-nearest neighbour points to the origin in this FCC lattice, at:

\[
(-0.5, 0.5, 0), \quad (0.5, 0.5, 0), \quad (0.5, -0.5, 0), \quad (-0.5, -0.5, 0), \\
(0, -0.5, 0.5), \quad (0, 0.5, 0.5), \quad (0, 0.5, -0.5), \quad (0, -0.5, -0.5), \\
(-0.5, 0, 0.5), \quad (0.5, 0, 0.5), \quad (0.5, 0, -0.5), \quad (-0.5, 0, -0.5).
\]

The Wigner-Seitz cell of the FCC lattice is constructed from the planes at 90° to the vectors from the origin of the lattice to the points listed above, thus giving a twelve-sided cell (Fig.2.4) which defines the first Brillouin zone of the cubic garnet structure.

As phonon frequencies vary as a function of wavevector \( \mathbf{k} \) across the Brillouin zone, it is essential to evaluate the frequencies throughout the entire zone in order to calculate the thermodynamic properties accurately. However due to computational constraints, this is impractical and hence, efficient Brillouin zone sampling methods are essential for economising computer time. Three main approaches to zone sampling have been developed: uneven grid sampling (Filippini et al., 1976); mean value points (Baldereschi, 1973); and special point sets (Chadi and Cohen, 1973).
Filippini et al. (1976) proposed a system of sampling points on a general grid throughout the Brillouin zone. As phonon dispersion is generally greatest near the zone centre, more dense sampling is required in that area and hence, the Filippini et al. (1976) proposed the idea of uneven Brillouin zone sampling. Sampling points are chosen by the division of each reciprocal axis into unequal intervals following the progression:

\[ x_i = \frac{1}{2} \cdot \frac{2^{(i-1)}}{2^n - 1} \]  

(2.50)

where \( n \) is the cube root of the number of points, \( i \), sampled. This progression may be used to establish the sampling points directly, in which interval borders are taken to be equidistant from adjacent points (Fig.2.5a), or to establish the intervals themselves, in which the sample points are taken as equidistant from adjacent borders (Fig.2.5b,c).

---

**Figure 2.4**: The Wigner-Seitz cell of the reciprocal lattice of the garnet structure.
Figure 2.5: a) and b) definition of points and intervals on the reciprocal axes for Brillouin zone sampling (see text), and c) application of $b$ to 2 reciprocal axes for two-dimensional sampling (after Filippini et al., 1976).
The coordinates of the \( i^{th} \) point at the centre of each interval are given by the equation:

\[
\frac{1}{2} \cdot \frac{2^{(i-1)}}{2^n - 1} + \frac{1}{2} \cdot \frac{2^{(i-1)}}{2(2^n - 1)}
\]  

(2.51)

In order to account for the disparity in the size of the intervals, a weighting factor \( M \) is assigned to each frequency, proportional to the extension or the volume of the interval surrounding a sampling point, given by:

\[
M = 2^{(i+j+k-3)}
\]  

(2.52)

where \( i, j, k = 1 \) to \( n \). In this sampling method it is important to establish the minimum number of points to be sampled. Thus, the structural, elastic and thermodynamic properties of pyrope were calculated at ambient conditions using this sampling technique with 1, 8, 27 and 64 points on the general grid for both the primitive and full body-centred cubic unit cells (see Table A1, Appendix 1).

b) Mean Value Point in the Brillouin zone

Baldereschi (1973) introduced a new high-symmetry special point in the Brillouin zone, termed the mean value point and defined as the point at which the value assumed by a given periodic function of the wavevector is an excellent approximation to the average value of the same function throughout the Brillouin zone. This approach was reported to be most valuable in studying phases of high-symmetry containing many atoms and hence, should be particularly applicable to the body-centred cubic garnet structure. The coordinates of the mean value point, \( \mathbf{k}^* \), are uniquely defined by the symmetry properties of the crystal lattice. For the BCC lattice, the mean value point is given by:

\[
\mathbf{k}^* = \left( \frac{2\pi}{a} \right) \left( \frac{1}{6}, \frac{1}{6}, \frac{1}{2} \right)
\]  

(2.53)

We have performed simulations of pyrope at 300K using \( \mathbf{k}^* \) defined in equation (2.53) and hypothetical mean value points located in the BCC unit cell at:
The results of which are shown in Table A2 (Appendix A).

c) Special Points in the Brillouin zone

Chadi and Cohen (1973) extended the work of Baldereschi (1973) by generating sets of special sampling points for cubic and hexagonal crystal lattices. The set of 8 special points $k_i$ (in units of $2\pi/a$), and their weighting factors $\alpha_i$, derived by Chadi and Cohen (1973) for the BCC Bravais lattice and used for our simulations of pyrope (Table A2) is given by:

$$k_1 = \left(\frac{1}{8}, \frac{1}{8}, \frac{1}{8}\right) \quad \alpha_1 = \frac{1}{16}$$

$$k_2 = \left(\frac{3}{8}, \frac{1}{8}, \frac{1}{8}\right) \quad \alpha_2 = \frac{3}{16}$$

$$k_3 = \left(\frac{3}{8}, \frac{3}{8}, \frac{1}{8}\right) \quad \alpha_3 = \frac{3}{16}$$

$$k_4 = \left(\frac{5}{8}, \frac{3}{8}, \frac{1}{8}\right) \quad \alpha_4 = \frac{1}{16}$$

$$k_5 = \left(\frac{5}{8}, \frac{1}{8}, \frac{3}{8}\right) \quad \alpha_5 = \frac{1}{16}$$

$$k_6 = \left(\frac{5}{8}, \frac{3}{8}, \frac{3}{8}\right) \quad \alpha_6 = \frac{3}{16}$$

$$k_7 = \left(\frac{7}{8}, \frac{1}{8}, \frac{1}{8}\right) \quad \alpha_7 = \frac{1}{16}$$

$$k_8 = \left(\frac{7}{8}, \frac{3}{8}, \frac{1}{8}\right) \quad \alpha_8 = \frac{1}{16}$$

2.3.3 Discussion of Results of Brillouin Zone Sampling Methods

The structural, elastic and thermodynamic properties of pyrope calculated using the 3 sampling methods described in the previous section (2.3.2) are shown in Tables A1-A2, and Figure 2.6. Simulations performed using the primitive cell of pyrope with the uneven grid sampling technique (Filippini et al., 1976) demonstrated that the use of different numbers of sampling points with this method resulted in only small variations in the calculated properties (Table A1). The greatest difference (excluding calculation time) was observed between the entropy values obtained using 1 and 64 sampling points, where the value determined from a single point (252.473 J/mol.K) is 0.44% larger than that calculated using 64 points (Fig.2.6f). The average
difference between the remaining properties is markedly lower, at 0.0132%. Simulations performed on the BCC cell using the same sampling technique (Table A1) also resulted in little variation in calculated values with increasing number of sampling points. The greatest difference (again excluding time) was observed between the calculated heat capacities, where the values obtained from 1 sampling point are 0.8% larger than those obtained using 64 points (Figs.2.6d,e); the average difference between the remaining calculated values is only 0.02%. Comparison of the primitive and BCC cell datasets derived from the Filippini et al. (1976) sampling method, shows that there is very little difference (0.08%) between the values calculated for each unit cell. The properties determined for the primitive cell are, in general, slightly larger, except for free energy, lattice parameter, volume and heat capacity, where the value calculated from one sampling point in the BCC cell is the greatest (Fig.2.6).

Simulations performed on the BCC cell using the mean value of Baldereschi (1973), designated MV1, and our theoretical mean value points, MV2 and MV3 (equation 2.54), also resulted in only small differences (0.07%) between calculated properties (Table A2; Fig.2.6). A greater deviation was observed between the calculated entropy in which the value determined using MV3 is 0.59% larger at 252.1716 J/mol.K than that obtained from MV1 and MV2 (Fig.2.6f). Comparison of the properties calculated from the mean value points with those obtained using the uneven grid sampling method (Filippini et al., 1976) and also the set of special points (Chadi and Cohen, 1973), shows that there is little variation in calculated values with sampling method used.

Properties such as the free energy, which are logarithmic functions of phonon frequency are expected to be fairly robust to Brillouin zone sampling, but properties such as volume can be affected. We suggest that the similarity of our results regardless of sampling technique employed illustrates the dense nature of the phonon dispersion relations of garnet, which consists of 240 vibrational modes showing little dispersion (see Figs.4.3b-4.5b), so that any point selected in the Brillouin zone will yield a good representation of the thermodynamic properties of this phase.

There is one important difference between the 3 Brillouin zone sampling methods used – the time taken to complete the calculation (Fig.2.6s). The time required for a calculation using the Filippini et al. (1976) sampling method appears to increase linearly with increasing number of sampling points. However, calculations
Figure 2.6a-f: Comparison of the properties of pyrope calculated at ambient conditions using the uneven grid (Filippini et al., 1976), mean values points MV₁ (Baldereschi, 1973), MV₂ and MV₃, and special point set (Chadi and Cohen, 1973) Brillouin zone sampling methods.
Figure 2.6g-l: Comparison of the properties of pyrope calculated at ambient conditions using the uneven grid (Filippini et al., 1976), mean values points MV$_1$ (Baldereschi, 1973), MV$_2$ and MV$_3$, and special point set (Chadi and Cohen, 1973) Brillouin zone sampling methods.
Seismic Velocity, $V_P$

Seismic Velocity, $V_S$

Thermal Expansion

Gruneisen Parameter

Static Dielectric Constant

High Frequency Dielectric Constant

Figure 2.6m-r: Comparison of the properties of pyrope calculated at ambient conditions using the uneven grid (Filippini et al., 1976), mean values points $MV_1$ (Baldereschi, 1973), $MV_2$ and $MV_3$, and special point set (Chadi and Cohen, 1973) Brillouin zone sampling methods.
performed on the BCC cell take more than 5 times longer to complete than a similar calculation using the primitive cell. For example, a simulation using a single sampling point in the primitive cell requires approximately 15 minutes for completion, while the equivalent calculation performed on the BCC cell requires approximately 45 minutes (a longer time is expected from consideration of the number of atoms in the BCC cell). Calculations performed using the MV1-MV3 single sampling points in the BCC unit cell require, on average, approximately 50 minutes for completion, while the sampling procedure using the special point set (Chadi and Cohen, 1973) takes in excess of 2 hours. Thus, we consider the use of a single sampling point within the primitive unit cell according to the uneven grid sampling method proposed by Filippini et al. (1976) to be the most efficient Brillouin zone sampling technique for pyrope as it yields simulated values representative of all the other sampling methods tested, and is also highly economic in terms of CPU time.
2.3.4 Comparison of Calculated Results with Experimental Data

In order to test the accuracy of the lattice dynamical model and the reliability of the potentials parameters used in describing the structural, elastic and thermodynamic properties of pyrope, comparisons with the available experimental data for this phase must be made. Table 2.3 shows the calculated properties of pyrope derived from a single Brillouin zone sampling point defined by Filippini et al. (1976) and applied to the primitive cell, compared with the experimental values obtained from both pure synthetic and natural pyrope samples. The calculated properties of pyrope are in reasonable agreement with the experimental data, underestimating the observed lattice parameter and heat capacities by approximately 1% (entropy is underestimated by 5%). The volume of pyrope is thus underestimated by approximately 3%, resulting in a simulated structure which is too dense, as confirmed by the discrepancies between the calculated and observed density values. Consequently, the calculated seismic velocities, $V_p$ and $V_s$, are overestimated (by approximately 10%) as the denser structure enhances their propagation through the crystal.

The elastic moduli, $C_{ij}$, $K$ and $\mu$, are also overestimated in our simulations, by an average of 18%, again indicative of the rigidity of the simulated structure. The observed elastic constant values $C_{ij}$ have been determined by a variety of experimental methods (e.g. Brillouin spectroscopy - O'Neill et al., 1991; Leitner et al., 1980; pulse-superposition ultrasonics - Bonczar et al., 1977; rectangular parallelepiped resonance - Babuška et al., 1978) which yield similar values for the $C_{11}$ and $C_{44}$ elastic constants. The experimental $C_{23}$ modulus data encompass a wider range of values (105-117 GPa) and this results in more favourable agreement with our calculated value of 118.9 GPa, with a difference of only 1.6% between our value and that reported by Leitner et al. (1980) for pure synthetic pyrope. However, the $C_{11}$ and $C_{44}$ values obtained by Leitner et al. (1980) for the same sample show the greatest deviations from our calculated values. The wide range of observed values for the $C_{23}$ modulus may be a consequence of the fact that $C_{23}$ is an off-diagonal modulus and therefore cannot be measured directly.

The experimental bulk moduli data also show a wide range of values (169-212 GPa). Our calculated value of 204.6 GPa shows the most favourable agreement with the value reported by Takahashi and Liu (1970), determined via static compression measurements. However, no gasket was used in their diamond-anvil cell experiments.
<table>
<thead>
<tr>
<th>Parameter:</th>
<th>Calculated Value</th>
<th>Experimental Value + References</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice Constant, $a$ (Å)</td>
<td>11.34404</td>
<td>11.454(5) $^{1,2,3}$</td>
<td>0.969</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.455(7) $^{4,5}$</td>
<td>0.978</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.456(1) $^{6,7,8}$</td>
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<tr>
<td></td>
<td></td>
<td>11.457(1) $^{9,10,11}$</td>
<td>0.996</td>
</tr>
<tr>
<td></td>
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<td>11.458(7) $^{12}$</td>
<td>1.011</td>
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<td>11.459(1) $^{13,14}$</td>
<td>1.013</td>
</tr>
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<td></td>
<td></td>
<td>11.490(3) $^{9}$</td>
<td>1.287</td>
</tr>
<tr>
<td>Volume ($Å^3$)</td>
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<td>1502.697(15) $^{1,2,3}$</td>
<td>2.936</td>
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<td>1503.091(21) $^{5,6}$</td>
<td>2.963</td>
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<td>1503.485(3) $^{6,7,8}$</td>
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<td>1516.911(15) $^{9}$</td>
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<td>326.05(1.3) $^{13}$</td>
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<td></td>
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<td>326.4 $^{15}$</td>
<td>0.912</td>
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<td>326.6 $^{16}$</td>
<td>0.974</td>
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<td></td>
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<td>330.1(3) $^{12}$</td>
<td>2.056</td>
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<td>Entropy, $S$ (J/mol.K)</td>
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<td>323.4(3) $^{17}$</td>
<td>0.503</td>
</tr>
<tr>
<td></td>
<td></td>
<td>323.5(5) $^{15}$</td>
<td>0.534</td>
</tr>
<tr>
<td>Elastic Constant, $C_{11}$ (GPa)</td>
<td>379.276</td>
<td>266.27(5) $^{1,18}$</td>
<td>5.465</td>
</tr>
<tr>
<td></td>
<td></td>
<td>266.3 $^{16}$</td>
<td>5.477</td>
</tr>
<tr>
<td>Elastic Constant, $C_{23}$ (GPa)</td>
<td>118.908</td>
<td>117.0(1) $^{22}$</td>
<td>1.631</td>
</tr>
<tr>
<td></td>
<td></td>
<td>111.1(6) $^{5}$</td>
<td>7.028</td>
</tr>
<tr>
<td></td>
<td></td>
<td>109.8(8) $^{9}$</td>
<td>8.295</td>
</tr>
<tr>
<td></td>
<td></td>
<td>109 $^{23}$</td>
<td>9.090</td>
</tr>
<tr>
<td></td>
<td></td>
<td>106.21(5) $^{21}$</td>
<td>11.956</td>
</tr>
<tr>
<td></td>
<td></td>
<td>105 $^{29}$</td>
<td>13.246</td>
</tr>
</tbody>
</table>

Table 2.3: Comparison of the properties of pyrope calculated using a single Brillouin zone sampling point in the primitive unit cell at ambient conditions, with the experimental data available for this phase. Bold-type indicates data obtained from natural samples; remaining data is from pure synthetic samples.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calculated Value</th>
<th>Experimental Value + References</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic Constant, $C_{44}$ (GPa)</td>
<td>104.020</td>
<td>$92.7(7)^9$ 92\textsuperscript{20} $91.64(13)^{21} 91.6(3)^9 91^{23} 90(3)^{22}$</td>
<td>12.211 13.065 13.509 13.559 14.308 15.578</td>
</tr>
<tr>
<td>Grüneisen Parameter, $\gamma$ (x10\textsuperscript{-5} K\textsuperscript{-1})</td>
<td>1.09837</td>
<td>1.05\textsuperscript{24} 1.19(36)\textsuperscript{25} 0.98(45)\textsuperscript{25} 1.43\textsuperscript{26}</td>
<td>4.607 8.342 12.079 30.193</td>
</tr>
<tr>
<td>Thermal Expansion, $\alpha$ (x10\textsuperscript{-5} K\textsuperscript{-1})</td>
<td>1.5717</td>
<td>1.90\textsuperscript{25} 1.98(6)\textsuperscript{14} 2.03(1)\textsuperscript{27} 2.10\textsuperscript{21} 2.36\textsuperscript{26}</td>
<td>20.888 25.978 29.159 33.613 50.156</td>
</tr>
<tr>
<td>Bulk Modulus, $K$ (GPa)</td>
<td>204.633</td>
<td>212(8)\textsuperscript{3} 190(6)\textsuperscript{3} 175.0(1)\textsuperscript{29,22} 174.0(1)\textsuperscript{30} 173(9)\textsuperscript{28} 171(3)\textsuperscript{11} 169.0\textsuperscript{26}</td>
<td>3.600 7.702 16.933 17.605 18.285 19.668 21.085</td>
</tr>
<tr>
<td>Shear Modulus, $\mu$ (GPa)</td>
<td>113.7990</td>
<td>93.2(2)\textsuperscript{9} 93.0(1)\textsuperscript{23} 92.6\textsuperscript{26} 92(1)\textsuperscript{27} 92.0(2)\textsuperscript{9} 89(1)\textsuperscript{52}</td>
<td>22.102 22.365 22.893 23.695 23.695 27.864</td>
</tr>
<tr>
<td>Density, $\rho$ (g/cm\textsuperscript{3})</td>
<td>3.6675</td>
<td>3.705\textsuperscript{26} 3.604(9)\textsuperscript{9} 3.582(3)\textsuperscript{29} 3.571(10)\textsuperscript{30} 3.567(1)\textsuperscript{9} 3.553(4)\textsuperscript{27} 3.510(2)\textsuperscript{33}</td>
<td>1.022 1.762 2.387 2.702 2.817 3.223 4.487</td>
</tr>
</tbody>
</table>

Table 2.3 (continued): Comparison of the properties of pyrope calculated using a single Brillouin zone sampling point in the primitive unit cell at ambient conditions, with the experimental data available for this phase. Bold-type indicates data obtained from natural samples; remaining data is from pure synthetic samples.
<table>
<thead>
<tr>
<th>Parameter</th>
<th>Calculated Value</th>
<th>Experimental Value + References</th>
<th>% Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seismic Velocity, $V_p$ (km/s)</td>
<td>9.8721</td>
<td>9.11(5) $^{22}$</td>
<td>8.306</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.08(3) $^{33}$</td>
<td>8.724</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.92 $^{26}$</td>
<td>10.674</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.9 $^{23}$</td>
<td>10.922</td>
</tr>
<tr>
<td></td>
<td></td>
<td>8.83(9) $^{21}$</td>
<td>11.688</td>
</tr>
<tr>
<td>Seismic Velocity, $V_s$ (km/s)</td>
<td>5.5703</td>
<td>5.07(3) $^{33}$</td>
<td>9.868</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.04(5) $^{22}$</td>
<td>10.522</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.00 $^{26}$</td>
<td>11.406</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.97(4) $^{21}$</td>
<td>11.988</td>
</tr>
<tr>
<td>Static Dielectric Constant, $\varepsilon$</td>
<td>9.6134</td>
<td>12.00(77) $^{34}$</td>
<td>24.826</td>
</tr>
</tbody>
</table>

Table 2.3 (continued): Comparison of the properties of pyrope calculated using a single Brillouin zone sampling point in the primitive unit cell at ambient conditions, with the experimental data available for this phase. Bold-type indicates data obtained from natural samples; remaining data is from pure synthetic samples. References are:

2. Geiger et al. (1987)
4. Eckert et al. (1992)
5. Mernagh and Liu (1990)
6. Hazen and Finger (1978)
8. Meagher (1975)
10. Newton et al. (1977a)
11. Sato et al. (1978)
12. Téquière et al. (1991)
15. Richet and Fiquet (1991)
16. Robie et al. (1978)
17. Saxena and Shen (1992)
20. Leitner et al. (1980)
21. Bonczar et al. (1977)
22. Isaak and Graham (1976)
23. Wang and Huang (1975)
25. Gillet et al. (1992)
26. Anderson et al. (1992)
27. Thiéblot et al. (1998)
28. Babuška et al. (1978)
29. Levien et al. (1978)
31. Hofmeister and Chopelas (1991a)
32. Stockwell (1927)
33. Ford (1915)
34. Shannon and Rossman (1992)
and extensive extrusion is thought to have occurred, together with bridging of the anvils at approximately 1 GPa where the relative volume appears to increase (see Fig.2.16), resulting in an unreliable bulk modulus value. The most precise bulk moduli values therefore appear to be those derived from Brillouin scattering (Leitner et al., 1980) and resonance (Babuška et al., 1978) experiments performed at ambient conditions which yield adiabatic bulk moduli values of around 175 GPa.

The calculated thermal expansion, which is also related to volume, underestimates the observed values by 20-50%. The experimental values listed in Table 2.3 are derived from natural samples which contain significant amounts of Fe and Ca, the addition of which into the garnet structure appears to decrease the thermal expansion at room temperature (e.g. Skinner, 1956; Anderson et al., 1991; Thiéblot et al., 1998). Hence, the thermal expansion of pure pyrope is expected to be greater than the experimental values given in Table 2.3, thus increasing the deviation between the calculated and observed values. The experimentally determined Grünneisen parameters also cover a relatively wide range of values (0.98-1.43) and our calculated Grünneisen parameter (1.09) thus lies within the range of experimental values, showing the most favourable agreement with the value of 1.05 determined by Anderson et al. (1991) for a natural pyrope sample containing significant amounts of Ca. According to Anderson et al. (1991), the addition of Ca into the garnet structure decreases γ and hence, the experimental value reported by Anderson et al. (1991) is expected to be larger for pure pyrope.

The calculated static dielectric constant underestimates the observed values by approximately 25% (Table 2.3). However the experimental values, measured by a two-terminal method (Shannon and Rossman, 1992), were obtained from a suite of natural pyropes containing significant proportions of Fe and minor amounts of Ca. The addition of Ca into the garnet structure appears to lower the static dielectric constant, with values of 8-9 reported for the Ca end-member garnet, grossular (Shannon and Rossman, 1992; Olhoeft, 1981; Bliss, 1989). In contrast, an increase in Fe-content of pyrope-almandine solid-solutions appears to increase the static dielectric constant (Shannon and Rossman, 1992), and hence, this parameter for pure pyrope is expected to be lower than the values reported for Fe-bearing pyropes by Shannon and Rossman (1992). However, the extent to which such impurities effect the static dielectric constant must be investigated, and
measurements of pure pyrope samples made in order to compare our calculated values directly.

2.4 Results of Simulations of Pyrope at Temperature

2.4.1 Introduction

Simulations of pyrope were performed at temperatures from 50K to 2000K using the Brillouin zone sampling method of Filippini et al. (1976) in both the primitive and BCC unit cells (with 1, 8, 27 and 64 sampling points) in order to model the temperature behaviour of this phase (Tables A3-A10, Appendix A). The results of our calculations again demonstrates that the use of different numbers of Brillouin zone sampling points in the garnet unit cell produces little difference in the simulated properties, with an average difference of 0.03% between the properties calculated using the primitive and BCC cells at each temperature stage. The greatest difference in the calculated properties is observed between the entropy values, which differ by an average of 2% at each temperature stage. The largest entropy value is consistently obtained using a single sampling point in the primitive cell, whereas the smallest value was calculated from one sampling point in the BCC cell. However, this difference corresponds to only approximately 1 J/mol.K. The most important difference between the datasets is again the time taken to complete the simulation. Calculations performed using a single sampling point in the primitive cell require an average of 10 minutes, while those performed using 64 points in the BCC cell require an average of 13.42 hours. Hence, the most representative and efficient temperature dataset appears to be that derived from a single sampling point in the primitive unit cell, as observed in our simulations performed at ambient conditions, as this provides a consistently higher calculated entropy, thus closer to the experimental values, and requires the shortest calculation time. The results of the calculations at temperature using the single sampling point are illustrated in Figure 2.7, which show that the calculated properties vary smoothly from zero Kelvin with temperature and that no phase changes were observed.
Figure 2.7: Variation of calculated structural, elastic and thermodynamic properties of pyrope with temperature, obtained from a single Brillouin zone sampling point (Filippini et al., 1976) in the primitive unit cell.
Figure 2.7 (continued): Variation of the calculated structural, elastic and thermodynamic properties of pyrope with temperature, obtained from a single Brillouin zone sampling point (Filippini et al., 1976) in the primitive unit cell.
Figure 2.7 (continued): Variation of calculated structural, elastic and thermodynamic properties of pyrope with temperature, obtained from a single Brillouin zone sampling point (Filippini et al., 1976) in the primitive unit cell.
The lattice constant, $a$, of pyrope has been determined by many authors at ambient conditions (Table 2.3). However, the effect of temperature on this parameter and hence the unit cell volume, has only been reported by Skinner (1956), who used powder x-ray diffraction (XRD) to measure the increase in $a$ of end-member garnets to 1030K, and more recently by Thiéblot et al. (1998), who used powder XRD with synchrotron radiation to measure the lattice parameter of natural pyrope (98.5 mol% pyrope) to 1630K. Comparison of our calculated temperature variation of the lattice parameter of pyrope with the experimental data of Skinner (1956) and Thiéblot et al. (1998), demonstrates that our simulated values consistently underestimate the observed data by approximately 0.12 Å (Fig.2.8a). This deviation, although only approximately 1%, results from the propagation of the difference observed at ambient conditions. However, the rate of change of the calculated lattice parameter with temperature is similar to that reported by Thiéblot et al. (1998) and Skinner (1956), at approximately 0.0001 Å/K to 1500K. Above this temperature, Thiéblot et al. (1998) reported a more rapid expansion of the lattice parameter and attributed this effect to the observed decomposition of pyrope to corundum + enstatite.

The thermal expansion coefficient, $\alpha$, of pyrope has also been measured experimentally by Skinner (1956) and Thiéblot et al. (1998). From molar volume measurements at temperature, Skinner (1956) derived the following equation to describe the thermal expansion of synthetic pyrope to 1023K:

$$\alpha = 2.311 \times 10^{-5} + 5.956 \times 10^{-9} T - 0.4538 \ T^{-2}$$  \hspace{1cm} (2.55)$$

Thiéblot et al. (1998) formulated a similar equation to describe the volume-temperature behaviour of a natural pyrope sample in the range 284-1454K. The thermal expansion equation derived by Thiéblot et al. (1998) included the data of Skinner (1956) in order to improve constraints on $\alpha$ at lower temperatures:

$$\alpha = 2.28 \times 10^{-5} + 5.17 \times 10^{-9} T - 0.369 \ T^{-2}$$  \hspace{1cm} (2.56)$$
Figure 2.8: Comparison of the calculated a) lattice parameter, and b) thermal expansion of pyrope with the experimental data at temperature.
Anderson et al. (1992) have also presented $\alpha$ values for pyrope from 100-1200K, using the primary data of Sumino and Anderson (1984), who studied a natural pyrope to 1000K. Comparison of our calculated $\alpha$ values for pyrope at temperature with the experimental data (Table 2.4; Fig.2.8b), shows that the simulated values underestimate the observed values by approximately 20%, as noted at ambient conditions (Table 2.3), but exhibit similar behaviour with increasing temperature.

<table>
<thead>
<tr>
<th>Temp (K)</th>
<th>This Work</th>
<th>Skinner (1956)</th>
<th>Anderson et al. (1992)</th>
<th>Thiéblot et al. (1998)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.5717</td>
<td>1.9855</td>
<td>2.36</td>
<td>2.0251</td>
</tr>
<tr>
<td>500</td>
<td>1.8850</td>
<td>2.4273</td>
<td>2.80</td>
<td>2.3909</td>
</tr>
<tr>
<td>800</td>
<td>2.0952</td>
<td>2.7166</td>
<td>3.03</td>
<td>2.6359</td>
</tr>
<tr>
<td>1200</td>
<td>2.2850</td>
<td>-</td>
<td>3.18</td>
<td>2.8478</td>
</tr>
<tr>
<td>1500</td>
<td>2.4287</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2000</td>
<td>2.7358</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 2.4: Comparison of the calculated and experimental thermal expansion coefficient of pyrope at temperature.

Comparison of the calculated Grüneisen parameter at temperature with the experimental data (Anderson et al., 1992) shows that above 200K, the calculated values underestimate the experimental results by approximately 20% (Fig.2.9a). However, it is not known to what extent the experimental data is affected by the presence of impurities (27 mol%) in the natural sample studied. Therefore, in order to make a direct comparison between calculated and observed results, experimental data for pure pyrope is required. Both $\gamma$ curves in Figure 2.9a do however exhibit similar temperature behaviour, increasing to a peak at low-temperatures, and subsequently decreasing as temperature increases, although the peak in the experimental curve is shifted to a higher temperature by approximately 100K, compared to the calculated data.

The heat capacity, $C_p$, of synthetic pyrope has been measured at low-temperatures (10-350K) by Haselton and Westrum (1980), via adiabatic calorimetry, with the lowest temperature data fitted to an equation of the form,
to permit extrapolation to zero Kelvin. Previous low-temperature \( C_p \) measurements of pyrope yielded anomalous heat capacity values in the range 10-30K (Kolesnik et al., 1977), not observed by Haselton and Westrum (1980). The data of Kolesnik et al. (1977) was obtained from natural sample containing 18.8 mol\% almandine, which is known to undergo paramagnetic to antiferromagnetic ordering at 7.5K (Prandl, 1971). This provides an additional entropy contribution of approximately 40 J/mol.K (Kittel, 1976; Ulbrich and Waldbaum, 1976), which also affects the heat capacity values. The data of Haselton and Westrum (1980) shows that for pure pyrope, there is no heat capacity anomaly, as confirmed in our calculations (Fig.2.9b) which, at very low-temperatures, were performed in steps of 5-10K to 100K.

Téqui et al. (1991) used drop-calorimetry to measure the high-temperature heat capacity of natural pyrope (98.8 mol\% pyrope) in the range 820-1300K, thus extending the previous work of Watanabe (1982) and Newton et al. (1977b), who used differential scanning calorimetry to measure \( C_p \) of synthetic pyrope to 600K and 1000K, respectively. Using the form of the \( C_p \) equation proposed by Richet and Fiquet (1991), which ensures both accurate representation of the experimental data and reliable high-temperature extrapolation, Téqui et al. (1991) formulated the following equation to describe the \( C_p \) of pyrope:

\[
C_p = -592.635 + 138.003 \ln T + 191.204 \times 10^3 T^{-1} - 72.066 \times 10^6 T^{-2} + 79.749 \times 10^8 T^{-3}
\]  

(2.58)

This equation was reported to give values deviating by 0.10% from those of Haselton and Westrum (1980) above 275K, and 1.39% from those of Newton et al. (1977b). Equation (2.58) is therefore considered to supersede previous equations derived by Berman and Brown (1985), Berman (1988) and Holland and Powell (1990), who used the limited dataset of Haselton and Westrum (1980) to extrapolate to high-temperatures. Comparison of the calculated \( C_p \) data with the experimental results of Haselton and Westrum (1980) and Téqui et al. (1991), shows that there is excellent agreement between the datasets (Fig.2.9b). However above approximately 900K,
Figure 2.9: Comparison of the calculated a) Grüneisen parameter, and b) heat capacity, $C_p$, of pyrope with the experimental data at temperature.
a greater deviation between the datasets is observed, with the calculated values underestimating the experimental results by approximately 2%. This is due to anharmonic effects which become important at high-temperatures, providing an additional contribution to the heat capacity not observed in the calculations because of our use of the quasi-harmonic approximation.

Anderson et al. (1992) presented both $C_P$ (Fig.2.9b) and $C_V$ (Fig.2.10) data for a natural pyrope sample (73 mol% pyrope). The $C_P$ values significantly underestimate both the calculated and previous experimental data by an average of 6%. This deviation may be related to the impurities present in the sample which have also resulted in large thermal expansion (Fig.2.8b) and Grüneisen parameter values (Fig.2.9), and an underestimation of the bulk modulus and heat capacities through equation (2.47), as compared to the values for pure pyrope.

Experimental entropy values, $S$, for pyrope have been derived from the heat capacity data of Haselton and Westrum (1980) and Téqui et al. (1991), through the integral relating these parameters:

$$S = \int_0^T \frac{C_V}{T} dT$$

Comparison of the calculated and experimentally-determined entropy of pyrope (Fig.2.11) shows that there is good agreement between the datasets, with the calculated data underestimating the observed values by approximately 5% below 600K. Above this temperature, the discrepancy increases and this is thought to be due to the differences observed between the experimental and calculated heat capacity values, propagated through the integral relating these parameters.

The entropy and heat capacity values of pyrope are reported to be anomalously high compared to those of grossular under the same conditions (Haselton and Westrum, 1980). Ca-bearing phases are expected to have higher heat capacities (and thus higher entropies) than their Mg-isomorphs, due to the lower vibrational frequencies associated with the larger mass of the Ca atom relative to Mg. The proposal of positional disorder of the divalent cations over 4 statistically occupied
Figure 2.10: Comparison of the calculated and experimentally-determined heat capacity, $C_V$ of pyrope.

Figure 2.11: Comparison of the calculated and experimentally-determined entropy of pyrope. Values below 350K are from Haselton and Westrum (1980); values above 400K are from Tequi et al. (1991).
general positions around the symmetry-fixed special 24c site (Zemann and Zemann, 1961; Kleber et al., 1969) as providing the additional entropy contribution has been discounted by Haselton and Westrum (1980), and by more recent low-temperature single-crystal XRD studies which have demonstrated that no lowering of symmetry is evident, but instead large and anisotropic displacements of the Mg-cations are observable. These displacements indicate that pyrope is characterized by substantial dynamic disorder of the dodecahedral cations (as opposed to static disorder), which gives rise to strongly anisotropic amplitudes within the dodecahedral site. These produce a rattling effect of the small Mg-cation within the relatively large dodecahedral site, and result in the observed large heat capacities and third law entropies of pyrope (Armbruster et al., 1992; Geiger et al., 1992; Armbruster and Geiger, 1993; Pavese et al., 1995). The anisotropy of the Mg-motions was reported to be particularly evident along the [110] and [001] axes, with the dominant motion of the Mg-atom lying within the (001) plane; within this plane, the largest component was reported to be parallel to [110] and the smallest parallel to [1̅10] (Pavese et al., 1995; Armbruster and Geiger, 1993). The anisotropic displacement appears to relax the strain of the strongly underbonded dodecahedral site, so that a more ideal bond valence is obtained (Armbruster et al., 1992; Geiger et al., 1992; Armbruster and Geiger, 1993). This is in agreement with the distortion theorem of Brown (1992b) which states that "If an atom is placed in a cavity that is too large, so that the average length of its bonds is too long to satisfy the Valence Sum Rule, the valence sum can be increased by making some bonds longer and others shorter, e.g. by allowing the atom to move off centre within the cavity".

The temperature dependence of the elastic constants, $C_y$, of a natural sample of pyrope (65 mol% pyrope) was investigated by Bonczar et al. (1977), who used pulse-superposition ultrasonic measurements to study the variation of $C_y$ in the temperature range 300-373K. Within the small temperature range studied, the elastic constants were reported by Bonczar et al. (1977) to show a linear decrease with increasing temperature, within experimental uncertainty. The temperature-derivatives of the adiabatic elastic constants were determined to be:

$$\left(\delta C_{11}/\delta T\right)_p = -0.0329 \pm 0.005 \text{ GPa/K}$$
$$\left(\delta C_{23}/\delta T\right)_p = -0.0118 \pm 0.008 \text{ GPa/K}$$
Comparison of the experimentally-determined and calculated temperature variation of $C_{ij}$ for pyrope (Fig.2.12 - in which the temperature-derivatives determined by Bonczar et al. (1977) have been projected to higher temperatures), demonstrates that the calculated $C_{ij}$ values consistently overestimate the observed values by an average of 15% as observed at ambient conditions, due to the rigidity of the simulated structure. However, comparison of the simulated and observed rate of change of $C_{ij}$ with temperature shows that there is good agreement between the calculated and experimental temperature-derivatives for $C_{11}$ (Fig.2.12a), with the calculated value approximately -0.027 GPa/K. The calculated temperature-derivatives for $C_{23}$ and $C_{44}$, at -0.0063 GPa/K and -0.0043 GPa/K respectively, are slightly lower than the experimental values (Figs.2.12b-c). However, more realistic comparisons of the temperature-dependence of the elastic constants of pyrope can only be made when the experimental temperature range is extended and data for pure pyrope is available.

Anderson et al. (1992) measured the temperature-dependence of the bulk modulus, $K$, of pyrope over the temperature range 100-1200K, thus extending the previous data of Bonczar et al. (1977). Using the primary data of Suzuki and Anderson (1983), derived from resonant ultrasound spectroscopy, Anderson et al. (1992) calculated both the adiabatic and isothermal bulk moduli of pyrope, which differ by approximately 2 GPa at 300K. Comparison of the calculated temperature variation of the bulk modulus with the experimental values (Fig.2.13a), shows that the calculated $K$ is overestimated by approximately 20%, as observed at ambient conditions. These differences are too great to be attributed to compositional differences alone and hence, are related to the stiffness of the simulated pyrope structure. The calculated rate of change of the bulk modulus with temperature (-0.0183 GPa/K) is in good agreement with the experimental data of Bonczar et al. (1977) who determined a temperature derivative of -0.0188 GPa/K for the range 300-373K. The data of Anderson et al. (1992) suggests a slightly greater rate of change with temperature, of approximately -0.025 GPa/K. However, the effect of impurities such as Ca, Fe and Cr, present in the sample used by Suzuki and Anderson (1983), on the temperature variation of $K$ is unknown, and hence, a detailed study of the elasticity of garnet solid-solution series at temperature is required.
Figure 2.12: Variation of the calculated and experimentally-determined elastic constants a) $C_{11}$, b) $C_{23}$ and c) $C_{44}$ of pyrope with temperature.
Figure 2.13: Variation of the calculated and experimental values of a) bulk modulus, and b) shear modulus of pyrope with temperature.
The temperature variations of the shear modulus, \( \mu \), density, \( \rho \), and seismic velocities, \( V_P \) and \( V_S \), of pyrope have been reported by Anderson et al. (1992) to be approximately linear over the temperature range 100-1250K. Comparison of the calculated temperature variation of these parameters with the experimental data (Fig.2.13b-d) shows that the calculated shear modulus is overestimated by approximately 20\%, although the calculated rate of change of \( \mu \) with temperature (approximately 0.01 GPa/K) is similar to the observed temperature behaviour (Fig.2.13b). The calculated seismic velocities are also overestimated at temperature (Fig.2.13c), as observed at ambient conditions, as a consequence of the rigidity of the simulated structure. The density determined by Anderson et al. (1992), shows a greater rate of change with temperature than our calculated density values, which underestimate the experimental data by approximately 1\% at 300K (Fig.2.13d). The agreement between the experimental and calculated density values therefore improves with increasing temperature, and based on the trends observed within the temperature ranges studied, it appears that the calculated and observed values will be identical at approximately 1500K.

2.4.3 Response of the Garnet Structure to Temperature from Previous XRD Studies

The structural response of pyrope to temperature has been determined from the single-crystal XRD studies of Meagher (1975), Armbruster et al. (1992), Armbruster and Geiger (1993), and Pavese et al. (1995). According to these studies, the expansion results primarily from dilation of the Al-O and in particular, the Mg-O bonds. There are 2 symmetrically non-equivalent Mg-O interatomic distances in the dodecahedral site (Zemann, 1962; Gibbs and Smith, 1965), denoted Mg-O(2) and Mg-O(4) (Fig.2.14). The Mg-O(4) distance is longer and increases at a greater rate with temperature than the Mg-O(2) distance, with a linear thermal expansion coefficient of 1.75(3)x10^{-5} \text{ K}^{-1}; the linear thermal expansion coefficient of the smaller Mg-O bond is 0.87(3)x10^{-5} \text{ K}^{-1} (Meagher, 1975). This yields an average thermal expansion coefficient of the mean Mg-O distance of 1.3x10^{-5} \text{ K}^{-1} which is in good agreement with the value reported by Pavese et al. (1995) of 1.31x10^{-5} \text{ K}^{-1}. The dodecahedral site is most sensitive to temperature variations because it involves the weakest bonds in
Figure 2.13: Variation of the calculated and experimental values of c) seismic velocities, and d) density of pyrope with temperature.
the structure. The volume change of this site has been calculated to be approximately 3.5% at 1000K, with respect to the volume at 30K, corresponding to the largest polyhedral volume expansion in the garnet structure (Pavese et al., 1995).

The AlO₆ octahedron is the most regular polyhedra in the structure, as indicated by its small octahedral angle strain (Robinson et al., 1971). Each octahedron has 6 edges, shared with adjacent dodecahedra, which are shorter at room temperature by 0.10 Å than the 6 unshared edges (Gibbs and Smith, 1965), as predicted by Pauling (1929). With increasing temperature, the expansion of the shared edge is significantly greater than that of the unshared edge (Meagher, 1975; Pavese et al., 1995), which causes the octahedral bond angle strain to decrease, leading to a more regular octahedron at higher temperatures. The thermal expansion coefficient of the mean Al-O distance has been reported by Pavese et al. (1995) to be 0.96x10⁻⁵ K⁻¹, in agreement with the value of 0.8x10⁻⁵ K⁻¹ obtained by Meagher (1975), resulting in a volume change of approximately 2% over the temperature range 30-1000K.

The Si-O interatomic distances and the tetrahedral O-Si-O angles are reported to show essentially no variation at low-temperatures (Armbruster et al., 1992; Pavese et al., 1995) and hence, the size and shape of the SiO₄ tetrahedra change little with increasing temperature. Instead they rotate about their central 4-axes by approximately 0.6° over an interval of 1000K (Meagher, 1975; Pavese et al., 1995), thus contributing to the enlargement of the dodecahedral sites (Fig.2.14). At higher temperatures, the Si-O bonds themselves dilate, with the larger unshared O-O edges expanding at a greater rate than those shared with the dodecahedra, thus increasing the tetrahedral distortion. Pavese et al. (1995) reported a mean thermal expansion coefficient of 0.51x10⁻⁵ K⁻¹ for the Si-O bonds in temperature range 300-1000K, which is slightly larger than the value determined by Meagher (1975), of 0.1x10⁻⁵ K⁻¹. These thermal expansion coefficients are small compared to those determined for the Mg-O and Al-O bonds, and hence, the SiO₄ tetrahedra behave more rigidly in comparison with the other polyhedra, with observed volume changes of approximately only 1% at 1000K.
Figure 2.14: Polyhedral model of the garnet structure (modified after Novak and Gibbs, 1971) showing the effects of temperature, with rotation of the SiO$_4$ tetrahedra (indicated by curved arrows) affecting the relative lengths of the AlO$_6$ and MgO$_8$ polyhedral edges. Numbers on oxygen atoms refer to cation-oxygen distances, with Mg-O(4) and symmetry equivalent bond distances longer than Mg-O(2), and increasing at a greater rate.


2.5.1 Introduction

Simulations of pyrope were performed using a single Brillouin zone sampling point in the primitive unit cell, according to the sampling technique proposed by Filippini et al. (1976), to pressures of 10 GPa (Table A11, Appendix A). The results of these simulations show that the calculated structural, elastic and thermodynamic properties of pyrope exhibit approximately linear variations with increasing pressure, with no phase changes observed in the pressure range studied. Calculated properties such as the free energy, density, elastic moduli, seismic velocities and high-frequency dielectric constant were observed to increase with increasing pressure, while the lattice parameter, unit cell volume, heat capacities, entropy, static dielectric constant, thermal expansion and the Grüneisen parameter were all observed to decrease with increasing pressure (Table A11; Fig.2.15).

2.5.2 Comparison of the Results of High-Pressure Calculations with Experimental Data

The unit cell volume and elastic moduli of pyrope are the only parameters which have been studied experimentally at high-pressure. Our calculations therefore extend the data available for this phase, as the pressure variation of the thermodynamic properties has now been determined (Table A11; Fig.2.15). The response of pyrope to pressure was first investigated by Bridgman (1928), who reported that the volume compressibility of a natural sample of pyrope could be described by the equation:

\[
\frac{\Delta V}{V_0} = -aP + bP^2
\]  

(2.63)

where \( a \) and \( b \) are the coefficients \( 5.379 \times 10^{-7} \) and \( 2.19 \times 10^{-12} \) (at \( 30^\circ C \)), respectively, and \( 5.439 \times 10^{-7} \) and \( 2.19 \times 10^{-12} \) (at \( 75^\circ C \)).
Figure 2.15: Variation of the properties of pyrope with pressure, calculated from the primitive unit cell, using a single Brillouin zone point according to the sampling method proposed by Filippini et al. (1976).
Figure 2.15 (continued): Variation of the properties of pyrope with pressure, calculated from the primitive unit cell, using a single Brillouin zone point according to the sampling method proposed by Filippini et al. (1976).
Figure 2.15 (continued): Variation of the properties of pyrope with pressure, calculated from the primitive unit cell, using a single Brillouin zone point according to the sampling method proposed by Filippini et al. (1976).
The variation of the unit cell volume of pyrope with pressure has since been investigated using modern static compression techniques by Takahashi and Liu (1970), Duba and Olinger (1972), Sato et al. (1978), Levien et al. (1979), Hazen and Finger (1978, 1989) and Leger et al. (1990), the details of which are shown in Table 2.5. A least-squares fit of the volume-pressure data to a third-order Birch-Murnaghan equation of state:

\[ P = \frac{3}{2} K_0 \left[ \left( \frac{V}{V_0} \right)^{7/3} - \left( \frac{V}{V_0} \right)^{5/3} \right] \cdot \left\{ 1 - \frac{3}{4} \left( 4 - K_0' \right) \left[ \left( \frac{V}{V_0} \right)^{2/3} - 1 \right] \right\} \]  

(2.64)

yields a value for the bulk modulus, \( K_0 \), and its pressure derivative \( K_0' \). Application of equation (2.64) to our calculated volume-pressure data for pyrope yields \( K = 207.2 \) GPa, and \( K_0' = 3.6 \). These results compare most favourably with the experimental data (Fig.2.16) of Takahashi and Liu (1970) who obtained an isothermal bulk modulus value of 212(8) GPa and \( K_0' \) of 3.5(6) for synthetic pyrope powder. However, the use of NaCl as the pressure-transmitting medium in the diamond-anvil cell (DAC) used by Takahashi and Liu (1970) has led to reported concerns over non-hydrostatic conditions within their experiments (Sato et al., 1978; Leitner et al., 1980; Levien et al., 1979; Leger et al., 1990). Takahashi and Liu (1970) also used no gasket in their DAC and hence, extensive extrusion and bridging of the anvils by the pyrope particles at approximately 1 GPa, demonstrated by the apparent volume increase at this pressure (Fig.2.16), is thought to have occurred, resulting in overestimation of \( K_T \) (Leger et al., 1990). The remaining static compression studies of pyrope (Table 2.5) have yielded isothermal bulk moduli values in the range 175-179 GPa, obtained from both natural and synthetic samples. (The value of 179 GPa reported by Hazen and Finger (1989), assuming \( K' = 4 \), supersedes their previous low value (Hazen and Finger, 1978) which was considered to be erroneous as the room-pressure and high-pressure volumes were determined using different sets of reflections under different conditions, resulting in larger volumes at ambient conditions relative to the high-pressure measurements.). These \( K_T \) values are in agreement with the adiabatic values determined from ultrasonic studies by Babuška et al. (1978), who suggested a \( K_S \) value of 173.0(9) GPa for end-member pyrope from measurements on natural samples.
<table>
<thead>
<tr>
<th>Author, Year</th>
<th>Technique</th>
<th>Sample Type</th>
<th>Sample Composition</th>
<th>P-transmitting medium</th>
<th>Internal Standard</th>
<th>Max. Pressure (GPa)</th>
<th>K_T (GPa)</th>
<th>K' (GPa)</th>
<th>Calculation Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Takahashi + Liu (1970)</td>
<td>DAC ; XRD (no gasket)</td>
<td>Powder</td>
<td>Synthetic</td>
<td>NaCl</td>
<td>NaCl</td>
<td>32.8</td>
<td>212(8)</td>
<td>3.5(6)</td>
<td>Birch-Murnaghan</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Natural (60mol% Pyr)</td>
<td>NaCl</td>
<td></td>
<td>32.4</td>
<td>205(6)</td>
<td>3(4)</td>
<td></td>
</tr>
<tr>
<td>Duba + Olinger (1972)</td>
<td>Pistons ; XRD</td>
<td>Powder</td>
<td>Natural (&lt;60mol% Pyr)</td>
<td>unspecified</td>
<td>NaF</td>
<td>10</td>
<td>175</td>
<td>-</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Hazen + Finger (1978)</td>
<td>DAC ; XRD</td>
<td>Single-crystal</td>
<td>Synthetic</td>
<td>Water + glycerin</td>
<td>Ruby</td>
<td>5.6</td>
<td>133(3)</td>
<td>-</td>
<td>Quadratic</td>
</tr>
<tr>
<td>Sato et al. (1979)</td>
<td>DAC ; XRD</td>
<td>Powder</td>
<td>Synthetic</td>
<td>Water + glycerin</td>
<td>Ruby</td>
<td>5</td>
<td>176(3)</td>
<td>1.9(8)</td>
<td>Birch-Murnaghan, 2^nd-order</td>
</tr>
<tr>
<td>Levien et al. (1989)</td>
<td>DAC ; XRD</td>
<td>Single-crystal</td>
<td>Synthetic</td>
<td>4:1 methanol:ethanol</td>
<td>Ruby</td>
<td>6</td>
<td>179(3)</td>
<td>-</td>
<td>Birch-Murnaghan, 3^rd-order</td>
</tr>
<tr>
<td>Hazen + Finger (1989)</td>
<td>DAC ; XRD</td>
<td>Single-crystal</td>
<td>Natural (67mol% Pyr)</td>
<td>4:1 methanol:ethanol</td>
<td>Ruby</td>
<td>5</td>
<td>175(1)</td>
<td>4.5(5)</td>
<td>Birch-Murnaghan, 3^rd-order</td>
</tr>
<tr>
<td>Leger et al. (1990)</td>
<td>DAC ; XRD</td>
<td>Powder</td>
<td>Synthetic</td>
<td>NaCl</td>
<td></td>
<td>23</td>
<td>-</td>
<td>3.4(1.0); 3.8</td>
<td>Birch-Murnaghan, 3^rd-order</td>
</tr>
</tbody>
</table>

Table 2.5: Details of the experimental techniques and samples used in recent static compression studies of pyrope, for the determination of the isothermal bulk modulus, K_T, and its pressure-variation, K'.
Figure 2.16: Comparison of the calculated and experimentally-determined relative volume change, \(V/V_0\), of pyrope with pressure.
of various compositions, and by Bonczar et al. (1977), who determined $K_S$ to be 168.21(36) GPa for a natural pyrope sample (94 mol% pyrope). Leitner et al. (1980) and O'Neill et al. (1991) used Brillouin spectroscopy to obtain $K_S$ values of 177(1) GPa and 172.8(3) GPa, respectively, for synthetic pyrope single-crystals. These $K_S$ values are related to $K_T$ via the equation:

$$K_T = K_S (1 + \alpha \gamma T)^{-1}$$

which yields $K_T$ values approximately 2 GPa lower than their corresponding $K_S$ values for pyrope. Thus, the $K_S$ value reported by Leitner et al. (1980), derived from the same crystal used by Levien et al. (1978) from velocity measurements in 3 crystallographic directions, was converted to a $K_T$ value of 175 GPa, identical to that obtained by Levien et al. (1979) from their static compression study.

These results demonstrate that our calculated bulk modulus is overestimated, again indicating that our simulated structure of pyrope is too rigid. However, the calculated rate of change of the bulk modulus with pressure, described by $K' = 3.6$, shows good agreement with the $K'$ value determined by Leger et al. (1990) of 3.4±1, assuming the bulk modulus value of 175(1) GPa of Leitner et al. (1980), or 3.8, assuming $K = 172.8(3)$ reported by O'Neill et al. (1991). Leger et al. (1990) suggested that the relatively low $K'$ value of pyrope (silicates usually have $K' = 4$) could be a consequence of the small size of the Mg-cation for which high-pressures are necessary for its accommodation in the highly coordinated dodecahedral site. These $K'$ values lie within the range of experimentally-determined values, extending from 1.9 (Sato et al., 1978) to approximately 4.6 (Levien et al., 1979; Bonczar et al., 1977), which demonstrates that further work must be done on pure samples under hydrostatic conditions over a much larger pressure range to obtain an accurate value of $K'$ for pyrope.

Bonczar et al. (1977) determined the pressure-dependence of the adiabatic elastic constants of a natural pyrope (65 mol% pyrope) to 1 GPa, via pulse-superposition ultrasonic measurements. Comparison of the calculated pressure variation of the elastic constants with the data of Bonczar et al. (1977) shows that the calculated elastic constants are overestimated by approximately 25% (Fig.2.17), as observed at ambient conditions (Table 2.3) and at temperature (Fig.2.12). This discrepancy becomes more pronounced with increasing pressure as the calculated and
experimentally-determined pressure derivatives for the elastic constants differ also. The agreement between the calculated and observed $C_{44}$ elastic constant pressure-variation is the most favourable (Fig. 2.17c), with a calculated pressure derivative of 0.32 GPa/GPa, compared to the value of 0.143(1) GPa/GPa reported by Bonczar et al. (1977). The calculated pressure derivatives for the $C_{11}$ and $C_{23}$ elastic constants are much greater, at 6.04 and 2.67 GPa/GPa respectively, than those determined by Bonczar et al. (1977) of 0.67 and 0.37 GPa/GPa, respectively (Fig. 2.17b-c). However, the experimental data was determined over limited pressure range (0-1 GPa) and has been extended over a greater range in this study for purposes of comparison. Also, it is not known to what extent the presence of the approximately 35 mol% almandine content of the sample studied affects the rates of change of the elastic constants with pressure. Therefore more detailed experimental studies of the elastic constants of pure pyrope over a greater pressure range are required for more realistic comparisons with the calculated data.

2.6 Optimization of Interatomic Potentials for Pyrope

Having observed the discrepancies between the calculated and experimental data for pyrope, Pavese et al. (1998) recently developed an interatomic potential set specifically for pyrope, determining its parameters through simultaneous fitting to observed room temperature structural, elastic and vibrational ($F_{2g}$ modes) data. With the potential parameters employed by Winkler et al. (1991) in their simulation study of aluminosilicate minerals used as the starting point, the optimization of the potential parameters was performed using the MINUIT code (James and Roos, 1975), adjusted to suit a modified version of PARAPICS (Pavese et al., 1996). The calculations were performed under the static-lattice approximation, thus neglecting thermal contributions. Although this reduces the capability of the potential to model mineral behaviour at high-temperature, it allows the minimization to be computationally possible and permits reliable room- or low-temperature simulations to be performed. During the optimization routine, all atomic charges were allowed to vary, constrained so as to maintain electroneutrality; the $A$, $\rho$ and $C$ terms of the Buckingham potential (equation 2.4) were refined for the O-O, Mg-O, Si-O and Al-O interactions, and the force constants of the O-Si-O, O-Al-O, and oxygen core-shell interactions were also optimized.
Figure 2.17: Comparison of the calculated and experimentally-determined variation of the a) $C_{11}$, b) $C_{23}$ and c) $C_{44}$ elastic constants of pyrope with pressure.
Pavese et al. (1998) reported that the optimized potential parameters for pyrope showed large changes compared to those used by Winkler et al. (1991), with the $A$ and $C$ parameters for the O-O interaction and the oxygen core-shell coupling coefficient showing the most significant changes from their initial values (Table 2.6). The coefficients of O-Al-O and O-Si-O interactions were reported to be rather small but were maintained as they provided a slight improvement in modelling the elastic constants. The optimized fractional charges were reported to significantly improve the capability of the potential to reproduce the experimental data, though at the expense of its transferability. The optimization resulted in the Si-cation retaining its formal charge, while the Al, O and in particular Mg, atoms clearly deviate from ideal ions in the pyrope structure (Table 2.6).

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$A$ (eV)</th>
<th>$\rho$ (Å)</th>
<th>$C$ (eV Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O - O</td>
<td>96461.7</td>
<td>0.1345</td>
<td>48.37</td>
</tr>
<tr>
<td>Mg - O</td>
<td>1261.7</td>
<td>0.2957</td>
<td>0.0</td>
</tr>
<tr>
<td>Al - O</td>
<td>1435.6</td>
<td>0.2998</td>
<td>0.0</td>
</tr>
<tr>
<td>Si - O</td>
<td>1245.8</td>
<td>0.3207</td>
<td>10.7</td>
</tr>
<tr>
<td>O - Si - O</td>
<td>3.57</td>
<td>109.47</td>
<td></td>
</tr>
<tr>
<td>O - Al - O</td>
<td>2.69</td>
<td>90.0</td>
<td></td>
</tr>
<tr>
<td>O core-shell</td>
<td>125.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Charge, $q$ (e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O shell</td>
</tr>
<tr>
<td>O core</td>
</tr>
<tr>
<td>Mg</td>
</tr>
<tr>
<td>Al</td>
</tr>
<tr>
<td>Si</td>
</tr>
</tbody>
</table>

Table 2.6: Optimized potential parameters for pyrope (Pavese et al., 1998).

Using the optimized potentials, Pavese et al. (1998) calculated the elastic constants of pyrope to be $C_{11} = 298.7$, $C_{23} = 112.6$ and $C_{44} = 90.6$ GPa, having adopted
the experimental structure at room temperature. The agreement between these values and those determined experimentally was reported to be very satisfactory, with the absolute difference within 3%, a marked improvement on the 20% difference reported in our work and that of Winkler et al. (1991). Comparison of the experimental room-temperature crystallographic data and the statically relaxed structure demonstrated that the cell edge was calculated to within 0.1%, with the calculated and experimental cation-oxygen distances in good agreement. The largest deviation was observed between the simulated and observed Mg-O bond (-3.7%), which, as Pavese et al. (1998) concluded, is the weakest interaction in the structure and thereby difficult to simulate accurately.

2.7 Summary and Conclusions

The atoms in a solid vibrate about their equilibrium positions and these atomic motions, which can be described within the framework of lattice dynamics, govern the bulk thermodynamic properties of the solid. We have performed lattice dynamical simulations of pyrope garnet, using interatomic potentials for simple binary oxides and the computer code PARAPACS (Parker and Price, 1989). We have shown that the use of different methods of sampling the Brillouin zone results in little difference in the calculated properties of pyrope, due to the dense nature of the phonon dispersion relations of garnet. Our calculated structural and thermodynamic properties of pyrope at ambient conditions, and at temperature and pressure, show good agreement with the experimental data. However, our calculated elastic moduli of pyrope are overestimated by an average of approximately 18%. This has also been a common result in previous simulation studies of pyrope which have employed several different methods of calculation (e.g. lattice dynamics, molecular dynamics, quantum mechanical), and is attributed to the weak bonding of the small Mg-cation in the large dodecahedral site which is difficult to simulate. Recently, Pavese et al. (1998) have refined a set of interatomic potentials specifically for pyrope, which are currently only valid for low-temperature and room-temperature simulations. These potentials are reported to accurately reproduce the observed elastic constants of pyrope at ambient conditions, but at the expense of the transferability of the potential. It is expected that these potentials will be further refined by Pavese et al. (1998) so that they may be employed in future high-temperature and high-pressure simulations of pyrope.
Atoms bonded together in molecular systems vibrate at frequencies of $10^{12}$-$10^{14}$ Hz, in the infrared (IR) region of the electromagnetic spectrum. The exact frequency of each vibration is controlled by the interatomic forces existing between the bonded atoms, and thus the mass and molecular geometry of the constituent atoms. Many of the bulk thermodynamic properties of a crystal are directly related to its vibrational properties (e.g. $E, C_V, S$), and hence a study of the vibrational characteristics of a system provides the important link between its micro- and macroscopic properties.

In the classical description of atomic vibrations, atoms are considered to be connected by springs whose stiffness represents the interatomic forces. If the spring obeys Hooke's Law (i.e. the restoring force is proportional to the displacement from the equilibrium position), the vibrational motions of the atoms or molecules are said to be harmonic, and under this approximation, atoms connected by weak springs or bonds will vibrate at lower frequencies than those connected by stronger, more rigid bonds. In the harmonic model, each vibrational frequency or mode is treated as a discrete oscillator, although in real systems, the oscillators may not act independently of each other, resulting in coupling of vibrational modes (to give combination modes or overtones) and transfer of energy between oscillators, producing anharmonic effects.

In a crystal system, each atom in the unit cell may be described as having 3 degrees of vibrational freedom (along the $x$-, $y$- and $z$-axes) so that the total number of vibrational modes in a unit cell of $n$ atoms, is $3n$. Three of these modes correspond to translations of the entire system in which the atoms in the unit cell move in the same direction, in phase and with the same amplitude (Fig.3.1a). These vibrations are known as acoustic modes as they are responsible for the propagation of sound waves through the lattice. The remaining $3n-3$ vibrational modes (ignoring system rotations) are termed normal or optic modes, because the atomic displacements involved in these vibrations generate an oscillating dipole moment (whose frequency is defined by the oscillation
frequencies of the individual atoms about their equilibrium positions) and hence, can interact with light. During a normal vibration, the atoms involved vibrate at the same frequency and move in phase although they may have different amplitudes and move in opposite directions (Fig.3.1b). In a crystal, because the arrangement of the atoms is periodic, the vibrational modes take the form of displacement waves travelling through the crystal, producing lattice vibrations. The normal modes are the long wavelength lattice vibrations with zero wavevector and are said to lie at the Brillouin zone centre. These lattice waves may be described as transverse, where the displacements are perpendicular to the propagation direction (Fig.3.1c,d), or longitudinal, where the atomic displacements are parallel to the wave propagation direction (Fig.3.1e).

![Figure 3.1: Lattice vibrations in which a) all atoms in the diatomic chain move in phase in the same direction to generate an acoustic mode, b) atoms in the diatomic chain move in opposing directions to generate an optic or normal mode, c) and d) atomic displacements of the monatomic chains are perpendicular to the wave propagation direction to produce transverse waves, and e) atomic displacements of the monatomic chain are parallel to the wave propagation direction to produce a longitudinal mode.](image-url)
The vibrational frequencies of a molecule or crystal may be measured using spectroscopy, an experimental technique which involves the interaction of radiation with matter. The vibrational frequencies throughout the Brillouin zone may be measured via inelastic neutron spectroscopy (see Chapter 4). However, this technique requires highly specialized facilities. Instead, selected modes at the Brillouin zone centre are more readily measured using vibrational spectroscopy in which the interaction between electromagnetic waves (light) and matter is studied. In such spectroscopic experiments, an incident beam of radiation is directed on to a sample which will either absorb or emit the radiation. Spectroscopy is used to measure the energy of the absorbed or emitted radiation when the molecules are excited to a higher energy state or as they decay back to the zero energy or ground state. As the rotations of molecular groups and the stretching and bending of atomic bonds occur in the IR range, transitions between the vibrational energy levels of a molecule can be induced by incident IR radiation, which will be absorbed or reflected by the sample at the frequencies corresponding to the vibrational modes of the sample (Infrared spectroscopy - section 3.2). Near-IR radiation (14-14.5 Hz) is used to determine vibrational frequencies in the 10,000-4000 cm\(^{-1}\) region, while mid-IR radiation (13-14 Hz) is used for the range 4000-400 cm\(^{-1}\) and far-IR radiation (11.5-13 Hz) for the range 400-10 cm\(^{-1}\). Zone centre vibrations may also be measured by Raman spectroscopy (section 3.3) in which an incident beam of radiation, usually in the visible region of the electromagnetic spectrum, has its energy changed by inelastic collision with the vibrating atoms, resulting in Raman scattering (Raman, 1928; Raman and Krishnan, 1928). The energy lost by the incident beam corresponds to the energy required to induce the phonon energy, while the energy gained by the beam corresponds to the energy required to allow a normal mode to decay to its non-vibrating state. Both of these vibrational spectroscopic techniques result in a set of absorption minima or scattering peaks as a function of energy, constituting a vibrational spectrum. Individual peaks or minima in the spectrum correspond to the energies of vibrational transitions within the sample and thus give the frequencies of its vibrational modes. The selection rules which govern which zone centre frequencies will be 'active' under IR or Raman light may be determined via Factor Group Analysis (e.g. Fateley et al., 1972; McMillan and Hess, 1988), from consideration of the crystal symmetry within the mathematical framework of Group theory (section 3.4).

Although pyrope-rich garnets have been the subject of many IR spectroscopic studies (Adler et al., 1950; Launer, 1952; Wickersheim et al., 1960; Tarte, 1965; Moore
et al., 1971; Cahay et al., 1981; McMillan et al., 1989; Geiger et al., 1989, 1992; Bosenick et al., 1995), these studies have failed to yield complete sets of IR-active modes, due to poor instrument resolution, difficulties in distinguishing weak modes from artifacts, overtones and combination modes, and intense scattering from the powder samples used. The single-crystal investigations by Hofmeister and Chopelas (1991a) and Hofmeister et al. (1996) are the only studies to have reported complete sets of IR-active frequencies for pyrope, although some regions of the spectra are still poorly resolved. Raman spectroscopic studies of pyrope are less well documented, but suffer similar problems. The Raman spectra of single-crystal pyrope-rich garnets have been recorded by Griffith (1969), Memagh and Liu (1990), Hofmeister and Chopelas (1991a), Gillet et al. (1992) and more recently, by Kolesov and Geiger (1998). These experiments again failed to report the full number of Raman-active modes for pyrope, except the polarized study by Hofmeister and Chopelas (1991a) which reported a complete set of bands.

In this chapter, we present the results of lattice dynamical simulations of the zone centre vibrational frequencies of pyrope, and the determination of their IR- and Raman-activity (section 3.5). This study is useful as it establishes the complete sets of IR- and Raman-active modes for pyrope, and facilitates the interpretation of poorly resolved regions of the experimental spectra. Several experimental studies have attempted to ascertain which atomic or site motions within the garnet structure generate the IR- and Raman-active modes, with the assignments determined from isotopic substitution data (Cahay et al., 1981; Kolesov and Geiger, 1998), or predictions from Group theory and assumptions based on relative cation masses, pure mode and solid-solution behaviour (Griffith, 1969; Moore et al., 1971; Hofmeister and Chopelas, 1991a; Hofmeister et al., 1996). In section 3.6, we examine the theoretical derivation of the vibrational modes of garnet, and in section 3.7, we present our assignments of the calculated modes of pyrope to specific atomic or site motions, determined from simulated displacements of the constituent atoms and the mode shifts arising from the simulated isotopic substitution of $^{26}$Mg and $^{30}$Si. Finally in section 3.8, we compare our results with the experimental data and assess the theoretical predictions of garnet vibrational behaviour.
3.2 Infrared Spectroscopy

The interaction of IR radiation with crystal lattices is described in detail by authors such as Lazarev (1972), Turrell (1972), Sherwood (1972), Farmer (1973), and McMillan and Hofmeister (1988). Briefly, in an infrared spectroscopic experiment, an incident beam of IR radiation with a range of frequency from a filament source is focused on to a powder or single crystal sample. The radiation is transmitted, absorbed, reflected or emitted by the sample, according to Kirchoff's Law:

\[ T(v) = 1 - A(v) - R(v) - \kappa(v) \]  

where \( v \) is the frequency of the incident beam, and \( T, A, R \) and \( \kappa \) are the coefficients of transmission, absorption, reflection and emission, respectively. IR absorption occurs when the oscillating electric field of the incident radiation resonates with a fluctuating electric dipole caused by a molecular vibration. If two atoms of equal and opposite charge \( \pm Q \), are separated by a distance \( r \), an electric dipole is generated with a dipole moment of magnitude:

\[ \mu = Q \cdot r \]  

If the two atoms are at rest \( (r = r_0) \), the equilibrium dipole moment is \( \mu_0 \). In a polyatomic molecule, each atom pair will generate a dipole moment, the vector sum of which gives the net molecular dipole moment. During a vibrational mode, the relative motion of the constituent nuclei may result in a change in the net dipole moment. Because the vibrational motion is oscillatory, a fluctuating electric field is generated and this field may interact with the electric part of the incident radiation. Thus absorption of IR radiation will only occur when:

\[ \frac{\delta \mu}{\delta r} = Q^* \neq 0 \]  

where \( Q^* \) is the magnitude of the effective charge, thus defining the selection rule for IR-activity. The intensity of IR absorption is related to the magnitude of the dipole change, so that small dipole changes are generally associated with weak IR bands, while asymmetric vibrations with large dipole moment changes are associated with stronger IR absorption. The most common method of obtaining IR spectra has been via a powder
transmission experiment (e.g. Berreman, 1963; Luxon and Summitt, 1969; Martin, 1970; Moore et al., 1971; Ohmori, 1971; Dietrich and Arndt, 1982; Gillet et al., 1992; Bosenick et al., 1995), in which the powdered sample is dispersed in a support medium and the IR beam is passed through both materials. The resulting spectra show minima in IR transmission, usually taken to correspond to bulk absorption peaks of the sample.

The vectors of the atomic displacements during an optic mode may be resolved into three components according to the propagation directions of their associated lattice waves, to give a longitudinal optic (LO) mode parallel to the wave-vector, \( \mathbf{k} \), and 2 transverse optic (TO) modes which are mutually perpendicular and at right-angles to \( \mathbf{k} \) (Fig.3.1). For \( \mathbf{k} < 0 \), the LO and TO components generally have different frequencies because they involve different types of wave propagation (compressional and shear) through adjacent unit cells. The two TO modes may themselves be degenerate, depending on the crystal symmetry and the propagation direction of the wave. At the Brillouin zone centre, where all unit cells should vibrate in phase, all three components of each optic mode should have the same frequency, based on mechanical forces alone. However, for polyatomic crystals it is observed that the frequency of the LO mode is different from that of the TO modes at \( \mathbf{k} = 0 \). This LO-TO splitting is usually interpreted within the ionic model of crystals which demonstrates that when adjacent ions of opposite charge are separated during an LO mode, an electric field opposing this separation is generated. This field provides an additional contribution to the mechanical restoring force so that the LO mode becomes raised in frequency. No such electric field is generated for the corresponding transverse modes and hence, these modes remain at the frequencies defined by the mechanical force constant (Born and Huang, 1954). The amount of LO-TO splitting that will occur is related to the refractive index and thus the dielectric character of the sample, which governs its reflective properties. The refractive index, \( n \), of a material is given by:

\[
n = \frac{c}{v}
\]

(3.4)

where \( c \) is the speed of light in a vacuum, and \( v \) is the velocity of the propagation of electromagnetic radiation within the material. The refractive index is always greater than 1 (except in the region of a resonance where \( n \) is undefined) because the incident beam is retarded by its interaction with matter. The dielectric constants, \( \varepsilon \), of a material are related to the refractive index by:
The propagation velocity, $v$, of a quantum unit of light within a material (a polariton) is dependent on the nature of the interaction between the light and the material (modulation), and also the wavelength of the incident electromagnetic radiation. Consequently, $n$ and $\varepsilon$ also vary with radiation wavelength. At high-frequency, the more massive nuclei remain stationary and modulation of the polariton occurs via electronic motions, defining the high-frequency (optical) dielectric constant, $\varepsilon_\infty$. At low-frequencies, there is dielectric contribution from both the relative displacements of the nuclei and the electrons, as the polariton is modulated by both of these motions. This defines the low frequency (static) dielectric constant, $\varepsilon_0$, which is thus larger than $\varepsilon_\infty$.

The powder IR absorption method suffers from significant problems due to shifting of TO (absorption) peaks towards the frequency of LO mode, splitting of a single absorption band into separate LO and TO components, and scattering due to the particulate nature of the sample. These effects result in major changes in the appearance of the true absorption spectrum, both in the number, position and shape of the bands observed, and may be dependent on shape and size of sample particles.

In contrast, IR reflectance experiments performed on single-crystal samples (e.g. Simon and McMahon, 1953; Gaskell, 1966; Servoin and Piriou, 1973; Piriou, 1974; Hofmeister and Chopelas, 1991a; Hofmeister et al., 1996) give more quantitative results although the spectra are more difficult to interpret as they do not simply consist of peaks corresponding to vibrational frequencies. An IR reflectance, $R(\nu)$ of a crystal, defined as

$$R = \frac{(n-1)^2}{(n+1)^2},$$

(3.6)

where $R$ is the reflectivity, has a characteristic form which can be analyzed to give the optical constants ($n$ and $\varepsilon$) as a function of wavelength, $\lambda$, of the incident light and the frequencies of the TO and LO modes via a Kramers-Kronig analysis. During an IR reflectance experiment, if the frequency of the incident beam directed on to the sample begins at low-frequency, dramatic changes are observed in the values of $n$, $\varepsilon$ and $R$ as the incident radiation increases in frequency and approaches the frequency, $\nu_0$, of a vibrational mode of the sample (Fig.3.2a). The polariton starts to drive the atomic
Figure 3.2: a) the hypothetical variation of the refractive index $n$, dielectric constant $\varepsilon$, and reflectivity $R$, with frequency, and b) the real variation of $n$, $\varepsilon$, and $R$ with frequency, with absorption of IR radiation by the sample through anharmonic processes included (after McMillan and Hofmeister, 1988).
displacements associated with a transverse normal vibrational mode of the lattice, creating a phonon. The phonon propagates more slowly through the lattice than the polariton, which is itself retarded by resonance with the phonon frequency, \( v_0 \). This causes the values of \( n \) and \( \varepsilon \) to increase asymptotically to infinity (Fig. 3.2a). At \( v_0 \), light can no longer propagate through the lattice so that its velocity tends to zero and the sample becomes totally reflecting \( (R = 1) \). On the high-frequency side of the resonance, the value of \( \varepsilon \) returns from negative infinity to cross the axis \( \varepsilon = 0 \), at a frequency which defines the LO mode, \( v_L \). IR reflection spectroscopy can therefore be used to determine the LO frequencies of a sample which cannot be measured directly from IR absorption experiments. A sample will usually have several such resonance regions in its IR reflectance spectrum, one corresponding to each of its IR-active modes. Between \( v_0 \) and \( v_L \), the refractive index is undefined, and at frequencies above \( v_L \), the dielectric constant and refractive index rise to their high-frequency values. Since electromagnetic radiation is a transverse wave, the incident IR beam may only interact with transverse optic vibrations, so that frequency \( v_0 \) is equivalent to the TO frequency at \( k = 0 \). The frequency interval between \( v_{TO} \) and \( v_{LO} \), in which the sample is totally reflecting, thus defines the amount of LO-TO splitting. The IR reflection spectra of real crystals rarely show complete reflection between \( v_0 \) and \( v_L \) due to some absorption of the radiation by the crystal and dissipation of energy along the crystal lattice vibrations through anharmonic processes (dielectric loss behaviour). By allowing the optical constants to become complex:

\[
n = n' + n^* \quad \text{and} \quad \varepsilon = \varepsilon' + i\varepsilon^*
\]

where:

\[
\varepsilon' = n'^2 - n^*^2 \quad \text{and} \quad \varepsilon^* = 2n'n^*
\]

(3.7)

(3.8)

the reflectivity may be defined as:

\[
R = \left\{ \frac{(n' - 1)^2 + (n^*)^2}{(n' + 1)^2 + (n^*)^2} \right\}
\]

(3.9)

The complex refractive indices may be calculated via the Fresnel equations:
\[ n' = \frac{(1 - r^2)}{(1 + r^2 - 2r \cos \theta)} \quad \text{and} \quad n'' = \frac{2r}{(1 + r^2 - 2r \cos \theta)} \]  \quad (3.10)

where \( r = \sqrt{R} \) is defined as the real part of the reflectivity, and \( r^* \) is the imaginary part, given by the equation:

\[ r^* = r \cdot e^{i\theta} \]  \quad (3.11)

where \( \theta \) is the phase shift between the real and imaginary parts of the reflectivity, and is proportional to the magnitude of the absorption coefficient, \( A(v) \), defined as:

\[ A(v) = 4\pi n^* v \]  \quad (3.12)

where \( v \) is the optical frequency. A Kramers-Kronig analysis (e.g. Anderman et al., 1965; Piriou and Cabannes, 1968) is used to calculate \( \theta \) from the measured reflection spectrum, \( R(v) \), via the equation:

\[ \theta(v_i) = \frac{2v_i}{\pi} \int_0^\infty \frac{\ln r(v) - \ln(v_i)}{v_i^2 - v^2} dv \]  \quad (3.13)

From these equations the TO and LO frequencies can be established: the dielectric loss function \( \varepsilon''(v) \) has a maximum at the transverse optical frequency \( (v_{TO}) \), and the absorption coefficient is determined by the magnitude of \( n'' \) at this point (Fig.3.2b). The LO frequency is determined by the point at which the real part of the complex optical constant, \( \varepsilon'(v) \), crosses the axis \( \varepsilon' = 0 \) after the \( \varepsilon' \) minimum. The reflectivity curve, \( R(v) \), may not increase perfectly to \( R = 1 \) and structures may be present in the 'forbidden' region between \( v_0 \) and \( v_L \) (Fig.3.2b).

### 3.3 Raman Spectroscopy

The Raman scattering of light by a crystal lattice has been described by Gilson and Hendra (1970), Hayes and Loudon (1970), Tobin (1971), Long (1977) and McMillan and Hofmeister (1988). Here briefly, in Raman spectroscopy the sample is
illuminated with monochromatic light with frequency \( v \), and photon energy \( E \), to which the sample is transparent. The majority of the incident light (approximately 99\%) is transmitted or scattered by elastic collision with the atoms in the sample with no energy change, producing *Rayleigh scattering*, with energy \( E \) and frequency \( v \). The remaining part of the incident light may gain or lose a small amount of energy, \( e \), through inelastic interactions with the vibrational modes of the crystal to give peaks in the Raman scattering spectrum at \( E + e \) and \( E - e \). These peaks correspond to *anti-Stokes* scattering and *Stokes* scattering, respectively (Fig. 3.3); the change in energy of the scattered light beam relative to the incident beam energy is termed the *Raman shift*. It is usual practice to measure the Stokes lines in the spectrum as these are generally more intense than the anti-Stokes lines. Raman scattering is a very weak effect with only \( 10^{-6}-10^{-7} \) of the intensity of the incident light involved. Thus, an intense light source (laser) must be used.

Figure 3.3: Theoretical Raman spectrum with a strong central peak due to elastic Rayleigh scattering of energy \( E \), and weaker Raman-shifted lines at \( E+e \) and \( E-e \) corresponding to anti-Stokes and Stokes scattering, respectively.
In the simple quantum mechanical description of a polyatomic system, the $3n-3$ independent harmonic oscillators each have a characteristic frequency $\nu_i = \lambda_i^{1/2}$. Each oscillator is associated with a set of quantum numbers, $n_i$, which define its vibrational energy states and its corresponding wavefunctions. The energy levels for the entire polyatomic system may be described by the function:

$$E = (n_1 + 0.5)\hbar\nu_1 + (n_2 + 0.5)\hbar\nu_2 + (n_3 + 0.5)\hbar\nu_3 \ldots$$  \hspace{1cm} (3.11)$$

so that for the zero point energy, $E_0$, all quantum numbers, $n_i$, are zero. The ground state wavefunction has an equal component of the atomic displacements for each vibrational normal mode, $i$. A fundamental transition is one from the ground state to a level with $n_i = 1$, with all other quantum numbers remaining at zero (combination transitions, in which more than one quantum number changes at the same time, may occur in anharmonic polyatomic systems). This approach provides the simplest explanation of the Rayleigh and Raman scattering effects: when a sample is illuminated with light of frequency $\nu$, the photon associated with this light has energy $\hbar\nu$, where $\hbar$ is Planck's constant. Such photons may interact with the molecules in the sample without a change in energy, producing Rayleigh scattering in all directions with the same frequency. However, if the molecule is in a low energy vibrational state, it may abstract a certain amount of energy from the incident photon in order to reach a higher energy state. If the frequency associated with such a transition is $\nu'$, then energy $\hbar\nu'$ is removed from the photon so that the scattered photon will have the decreased energy $\hbar(\nu-\nu')$, producing a Stokes line in the Raman spectrum, with frequency $\nu-\nu'$. In contrast, if the molecule is in a vibrationally excited state, it may impart energy $\hbar\nu'$ to the photon, so that an anti-Stokes line of energy $\hbar(\nu+\nu')$ is observed in the Raman spectrum. As a greater number of molecules are always in lower energy states than higher states, the Stokes lines are more intense than the anti-Stokes lines in the Raman spectrum.

In the simple classical description of Rayleigh and Raman scattering, the incident beam is said to induce an instantaneous dipole moment in the molecule by deforming its electronic wavefunction or electron cloud during photon-molecular collision. Subsequently, the heavier nuclei move to follow the new deformed electronic distribution. In most cases, the photon leaves the molecule and the nuclei relax back to their original positions, and the collision is said to be elastic (generating Rayleigh scattering). However, if the displacement of the electron cloud and the nuclei...
corresponds to their displacement during a vibrational mode and the perturbation is sufficient, the normal mode is stimulated and becomes Raman-active. The energy required for the vibrational transition is subtracted from the incident photon to give Stokes scattering. If the molecule is originally in an excited state and interaction with an incident phonon produces a transition to a lower state, anti-Stokes scattering occurs. The magnitude of the instantaneous dipole moment, \( \mu_{\text{ind}} \), produced by the incident light is dependent on the ease with which the electron cloud can be deformed, i.e. by the molecular polarizability, \( \alpha \), and is defined to the first approximation as:

\[
\mu_{\text{ind}} = \alpha \cdot E \tag{3.12}
\]

where \( E \) is the oscillating electric field of the photon, with frequency \( \nu \), and amplitude \( E_0 \), and varies according to the relationship,

\[
E = E_0 \cos 2\pi \nu t \tag{3.13}
\]

These equations form the classical expression for Rayleigh scattering, with no change in frequency involved, and in this case, the polarizability \( \alpha \), represents the equilibrium polarizability (\( \alpha_0 \)) of the static molecule. If the molecule undergoes a vibration of frequency \( \nu' \), which causes its polarizability to change, the time-dependent polarizability of the molecule (assuming electrical harmonicity) is described by:

\[
\alpha(t) = \alpha_0 + \beta \cos 2\pi \nu' t \tag{3.14}
\]

where \( \beta \) is the rate of change of polarizability with the vibration. Thus, the induced dipole may be expressed as:

\[
\mu_{\text{ind}} = E_0 \cos 2\pi \nu t (\alpha_0 + \beta \cos 2\pi \nu' t) \tag{3.15}
\]

Expansion of equation (3.15) yields the 3 separate parts of the equation which describe the Rayleigh, Stokes (\( \nu - \nu' \)) and anti-Stokes (\( \nu + \nu' \)) scattering:

\[
\mu_{\text{ind}} = \alpha_0 E_0 \cos 2\pi \nu t + \frac{1}{2} \beta E_0 \left[ \cos 2\pi (\nu - \nu') t + \cos 2\pi (\nu + \nu') t \right] \tag{3.16}
\]
This equation defines the basic selection rules for the Raman activity of vibrational modes, so that vibrations which involve a change in polarizability, \( \beta \), will be Raman-active. The disadvantage of this equation is that it predicts that the Stokes and anti-Stokes scattering will be of equal intensity. The intensity, \( I \), of the scattering is determined by the power spectrum of \( \alpha(t) \) and is proportional to:

\[
\int \langle \alpha_0 \alpha(t) \rangle \exp(-i\omega t) dt = \alpha_0^2 \delta(\nu) + \sum_{k,v} \gamma(k,v) \left[ n(\omega, T) + \delta(\omega - \omega(k, v)) \right] n(\omega, T) \delta(\omega + \omega(k, v)) \]

(3.17)

where \( \exp(-i\omega t) = \cos 2\pi\nu t \). The expression \( \alpha_0^2 \delta(\nu) \) represents Rayleigh scattering, and the coefficient \( \gamma(k, v) \), subsumes the parameter \( \alpha' \), and therefore takes into account the polarizability for the specific scattering geometry. The process of phonon creation and absorption are weighted by different thermal factors \( n(\omega, T) + 1 \) and \( n(\omega, T) \), (where \( \omega \) is the photon angular frequency) and thus represent Stokes and anti-Stokes scattering, respectively.

Equations (3.12-3.16) are based on the assumption that the electric vector \( E \), induces a dipole vector \( \mu \) in the same direction as \( E \). However, the polarizability within a molecule is generally greater in one direction than in another. Thus, the induced dipole tends to align itself with the direction of greatest polarizability in the molecule rather than with \( E \). Therefore, the simplicity of equation (3.12) must be replaced by a more complex set of equations based on the Cartesian axes \( x, y \) and \( z \):

\[
\begin{align*}
\mu_x &= \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \\
\mu_y &= \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \\
\mu_z &= \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z
\end{align*}
\]

(3.18)

where \( \alpha_{xy} = \alpha_{yx}, \ \alpha_{yz} = \alpha_{zy}, \ \alpha_{xz} = \alpha_{zx} \). The second-rank polarizability tensor derived from the matrix of \( \alpha_0 \) components is given by:
Vibrational modes will be Raman-active if they have the same symmetry as one or more of the elements of the polarizability tensor. If only one of the six derivatives is non-zero for a given mode then that mode will only be weakly Raman-active. The diagonal components of the tensor are always associated with the highest symmetry Raman-active modes and usually generate the most intense bands in the Raman spectrum as they are associated with the greatest changes in polarizability. The strength of the Raman activity of a mode can therefore be related to the number and symmetry of the tensor elements which are non-zero for that mode. The polarizability tensor can be used to obtain spectra containing modes of a particular symmetry by using oriented crystals and polarizing both the incident and scattered beams; laboratory geometry can be used to define particular polarizability elements and obtain the corresponding mode symmetries. If the polarizations of the beams are parallel to the diagonal elements of the scattering tensor, then xx, yy or zz are selected. If the polarizations are at right-angles, off-diagonal elements xy, xz or yz are selected. For example, if the incident laser beam lies along y and is polarized parallel to z, and the scattered radiation is collected along x and is also polarized parallel to z, then the scattering geometry may be written as y(zz)x in Porto notation (Damen et al., 1966). This selects polarizability tensor element αzz so that modes corresponding to this symmetry will be recorded in the Raman spectrum.

3.4 Prediction of the Infrared- and Raman-Activity of Molecules and Crystals

3.4.1 Introduction

Prediction of the IR- and Raman-activity of the vibrational modes of a molecule or crystal is accomplished using the mathematical approach known as Group theory (e.g. Hammermesh, 1962; Cotton, 1971; Birman, 1984; McMillan and Hess, 1988). In this method, the symmetry of a molecule or unit cell is described in terms of a set of
conventionally selected symmetry elements which define the spatial relations between different parts of the system, and collectively form a mathematical group. The five conventional symmetry elements are:

1) **Identity** (I or E) - the operation which involves no movement but is introduced to satisfy the algebraic requirements of the group.

2) **Proper rotation axis** \((C_n^m)\) - an operation which involves a rotation of \(360°m/n\) about the \(C_n\) axis.

3) **Mirror plane** \((\sigma)\) - an operation involving the reflection of points across a plane which may be vertical \((\sigma_v)\), horizontal \((\sigma_h)\) or diagonal \((\sigma_d)\).

4) **Improper rotation axis** \((S_n^m)\) - this operation is defined as a combination of a rotation about a proper rotation axis \(C_n\), followed by a reflection in a mirror plane perpendicular to that axis (also termed a roto-reflection).

5) **Inversion centre** \((i)\) - the operation corresponding to reflection about a point.

A molecule or unit cell will contain a set of one or more of these five symmetry elements (each part of a rotation operation is counted as a separate member of a set, so that \(C_1^1\) and \(C_3^2\), corresponding to rotations of \(120°\) and \(240°\) respectively about a 3-fold axis, count as 2 separate members). For example, the \(\text{H}_2\text{O}\) molecule may be described by the set:

\[
\{I, C_2, \sigma_v(xz), \sigma_v(yz)\}
\]  

(3.20)

where \(I\) is the identity, \(C_2\) is a 2-fold rotation axis, and \(\sigma_v(xz)\) and \(\sigma_v(yz)\) are mirror planes in the \(xz\)- and \(yz\)-planes, respectively. The sets of symmetry operations which correspond to the symmetries of all known molecular systems form special sets known as **groups**. For each group, Schonflies notation is used in spectroscopic applications to denote the particular set of elements present for the symmetry group. For example, the symbol describing the symmetry of \(\text{H}_2\text{O}\) is \(C_{2v}\), and the symbol for a \(\text{BF}_3\) molecule is \(D_{3h}\). These symbols are constructed in a systematic way according to the number and type of symmetry elements present, and range from \(C_v\) (containing I and \(\sigma_h\) symmetry elements only) to \(O_h\) (which contains 48 different symmetry elements). In crystallography, where translational symmetry operations are considered explicitly, the symmetry group is known as a **space group**; in molecular symmetry groups, in which
such translations are disregarded, at least one point of the molecule remains invariant under all operations, and these groups are termed point groups.

3.4.2 Matrix Representations of Symmetry Operations

The interrelations between members of a point group may be expressed numerically by using transformation matrices. The general matrix representations for the 5 main symmetry operations are generated by investigating the effect of the operations on a general point \( P(x, y, z) \) relative to the 3 Cartesian axes:

1) *Identity operation*, \( I: P(x, y, z) \rightarrow P(x', y', z') \) via the matrix:

\[
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
\begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x' \\
y' \\
z'
\end{pmatrix}
\]

\[ (3.21) \]

2) *Proper rotation*, \( C_n \): the clockwise rotation of point \( P(x, y, z) \) by \( \theta \)° about the z-axis (Fig.3.4) generates new coordinates \( P(x', y', z') \) via the matrix:

\[
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
\begin{pmatrix}
\cos \theta & \sin \theta & 0 \\
-\sin \theta & \cos \theta & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x' \\
y' \\
z'
\end{pmatrix}
\]

\[ (3.22) \]

For example, a \( C_n^m \) rotation operation corresponding to a rotation of \( \theta = (360m)°/n \) about the z-axis, is described by the matrix:

\[
\begin{pmatrix}
x \\
y \\
z
\end{pmatrix}
\begin{pmatrix}
\cos m\theta & \sin m\theta & 0 \\
-\sin m\theta & \cos m\theta & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
x' \\
y' \\
z'
\end{pmatrix}
\]

\[ (3.23) \]
3) Improper rotation $S_0$: the clockwise rotation of point $P(x, y, z)$ by $\theta^\circ$ about the $z$-axis, followed by a reflection in the plane perpendicular to $z$ transforms point $P(x, y, z)$ to new coordinates $P(x', y', z')$ via the matrix:

$$
\begin{pmatrix}
  x \\
  y \\
  z
\end{pmatrix}
\begin{pmatrix}
  \cos \theta & \sin \theta & 0 \\
  -\sin \theta & \cos \theta & 0 \\
  0 & 0 & -1
\end{pmatrix}
\begin{pmatrix}
  x' \\
  y' \\
  z'
\end{pmatrix}
$$

(3.24)

Figure 3.4: General rotation of point $P(x, y, z)$ through $\theta^\circ$ about the $z$-axis (after McMillan and Hess, 1988).

4) Mirror plane: the reflection of point $P(x, y, z)$ in mirror planes $xy$, $xz$, and $yz$ produce the new Cartesian coordinates $P(x', y', z')$ via the matrices:

$$
\sigma_{(xy)} = \begin{pmatrix}
  1 & 0 & 0 \\
  0 & 1 & 0 \\
  0 & 0 & -1
\end{pmatrix} \quad \sigma_{(xz)} = \begin{pmatrix}
  1 & 0 & 0 \\
  0 & -1 & 0 \\
  0 & 0 & 1
\end{pmatrix} \quad \sigma_{(yz)} = \begin{pmatrix}
  -1 & 0 & 0 \\
  0 & 1 & 0 \\
  0 & 0 & 1
\end{pmatrix}
$$

(3.25)
5) *Inversion centre, i:* the inversion of point \( P(x, y, z) \) through a centre produces the new coordinates \( P(-x, -y, -z) \) via the matrix:

\[
i = \begin{pmatrix}
-1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & -1
\end{pmatrix}
\]

(3.26)

The symmetry operations of a point group may be expressed in terms of a list of transformation matrices. For example, the matrix representation for the \( \text{H}_2\text{O} \) molecule which belongs to point group \( C_{2v} \), is:

\[
I = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
C_2 = \begin{pmatrix}
1 & 0 & 0 \\
0 & -1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
\sigma_{(xz)} = \begin{pmatrix}
1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

\[
\sigma_{(yz)} = \begin{pmatrix}
-1 & 0 & 0 \\
0 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

(3.27)

### 3.4.3 Irreducible Representations

In order to simplify the matrix representation of a point group, the representation is rewritten using \([1x1]\) matrices for each symmetry operation associated with each of the individual basis vectors \( x, y \) and \( z \), which originate from the invariant point of the system. Thus, the reduced representation of point group \( C_{2v} \) is:

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>I</th>
<th>( C_2 )</th>
<th>( \sigma(xz) )</th>
<th>( \sigma(yz) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basis ( x = \Gamma_x ):</td>
<td>{1, \ -1}</td>
<td>1, \ -1, \ 1</td>
<td>{1}</td>
<td></td>
</tr>
<tr>
<td>Basis ( y = \Gamma_y ):</td>
<td>{1, \ -1}</td>
<td>1, \ -1, \ 1</td>
<td>{1}</td>
<td></td>
</tr>
<tr>
<td>Basis ( z = \Gamma_z ):</td>
<td>{1}</td>
<td>1, \ 1, \ 1</td>
<td>{1}</td>
<td></td>
</tr>
</tbody>
</table>

These one-dimensional representations cannot be reduced further by a different choice of basis vectors and are therefore known as the *irreducible representations* of the group. The number of possible irreducible representations for any point group is governed by the properties of the group. For point group \( C_{2v} \), there are actually four irreducible representations derived from combinations of behaviour with respect to the symmetry operations.
The values +1 and -1 are taken to represent symmetric and antisymmetric behaviour with respect to each operation, respectively *(i.e. the basis vectors remain the same or change direction)*; all members of the basis must be symmetric to the identity operation. For the H$_2$O molecule, it is impossible to be simultaneously antisymmetric with respect to the C$_2$ axis and both mirror planes. Hence {1,-1,-1,-1} does not constitute a valid irreducible representation. Therefore, $\Gamma_1$-$\Gamma_4$ are the only possible irreducible representations for H$_2$O, and these are given the conventional spectroscopic symbols $A_1$, $A_2$, $B_1$ and $B_2$. In this example, only 3 Cartesian vectors were used as a basis for the matrix representation. In molecular systems, it is more common to place 3 such vectors on each of the atoms, producing a much larger basis set. Thus, a [9x9] matrix is generated to represent an H$_2$O molecule, although all matrix representations may be expressed in terms of a number of elementary irreducible representations. In large matrices, the irreducible representations may not be immediately deduced as the coefficients of the matrix representations may not lie along the diagonal as before. In order to reduce such matrices, a different set of basis vectors must be chosen which results in all matrix coefficients positioned along the matrix diagonals. For H$_2$O, the new basis set, $\xi_n$, may be derived from linear combinations of the Cartesian vectors for the 2 hydrogen atoms, with the basis vectors for the oxygen atom remaining unchanged. The diagonalized matrices generated by these new basis vectors allow the [1x1] matrix representations corresponding to each $\Gamma(\xi_i)$, and thus the irreducible representations of the point group to be deduced.
The irreducible representations of this point group may be written in terms of their conventional spectroscopic symbols, which denote their *symmetry species*:

\[ \Gamma = 3A_1 + A_2 + 2B_1 + 3B_2 \]  

(3.28)

In more complex molecular systems, the matrix representations cannot be diagonalized simply from linear combinations of the original basis vectors. Instead, more efficient and sophisticated methods for the reduction of group representations have been developed, based on the algebraic relations inherent in Group theory. In general, once a basis set is defined, an associated transformation matrix \( A_R \), exists for each symmetry operation \( R \), of the point group:

\[
A_R = \begin{pmatrix}
    a_{11} & a_{12} & a_{13} & a_{14} & \ldots & a_{1n} \\
    a_{21} & a_{22} & a_{23} & \ldots & \ldots & \ldots \\
    a_{31} & a_{32} & \ldots & \ldots & \ldots & \ldots \\
    a_{41} & \ldots & \ldots & \ldots & \ldots & \ldots \\
    \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\
    a_{n1} & \ldots & \ldots & \ldots & \ldots & a_{nn}
\end{pmatrix}
\]  

(3.29)

A transformation matrix \( S \), must then be determined which will simultaneously diagonalize all matrices \( A_R \) and reduce them to block diagonal form \( D_R \), using the similarity transformation:

\[
D_R = S^{-1} A_R S
\]  

(3.30)

where \( S^{-1} \) is the inverse of matrix \( S \). The irreducible representations of point groups such as \( C_{2v} \) are all one-dimensional or *singly degenerate*, and complete reduction of the matrix representation leads to fully diagonal matrices \( D_R \), with \( \pm 1 \) along the diagonal. This is also true for point groups \( C_1, C_2, C_{nv}, C_2, C_{2h}, D_2 \) and \( D_{2h} \). For the remaining point groups, complete reduction of the original matrix representation leads to block-factored matrices \( D_R \), which contain \([2x2] \) or \([3x3] \) blocks along the leading diagonal that cannot be reduced further by any transformation. For example, an \( \text{NH}_3 \) molecule which has \( C_{3v} \) point group symmetry (with the \( C_3 \) rotation axis coincident with the \( z \)-axis) has the following matrix representations for its symmetry operations:
The irreducible representation for the basis vector \( \Gamma_x \) is easily determined as it is one-dimensional already: \( \Gamma_x = \{1, 1, 1, 1, 1, 1\} = A_1 \). The representations for basis vectors \( \Gamma_x \) and \( \Gamma_y \) are all two-dimensional:

\[
\sigma_{(\varphi)} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{(\psi)} = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix} \quad \sigma_{(\chi)} = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}
\]

These representations cannot be reduced further by a similarity transformation and are thus termed *doubly degenerate* and given the symbol \( E \). In the cubic point groups (e.g. \( O_h \)), all 3 directions in space are equivalent and so *triply* degenerate representations occur and these are given the symbols \( F \) or \( T \). In point groups which contain a centre of inversion, \( i \), the subscripts \( g \) (for *gerade* meaning even) and \( u \) (for *ungerade* meaning uneven) are used to refer to modes which show symmetric and antisymmetric behaviour about the inversion centre, respectively.

When two- and three-dimensional representations are deduced, it is more convenient to give the *character* or *trace* of each symmetry operation matrix as the irreducible representation. The character, \( \chi(A_\beta) \), of a square matrix is the sum of the elements along its leading diagonal, and remains unaffected by a similarity transformation. Thus, in terms of matrix characters, the irreducible representations for point group \( C_{3v} \) are shown in Table 3.1, and together constitute the \( C_{3v} \) point group character table. The subsets of symmetry elements \( \{ C_3^1, C_3^2 \} \) and \( \{ \sigma_v, \sigma_v, \sigma_v \} \) of the \( C_{3v} \) point group have the same character and thus behave in exactly the same way for each of the symmetry species, \( A_1 \), \( A_2 \) and \( E \). These subsets from classes within the point group and their characters may be grouped together in a shortened form of the character table (Table 3.2).
3.4.4 Prediction of Infrared- and Raman-Activity

The point group character tables have been derived for all symmetry groups (e.g. Adams and Newton, 1970; Fateley et al., 1972; Salthouse and Ware, 1972) and always indicate the symmetry species present and their relationship with the x, y, and z translations of the origin (T_{x}, T_{y}, T_{z}), rotations about the x-, y- and z-axes (R_{x}, R_{y}, R_{z}), and quadratic combinations of x, y and z. This information can be used to determine the IR- and Raman-activity of the symmetry species. The IR-active vibrations of a molecule belong to those symmetry species which correspond to T_{x}, T_{y}, and T_{z}. The dipole moment change \( \Delta \mu \), which must occur for a vibration to be IR-active, is a vector quantity which may be expressed in terms of Cartesian components \( \Delta \mu_x, \Delta \mu_y \) and \( \Delta \mu_z \). These components belong to the same symmetry species as Cartesian translations of the origin x, y and z and so will be active under IR light. For example, the complete \( C_{3v} \) point group character table (Table 3.2) shows that molecular vibrations corresponding to the \( A_1 \) and \( E \) symmetry species will be IR-active as they are associated with \( T_{z} \), \( T_{x} \), \( T_{y} \), respectively.

<table>
<thead>
<tr>
<th>( C_{3v} )</th>
<th>I</th>
<th>2C_{3}</th>
<th>3\sigma_{v}</th>
<th>Translations/Rotations</th>
<th>Raman-activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( T_z )</td>
<td>( \alpha_{xx} + \alpha_{yy} + \alpha_{zz} )</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>( R_z )</td>
<td></td>
</tr>
<tr>
<td>( E )</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>( (T_x, T_y) ); ( (R_x, R_y) )</td>
<td>( (\alpha_{xx}, \alpha_{yy}, \alpha_{xy}), (\alpha_{xz}, \alpha_{yz}) )</td>
</tr>
</tbody>
</table>

Table 3.2: The \( C_{3v} \) point group character table, showing the IR- and Raman-activity of the symmetry species.
Point group character tables show explicitly which symmetry species will be Raman-active from the listed polarizability tensor elements $\alpha_{xx}$, $\alpha_{yy}$, $\alpha_{zz}$, $\alpha_{xy}$, $\alpha_{xz}$ and $\alpha_{yz}$. These expressions of polarizability change transform in the same way as the quadratic combinations of x, y and z within the point group, and symmetry species corresponding to these combinations will be Raman-active. For point group $C_{3v}$ (Table 3.2), vibrations with $A_1$ or $E$ symmetry will be Raman-active, as they are associated with components of the polarizability tensor. For this point group, modes with $E$ symmetry will therefore be both IR- and Raman-active. Molecules or unit cells which belong to point groups containing a centre of inversion $i$, have IR-active vibrations which are never Raman-active, and vice versa; vibrational modes which are neither IR- or Raman-active are said to be inactive. The quadratic combinations of x, y and z also indicate which polarization directions may be used in Raman spectroscopic experiments in order to obtain spectra containing vibrational modes of specific symmetry species. Thus, for point group $C_{3v}$, the $\alpha_{xz}$ polarization direction may be used to obtain a spectrum with vibrational modes of $A_1$ symmetry, while the $\alpha_{xy}$ polarization direction could be used to determine the frequencies with $E$ symmetry.

3.5 Simulation of the Infrared- and Raman-Active Modes of Pyrope Garnet

3.5.1 Introduction

The aluminosilicate garnets have a cubic structure and belong to space group $Ia\overline{3}d$ (No.230) and point group $O_{h}^{10}$. The highly symmetric structure contains 48 symmetry elements, the symmetry operations of which transform a point $P(x, y, z)$ to new coordinates as follows:

<table>
<thead>
<tr>
<th>Operation:</th>
<th>Transformation:</th>
<th>Axis:</th>
<th>Rotation:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity, $I$:</td>
<td>$P(x, y, z) \rightarrow (x, y, z)$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Inversion, $i$:</td>
<td>$P(x, y, z) \rightarrow (\overline{x}, \overline{y}, \overline{z})$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Operation:</td>
<td>Transformation:</td>
<td>Axis:</td>
<td>Rotation:</td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
<td>------</td>
<td>----------</td>
</tr>
<tr>
<td>2-fold rotations, $C_2$:</td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{2}x, \ y, \ \frac{1}{2}z\right)$</td>
<td>[001]</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{2}+x, \ \frac{1}{2}+y, \ \frac{1}{2}-z\right)$</td>
<td>[100]</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\bar{x}, \ \frac{1}{2}+y, \ \frac{1}{2}-z\right)$</td>
<td>[010]</td>
<td>-</td>
</tr>
<tr>
<td>2-fold rotations, $C'_{2}$:</td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}+y, \ \frac{1}{4}+x, \ \frac{1}{4}-z\right)$</td>
<td>[110]</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}-y, \ \frac{1}{4}-x, \ \frac{1}{4}+z\right)$</td>
<td>[1\bar{1}0]</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}+x, \ \frac{1}{4}+z, \ \frac{1}{4}+y\right)$</td>
<td>[011]</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}-x, \ \frac{1}{4}-z, \ \frac{1}{4}-y\right)$</td>
<td>[01\bar{1}]</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}+z, \ \frac{1}{4}-y, \ \frac{1}{4}+x\right)$</td>
<td>[101]</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}-z, \ \frac{1}{4}-y, \ \frac{1}{4}-x\right)$</td>
<td>[\bar{1}01]</td>
<td>-</td>
</tr>
<tr>
<td>3-fold rotations, $C_{3}$:</td>
<td>$P(x, y, z) \rightarrow (y, \ z, \ x)$</td>
<td>[111]</td>
<td>$3^1$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow (x, \ y, \ z)$</td>
<td>[111]</td>
<td>$3^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{2}-z, \ \frac{1}{2}+x, \ \frac{1}{2}+y\right)$</td>
<td>[\bar{1}11]</td>
<td>$3^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\bar{y}, \ \frac{1}{2}+z, \ \frac{1}{2}-x\right)$</td>
<td>[\bar{1}1\bar{1}]</td>
<td>$3^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{2}+y, \ \frac{1}{2}-z, \ \bar{x}\right)$</td>
<td>[1\bar{1}1]</td>
<td>$3^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{2}+z, \ \frac{1}{2}-x, \ \bar{y}\right)$</td>
<td>[1\bar{1}\bar{1}]</td>
<td>$3^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{2}y, \ \bar{z}, \ \frac{1}{2}+x\right)$</td>
<td>[1\bar{1}1]</td>
<td>$3^{-1}$</td>
</tr>
<tr>
<td>4-fold rotations, $C_{4}$:</td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}+y, \ \frac{1}{4}-x, \ \frac{1}{4}+z\right)$</td>
<td>[001]</td>
<td>$4^1$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}-y, \ \frac{1}{4}+x, \ \frac{1}{4}+z\right)$</td>
<td>[001]</td>
<td>$4^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}+x, \ \frac{1}{4}+z, \ \frac{1}{4}-y\right)$</td>
<td>[100]</td>
<td>$4^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}+x, \ \frac{1}{4}-z, \ \frac{1}{4}+y\right)$</td>
<td>[100]</td>
<td>$4^1$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}-z, \ \frac{1}{4}+y, \ \frac{1}{4}+x\right)$</td>
<td>[010]</td>
<td>$4^{-1}$</td>
</tr>
<tr>
<td></td>
<td>$P(x, y, z) \rightarrow \left(\frac{1}{4}+z, \ \frac{1}{4}+y, \ \frac{1}{4}-x\right)$</td>
<td>[010]</td>
<td>$4^1$</td>
</tr>
</tbody>
</table>
### Operation: 3-fold roto-inversions, $S'_6$:

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Axis: $[111]$</th>
<th>Rotation: $3^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(x, y, z) \rightarrow (\bar{y}, \bar{z}, \bar{x})$</td>
<td>$[111]$ x $i$</td>
<td>$3^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\bar{z}, \bar{x}, \bar{y})$</td>
<td>$[111]$ x $i$</td>
<td>$3^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (y, \frac{1}{2}-z, \frac{1}{2}+x)$</td>
<td>$[\bar{1}11]$ x $i$</td>
<td>$3^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{2}+z, x, \frac{1}{2}-y)$</td>
<td>$[\bar{1}11]$ x $i$</td>
<td>$3^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (z, \frac{1}{2}-x, \frac{1}{2}+y)$</td>
<td>$[\bar{1}11]$ x $i$</td>
<td>$3^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{2}-y, \frac{1}{2}+z, x)$</td>
<td>$[\bar{1}11]$ x $i$</td>
<td>$3^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{2}-z, \frac{1}{2}+x, y)$</td>
<td>$[\bar{1}11]$ x $i$</td>
<td>$3^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{2}+y, z, \frac{1}{2}-x)$</td>
<td>$[\bar{1}11]$ x $i$</td>
<td>$3^1$</td>
</tr>
</tbody>
</table>

### Operation: 4-fold roto-inversions, $S'_4$:

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Axis: $[001]$</th>
<th>Rotation: $4^1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{4}-y, \frac{3}{4}+x, \frac{1}{4}-z)$</td>
<td>$[001]$</td>
<td>$4^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{3}{4}+y, \frac{1}{4}-x, \frac{1}{4}-z)$</td>
<td>$[001]$</td>
<td>$4^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{4}-x, \frac{3}{4}-z, \frac{3}{4}+y)$</td>
<td>$[100]$</td>
<td>$4^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{4}-x, \frac{3}{4}+z, \frac{1}{4}-y)$</td>
<td>$[100]$</td>
<td>$4^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{3}{4}+z, \frac{1}{4}-y, \frac{1}{4}-x)$</td>
<td>$[010]$</td>
<td>$4^1$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{4}-z, \frac{3}{4}-y, \frac{3}{4}+x)$</td>
<td>$[010]$</td>
<td>$4^1$</td>
</tr>
</tbody>
</table>

### Horizontal mirror planes, $\sigma_h$:

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Axis: $[100]$</th>
<th>Rotation: $\bar{4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{2}-x, \frac{1}{2}+y, z)$</td>
<td>$[100]$</td>
<td>$\bar{4}$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{2}+x, y, \frac{1}{2}-z)$</td>
<td>$[001]$</td>
<td>$\bar{4}$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (x, \frac{1}{2}-y, \frac{1}{2}+z)$</td>
<td>$[010]$</td>
<td>$\bar{4}$</td>
</tr>
</tbody>
</table>

### Diagonal mirror planes, $\sigma_d$:

<table>
<thead>
<tr>
<th>Transformation</th>
<th>Axis: $[011]$</th>
<th>Rotation: $\bar{4}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{4}+x, \frac{1}{4}+z, \frac{1}{4}+y)$</td>
<td>$[011]$</td>
<td>$\bar{4}$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{4}+y, \frac{1}{4}+x, \frac{1}{4}+z)$</td>
<td>$[110]$</td>
<td>$\bar{4}$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{4}+z, \frac{1}{4}+y, \frac{1}{4}+x)$</td>
<td>$[101]$</td>
<td>$\bar{4}$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{1}{4}-y, \frac{3}{4}-x, \frac{3}{4}+z)$</td>
<td>$[010]$</td>
<td>$\bar{4}$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{3}{4}+x, \frac{1}{4}-z, \frac{3}{4}-y)$</td>
<td>$[011]$</td>
<td>$\bar{4}$</td>
</tr>
<tr>
<td>$P(x, y, z) \rightarrow (\frac{3}{4}-z, \frac{3}{4}+y, \frac{3}{4}-x)$</td>
<td>$[101]$</td>
<td>$\bar{4}$</td>
</tr>
</tbody>
</table>

The $O_h$ point group character table, derived from the traces of the irreducible representations of the transformation matrices describing these symmetry operations, is
shown in Table 3.3, with the IR and Raman selection rules for the symmetry species indicated. The first step in simulating the IR- and Raman-activity of any crystalline solid is to determine fully the symmetry relations between the atoms in the crystal structure. For garnet, this analysis demonstrated that the Mg- and Si-cations, are related to all other Mg- and Si-cations, respectively, by the set of symmetry elements:

\[ \{I, i, C_2, 4C'_2, 4C_3, 2C_4, 4S'_6, 4S'_4, \sigma_h, 2\sigma_d\} \] (3.33)

Each oxygen atom is related to 35 other oxygens by either:

\[ \{I, i, 3C_2, 8C_3, 8S'_6, 6S'_4, 3\sigma_h, 6\sigma_d\} \text{ or } \{I, i, 3C_2, 6C'_2, 8C_3, 6C_4, 8S'_6, 3\sigma_h\} \] (3.34)

The 4 Al-cations located at \((0, 0, 0), (0, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, 0, \frac{1}{2})\) and \((\frac{1}{2}, \frac{1}{2}, 0)\) have the highest symmetry in the garnet structure, and are related to each other and the remaining Al-cations by the symmetry element set:

\[ \{I, i, 3C_2, 6C'_2, 8C_3, 6C_4, 8S'_6, 6S'_4, 3\sigma_h, 6\sigma_h\}\] (3.35)

The other 4 Al-cations positioned at \((\frac{1}{4}, \frac{1}{4}, \frac{1}{4}), (\frac{1}{4}, \frac{3}{4}, \frac{3}{4}), (\frac{3}{4}, \frac{1}{4}, \frac{3}{4})\) and \((\frac{3}{4}, \frac{3}{4}, \frac{1}{4})\) are related to each other and the aforementioned Al atoms via the symmetry element set:

\[ \{I, i, 3C_2, 6C'_2, 8C_3, 6C_4\} \] (3.36)

Once the atomic interrelations are known, the vibrational frequencies and the Cartesian components of the atomic displacements under each frequency (eigenvectors) may be calculated and subsequently analyzed in order to ascertain the symmetry of the vibrations and hence, their IR- or Raman-activity.
Table 3.3: The $O_h$ point group character table (after Fateley et al., 1972) indicating the symmetry species present in garnet, and the selection rules governing the infrared- and Raman-activity, or inactivity of the symmetry species. The positive values in the table indicate which symmetry elements must be maintained in order for a mode to belong to a particular symmetry species; the negative values show which symmetry elements are destroyed during a vibration associated with a particular symmetry species.

<table>
<thead>
<tr>
<th>Symmetry Species</th>
<th>Character</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>Raman-active $\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>1</td>
<td>Inactive</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1</td>
<td>Inactive</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>Inactive</td>
</tr>
<tr>
<td>$E_{g}$</td>
<td>2</td>
<td>Raman-active $\alpha_{xx} + \alpha_{yy} - 2\alpha_{zz}, \alpha_{xx} - \alpha_{yy}$</td>
</tr>
<tr>
<td>$E_{u}$</td>
<td>2</td>
<td>Inactive</td>
</tr>
<tr>
<td>$F_{1g}$</td>
<td>3</td>
<td>Inactive (R_x, R_y, R_z)</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>3</td>
<td>Infrared-active (T_x, T_y, T_z)</td>
</tr>
<tr>
<td>$F_{2g}$</td>
<td>3</td>
<td>Raman-active $\alpha_{xy}, \alpha_{xz}, \alpha_{yz}$</td>
</tr>
<tr>
<td>$F_{2u}$</td>
<td>3</td>
<td>Inactive</td>
</tr>
</tbody>
</table>
3.5.2 Calculation and Analysis of Vibrational Frequencies and Eigenvectors

The PARAPoCS code (Parker and Price, 1989) was used to calculate the 240 vibrational frequencies and associated eigenvectors (see equations 2.28-2.37) of the primitive unit cell of pyrope, using the same interatomic potentials as employed in our previous simulations (Table 2.2). Although these potentials do not fully describe the elastic behaviour of pyrope, they provide a good description of its vibrational properties, from consideration of the parameters calculated from the vibrational density of states. The calculations were performed at a point close to the Brillouin zone centre, at \( \mathbf{k} = (0.0, 0.0, 0.0001) \). Simulations of this type cannot be made at precisely the zone centre, where the acoustic modes are zero, due to poorly-constrained calculation of the optic modes at this point. The LO acoustic mode was calculated to be 0.06 cm\(^{-1}\) at this point, suggesting that this is the maximum error in the calculated frequencies of the vibrational modes. The optic modes of pyrope were calculated to lie in the range 150-1070 cm\(^{-1}\) (with a frequency gap of approximately 100 cm\(^{-1}\) observed between 709 and 804 cm\(^{-1}\)), in good agreement with the experimental observations using IR spectroscopy (e.g. Moore et al., 1971; Hofmeister and Chopelas, 1991; Hofmeister et al., 1996).

The eigenvectors calculated for each frequency were analyzed in order to ascertain which symmetry elements were maintained or destroyed after the displacements of the atoms had occurred. This procedure allows the symmetry species for each vibrational mode to be identified and hence, the IR- or Raman-activity (or inactivity) of the modes to be determined. This was achieved using the \( \text{Oh} \) point group character table (Table 3.3), in which the positive values contained in the table indicate those symmetry elements which are maintained during a vibration associated with a particular symmetry species. Similarly, the negative values in the character table show which symmetry elements must be destroyed in order for a vibration to belong to a particular symmetry species. For example, for a vibrational mode to have \( A_{1g} \) symmetry, all symmetry elements must be maintained (as indicated by positive values for all symmetry elements in Table 3.3). The zero values contained in the table are less straightforward to interpret and so were not used in the analysis. The following sequence of tests was performed in order to ascertain which symmetry elements were maintained or destroyed during each vibrational frequency, so that the symmetry species of each vibrational mode of pyrope could be determined.
To separate 'g' and 'u' modes:

- Inversion, $i$ -
  - maintenance $\rightarrow$ 'g' modes
  - destruction $\rightarrow$ 'u' modes

To separate $A$, $E$ and $F$ modes:

- 3-fold rotations, $C_3$ -
  - maintenance $\rightarrow$ 'A' modes
  - destruction $\rightarrow$ 'E/F' modes

To subdivide 'g' modes:

- Diagonal mirror planes, $\sigma_d$ -
  - maintenance $\rightarrow$ 'A$_{1g}$' modes; 'F$_{2g}$' modes
  - destruction $\rightarrow$ 'A$_{2g}$' modes; 'F$_{1g}$' modes

To subdivide 'u' modes:

- Diagonal mirror planes, $\sigma_d$ -
  - maintenance $\rightarrow$ 'A$_{2u}$' modes; 'F$_{1u}$' modes
  - destruction $\rightarrow$ 'A$_{1g}$' modes; 'F$_{2u}$' modes

This was achieved by analyzing the sum of the eigenvectors for pairs of atoms known to be related by the symmetry element under investigation, which yields +1 for the maintenance of the symmetry element, or -1 for its destruction. Once the symmetry species of each vibrational frequency had been ascertained by this method, groupings of the $E$ and $F$ frequencies into their doubly- and triply-degenerate sets, respectively, was required. This was simple for the $E_u$, $F_{2u}$, $E_g$ and $F_g$ modes as the frequencies in each group are identical. However for the $F_{1u}$ modes, the situation is more complex, as these modes are IR-active (Table 3.3) and therefore have an LO-TO splitting. The 2 TO components are identical in value, but the corresponding LO component is expected to be raised in frequency relative to the TO pair (Born and Huang, 1954). Further analysis of the calculated eigenvectors for the $F_{1u}$ modes demonstrated that the column sum of the eigenvector matrix for each atom species gives values $x$, $y$, and $z$ for the first TO component, and $-y$, $x$, $z$ for the second TO component, where $z$ is always zero. The corresponding LO mode has eigenvector matrix column totals which are $z$, $z$, $|y-x|$, as required by the propagation directions of the longitudinal and transverse wave components. Thus, the frequencies of the IR-active (with LO-TO splittings), Raman-active and inactive modes determined from our analysis of the calculated eigenvectors of pyrope are shown in Tables 3.4-3.5. Our calculated IR-active TO modes show good agreement with those reported by Winkler et al. (1991) from their lattice dynamical simulations of pyrope, with an average difference of 7 cm$^{-1}$.  

126
<table>
<thead>
<tr>
<th>Infrared-Active Modes</th>
<th>Raman-Active Modes</th>
</tr>
</thead>
<tbody>
<tr>
<td>TO Modes</td>
<td>LO Modes</td>
</tr>
<tr>
<td>153.14</td>
<td>155.97</td>
</tr>
<tr>
<td>170.39</td>
<td>172.80</td>
</tr>
<tr>
<td>230.87</td>
<td>231.03</td>
</tr>
<tr>
<td>234.58</td>
<td>257.45</td>
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<td></td>
<td>850.52</td>
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<td>307.72</td>
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<td></td>
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<td>367.28</td>
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<td></td>
<td>875.81</td>
</tr>
<tr>
<td></td>
<td>1061.83</td>
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Table 3.4: Calculated IR- and Raman-active modes for pyrope (units: cm⁻¹).
<table>
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<td>$F_{lg}$</td>
<td>219.31</td>
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<tr>
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<td>313.92</td>
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<table>
<thead>
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<tr>
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<td>1001.14</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>1051.50</td>
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</tbody>
</table>

Table 3.5: Calculated inactive modes for pyrope (units: cm$^{-1}$) and their respective symmetry species.
The results of this analysis show that the total number of symmetry species for pyrope is:

\[
\Gamma_{\text{vib}} = 3A_{1g} + 5A_{2g} + 8E_g + 14F_{1g} + 14F_{2g} + 5A_{1u} + 5A_{2u} + 10E_u + 18F_{1u} + 16F_{2u}
\]  
(3.37)

in agreement with the Group theoretical determinations by Fateley et al. (1972) and Moore et al. (1971). Memagh and Liu (1990) used the factor group analysis method of Adams and Newton (1970) which predicts the total number of symmetry species for garnet to be:

\[
\Gamma_{\text{vib}} = 3A_{1g} + 4A_{2g} + 7E_g + 14F_{1g} + 15F_{2g} + 5A_{1u} + 4A_{2u} + 9E_u + 18F_{1u} + 17F_{2u}
\]  
(3.38)

This method yields a total of 95 vibrational modes (with one less $A_{2g}$, $E_g$, $A_{2u}$ and $E_u$ mode, and additional $F_{2g}$ and $F_{2u}$ modes) compared to that used by Moore et al. (1970) and Fateley et al. (1972), which predicts a total of 97 modes. Memagh and Liu (1990) introduced this method to account for the observed splitting of a single low-frequency $E_g$ mode into 2 separate peaks in the Raman spectrum at pressure, suggesting a lowering of the dodecahedral site symmetry responsible for this mode. However, our calculated coefficients for each symmetry species agree entirely with the analyses of Moore et al. (1971) and Fateley et al. (1972), and suggest that the factor group analysis reported by Memagh and Liu (1990) is not applicable to pyrope at ambient conditions.

Our calculated inactive modes of pyrope (Table 3.5) are of use in analyzing the calculations of Hofmeister and Chopelas (1991b), who constructed a Kieffer model (Kieffer, 1979, 1980) for pyrope from observed IR- and Raman-active vibrational frequencies. The underestimation of heat capacity and entropy by their model was partly attributed by Hofmeister and Chopelas (1991b) to inactive frequencies not included in the model. The upper cut-off frequency of the optic continuum chosen by Hofmeister and Chopelas (1991b) as 667 cm\textsuperscript{-1} appears to be too low, as our calculations suggest that the highest energy external mode occurs at approximately 710 cm\textsuperscript{-1}, marking the start of the calculated frequency gap. In the frequency interval between 667 and 710 cm\textsuperscript{-1}, there are 3 inactive modes (at 671, 685 and 694 cm\textsuperscript{-1}) and 1 IR-active mode (at 681-710 cm\textsuperscript{-1}) not included by Hofmeister and Chopelas (1991b), which will each provide an additional contribution to $C_p$ and $S$. Our calculations also show that the frequency range of the 4 Einstein oscillators selected
for the Kieffer model (890-1033 cm⁻¹), should be extended to 805-1068 cm⁻¹, a region which contains 3 IR-active, 3 Raman-active, and 11 inactive modes, suggesting that this part of the density of states cannot be modelled by four oscillators alone.

3.6 Derivation of the Vibrational Modes of Garnet from Atomic or Site Motions

3.6.1 Introduction

The factor group analysis used in the previous section is useful for ascertaining the correct symmetry of the vibrational modes and the selection rules which govern them. However, it provides little information regarding which atomic motions give rise to which vibrational frequencies. Instead a further site group to factor group correlation, as demonstrated by authors such as Moore et al. (1971) and Fateley et al. (1972), yields the theoretical derivation of the vibrational modes. Menzer (1926) established that in the garnet structure, the X-cations have D₂ site symmetry, the Y-cations S₆ symmetry, the Si-cations S₄ symmetry, with the oxygen atoms in general sites, C₁. By correlating the symmetry species of the individual site groups with those of the factor group (Oₘ), the symmetry of the modes arising from each site may be determined.

3.6.2 Mg-Cations in Site D₂

The D₂ site group character table (Table 3.6) shows that the singly-degenerate B₁, B₂ and B₃ modes are related to the x, y, and z translations of the origin Tₓ, Tᵧ, and Tₚ, respectively.

<table>
<thead>
<tr>
<th></th>
<th>D₂</th>
<th>I</th>
<th>C₂(z)</th>
<th>C₂(y)</th>
<th>C₂(x)</th>
<th>Translations/ Rotations</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
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<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>B₁</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>Tₓ, Rₓ</td>
</tr>
<tr>
<td>B₂</td>
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<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>Tᵧ, Rᵧ</td>
</tr>
<tr>
<td>B₃</td>
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<td>-1</td>
<td>-1</td>
<td>1</td>
<td></td>
<td>Tₓ, Rₓ</td>
</tr>
</tbody>
</table>

Table 3.6: The D₂ point group character table (from Fateley et al., 1972).
Correlation of these species with the $O_h$ factor group, using the $D_2\rightarrow O_h$ correlation table (Table 3.7) establishes which of the symmetry species of the factor group have the same character as the symmetry operations of point group $D_2$.

<table>
<thead>
<tr>
<th></th>
<th>$O_h$</th>
<th>$3C_2$</th>
<th>$D_2$</th>
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<tr>
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<td>1</td>
<td>$A$</td>
</tr>
<tr>
<td>$A_{2g}$</td>
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<td>2</td>
<td>2</td>
<td>$A+B_1$</td>
</tr>
<tr>
<td>$F_{1g}$</td>
<td>3</td>
<td>-1</td>
<td>$B_1+B_2+B_3$</td>
</tr>
<tr>
<td>$F_{2g}$</td>
<td>3</td>
<td>-1</td>
<td>$A+B_2+B_3$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
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<td>1</td>
<td>$A$</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>1</td>
<td>$B_1$</td>
</tr>
<tr>
<td>$E_u$</td>
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<td>$A+B_1$</td>
</tr>
<tr>
<td>$F_{1u}$</td>
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<td>-1</td>
<td>$B_1+B_2+B_3$</td>
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<tr>
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<td>3</td>
<td>-1</td>
<td>$A+B_2+B_3$</td>
</tr>
</tbody>
</table>

Table 3.7: The correlation table for correlation between site group $D_2$ and factor group $O_h$ symmetry species (from Fateley et al., 1972).

Table 3.7 shows that the $D_2$ site symmetry species can be correlated with those of the $O_h$ factor group as follows:

$$
\begin{align*}
B_1 & \rightarrow A_{2g} + E_g + F_{1g} + A_{2u} + E_u + F_{1u} \\
B_2 & \rightarrow F_{1g} + F_{2g} + F_{1u} + F_{2u} \\
B_3 & \rightarrow F_{1g} + F_{2g} + F_{1u} + F_{2u}
\end{align*}
$$

Thus, the site group analysis (SGA) predicts the total number of translatory modes arising from the motions of the Mg-cations in the $D_2$ sites to be:

$$
\Gamma_{T(Mg)} = A_{2g} + E_g + 3F_{1g} + 2F_{2g} + A_{2u} + E_u + 3F_{1u} + 2F_{2u}
$$

(3.40)
3.6.3 Si-Cations in Site $S_4$

The $S_4$ site group character table (Table 3.8) shows that the singly-degenerate $B$, and doubly-degenerate $E$ symmetry species are associated with the $T_z$, and $T_x$ and $T_y$ translation components, respectively.

<table>
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<th>$I$</th>
<th>$S_4$</th>
<th>$C_2$</th>
<th>$S_4^3$</th>
<th>Translations/ Rotations</th>
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</thead>
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<tr>
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<td>-i</td>
<td>($T_x$, $T_y$)</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>-i</td>
<td>-1</td>
<td>i</td>
<td>($R_x$, $R_y$)</td>
</tr>
</tbody>
</table>

Table 3.8: The $S_4$ character table (after Fateley *et al.*, 1972).

As the $E$ modes are associated with both the $T_x$ and $T_y$ translational components, the coefficients of the corresponding modes in the $O_h$ factor group must be doubled. Correlation of the $S_4$ site group symmetry species with those of the $O_h$ factor group (Table 3.9) again establishes which of the symmetry species of the factor group have the same character as the symmetry operations of point group $S_4$.

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$S_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$A$</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>$B$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$A + B$</td>
</tr>
<tr>
<td>$F_{1g}$</td>
<td>$A + E$</td>
</tr>
<tr>
<td>$F_{2g}$</td>
<td>$B + E$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>$B$</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>$A$</td>
</tr>
<tr>
<td>$E_u$</td>
<td>$A + B$</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>$B + E$</td>
</tr>
<tr>
<td>$F_{2u}$</td>
<td>$A + E$</td>
</tr>
</tbody>
</table>

Table 3.9: Correlation between site group $S_4$ and factor group $O_h$ (after Fateley *et al.*, 1972).
This correlation yields:

\[ B \rightarrow A_{2g} + E_g + F_{2g} + A_{1u} + E_u + F_{1u} \]
\[ E \rightarrow 2F_{1g} + 2F_{2g} + 2F_{1u} + 2F_{2u} \]  
(3.41)

Thus, the total number of translatory modes arising from the motions of the Si-cations is predicted to be:

\[ \Gamma_{T(Si)} = A_{1g} + E_g + 2F_{1g} + 3F_{2g} + A_{1u} + E_u + 3F_{1u} + 2F_{2u} \]  
(3.42)

3.6.4 Al-Cations in Site \( S_6 \)

The \( S_6 (= C_{3i}) \) site group character table (Table 3.10) indicates that the symmetry species \( A_u \) and \( E_u \) are associated with translational components \( T_z \), \( T_x \), and \( T_y \), respectively.

<table>
<thead>
<tr>
<th>( S_6 )</th>
<th>I</th>
<th>( C_3 )</th>
<th>( C_3^2 )</th>
<th>( i )</th>
<th>( S_6^5 )</th>
<th>( S_6 )</th>
<th>Translations/ Rotations</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( R_z )</td>
</tr>
<tr>
<td>( E_g )</td>
<td>1</td>
<td>( \varepsilon )</td>
<td>( \varepsilon^* )</td>
<td>( \varepsilon )</td>
<td>1</td>
<td>( \varepsilon )</td>
<td>( \varepsilon^* )</td>
</tr>
<tr>
<td>( A_u )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>( T_z )</td>
</tr>
<tr>
<td>( E_u )</td>
<td>1</td>
<td>( \varepsilon )</td>
<td>( \varepsilon^* )</td>
<td>( \varepsilon )</td>
<td>-1</td>
<td>-( \varepsilon )</td>
<td>-( \varepsilon^* )</td>
</tr>
</tbody>
</table>

Table 3.10: The \( S_6 \) point group character table (from Fateley et al., 1972), where \( \varepsilon = e^{2\pi/3} \).

As the \( E_u \) modes are associated with both \( T_x \) and \( T_y \) translations, the coefficients of the \( O_h \) symmetry species correlated to these modes (Table 3.11) must again be multiplied by a factor of 2.
Table 3.11: Correlation of the $S_6$ site group to the $O_h$ factor group (after Fateley et al., 1972).

<table>
<thead>
<tr>
<th>$O_h$</th>
<th>$S_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$A_g$</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>$A_g$</td>
</tr>
<tr>
<td>$E_g$</td>
<td>$E_g$</td>
</tr>
<tr>
<td>$F_{1g}$</td>
<td>$A_g + E_g$</td>
</tr>
<tr>
<td>$F_{2g}$</td>
<td>$A_g + E_g$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>$A_u$</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>$A_u$</td>
</tr>
<tr>
<td>$E_u$</td>
<td>$E_u$</td>
</tr>
<tr>
<td>$F_{1u}$</td>
<td>$A_u + E_u$</td>
</tr>
<tr>
<td>$F_{2u}$</td>
<td>$A_u + E_u$</td>
</tr>
</tbody>
</table>

The $S_6$ site group to $O_h$ factor group correlation yields:

\[
A_u \rightarrow A_{1u} + A_{2u} + F_{1u} + F_{2u} \\
E_u \rightarrow 2E_u + 2F_{1u} + 2F_{2u}
\]  

(3.43)

Thus, the total number of translatory modes arising from the motions of the Al-cations in the $S_6$ sites is:

\[
\Gamma_{T(Al)} = A_{1u} + A_{2u} + 2E_u + 3F_{1u} + 3F_{2u}
\]

(3.44)

3.6.5 Oxygen Atoms in $C_1$ Sites

The singly-degenerate $A$ symmetry species of the $C_1$ site group is associated with all three translational components $T_x$, $T_y$ and $T_z$. Thus, the coefficients of the corresponding $O_h$ factor group symmetry species must be multiplied by a factor of 3. Correlation of the symmetry species of the $C_1$ site group with those of the $O_h$ character
Table 3.12 (Table 3.12) yields the following total number of modes predicted to arise from the motions of the oxygen atoms:

\[ \Gamma_{Ox} = 3A_{1g} + 3A_{2g} + 6E_g + 9F_{1g} + 9F_{2g} + 3A_{1u} + 3A_{2u} + 6E_u + 9F_{1u} + 9F_{2u} \]  

(3.45)

<table>
<thead>
<tr>
<th>( O_h )</th>
<th>( C_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_{1g} )</td>
<td>A</td>
</tr>
<tr>
<td>( A_{2g} )</td>
<td>A</td>
</tr>
<tr>
<td>( E_g )</td>
<td>2A</td>
</tr>
<tr>
<td>( F_{1g} )</td>
<td>3A</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>3A</td>
</tr>
<tr>
<td>( A_{1u} )</td>
<td>A</td>
</tr>
<tr>
<td>( A_{2u} )</td>
<td>A</td>
</tr>
<tr>
<td>( E_u )</td>
<td>2A</td>
</tr>
<tr>
<td>( F_{1u} )</td>
<td>3A</td>
</tr>
<tr>
<td>( F_{2u} )</td>
<td>3A</td>
</tr>
</tbody>
</table>

Table 3.12: Correlation of the translational symmetry species between site group \( C_1 \) and factor group \( O_h \).

The vibrational modes predicted to arise from the motions of the oxygen atoms may also be described in terms of the motions of the SiO\(_4\) tetrahedra, which are considered to behave almost independently of the remaining structural components. These discrete tetrahedral motions are commonly described in terms of external (rotations of the entire tetrahedron) and internal (bending and stretching of the Si-O bonds) modes. The translatory modes associated with this molecule have previously been derived from the motions of the Si-cations in the S\(_4\) sites. The internal modes of the SiO\(_4\) tetrahedra (Fig.3.5) consist of symmetric and antisymmetric stretching vibrations (denoted as \( \nu_1 \) and \( \nu_3 \) modes, respectively), and symmetric and antisymmetric bending vibrations (\( \nu_2 \) and \( \nu_4 \) modes, respectively).
The distinction between symmetry species arising from the internal and external modes of the SiO$_4$ tetrahedra may be made by analyzing the symmetry species associated with the $v_1$-$v_4$ modes. The SiO$_4$ tetrahedral molecule usually has $T_d$ site symmetry, but within the garnet structure, the symmetry of this molecule is reduced to $S_4$, due to distortion along the 4-fold roto-inversion axis located through its centre (Fig. 3.6). This distortion results in 2 of the O-O distances being considerably shorter (2.494 Å) than the 4 remaining distances (2.751 Å) (Abrahams and Geller, 1958; Novak and Gibbs, 1971; Meagher, 1975). Thus, in order to derive the symmetry species associated with the $v_1$-$v_4$ motions, a further correlation between the $T_d$ and $S_4$ site groups must be made (Table 3.13) through which, removal of some of the degeneracy or site splitting occurs by the descent in symmetry.

<table>
<thead>
<tr>
<th>Mode</th>
<th>$T_d$</th>
<th>$S_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>$12A_{1g}$</td>
<td>$12A$</td>
</tr>
<tr>
<td>$v_2$</td>
<td>$12E_g$</td>
<td>$12A + 12B$</td>
</tr>
<tr>
<td>$v_3$</td>
<td>$12F_{2g}$</td>
<td>$12B + 12E$</td>
</tr>
<tr>
<td>$v_4$</td>
<td>$12F_{2g}$</td>
<td>$12B + 12E$</td>
</tr>
</tbody>
</table>

Table 3.13: Symmetry species associated with the $v_1$-$v_4$ vibrations of the SiO$_4$ molecule in the garnet structure for the $T_d$ and $S_4$ site groups.
By reversal of this correlation, the $O_h$ factor group species to which these internal modes belong may be determined (Fig. 3.7). Thus, the symmetry species arising from the internal modes of the SiO$_4$ tetrahedra are predicted to be:

$$\Gamma_{\text{internal}} = 2A_{1g} + 3A_{2g} + 5E_g + 6F_{1g} + 7F_{2g} + 3A_{1u} + 2A_{2u} + 5E_u + 7F_{1u} + 6F_{2u} \quad (3.46)$$

Consequently, the rotatory modes arising from SiO$_4$ motions are predicted to be:

$$\Gamma_{R(\text{SiO}_4)} = A_{1g} + E_g + 3F_{1g} + 2F_{2g} + A_{2u} + E_u + 2F_{1u} + 3F_{2u} \quad (3.47)$$
In summary, the predicted number of modes arising from the translatory motions of the cations, and the internal and external modes of the SiO$_4$ tetrahedra in garnet determined from the site group to factor group correlation are (Table 3.14):

<table>
<thead>
<tr>
<th>$S_4$</th>
<th>$T_d$</th>
<th>$O_h$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>12A</td>
<td>$2A_{1g}$ $2E_g$ $2F_{1g}$</td>
</tr>
<tr>
<td></td>
<td>12B</td>
<td>$2A_{2g}$ $2E_g$ $2F_{2g}$</td>
</tr>
<tr>
<td>$v_3, v_4$</td>
<td>12E</td>
<td>$4F_{1g}$ $4F_{2g}$</td>
</tr>
</tbody>
</table>

**Figure 3.7**: Site to factor group correlation for the $v_1$-$v_4$ internal SiO$_4$ modes.
Table 3.14: Summary of the cation and SiO₄ tetrahedral site motions associated with the symmetry species of the O₅ point group for pyrope.

<table>
<thead>
<tr>
<th></th>
<th>T(Mg)</th>
<th>T(Al)</th>
<th>T(SiO₄)</th>
<th>R(SiO₄)</th>
<th>v₁</th>
<th>v₂</th>
<th>v₃</th>
<th>v₄</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁g</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>A₂g</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>E₉</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>8</td>
</tr>
<tr>
<td>F₁g</td>
<td>3</td>
<td>0</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>14</td>
</tr>
<tr>
<td>F₂g</td>
<td>2</td>
<td>0</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>14</td>
</tr>
<tr>
<td>A₁u</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>5</td>
</tr>
<tr>
<td>A₂u</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>E₉</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td>F₁u</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>18</td>
</tr>
<tr>
<td>F₂u</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>16</td>
</tr>
</tbody>
</table>

3.7 Assignment of Calculated Modes to Specific Atomic/Site Motions

3.7.1 Introduction

The calculated eigenvectors for the IR- and Raman-active vibrational modes of pyrope were further analyzed, together with the mode shifts arising from simulated isotopic substitutions, in order to establish the dominant site or atomic motions contributing to each mode, and to test the validity of the site group model described in section 3.6.

3.7.2 Calculation of Mode Shifts Due to Isotopic Substitution

The IR and Raman modes of pyrope were recalculated using the same interatomic potentials (Table 2.2), with substitution of the Mg- and Si-cations by
isotopes $^{26}\text{Mg}$ and $^{30}\text{Si}$, in order to determine which frequencies were affected by the substitution, thus allowing the modes arising from Mg- or Si-cation motions to be identified. The calculated mode shifts (Tables 3.15-3.16) show good agreement with those determined experimentally by Kolesov and Geiger (1998), who investigated the effect of $^{26}\text{Mg}$ substitution on the Raman modes of pyrope, and Cahay et al. (1981), who studied the effects of both $^{26}\text{Mg}$ and $^{30}\text{Si}$ substitutions on the IR-active modes of pyrope. Our calculations therefore extend the previous experimental work by including the effect of $^{30}\text{Si}$ substitution on the Raman modes of pyrope.

<table>
<thead>
<tr>
<th>$^{26}\text{Mg}_3\text{Al}_2\text{Si}<em>3\text{O}</em>{12}$</th>
<th>$^{26}\text{Mg}_3\text{Al}_2^{30}\text{Si}<em>3\text{O}</em>{12}$</th>
<th>$^{26}\text{Mg}_3\text{Al}_2\text{Si}<em>3\text{O}</em>{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$ (cm$^{-1}$)</td>
<td>$\nu$ (cm$^{-1}$)</td>
<td>$\Delta\nu$ (cm$^{-1}$)</td>
</tr>
<tr>
<td>973.8</td>
<td>954.3</td>
<td>19.5</td>
</tr>
<tr>
<td>878.3</td>
<td>872.3</td>
<td>6.0</td>
</tr>
<tr>
<td>841.2</td>
<td>829.0</td>
<td>12.2</td>
</tr>
<tr>
<td>681.3</td>
<td>680.6</td>
<td>0.7</td>
</tr>
<tr>
<td>610.5</td>
<td>609.7</td>
<td>0.8</td>
</tr>
<tr>
<td>556.1</td>
<td>554.4</td>
<td>1.7</td>
</tr>
<tr>
<td>493.8</td>
<td>493.1</td>
<td>0.7</td>
</tr>
<tr>
<td>475.5</td>
<td>474.4</td>
<td>1.1</td>
</tr>
<tr>
<td>432.1</td>
<td>430.6</td>
<td>1.5</td>
</tr>
<tr>
<td>417.0</td>
<td>416.9</td>
<td>0.1</td>
</tr>
<tr>
<td>380.7</td>
<td>379.4</td>
<td>1.3</td>
</tr>
<tr>
<td>316.9</td>
<td>315.6</td>
<td>1.3</td>
</tr>
<tr>
<td>273.3</td>
<td>272.8</td>
<td>0.5</td>
</tr>
<tr>
<td>234.6</td>
<td>233.8</td>
<td>0.8</td>
</tr>
<tr>
<td>230.9</td>
<td>229.1</td>
<td>1.8</td>
</tr>
<tr>
<td>170.4</td>
<td>170.1</td>
<td>0.3</td>
</tr>
<tr>
<td>153.1</td>
<td>152.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 3.15: Calculated $F_{1u}$ IR-active TO frequencies of pyrope with isotopic substitution of $^{30}\text{Si}$ and $^{26}\text{Mg}$. 
<table>
<thead>
<tr>
<th>Species</th>
<th>( \gamma ) (cm(^{-1}))</th>
<th>( \Delta \gamma ) (cm(^{-1}))</th>
<th>( \Delta \gamma ) (%)</th>
<th>( \gamma ) (cm(^{-1}))</th>
<th>( \Delta \gamma ) (cm(^{-1}))</th>
<th>( \Delta \gamma ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{2g} )</td>
<td>1061.8</td>
<td>1044.0</td>
<td>17.8</td>
<td>1.70</td>
<td>1060.9</td>
<td>0.9</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>943.1</td>
<td>925.1</td>
<td>18.0</td>
<td>1.95</td>
<td>941.5</td>
<td>1.6</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>875.8</td>
<td>863.7</td>
<td>12.1</td>
<td>1.40</td>
<td>875.6</td>
<td>0.2</td>
</tr>
<tr>
<td>( A_{1g} )</td>
<td>850.5</td>
<td>850.5</td>
<td>0.0</td>
<td>0.00</td>
<td>850.5</td>
<td>0.0</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>844.3</td>
<td>838.7</td>
<td>5.6</td>
<td>0.67</td>
<td>844.2</td>
<td>0.1</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>816.3</td>
<td>816.2</td>
<td>0.1</td>
<td>0.01</td>
<td>816.3</td>
<td>0.0</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>643.8</td>
<td>642.0</td>
<td>1.8</td>
<td>0.28</td>
<td>643.7</td>
<td>0.1</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>633.2</td>
<td>631.5</td>
<td>1.7</td>
<td>0.27</td>
<td>630.7</td>
<td>2.5</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>607.2</td>
<td>605.9</td>
<td>1.3</td>
<td>0.21</td>
<td>607.1</td>
<td>0.1</td>
</tr>
<tr>
<td>( A_{1g} )</td>
<td>524.0</td>
<td>524.0</td>
<td>0.0</td>
<td>0.00</td>
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<td>0.0</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>514.9</td>
<td>511.8</td>
<td>3.1</td>
<td>0.61</td>
<td>514.7</td>
<td>0.2</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>506.8</td>
<td>506.5</td>
<td>0.3</td>
<td>0.06</td>
<td>506.8</td>
<td>0.0</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>473.2</td>
<td>471.8</td>
<td>1.4</td>
<td>0.30</td>
<td>473.1</td>
<td>0.1</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>430.6</td>
<td>429.4</td>
<td>1.2</td>
<td>0.28</td>
<td>421.1</td>
<td>9.5</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>367.3</td>
<td>367.0</td>
<td>0.3</td>
<td>0.08</td>
<td>367.0</td>
<td>0.3</td>
</tr>
<tr>
<td>( E_{g} )</td>
<td>363.8</td>
<td>363.4</td>
<td>0.4</td>
<td>0.11</td>
<td>363.2</td>
<td>0.6</td>
</tr>
<tr>
<td>( F_{2g} )</td>
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<td>0.26</td>
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<td>0.00</td>
<td>342.7</td>
<td>0.0</td>
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<tr>
<td>( F_{2g} )</td>
<td>323.1</td>
<td>320.6</td>
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<td>0.78</td>
<td>322.7</td>
<td>0.4</td>
</tr>
<tr>
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<td>0.00</td>
<td>304.4</td>
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<td>0.37</td>
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<td>0.6</td>
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<td>0.3</td>
<td>0.16</td>
<td>188.8</td>
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Table 3.16: Calculated Raman-active frequencies of pyrope with isotopic substitution of \(^{30}\)Si and \(^{26}\)Mg.
3.7.3 Assignment of the SiO$_4$ Internal Modes

The calculated frequency shifts arising from the isotopic substitutions (Tables 3.15-3.16) demonstrate that the majority of high-frequency modes (>700 cm$^{-1}$) are significantly affected by the $^{30}$Si substitution, with frequency shifts of up to 20 cm$^{-1}$ (2%), indicating that these modes are dominated by SiO$_4$ tetrahedral $v_3$ asymmetric stretching motions (Fig.3.5). Analysis of the calculated eigenvectors associated with these frequencies confirms these modes as $v_3$, from the relative movements of the oxygen atoms of each tetrahedra with respect to the Si-cations, and in particular, the large displacements of the Si-cations themselves. Two of the high-frequency Raman modes (850.5 and 816.3 cm$^{-1}$) show little or no shift with $^{30}$Si (or $^{26}$Mg) substitution. The eigenvectors for these frequencies indicate them to be $v_1$ symmetric stretching modes, demonstrating that it is the movement of the oxygen atoms relative to the Si-cations that generate these vibrations. In the central frequency ranges (490-700 cm$^{-1}$ for the IR modes; 430-700 cm$^{-1}$ for the Raman modes), the mode shifts associated with $^{30}$Si substitution are smaller, with a maximum shift of 3 cm$^{-1}$ (0.6%), but indicate that SiO$_4$ tetrahedral motions still dominate at these energy levels. The calculated eigenvectors demonstrate, via the relative movement of the oxygen and Si atoms, that the vibrations in these frequency ranges are dominated by $v_2$ and $v_4$ tetrahedral bending motions, with the final assignments of the internal modes shown in Tables 3.17-3.18. For each symmetry species, our assignments are consistent with the assumption that $v_3 > v_1 > v_2 > v_4$ (Woodward and Roberts, 1956), and show that the correct number of $v_1$-$v_4$ motions as predicted by SGA (Table 3.14) have been assigned, indicating that this model is applicable at high-frequencies.

3.7.4 Assignment of the External IR-Active Modes to Dominant Site/Atomic Motions

Site group analysis of pyrope (Table 3.14) predicts that the external IR-active vibrations should arise from 3T(Al), 2R(SiO$_4$), 3T(SiO$_4$) and 3T(Mg). Our assignments of the Al-translations were made by analyzing the calculated eigenvectors (no known Al-isotope effects have been identified), which explicitly show any movement of the Al-cations. This analysis resulted in the assignment of the calculated mode at 475.5 cm$^{-1}$ to T(Al). However, no other modes arising purely from Al-cation motions could be
identified. Thus, from consideration of the eigenvectors and isotopic substitution data (Table 3.15), the calculated modes at 432.1 and 380.7 cm$^{-1}$ were assigned as T(Al) mixed with T(Mg) and T(SiO$_4$), and T(Mg) components, respectively. Therefore, although we have assigned 3 modes to T(Al), as predicted by SGA, they are not all pure modes and are heavily mixed with other atomic motions (Table 3.17). Similarly, no vibrations arising purely from SiO$_4$-rotations or translations could be identified. The calculated modes at 417.0 and 316.9 cm$^{-1}$ contain significant components of R(SiO$_4$), determined from the eigenvector analysis, and constitute the 2 modes predicted by SGA. However, these modes are mixed with T(Mg) and T(SiO$_4$) components, respectively, as evidenced from their associated frequency shifts. The isotopic substitution data also demonstrates that the calculated modes at 230.9 and 153.1 cm$^{-1}$ consist of SiO$_4$ translatory motions, but that these vibrations are again partly attributable to Mg-cation motions. The 3 pure modes predicted by SGA as generated by T(Mg) could be identified from the $^{26}$Mg isotopic substitution calculations as 273.3, 234.6 and 170.4 cm$^{-1}$ (Table 3.17), with average frequency shifts of 3 cm$^{-1}$ (1.4%). However, other vibrations in addition to these have been shown to contain T(Mg) and thus, our calculations suggest that the site group model is not applicable for the low-frequency IR modes due to the observed mode mixing.

3.7.5 Assignment of the External Raman-Active Modes to Dominant Site/Atomic Motions

The Al-cations remain relatively stationary during the Raman-active vibrations in garnet and hence, the atomic motions generating the external Raman modes are R(SiO$_4$), T(SiO$_4$) and T(Mg). Our calculated eigenvectors and isotopic substitution data (Table 3.16) demonstrate that the single external Raman-active A$_{1g}$ mode (342.7 cm$^{-1}$) is generated by R(SiO$_4$), in agreement with the prediction by SGA (Table 3.14). The external Raman-active E$_g$ modes are predicted to arise from 1R(SiO$_4$), 1T(SiO$_4$) and 1T(Mg). The single mode derived purely from R(SiO$_4$) could be identified at 363.8 cm$^{-1}$ from analysis of the relative motions of the oxygen atoms surrounding the SiO$_4$ tetrahedra. However, the same analysis demonstrated that the E$_g$ mode at 307.7 cm$^{-1}$ also contains an element of R(SiO$_4$). The $^{26}$Mg isotopic substitution calculations suggest that this mode is also partly attributable to Mg-translatory motions due to the associated 3.3 cm$^{-1}$ (1.08%) frequency shift. The lowest frequency E$_g$ mode (207.2 cm$^{-1}$) was also
determined to be a mixed mode, consisting of both Si- and Mg-cation translations from the 1% frequency shifts calculated for both substitutions. Hence, no pure T(SiO$_4$) or T(Mg) modes as predicted by SGA, could be determined.

The origins of the external F$_{2g}$ Raman modes are predicted to be 2R(SiO$_4$), 3T(SiO$_4$) and 2T(Mg). Our analysis of the calculated eigenvectors and mode shifts demonstrates that the calculated mode at 367.3 cm$^{-1}$ can be solely attributed to R(SiO$_4$). However, the remaining pure R(SiO$_4$) mode predicted by SGA could not be identified. The calculated mode at 353.1 cm$^{-1}$ certainly contains an element of R(SiO$_4$), but is mixed with T(Mg), as indicated by the relatively large frequency shift (5.7 cm$^{-1}$; 1.64%) associated with $^{26}$Mg substitution. The calculated mode at 323.1 cm$^{-1}$ is dominated by T(SiO$_4$) motions, but may contain an element of R(SiO$_4$), because the frequency shift caused by the $^{30}$Si substitution suggests that this mode is not pure T(SiO$_4$). The two pure T(Mg) modes predicted by SGA were identified at 227.4 and 192.6 cm$^{-1}$ from the large frequency shifts (1-2%) associated with $^{26}$Mg substitution. However, two additional modes containing Mg-translatory components could also be identified, at 297.2 and 246.6 cm$^{-1}$. The calculated mode shifts due to $^{30}$Si substitution suggests that these modes are mixed with SiO$_4$-translatory motions and hence, no pure T(SiO$_4$) modes could be identified (Table 3.18).

Hence, our assignments of the calculated IR- and Raman-active modes demonstrates that origin of the vibrational modes of pyrope predicted by the SGA model, in which the SiO$_4$ tetrahedra are assumed to behave independently of the other structural features, is applicable at high-frequencies, where the SiO$_4$ internal bending and stretching motions dominate. However at lower frequencies, the number of modes predicted by SGA to arise from each site or atomic motion is not adhered to, due to substantial mixing of modes, in particular T(Mg) and T(SiO$_4$), dominating these energy levels. The calculated eigenvectors and mode shifts due to $^{26}$Mg and $^{30}$Si isotopic substitutions also show that several cation species may undergo simultaneous movement, hindering assignment to specific atomic motions. However, from consideration of the garnet structure, in which the SiO$_4$ tetrahedra share opposite edges with the Mg-cation sites and corners with Al-cation sites, kinematic coupling of modes is to be expected as any motion of the Si-O bonds will affect the adjacent sites and vice versa.
<table>
<thead>
<tr>
<th>LO Modes (cm(^{-1}))</th>
<th>TO Modes (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
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<tr>
<td>1068.1</td>
<td>973.8</td>
<td>(v_3)</td>
</tr>
<tr>
<td>913.4</td>
<td>878.3</td>
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<td>T(Mg)</td>
</tr>
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<tr>
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<td>T(Mg)</td>
</tr>
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<td>380.7</td>
<td>T(Al)</td>
</tr>
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<td></td>
<td></td>
<td>T(Mg), T(SiO(_4))</td>
</tr>
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<td>T(Mg)</td>
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<td>T(SiO(_4))</td>
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<td></td>
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</tr>
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Table 3.17: Calculated \(F_{1g}\) LO and TO IR-active frequencies of pyrope, with assignment of modes to specific site or atomic motions.
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<th>Symmetry Species</th>
<th>Calculated Modes</th>
<th>Assignments</th>
</tr>
</thead>
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<td>( A_{1g} )</td>
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</tr>
<tr>
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<td>342.7 ( R(SiO_4) )</td>
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<td>( E_g )</td>
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<tr>
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<td>307.7 ( R(SiO_4) ) ( T(Mg) )</td>
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</tr>
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<td></td>
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<td>( F_{2g} )</td>
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<td>323.1 ( T(SiO_4) ) ( ?R(SiO_4) )</td>
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<tr>
<td></td>
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<tr>
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<td>192.6 ( T(Mg) )</td>
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Table 3.18: Calculated Raman-active modes and assignments to site/atomic motions.
3.8 Comparison of Calculated IR- and Raman-active Modes and Assignments with the Experimentally-Determined Values

3.8.1 Infrared-Active Modes

The IR spectra of pyrope-rich garnets obtained via the powder dispersion method (Adler et al., 1950; Launer 1952; Wickersheim et al., 1960; Tarte 1965; Moore et al., 1971; Cahay et al., 1981; Geiger et al., 1989, 1992; Bosenick et al., 1995) commonly yield fewer than the expected 17 IR-active modes predicted by factor group analysis (one additional F1u mode is also acoustic in character). Measurements of this type encounter significant scattering from sample particle surfaces and result in peak positions which lie between the LO and TO frequencies according to the amount and particle size of the powder used. In contrast, the single-crystal reflectance studies of Hofmeister and Chopelas (1991a) and Hofmeister et al. (1996) give quantitative and complete sets of IR-active bands for pyrope, in which the frequencies have been determined via a Kramers-Kronig analysis, defining the LO and TO positions of the IR modes by the minima of the imaginary part of \(1/\varepsilon\), and the maxima in the dielectric function \(\varepsilon''\), respectively (see Fig. 3.2).

Our eigenvector analysis of the calculated IR modes of pyrope (section 3.5.2) has demonstrated that these modes are characterized by 3 components: a single longitudinal optic (LO) mode, associated with a doubly-degenerate transverse optic (TO) mode, which is always lower in frequency than the LO mode. Consequently, no LO-TO reversals, in which the TO component of an LO-TO pair is higher in frequency than its associated LO mode, were identified. Such reversals have been suggested in quartz (Scott and Porto, 1967) and garnet (Hofmeister and Chopelas, 1991a; Hofmeister et al. 1996) when a high-intensity band occurs just above and very close to a band of low-intensity, resulting in the TO frequency of the weaker band being greater than its corresponding LO component. We suggest that such a reversal is an artifact due to the mathematical requirement that TO frequencies must always be separated by LO frequencies. Although four such reversals were reported by Hofmeister and Chopelas (1991a) for LO-TO pairs at 889-906, 528-536, 474-478 and 422-423 cm\(^{-1}\) in pyrope, this number was reduced to two by Hofmeister et al. (1996) for the bands at 902-890 and 478-475 cm\(^{-1}\). However, this has recently been reduced to a single reversal at 475-478 cm\(^{-1}\) (A. Hofmeister, personal communication, 1998). The calculated eigenvectors
unambiguously show that no reversals are present in the calculated modes and hence, we do not support the observation that LO-TO reversals occur in pyrope. We therefore suggest that these reversals are unphysical and are artifacts of the experimental procedure or the Kramers-Kronig analysis.

The calculated IR-active $F_{1u}$ frequencies generally show very good agreement with those reported by Hofmeister et al. (1996). For example, the calculated LO-TO pairs at 1068.1-973.8 cm$^{-1}$ and 402.5-380.7 cm$^{-1}$ differ only slightly from the observed pairings at 1060-972 cm$^{-1}$ and 400-383 cm$^{-1}$, respectively (Table 3.19). However, our calculated LO-TO pair at 709.6-681.4 cm$^{-1}$ shows rather poor agreement with the mode at 650 cm$^{-1}$ reported by Hofmeister et al. (1996). This may be because the position of this observed mode is approximate, and a better comparison may be made with the LO-TO pair reported at 667-664 cm$^{-1}$ by Hofmeister and Chopelas (1991a). The calculated LO-TO pair at 442.9-432.1 cm$^{-1}$ has no comparable pairing in the reflectance datasets of Hofmeister et al. (1996) or Hofmeister and Chopelas (1991a). An $F_{1u}$ mode of similar energy (450 cm$^{-1}$) was reported in the calculated dataset of Winkler et al. (1991), and the small calculated LO-TO splitting for this mode suggests that it may be more favourably compared with the bands at approximately 455 cm$^{-1}$ reported by Moore et al. (1971) for pyrope-rich samples. The LO-TO pair reported by Hofmeister et al. (1996) at 357.3-336.2 cm$^{-1}$ does not compare well with our calculated LO-TO pair at 318.8-316.9 cm$^{-1}$; the calculated pair at 273.4-273.3 cm$^{-1}$ also has no experimental equivalent. This may be related to the accidental degeneracies reported by Hofmeister et al. (1996) for the modes at 357.3-336.2 and 152.2-134.4 cm$^{-1}$ from their observation that pairs of peaks coalesced in the very pyrope-rich spectrum of the pyrope-almandine solid-solution. However, the very small LO-TO splitting of the calculated mode at 318.8-316.9 cm$^{-1}$ suggests that it may be more favourably compared with the modes reported by Moore et al. (1971) in the range 308-325 cm$^{-1}$ for pyralspite garnets; the calculated LO-TO pair at 273.4-273.3 cm$^{-1}$ is highly comparable with the mode reported by Hofmeister and Chopelas (1991a) at approximately 272 cm$^{-1}$. Similarly, the calculated LO-TO pair at 172.8-170.4 cm$^{-1}$ shows better agreement with bands reported by Moore et al. (1971) to occur in the range 160-180 cm$^{-1}$ for all common silicate garnets.

Previous assignments of the experimentally-determined IR modes of pyrope-rich garnets to specific site or atomic motions have been based on symmetry analysis, observed trends in garnet solid-solution series (Moore et al., 1971; Geiger et al., 1989;
<table>
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<tr>
<th>Assignment</th>
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<th>TO Modes</th>
<th>LO Modes</th>
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Table 3.19: Comparison of the calculated and observed (Hofmeister et al., 1996) IR-active F\_\text{\textsubscript{i}}\text{\textsubscript{u}} LO and TO frequencies of pyrope, with assignment of modes to dominant site or cation motions (units: cm\textsuperscript{-1}). Note: *Previous LO and TO reversal was eliminated as this assignment was equivocal (Hofmeister, personal communication, 1998); **Degeneracies determined from the solid-solution of pyrope and almandine (Hofmeister et al., 1996).
Hofmeister and Chopelas, 1991a; Hofmeister et al., 1996), or isotopic substitution data (Cahay et al., 1981; Kolesov and Geiger, 1998), with the assumptions that:

- The atomic motions predicted by FGA are relatively pure, with no mode mixing;
- All Mg- and Al-cation motions are restricted to translations;
- Vibrational modes decrease in energy in the order: SiO$_4$-(internal) $>$ SiO$_4$-(rotations) $>$ heavy cations; and $\nu_3 > \nu_1 > \nu_4 > \nu_2$;
- For pure translational modes, the frequencies should increase with decreasing cation mass;
- The low mass of the Al-cation combined with its smaller octahedral site places Al-translations at higher frequencies than SiO$_4$-rotations.

Comparison of the assignments from the most comprehensive IR spectroscopic study (Hofmeister et al., 1996) with those of our calculated modes (Table 3.19) derived from analysis of the calculated eigenvectors and mode shifts with isotopic substitution of $^{26}\text{Mg}$ and $^{30}\text{Si}$, shows that there is excellent agreement between the assignments of the high-frequency internal modes of the SiO$_4$ tetrahedra, and the also the number of $\nu_1$-$\nu_4$ modes predicted by SGA. The assignments of Hofmeister et al. (1996) were made by counting down from the highest energy fundamental modes assuming the sequence $\nu_3 > \nu_1 > \nu_4 > \nu_2$. Our calculations demonstrate that this sequence of modes is valid for pyrope, although no $\nu_1$ modes were identified for the F$_{1u}$ symmetry species, as predicted by SGA. However, the assignments of the external modes show some differences. From our analysis of the eigenvectors, we have identified the 2 highest frequency modes generated by Al-cation translations to be positioned directly below the SiO$_4$ internal modes, in agreement with Hofmeister et al. (1996) and the assumption that T(A1) will occur at higher frequencies than R(SiO$_4$) from consideration of the relative cation masses. However, we have assigned the calculated LO-TO pair at 442.9-432.1 cm$^{-1}$, not observed by Hofmeister et al. (1996), as the second highest energy T(A1), in agreement with the assignment by Moore et al. (1971) for their mode at observed 458 cm$^{-1}$. The assignment by Hofmeister et al. (1996) of the observed LO-TO pair at 423.0-421.7 cm$^{-1}$ as the second T(A1) therefore disagrees with our own. Analysis of the eigenvectors for the mode at 431.5-417.1 cm$^{-1}$, considered to correspond to this observed mode, indicates that it is dominated by SiO$_4$-rotatory motions (with some Mg-cation movement), with little involvement of the Al-cations during this vibration. We have assigned the
calculated LO-TO pair at 402.5-380.7 cm\(^{-1}\) as the lowest energy T(Al) vibration. This differs significantly from the assignment of Hofmeister et al. (1996), who designated their observed mode at 263.0-258.5 cm\(^{-1}\) as dominated by the final T(Al) mode, based on compositional/TO positional trends in the IR spectra of pyrope-almandine garnets. Our calculations show that there is substantial movement of the Al-cations during the vibration at 402.5-380.7 cm\(^{-1}\), indicating it to be the position of the final T(Al) mode. The calculated isotopic substitution data also shows that this mode is mixed with both Mg- and Si-cation translatory motions. The eigenvectors for the calculated mode at 257.4-234.6 cm\(^{-1}\), considered to correspond to the observed mode at 263.0-258.5 cm\(^{-1}\), indicate that there is only very slight movement of the Al-cations during this vibration with translations of the Mg-cations dominating, as confirmed by the calculated 1.3\% mode shift arising from \(^{26}\text{Mg}\) isotopic substitution. All datasets have, however, shown that T(Al) are present in pyrope at frequencies below 400 cm\(^{-1}\), which is considerably lower than the commonly assumed 500-550 cm\(^{-1}\) lower limit.

Comparison of the assignment of the vibrational modes to SiO\(_4\)-rotations shows that both this study and Hofmeister et al. (1996) have placed the rotations directly below the first two T(Al) modes. We determined 2 modes to be attributable to R(SiO\(_4\)), as predicted by SGA, but these modes (431.5-417.1 cm\(^{-1}\) and 318.8-316.9 cm\(^{-1}\)) are mixed with T(Mg) and T(SiO\(_4\)) components, respectively. Hofmeister et al. (1996) assigned the mode at 357-336 cm\(^{-1}\) as R(SiO\(_4\)) mixed with T(SiO\(_4\)) also, from the observed degeneracy, in agreement with our own assignment. Assignment of the calculated modes to SiO\(_4\)-translations demonstrated that no pure T(SiO\(_4\)) modes could be identified, in agreement with the observations of Hofmeister et al. (1996). We identified 4 modes as dominated by SiO\(_4\) translatory motions from the calculated frequency shifts with isotopic substitution, but again these were observed to be mixed with either R(SiO\(_4\)), T(Al) or T(Mg). Our assignment of the calculated LO-TO pair at 156.0-153.1 cm\(^{-1}\) as a mixed mode consisting of both T(SiO\(_4\)) and T(Mg) is in excellent agreement with the assignment by Hofmeister et al. (1996). Assignment of the calculated modes to T(Mg) shows that 3 relatively pure modes could be identified, as predicted by SGA. The assignment of the calculated mode at 172.8-170.4 cm\(^{-1}\) to T(Mg) is in excellent agreement with that of Hofmeister et al. (1996), and the similar assignment of the calculated mode at 273.4-273.3 cm\(^{-1}\), which was not formally identified by Hofmeister et al. (1996), shows excellent agreement with the assignment of Hofmeister and Chopelas (1991a). (Assignment of the mode at 257.4-234.6 cm\(^{-1}\) has already been discussed).
Hofmeister et al. (1996) reported that the mode at 221 cm$^{-1}$ showed two-mode behaviour in pyrope-almandine solid-solutions, suggesting that this mode cannot be mixed. However, the calculated frequency shifts for the mode at 231.0-230.9 cm$^{-1}$ clearly show that this mode is related to movements of both the Si- and Mg-cations. We suggest that this, together with the observed mode mixing, is evidence of the kinematic coupling within the garnet structure whereby movement of one set of bonds or cations affects adjacent structural components.

3.8.2 Raman-Active Modes

Only 5 Raman spectroscopic studies of pyrope-rich garnets have been documented to date. Griffith (1969) presented 6 Raman-active bands in the range 300-1000 cm$^{-1}$, and subsequent Raman studies were still limited when Memagh and Liu (1990) reported only 7 out of the expected 25 Raman-active modes in the range 100-1200 cm$^{-1}$. Hofmeister and Chopelas (1991a) obtained polarized single-crystal Raman measurements of pyrope and reported the first complete set of 25 Raman-active bands. Later studies by authors such as Gillet et al. (1992) and Kolesov and Geiger (1998) have presented a maximum of 19 and 17 bands, respectively, in the same range.

Comparison of the calculated Raman-active modes of pyrope with the experimentally-determined modes reported by Hofmeister and Chopelas (1991a) and Kolesov and Geiger (1998) from their fully polarized studies of natural single-crystals is shown in Tables 3.20-3.21. The symmetry species of the observed modes were determined through the polarizing geometry: the $A_{1g}$ and $E_g$ modes were determined via $x(zz)y$ geometry (polarization parallel to incident laser polarization); the $F_{2g}$ modes were determined via $x(zx)y$ geometry (polarization perpendicular to laser polarization). The $A_{1g}$ and $E_g$ modes were distinguished between by rotating the crystal through 45° about a 4-fold axis and using crossed-polarization geometry to observe the $E_g$ modes.

The calculated Raman modes may be grouped into 3 distinct regions: low-frequency peaks (192-431 cm$^{-1}$); medium-energy peaks (473-644 cm$^{-1}$); and high-energy peaks (815-1062 cm$^{-1}$), with one $A_{1g}$ peak located in each region. These groupings show excellent agreement with those made by Hofmeister and Chopelas (1991a). The calculated $A_{1g}$ modes show reasonable agreement with the $A_{1g}$ modes reported by Kolesov and Geiger (1998) and Hofmeister and Chopelas (1991a), with the calculated
modes lower in frequency than the observed bands (Table 3.20). The agreement between
the datasets was observed to improve at lower frequencies. The discrepancies between
the observed and calculated data may be related to the Si-O interatomic potential or the
three-body bending term employed in our lattice dynamical model which may not fully
describe the behaviour of the SiO$_4$ tetrahedra in this case.

Comparison of the calculated $E_g$ modes with the observed modes (Table 3.20)
shows that there is excellent agreement between the datasets, with an average difference
of approximately 7 cm$^{-1}$, except for the calculated modes at 307 and 816 cm$^{-1}$, which
show greater deviations from the observed modes. However, the corresponding observed
Raman modes at 342 and 911 cm$^{-1}$ have recently been revised to 309 and 867 cm$^{-1}$,
respectively (Chopelas, Hofmeister and Kenneally, in preparation), which greatly
improves the agreement with the calculated data.

The calculated $F_{2g}$ modes show very good agreement with the observed modes
listed in Table 3.21, with an average difference of 10 cm$^{-1}$ between the datasets. Kolesov
and Geiger (1998) reported a low-energy Raman mode at 135 cm$^{-1}$ in their $F_{2g}$ spectrum,
which was not reported by previous authors. It was attributed to the anisotropic dynamic
disorder within the dodecahedral site which causes the Mg-cation to undergo a "rattling"
motion in the site (Armbruster et al., 1992). We did not observe this mode in our
simulations and this may be due to our use of the quasi-harmonic approximation which
does not include anharmonic effects. However, this mode may be related to the lowest
energy IR mode observed at 134 cm$^{-1}$ (Hofmeister et al., 1996) leaking through into the
Raman spectrum (Hofmeister, personal communication, 1998).

Comparison of the assignments of the calculated modes and those made by
Hofmeister and Chopelas (1991a) and Kolesov and Geiger (1998), who used $^{26}$Mg
isotopic substitution data to assist in their assignments, demonstrates that there is
complete agreement between all assignments of the $A_{1g}$ modes (Table 3.20) and also
those predicted by SGA. Comparison of the assignments of the calculated internal $E_g$
modes shows that there is also excellent agreement with the assignments of the
experimentally-determined modes and those predicted by SGA, with the assumption
$v_3>v_1>v_4>v_2$ fully supported. However, the assignments of the external $E_g$
modes show some differences (Table 3.20). Our assignment of the calculated mode at 363.8 cm$^{-1}$ to
$R$(SiO$_4$) is in agreement with that of Hofmeister and Chopelas (1991a), and we would
suggest that the mode reported by Kolesov and Geiger (1998) at 375 cm$^{-1}$ is also
<table>
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<th>Species</th>
<th>Observed Modes and Assignments</th>
<th>Calculated Modes and Assignments</th>
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</thead>
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<td></td>
<td>Kolesov and Geiger (1998)</td>
<td>Hofmeister and Chopelas (1991)</td>
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<td></td>
<td>(Si-O)$_\text{str}$ 928</td>
<td>$\nu_1$ 925</td>
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<tr>
<td></td>
<td>(Si-O)$_\text{bend}$ 563</td>
<td>$\nu_2$ 562</td>
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<td>R(SiO$_4$) 362</td>
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<td>A$_{1g}$</td>
<td>(Si-O)$_\text{str}$ 945</td>
<td>$\nu_3$ 938</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\nu_1$ 911(867*)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\nu_4$ 626</td>
</tr>
<tr>
<td></td>
<td>R(SiO$_4$) 375</td>
<td>R(SiO$_4$) 365(379*)</td>
</tr>
<tr>
<td></td>
<td>(Si-O)$_\text{bend}$ 525</td>
<td>$\nu_2$ 524</td>
</tr>
<tr>
<td></td>
<td>T(Si$_4$O$_4$) 211</td>
<td>T(Mg) 203</td>
</tr>
<tr>
<td>E$_g$</td>
<td>(Si-O)$_\text{bend}$ 375</td>
<td>T(Si$_4$O$_4$) 342(309*)</td>
</tr>
<tr>
<td></td>
<td>T(Mg) 284</td>
<td>T(Mg)</td>
</tr>
</tbody>
</table>

Table 3.20: Comparison of the observed and calculated A$_{1g}$ and E$_g$ Raman-active modes of pyrope (units cm$^{-1}$) and their mode assignments. *Revisions in frequency (Chopelas, Hofmeister and Kenneally, in preparation).

attributable to R(SiO$_4$), as originally suggested by them. The calculated mode at 307.7 cm$^{-1}$, also assigned as R(SiO$_4$), shows good agreement with the assignment of the corresponding mode by Kolesov and Geiger (1998). However, this disagrees with the number of R(SiO$_4$) predicted by SGA and the assignment made by Hofmeister and Chopelas (1991a) to T(SiO$_4$). Our calculated frequency shifts for $^{26}$Si substitution, together with analysis of the calculated eigenvectors, show that there is little or no movement of the Si-cations during this vibration and hence, we suggest that is attributable to SiO$_4$-rotatory motions. The $^{26}$Mg substitution data also suggests that this mode may contain Mg-translatory components. The calculated lowest energy E$_g$ mode has also been assigned as a mixed mode, consisting of both SiO$_4$- and Mg-translatory motions, from analysis of the calculated frequency shifts due to both $^{26}$Mg and $^{30}$Si.
isotopic substitutions. Kolesov and Geiger (1998) also observed a similar shift of approximately 1% with $^{26}$Mg substitution, but assigned this mode as T(SiO$_4$) as the mode was not pure.

Comparison of the assignments of the calculated F$_{2g}$ internal modes with the observed modes (Table 3.21) shows that there is excellent agreement between the datasets and the assignments predicted by SGA. Assignment of the F$_{2g}$ modes to R(SiO$_4$) shows that there is excellent agreement between all datasets for the 2 external modes of highest frequency (range 350-380 cm$^{-1}$). However, our calculated frequency shifts suggest that the mode at 353.1 cm$^{-1}$ may also be partly attributable to T(Mg). Below 350 cm$^{-1}$, assignment of the calculated and observed external modes again differs. Our calculations suggest that the mode at 323 cm$^{-1}$ is dominated by T(SiO$_4$), with a resultant frequency shift of approximately 1% due to $^{30}$Si substitution. This is in agreement with the assignment made by Hofmeister and Chopelas (1991), but differs from that made by Kolesov and Geiger (1998), who assigned this mode as an SiO$_4$-rotation. As the calculated frequency shift indicates that the mode is not pure T(SiO$_4$), we also suggest that it may be associated with some SiO$_4$-rotational motions, as there is little movement of the Mg-cations at this energy level. We have designated the remaining calculated F$_{2g}$ modes in the range 100-300 cm$^{-1}$ as dominated by relatively pure Mg-translations due to the large calculated frequency shifts (1-2%) associated with the $^{26}$Mg substitution. However, the calculated mode shifts suggest that these modes may contain smaller components of T(SiO$_4$). This is in agreement with the assignments of Hofmeister and Chopelas (1991). Kolesov and Geiger (1998) reported a frequency shift of nearly 1% with $^{26}$Mg substitution for their observed mode at approximately 212 cm$^{-1}$, but assigned it as T(SiO$_4$) because the mode was not pure T(Mg). However, our calculated frequency shift of 0.16% for this mode with $^{30}$Si substitution suggests that it is in fact dominated by Mg-cation motions, and should be designated T(Mg).

3.9 Summary and Conclusions

Lattice dynamical calculations of the Brillouin zone centre phonon frequencies of pyrope have been performed in order to simulate the IR- and Raman-activity of this phase. Using Group theoretical analysis and simulated atomic displacement parameters,
<table>
<thead>
<tr>
<th>Species</th>
<th>Observed Modes and Assignments</th>
<th>Calculated Modes and Assignments</th>
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<tr>
<td></td>
<td>Kolesov and Geiger (1998)</td>
<td>Hofmeister and Chopelas (1991a)</td>
</tr>
<tr>
<td>F$_{2g}$</td>
<td>(Si-O)$_{str}$ 1066 $\nu_3$ 1062</td>
<td>$\nu_3$ 899 866 844.4 $\nu_3$</td>
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<td></td>
<td>(Si-O)$_{str}$ 902 $\nu_3$ 902</td>
<td>875.8 $\nu_3$ 844.4 $\nu_3$</td>
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<tr>
<td></td>
<td>(Si-O)$_{str}$ 871 $\nu_3$ 871</td>
<td>844.4 $\nu_3$ 844.4 $\nu_3$</td>
</tr>
<tr>
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<td>(Si-O)$_{bend}$ 650 $\nu_4$ 648</td>
<td>643.8 $\nu_4$ 643.8 $\nu_4$</td>
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<tr>
<td></td>
<td>(Si-O)$_{bend}$ 598 $\nu_4$ 598</td>
<td>607.2 $\nu_4$ 607.2 $\nu_4$</td>
</tr>
<tr>
<td></td>
<td>(Si-O)$_{bend}$ 512 $\nu_4$ 512</td>
<td>514.9 $\nu_4$ 514.9 $\nu_4$</td>
</tr>
<tr>
<td></td>
<td>(Si-O)$_{bend}$ 492 $\nu_2$ 490</td>
<td>473.2 $\nu_2$ 473.2 $\nu_2$</td>
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<tr>
<td></td>
<td>R(SiO$_4$) 383 R(SiO$_4$) 379</td>
<td>367.3 R(SiO$_4$) 367.3 R(SiO$_4$)</td>
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<tr>
<td></td>
<td>R(SiO$_4$) 353 R(SiO$_4$) 350</td>
<td>353.1 R(SiO$_4$) 353.1 R(SiO$_4$)</td>
</tr>
<tr>
<td></td>
<td>R(SiO$_4$) 322 T(SiO$_4$) 318(342*)</td>
<td>323.1 T(SiO$_4$) 323.1 T(SiO$_4$)</td>
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<td>- - T(SiO$<em>4$)$</em>{mix}$ 285(318*)</td>
<td>297.2 T(Mg) 297.2 T(Mg)</td>
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<tr>
<td></td>
<td>- - T(SiO$<em>4$)$</em>{mix}$ 230</td>
<td>227.4 T(Mg) 227.4 T(Mg)</td>
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<td></td>
<td>T(SiO$_4$) 212 T(Mg) 208</td>
<td>192.6 T(Mg) 192.6 T(Mg)</td>
</tr>
<tr>
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<td>T(Mg) 135</td>
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Table 3.21: Comparison of the observed and calculated F$_{2g}$ Raman-active modes of pyrope (units cm$^{-1}$) and their mode assignments. Note: * Revisions in frequency (Chopelas, Hofmeister and Kenneally, in preparation).

The symmetry species of each vibrational mode has been identified and hence, its IR- or Raman-activity (or inactivity) determined. Comparison of the calculated and experimentally-determined IR- and Raman-active modes of pyrope shows that there is generally very good agreement between the datasets, indicating that the lattice dynamical model and the interatomic potentials employed provide a good description of the vibrational behaviour of pyrope. There is more favourable agreement between the
calculated and observed Raman modes than between the calculated and observed IR
modes, and this may be because the perturbation of the IR modes by the electric field of
the light is not accounted for in the calculations.

The calculated mode shifts of the zone centre frequencies of pyrope due to the
isotopic substitutions of $^{26}\text{Mg}$ and $^{30}\text{Si}$, together with further analysis of the calculated
eigenvectors, enabled the dominant site or atomic motions contributing to each
vibrational mode to be identified. Comparison of the assignments of the calculated and
observed IR and Raman modes demonstrates that there is excellent agreement between
the datasets and with the theoretical number of modes predicted by SGA for the SiO$_4$
internal modes, suggesting that the Group theoretical model, in which the SiO$_4$
tetrahedra are treated as isolated structural features, is applicable at high-frequencies.
Comparison of the assignments of the lower frequency external modes shows that the
agreement is less favourable. This is considered to be due to the fact that the assignments
of the experimentally-determined modes have been based predominantly on the SGA
model, which implies that all modes are relatively pure, and certain assumptions
regarding the relative energies of the external modes. Although mixing of modes has
been suggested for some of the observed modes, our calculations explicitly show that
significant amounts of mode mixing occur for the majority of low-frequency modes for
pyrope, and that the contribution to each vibration from each set of cations can be
unambiguously established. Thus, the number of vibrations predicted by the SGA model
to arise from each site/cation motion is not adhered to for the low-frequency modes,
suggesting that this model is not applicable at these energy levels. From consideration of
the garnet structure, in which the SiO$_4$ tetrahedra share opposite edges with the MgO$_6$
dodecahedra and corners with the AlO$_6$ octahedra, this kinematic coupling is to be
expected as any motion of the Si-O bonds will affect adjacent cation sites, and vice
versa.

Having established that our lattice dynamical model provides a good description
of the Brillouin zone centre vibrational behaviour of pyrope, we can now extend this
type of modelling to the non-zone-centre phonons of pyrope - those attributable to
phonon dispersion - which can be measured experimentally using the technique of
coherent inelastic neutron scattering.
4.1 Introduction

In the previous chapter, the calculated vibrational modes of pyrope were compared with the Brillouin zone centre frequencies determined via infrared (IR) and Raman spectroscopies. These vibrational spectroscopic methods, although widely available in many laboratories, provide only a limited number of phonon frequencies, due to the long wavelength of the incident radiation used (typically $10^5$ Å for IR-light, 5000 Å for Raman-light), and the symmetry-based selection rules which govern the IR- and Raman-activity of the long wavelength vibrational modes. It is possible to measure the general distribution of the phonon frequencies throughout the Brillouin zone - the vibrational density of states - using the technique of coherent inelastic neutron scattering (INS). However, this experimental method requires highly specialized facilities (e.g. a neutron source, extensive radiation shielding, sophisticated detection equipment) which are only available at a few installations worldwide (e.g. Los Alamos and Argonne National Laboratories, USA; Rutherford-Appleton Laboratory, UK; ILL, Grenoble, France). In this chapter, we discuss the scattering of neutrons by crystals (section 4.2) and present the results of density of states measurements of pyrope and grossular, obtained using coherent INS, thus extending the previous INS measurements of garnet reported by Pavese et al. (1998) (sections 4.3-4.5); we also compare our empirical results with lattice dynamical simulations of the INS experiments and phonon dispersion calculations (section 4.5). Finally in section 4.6, we present a summary of our INS study and the conclusions we can draw from it.

4.1.1 Why Use Neutrons?

A neutron is a subatomic particle with zero charge, spin $\frac{1}{2}$, mass $m = 1.0087$ amu and magnetic moment $\mu_n = -1.9132$ nuclear magnetons, and the combination of these four properties make the neutron a highly effective probe of condensed matter. The zero charge of the neutron confines its interactions with matter to short-ranged nuclear and...
magnetic interactions, resulting in a small interaction probability, enabling the neutron to penetrate the bulk of the sample. As the interactions are nuclear rather than electronic, the neutron scattering power of an atom is not strongly related to its atomic number (unlike x-ray and electronic scattering), thus allowing light elements such as hydrogen to be readily detected in the presence of heavier atoms, and because of differences in nuclear structure, atoms of similar mass can also be easily distinguished between. The spin of the neutron permits investigation of nuclear spin correlation and ordering at low-temperatures, because the strength of the interaction between a neutron and a nucleus with non-zero spin depends on the relative orientations of the neutron and nuclear spins. The mass of the neutron means that neutrons have a sizeable momentum which may be imparted to a nucleus in a material during a collision event. The magnetic moment of the neutron makes it a unique probe of magnetism on an atomic scale, allowing the magnetic structure (spin arrangement) and dynamics of the spin system in magnetically ordered minerals to be studied, as neutrons may be scattered from the magnetic moments associated with transition metal ions with unpaired electron spins in magnetic samples.

Neutrons can have energies similar to those associated with atomic motions (i.e. in the meV to eV range), thus allowing the energy levels from the \( \mu \text{eV} \) of quantum tunnelling, through molecular transitions, rotations, vibrations and lattice modes, to eV energy transitions within the electronic structure of materials to be studied by neutron scattering. Neutrons are classified according to their energies as ultracold (0.00025 meV), cold (1 meV), thermal (25 meV) and epithermal (1000 meV). Consideration of the wave nature of the neutron shows that its energy, \( E \), may be described by (Halban and Preiswork, 1936; Mitchell and Powers, 1936):

\[
E = \frac{\hbar^2}{2m\lambda^2} \approx k_B T ; \quad p = \hbar k
\]

where \( \hbar \) is Planck's constant (= \( \hbar/2\pi \)), \( m \) and \( p \) are the mass and momentum of the neutron, respectively, and \( \lambda \) is the neutron wavelength. Thermal neutrons have energies typical of those associated with collective excitations in solids and liquids, and at approximately 300K, the mass of the neutron is such that it also has a wavelength of 1.8 Å, comparable to the interatomic spacings in solids or dense fluids, thus permitting diffraction measurements to be performed. Hence, thermal neutrons have both wavelengths and energies that closely match interatomic distances and excitations.
respectively, in condensed matter, allowing the simultaneous measurement of molecular structure and dynamics. This is in contrast to other probes which typically have either the appropriate wavelength range (x-rays) or energy range (photons).

4.1.2 Neutron Sources

Most neutron sources are ultimately based on nuclear reactions which free neutrons bound in nuclei. The mechanisms by which this may be done are: fission chain and fusion reactions (nuclear reactor-based processes), electron-Bramsstrahlung induced photo-neutron and photo-fission reactions, charged-particle nuclear reactions, and spallation (accelerator-based processes). Sources for high-flux neutron beams suitable for neutron scattering experiments are usually derived from two of these mechanisms:

1. **Steady-state sources** - derived from nuclear fission reactors via the splitting of heavy nuclei, such as $^{235}\text{U}$, into smaller lighter nuclei with an associated release of neutrons (an average of 2-3 neutrons per $^{235}\text{U}$ splitting event). This results in a continuous flux which is nearly isotropic, with a Maxwellian thermal distribution dominating the spectrum.

2. **Pulsed spallation sources** - These are the more modern and more efficient accelerator-based sources, in which an accelerated beam of protons or electrons is fed into a resonant accelerator and groups of particles are accelerated to frequencies of a few MHz by rapid cycling, resulting in short pulses of charged particles. The accelerated beam is then directed on to a heavy metal target, and the violent interaction (spallation) between the incident protons and the nuclei of the target results in the emission of neutrons, with several tens of neutrons released per proton (approximately 25 neutrons for $^{238}\text{U}$). This process is repeated at a rate of 24-50 Hz, resulting in a pulsed neutron beam. In contrast to the steady-state sources, pulsed sources operate briefly (0.4-1 µs) at high-power, producing momentarily higher flux than nuclear reactors, and then switch off allowing the heat to be dissipated.

The high-energy neutrons produced by these methods are slowed down to thermal energies for use in neutron scattering experiments by means of inelastic
collisions with a moderating material. The fast neutrons produced by nuclear fission are retarded by heavy water or graphite moderators; those produced by pulsed spallation sources are usually retarded by collisions with moderators composed of hydrogenous materials, such as water, polyethylene, liquid hydrogen or liquid methane. Most of the slow neutrons thus produced have speeds which are described by a Maxwell distribution, and their corresponding spectrum is white. Monochromators (most commonly single-crystals of Ge, Cu, Zn, Pb, Si, SiO₂ (quartz), Al₂O₃ (sapphire) or MgO) may then be encountered in the thermal neutron beam to act as filters which select the desired neutron wavelength.

4.2 Neutron Scattering

4.2.1 Introduction

When a beam of neutrons is directed on to a sample, some of the incident neutrons may be scattered by collision with nuclei in the sample. Analysis of the energy and momentum of the scattered neutrons can provide information about the microscopic structure and dynamics of the sample system. In a hypothetical neutron scattering experiment (Fig.4.1), a beam of neutrons characterized by wavevector \( k_0 \), is incident on a sample. The probability of neutron-nuclei interaction is small and hence, most neutrons are transmitted directly without any interaction. However, a small proportion of the incident neutrons will be scattered, and these may be measured by a detector placed for example, along wavevector \( k_1 \) (Fig.4.1). If the incident beam is characterized by a uniform flux \( \Phi \), the sample has \( N \) identical atoms in the beam, and the detector, with efficiency \( \eta \), subtends a solid angle \( \Delta \Omega \), the count rate, \( C \), in the detector is expected to be proportional (if \( \Delta \Omega \) is sufficiently small) to all these quantities. This constant of proportionality is termed the differential cross-section and is a function of the magnitude and direction of \( k_0 \), and the direction of \( k_1 \), and is a property of the sample being measured; it is defined as:

\[
\frac{d\sigma}{d\Omega} = \frac{C}{\Phi N (\Delta \Omega) \eta} = |b|^2
\]

(4.2)
where $\sigma$ is the neutron scattering cross-section for identical, non-interacting atoms in a sample, and $b$ is the nuclear scattering length, dependent upon atomic number ($Z$), atomic weight ($A$) and the relative spin states (parallel or anti-parallel) of the neutron and scattering nucleus. The scattering powers for the two spin states, $I = \pm \frac{1}{2}$, of the neutron-nucleus system are generally quite different (e.g. for hydrogen, the spin states $I = +\frac{1}{2}$ and $I = -\frac{1}{2}$ give neutron scattering cross-sections of 2 barns ($10^{-24}$ cm$^2$) and 79.1 barns, respectively), and this gives rise to coherent and incoherent scattering. (In coherent scattering, each nucleus of the same atom type in each unit cell contributes an equal amount of scattering power; in incoherent scattering, different nuclei of the same atom type (isotope effects, different spin states) scatter differently.) The total neutron scattering cross-section of an atom, $\sigma_{tot}$, which expresses the strength of the interaction between neutron and an atomic nucleus, is related to the nuclear scattering length via the expression:

$$\sigma_{tot} = 4\pi |b|^2$$

and is the sum of the two terms due to the spin combinations $I = +\frac{1}{2}$ and $I = -\frac{1}{2}$, such that:

Figure 4.1: Schematic diagram of a neutron scattering experiment (after Price and Sköld, 1986).
This separation of $\sigma_{\text{tot}}$ into two parts gives rise to two mechanisms which may be used to study different scattering processes. For example, the collective atomic or spin motions in a solid are studied by coherent neutron spectroscopy (e.g. phonon dispersion in calcite - Dove et al., 1992b; phonon density of states of fayalite - Rao et al., 1988), whereas individual atomic motions are studied by incoherent neutron spectroscopy (e.g. water molecules in a zeolite - Fuess et al., 1986; rotational tunnelling - Press, 1981). The details of the neutron-nucleus interaction are complex (e.g. Sears, 1986; Lovesey, 1984) and hence, there is no simple way of determining \textit{a priori} which nuclei have large or small neutron scattering lengths. Thus, these properties are usually determined experimentally and tabulated (e.g. Sears, 1986; Koester, 1977; Bacon, 1975).

Figure 4.1 illustrates that neutrons scattered by a sample involve a change in the neutron wavevector $k_0$, caused by a change in neutron momentum which, from classical mechanics, must be exchanged with the sample. The transfer of momentum to the sample is conventionally described in terms of the wave-vector $Q$, and the law of conservation of momentum is written as:

$$Q = k_0 - k_1$$

(4.5)

The scattering of a neutron by a nucleus also involves a change in neutron energy $\hbar \omega$, which has a value of zero for elastic scattering, and a non-zero value (positive or negative) for inelastic scattering. The most general neutron scattering processes are thus described by:

$$\hbar \omega = E_0 - E_1 \quad \text{and} \quad \hbar Q = \hbar (k_0 - k_1)$$

(4.6)

where $E$ is the neutron energy ($= h^2 k_0^2 / 2m$), $k$ is the neutron wavevector, $Q$ is the momentum transferred to/from the neutron to/from the scatterer; and subscripts 0 and 1 refer to the incident and final states, respectively.
4.2.2 Elastic and Quasi-Elastic Neutron Scattering

In elastic neutron scattering, there is no transfer of energy between the neutrons and the sample nuclei. Hence, the scattered neutrons have the same energy as the incident neutrons and the magnitude of $k_0$ does not change, so that $|k_1| = |k_0|$ and:

$$2k_0 \sin \left( \frac{\Phi}{2} \right) = Q \quad (4.7)$$

In crystalline solids, strong elastic scattering occurs when $Q$ is equal to the reciprocal lattice vector of the crystal, $\tau$, such that:

$$Q = \frac{2\pi}{d} \left( \frac{h}{a}, \frac{k}{b}, \frac{l}{c} \right) \quad \text{or} \quad Q = \frac{2\pi}{d} \quad (4.8)$$

where $d$ is the spacing of the $(h, k, l)$ set of crystal planes. Thus, elastic scattering occurs at a lattice point. The neutron wavelength, $\lambda$, is related to its wavevector, $k_0$, by:

$$k_0 = \frac{2\pi}{\lambda_0} \quad (4.9)$$

The combination of equations (4.7-4.9) yields the Bragg condition for diffraction (Bragg, 1913):

$$\lambda_0 = 2d \sin \left( \frac{\phi}{2} \right) \quad (4.10)$$

which describes the circumstances under which waves scattered from successive Bragg planes interfere constructively to give an intensity maximum in the diffraction pattern. As elastic scattering involves no change in energy between the neutron and nuclei, it provides no information on the internal dynamics of the sample. Thus, elastic neutron scattering is mainly used to determine the structural properties of a solid.

Quasi-elastic neutron scattering also involves no transfer of energy within the neutron-nuclei system. The sharp line in the scattered neutron spectrum centred at zero
energy transfer (elastic neutron scattering) becomes broadened in quasi-elastic scattering as the energy of the incident neutron is effectively Doppler-shifted by a particle in the sample undergoing diffusive motion. Thus, quasi-elastic neutron scattering is used to determine diffusion rates of particles between equilibrium sites (via analysis of the width of the broadened peak), and the geometry of non-periodic molecular motions. For example, this process is used in the study of fast-ion conductors in which the conducting ions are highly mobile \( \text{e.g.} \) CaF\(_2\) - Hutchings et al., 1984), and in the determination of the diffusion coefficients of water molecules between layers of a clay mineral \( \text{e.g.} \) Olejnik and White, 1972; Fuess and Stuckenschmidt, 1987).

4.2.3 Inelastic Neutron Scattering

In inelastic neutron scattering (INS), both energy, \( \hbar \omega \), and momentum, \( \hbar \mathbf{Q} \), are exchanged with the sample, so that the incident and scattered neutron energies are not equal \( (E_0 \neq E_1) \). Thus, the law of conservation of energy and momentum for INS is written as:

\[
\hbar \omega (\mathbf{Q}) = E_0 - E_1 = \frac{\hbar^2}{2m} \left( k_0^2 - k_1^2 \right)
\]

(4.11)

The energy transferred to (or from) the incident neutron during collision with a sample nucleus may be absorbed (or emitted) by a single elementary thermal excitation such as a quantum of a normal vibrational mode of the sample, with mode frequency, \( \omega \), and phonon energy, \( \hbar \omega \) (one-phonon scattering). Thus, analysis of the energy of the inelastically scattered neutron provides information on the microscopic dynamics of the sample, and the exchange of energy may occur away from the lattice point, within the first Brillouin zone. Coherent INS may be used to determine: the phonon dispersion relations or phonon density of states of a crystalline system; the temperature- and pressure-dependencies of the phonon frequencies, giving the mode Grüneisen parameters; soft modes; phonon intensities, peak shapes and lifetimes as a function of temperature or pressure, to provide information on the dynamical structure factor, anharmonicity and phonon-phonon interaction; electron-phonon interactions (Kohn anomalies) in metals and semi-conductors; energy-level separation in transition metal
ions in magnetic materials; and magnon (spin wave) dispersion relations and magnon
density of states in ferro-, ferri- and antiferro-magnetic materials.

From equation (4.11), it may be seen that a process in which a neutron is
scattered from \( k_0 \) to \( k_1 \) is associated with a set of values of \( Q \) and \( E \). The intensity of the
scattering as a function of the scattering vector \( Q = k_0 - k_1 \) and energy transfer \( h \omega = (E_0 - E_1) \) is proportional to the scattering function, \( S(Q, \omega) \), and is the property measured
during an INS experiment. It is dependent on the sample composition and experimental
environment (e.g. temperature, pressure, magnetic field) and is defined as (e.g. Marshall
and Lovesey, 1971; Bacon, 1975; Squires, 1978; Lovesey, 1984; Price and Sköld, 1986;
Dove, 1993):

\[
S(Q, \omega) = \int I(Q, t) \exp^{-\omega t} dt \tag{4.12}
\]

where \( I(Q, t) \) is the intermediate scattering function, given as:

\[
I(Q, t) = \langle \rho(Q, t) \rho(-Q, 0) \rangle \tag{4.13}
\]

where \( \rho(Q, t) \) is the density function and is defined as the Fourier transform of the
instantaneous nuclear density, weighted by the scattering length, \( b \):

\[
\rho(Q, t) = \sum_j b_j \exp(i Q \cdot r_j(t)) \tag{4.14}
\]

The instantaneous position of the \( j \)th nucleus, \( r_j(t) \), may be written as:

\[
r_j(t) = R_j + u_j(t) \tag{4.15}
\]

where \( R_j \) is the mean equilibrium position of the \( j \)th nucleus and \( u_j(t) \) is its instantaneous
displacement. Thus,

\[
S(Q, \omega) = \sum_{i,j} [b_i b_j \exp(iQ \cdot [R_i - R_j])] \times \int \{\exp(iQ \cdot [u_i(t) - u_j(0)])\} \exp(i\omega t) dt \tag{4.16}
\]
This expression includes the condition for elastic scattering and inelastic scattering involving one, two or more phonons. The dynamic information in equation (4.16) is contained in the time correlation function $G_y(Q,t)$, defined as:

$$G_y(Q,t) = \exp\left(\langle Q \cdot [u_i(t) - u_j(0)] \rangle\right) \tag{4.17}$$

In a harmonic crystal, the position of any nucleus at time $t$ is a linear function of the positions and momenta of all nuclei at time zero. Thus, it may be proved (e.g. Mermin, 1966; Ashcroft and Mermin, 1976; Squires, 1978) that for a harmonic oscillator, thermal averages involving two variables (or operators in the quantum case) $A$ and $B$, may be expressed as:

$$\langle e^A e^B \rangle = e^{\langle A B \rangle} \tag{4.18}$$

The time correlation function in equation (4.17) may be re-expressed using equation (4.18) as:

$$\langle \exp\left(iQ \cdot [u_i(t) - u_j(0)]\right) \rangle = \exp\left(-\frac{1}{2} \langle Q \cdot u_i(t) \rangle^2 - \frac{1}{2} \langle Q \cdot u_j(0) \rangle^2 \right) + \langle Q \cdot u_i(t) \rangle \langle Q \cdot u_j(0) \rangle \tag{4.19}$$

where $\langle Q \cdot u_i(t) \rangle^2$ and $\langle Q \cdot u_j(0) \rangle^2$ are the time-dependent Debye-Waller factors, describing the effect of the thermal vibrations of the nuclei about their equilibrium positions, such that:

$$\langle Q \cdot u_i(t) \rangle^2 = \langle Q \cdot u_i(0) \rangle^2 = 2W_i \quad ; \quad \langle Q \cdot u_j(0) \rangle^2 = 2W_j \tag{4.20}$$

Thus, equation (4.17) may be written as:

$$G_y(Q,t) = \exp\left(-[W_i + W_j]\right) \exp\langle Q \cdot u_i(t) \rangle \langle Q \cdot u_j(0) \rangle \tag{4.21}$$

The final exponential term of equation (4.21) may be expanded as a power series.
\[
\exp(\{Q \cdot u_i(t)\} \{Q \cdot u_j(0)\}) = \sum_{m=0}^{\infty} \frac{1}{m!} \langle \{Q \cdot u_i(t)\} \{Q \cdot u_j(0)\} \rangle^m
\]  

(4.22)

which yields:

\[
S(Q,\omega) = \sum_{m=0}^{\infty} S_m(Q,\omega)
\]

(4.23)

where:

\[
S_m(Q,\omega) = \frac{1}{m!} \sum_{ij} \{b_i b_j \exp(iQ \cdot [R_i - R_j]) \exp(-[W_i + W_j]) \times \int \langle \{Q \cdot u_i(t)\} \{Q \cdot u_j(0)\} \rangle^m \exp(-i\omega t) dt \}
\]

(4.24)

In this series, the most important information relevant to inelastic neutron scattering is contained in the terms, \( m \geq 1 \) (for the case where \( m = 0 \), the contribution to the scattering function is purely elastic, involving no scattering from phonons). The term for \( m = 1 \) involves the interaction between the neutron and a single phonon (one-phonon scattering), given by:

\[
S_1(Q,\omega) = \sum_{ij} \{b_i b_j \exp(iQ \cdot [R_i - R_j]) \exp(-[W_i + W_j]) \times \int \langle \{Q \cdot u_i(t)\} \{Q \cdot u_j(0)\} \rangle \exp(-i\omega t) dt \}
\]

(4.25)

Insertion of quantum mechanical expressions for the instantaneous displacements \( u(t) \) and amplitudes for the \([Q,u]\) terms in equation (4.25),

\[
u(t) = \frac{1}{\sqrt{N}} \sum_{ks} \sqrt{\frac{\hbar}{2m\omega_s(k)}} (a_{ks} + a_{ks}^*) \epsilon_s(k)e^{-ik \cdot R}
\]

(4.26)

where \( \omega_s(k) \) and \( \epsilon_s(k) \) are the frequency and polarization vectors \((\epsilon_s(k), \omega_s(k) = \delta_{ss})\) for the classical normal mode with polarization \( s \) and wavevector \( k \), \( a \) and \( a^* \) are the lowering and adjoint raising operators, respectively, of the simplified Hamiltonian describing the harmonic oscillator, such that \([a, a^*] = 1\), with consideration of the relations:
\[ a_{ks}(t) = a_{ks}e^{-i\omega_s(k)t} \]
\[ a_{ks}^*(t) = a_{ks}^*e^{-i\omega_s(k)t} \]
\[ \langle a_{ks} a_{k's}^* \rangle = 0 \] ; \[ \langle a_{ks} a_{k's} \rangle = [1 + n_s(k)]\delta_{kk'}\delta_{ss'} \quad (4.27) \]
\[ \langle a_{ks}^* a_{k's} \rangle = 0 \] ; \[ \langle a_{ks}^* a_{k's}^* \rangle = n_s(k)\delta_{kk'}\delta_{ss'} \]
yields the result (Dove, 1993):

\[ S_1(Q, \omega) = \sum_v \frac{\hbar}{2\omega(k)} |F_v(Q)|^2 \]
\[ \times \left([1 + n(k)]\delta(\omega + \omega(k)) + n(k)\delta(\omega - \omega(k))\right) \quad (4.28) \]

where \( Q = k + G \) (where \( G \) is a reciprocal lattice vector), \( n(k) \) is the Bose-Einstein factor, describing the mean number of phonons of type \( \omega \) present in thermal equilibrium, where \( n(k) \) and \( 1 + n(k) \) are the thermal factors describing the processes in which phonons are created or annihilated, respectively; the delta functions are present because the scattering only involves one phonon so that the scattering function will only be non-zero for values of the phonon mode frequencies, \( \omega = \pm \omega(k) \); the \( F_v(Q) \) term is the inelastic structure factor for the \( v \)th normal mode, defined by:

\[ F_v(Q) = \sum_j \frac{b_{mj}}{m_j} \exp(-W_j) \exp(iQ \cdot R_j)Q \cdot e_v^j(k) \quad (4.29) \]

where \( e \) is a vector that lies along the direction of motion of the atom. This expression determines the intensity of the one-phonon scattering, as it is a function of the scattering length, \( b \) (and thus the scattering cross-section - equation 4.3), the Debye-Waller factor, \( W_j \), and vectors \( Q \) and \( e \). The Debye-Waller factor results in attenuation of first-order scattering intensity as function of \( Q^2 \), resulting in greater attenuation at higher frequencies; the factor \( Q \cdot e \) results in the intensity of the one-phonon scattering being greatest if \( Q \) is approximately parallel to \( e \), and weakest if \( Q \) is approximately perpendicular to \( e \). Equation (4.28) also shows that the probability of scattering for \( \omega > 0 \), corresponding to the creation of a phonon, is always a greater than \( \omega < 0 \), corresponding to absorption of a phonon. This is to be expected because at low-temperatures, there is a limited number of thermally excited phonons and thus, very little chance of a neutron absorbing a phonon; however, it is always possible for a
neutron to lose energy by creation of a phonon. The probability of phonon annihilation occurring during inelastic scattering will therefore increase with temperature.

For the case where \( m > 1 \), each term corresponds to a scattering process involving \( m \) phonons (multi-phonon scattering), and the scattering function has only a weak structure in the frequency domain so that these higher-order terms will only usually contribute to the background scattering.

The scattering function, \( S(Q, \omega) \) is related to the double differential cross-section via the equation (e.g. Squires, 1978; Lovesey, 1984):

\[
\frac{d^2\sigma}{d\Omega dE} = \frac{k_1}{k_0^2} F^2 S(Q, \omega) \tag{4.30}
\]

Measurement of this function for all energy transfers \( E \) at a fixed \( k_0 \) and fixed direction \( k_1 \) yields the (single) differential cross-section, \( d\sigma/d\Omega \); if this property is measured over all scattering angles, then the total scattering-cross section, \( \sigma_{\text{tot}} \), for the system is obtained:

\[
\frac{d\sigma}{d\Omega} = \int_{-\infty}^{\infty} \frac{d^2\sigma}{d\Omega dE} dE \quad ; \quad \sigma_{\text{tot}} = \int \frac{d\sigma}{d\Omega} d\Omega \tag{4.31}
\]

4.2.4 Determination of the Magnitudes of Neutron Wavevectors

In INS, scattered groups of neutrons are observed whenever the energy and momentum conservation laws (equation 4.11) are simultaneously satisfied at certain \( \omega \) and \( Q \). An INS experiment involves the determination of the magnitudes of \( k_0 \) and \( k_1 \) and the scattering angle for each scattering event recorded, in order to obtain the energies of the scattered neutrons, \( E_i \). The directions of \( k_0 \) and \( k_1 \), and the scattering angles are determined from the geometry of the experimental arrangement, while the magnitudes of \( k_0 \) and \( k_1 \) are obtained by measuring either the wavelength or velocity of the neutrons. The first method uses a crystal spectrometer (the triple-axis spectrometer - Brockhouse, 1961), based on the Bragg law of scattering (equation 4.10). This spectrometer operates on a steady-state neutron source and uses the first of its 3 axes to give the orientation of the single-crystal monochromator (e.g. graphite, beryllium, germanium) which selects
the incident wavevector, \( \mathbf{k}_0 \), by normal Bragg scattering; the second axis gives the orientation of the sample, and the angles subtended by the incident and scattered neutron beams; the third axis gives the angle of a second monochromator (analyser) crystal which scatters neutrons of only one final wavevector (\( \mathbf{k}_1 \)) into the detector (Fig.4.2a). This scattering geometry is based on the momentum conservation law (equation 4.5) in which the neutron wave-vectors \( \mathbf{k}_1 \) and \( \mathbf{k}_0 \) form a closed triangle (Fig.4.2b). All 3 axes of the spectrometer are perpendicular to the scattering plane and all angles are variable (the second axis moves in an arc about the first, and the third axis moves in an arc about the second) to allow the exploration of \((Q, \omega)\) space.

The second method involves the electronic measurement of the transit time of neutrons over a finite flight path (the time-of-flight method), from which the neutron velocities may be determined. This method exploits the time structure of the neutron pulses produced by a spallation source, which have a narrow pulse width and a relatively large time interval between pulses (e.g. pulses of neutrons with time width of 20 \( \mu \)s are produced every 20 ms at the ISIS spallation source, RAL). The flight time, \( \tau \), for which a neutron of energy \( E \) and wavevector \( \mathbf{k} \) travels the distance \( L \), is given by:

\[
\tau = \frac{mL}{\hbar k} = L \left( \frac{m}{2E} \right)^{1/2}
\]  

(4.32)

As the initial pulse width is relatively narrow, it is possible to separate the different incident neutron energies by their flight times, and use them simultaneously in a measurement. This approach is generally used in time-of-flight spectrometer designs based on the principle of indirect geometry (e.g. the TFXA spectrometer, Figure 4.9), in which the crystal orientation and analyser angle remain fixed throughout the experiment, so that \( \mathbf{k}_1 \) is constant. Subtraction of \( \tau_1 \) (the time taken for the neutron to travel distance \( L_1 \) from the crystal to the detector) from the total time taken for the neutron to travel from the target to the detector, gives the time taken for the neutrons to travel from the target to the crystal, thus yielding the incident neutron wavevector \( \mathbf{k}_0 \). By measuring the intensity of the scattered neutrons as a function of flight time, equations (4.5) and (4.11) show that the intensity is actually measured as a function of a parabolic locus in \((Q, \omega)\) space. This is in contrast to measurements using a triple-axis spectrometer which record neutron scattering intensity as a function of \( Q \) or \( \omega \) only. Thus, the time-of-flight method allows a
wider area of \((Q, \omega)\) space to be explored in a single measurement, compared to measurements using a triple-axis spectrometer which require a large number of geometrical configurations to achieve the same result.

4.3 Previous Coherent INS Measurements

Coherent INS has been used predominantly in the determination of the phonon dispersion curves and density of states of molecular crystals for biochemical and
industrial applications (e.g. naphthalene - Natkaniec et al., 1980; anthracene - Dorner et al., 1982; HCN - Mackenzie and Pawley, 1979; C\textsubscript{10}H\textsubscript{6}(CH\textsubscript{3})\textsubscript{2} - Worlen et al., 1988; C\textsubscript{20}H\textsubscript{12} - Schleifer et al., 1989; C\textsubscript{3}N\textsubscript{3}H\textsubscript{3} - Heilmann et al., 1979; dispersed silica - Sheka et al., 1990; Cs\textsubscript{2}NaBiC\textsubscript{6} - Prokert and Aleksandrov, 1984; KSCN - Cookson et al., 1987; SnSe\textsubscript{2} - Harbec et al., 1983; UC, UAs - Jackman et al., 1986). Thus, studies of mantle-relevant silicate minerals using this technique are restricted, and limited to olivine (Ghose et al., 1991; Price et al., 1991; Rao et al., 1988), enstatite (Boysen et al., 1991), pyrope (Pavese et al., 1998) and quartz (e.g. Dolino et al., 1992; Berge et al., 1986; Boysen et al., 1980; Dorner et al., 1980). Thus, there has only been one previous determination of the vibrational density of states of garnet (by Pavese et al., 1998) and this was obtained from a powder sample of natural pyrope at 30K via the time-of-flight method, using the inverse geometry TFXA (Penfold and Tomkinson, 1986) and direct geometry MARI (Bennington and Eccleston, 1994) spectrometers with the ISIS pulsed neutron source (RAL). The experimental spectra were compared with the results of lattice dynamical simulations which employed the fully optimized interatomic potentials for pyrope (Table 2.6). The calculations by Pavese et al. (1998) were performed using a modified version of PARAPORS (Parker and Price, 1989; Pavese et al., 1996), in conjunction with the NEUTRONS code specifically written to simulate the INS patterns measured by the MARI and TFXA spectrometers (A. Pavese, personal communication, 1998), and based on the expression:

\[
P(\omega) = \sum_{j,Q} g[\omega - \omega_j(q)]\sigma[\omega_j(q)]|I_j(Q)|
\]  \hspace{1cm} (4.33)

where the summation is performed over the \(Q\) momentum transfer vectors accessed by the instrument, and over \(j\) phonons in the range 1 to \(3n\), where \(n\) is the number of atoms per primitive unit cell; and \(g(\omega)\) is a profile function defined as a normalized Gaussian function centred on each frequency, with a width given by:

\[
\sigma[\omega_j(q)] = \omega_j(q) \times 0.1
\]  \hspace{1cm} (4.34)

where each \(q\)-vector lies within the first Brillouin zone and is related to \(Q\) by a reciprocal lattice translation. The intermediate scattering function, \(I_j(Q)\), in equation (4.33) is defined as (Lovesey, 1984; c.f. equations 4.28 and 4.29):
\[
I_j(Q) \propto \left| \frac{k_1}{k_0} \right| \sum_d b_d \exp(-W_d(Q) + iQ \cdot d) \mathbf{k} \cdot \mathbf{e}^j_d(q) M^{-1/2}_d \right|^2 \left[ n(\omega_j(q)) \delta(\omega + \omega_j(q)) + (1 + n(\omega_j(q)) \delta(\omega - \omega_j(q))) \right] / \omega_j(q)
\]

(4.35)

where \( k_0 \) and \( k_1 \) are the initial and final neutron wavevectors, respectively; \( d \) is an atom in the primitive cell; \( n(\omega) \) is the Bose-Einstein distribution; \( \mathbf{e}^j_d(q) \) is a component of the dynamical matrix eigenvector of the \( j \)th phonon at wavevector \( q \), related to the \( d \)th atom; and \( M_d, W_d \) and \( b_d \) are the mass, Debye-Waller factor and scattering length of the \( d \)th atom, respectively.

Comparison of the experimentally-determined and simulated INS profiles demonstrated that there was reasonable agreement between all spectra, except in the high-energy region, where the simulations underestimated the intensities of the high-energy peaks. The atomic displacement parameters, obtained from the calculations and used to compute the intensity of each one-phonon inelastic process were underestimated by approximately 10% in comparison with those determined by a low-temperature XRD study (Pavese et al., 1995), suggesting that the disagreement between the profiles was not due to a loss of intensity from overestimation of the Debye-Waller term. Thus, the disagreement was attributed to multi-phonon effects in the experimental spectra, which become particularly significant in the high-energy range (Sjolander, 1958) and were unaccounted for in the harmonic approach of the simulations. The limited resolution of the experimental spectra was attributed to the quality of the sample which contained impurities not fully discarded during the sample preparation, resulting in the peaks in the experimental pattern being broad and overlapping. A lower theoretical resolution (10%) was used in the simulated profiles in order to provide a better separation of some of the frequency bands in the calculated profiles. The TFXA spectrum was reported to be better resolved than the MARI spectrum, particularly in the low-energy region (10-30 meV). This was suggested to be due to difficulties in correctly simulating the scattering intensities because of the averaging of the neutron counts in the detector array placed in space around the sample station on the MARI spectrometer. From the TFXA spectrum, Pavese et al. (1998) reported 13 peak positions which were dissimilar in energy to the Brillouin zone centre vibrational frequencies determined via IR and Raman spectroscopies, and therefore suggested that these must be a consequence of phonon
dispersion. Although this may be true for the low-frequency modes identified by Pavese et al. (1998) in the range 12-17 meV (98-135 cm\(^{-1}\)), our lattice dynamical calculations of the zone centre phonon frequencies of pyrope (Chapter 3) indicate that several of the higher frequency modes observed in the TFXA spectrum (at 22.8, 23.7, 62.0, 86.7 and 103.3 meV) may actually correspond to zone centre phonon frequencies which are inactive under IR or Raman light (Table 3.5) and therefore not observed in the spectroscopic datasets.

4.4 Present Coherent INS Measurements of Garnet

4.4.1 Introduction

In our INS study of garnet, discussed below, we have extended the INS work of Pavese et al. (1998) by performing coherent INS measurements of the density of states of pyrope along 3 crystallographic directions, [100], [110] and [111], in order to determine the variation of the phonon frequencies along specific wavevectors in the Brillouin zone; we have also performed the first coherent INS measurements of grossular garnet, \(\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}\). This is complemented by lattice dynamical calculations based on the computer codes and optimized potentials devised by Pavese et al. (1998), to assist in the interpretation of the experimental spectra. The 3 selected crystallographic directions are symmetrically distinct: the [100] direction, is dominated by 4-fold rotation and 4-fold roto-inversion axes centred on the SiO\(_4\) tetrahedra, with 2-fold rotation axes centred on the AlO\(_6\) octahedra (Fig.4.3a); the [110] direction is dominated by 2-fold rotation axes centred on the MgO\(_6\), AlO\(_6\) and SiO\(_4\) sites (Fig.4.4a); and the [111] direction is dominated by 3-fold rotations and 3-fold roto-inversions axes centred on the AlO\(_6\) sites (Fig.4.5a). Preliminary calculations of the phonon dispersion relations of pyrope along the [100] (Fig.4.3b), [110] (Fig.4.4b) and [111] (Fig.4.5b) directions, using the set of interatomic potentials defined in Table 2.2, show that there is relatively little dispersion of the vibrational modes in pyrope, compared to phases such as calcite (Dove et al., 1992b), quartz (Berger et al., 1986; Dolino et al., 1992) and olivine (e.g. Rao et al., 1988; Price and Parker, 1988; Ghose et al., 1991). The phonon dispersion relations of pyrope are particularly dense due to the large number vibrational modes present (240), but clearly
show the degeneracies of the modes at the Brillouin zone boundaries. Comparison of
the calculated dispersion relations along the 3 crystallographic directions shows that
the greatest amount of dispersion occurs for the internal modes above 900 cm\(^{-1}\), those
modes in the 500-700 cm\(^{-1}\) region and those below 200 cm\(^{-1}\), and the variations in the
calculated phonon dispersion relations are expected to be observable in the INS
spectra. The calculated dispersion relations were used to construct the vibrational
density of states of pyrope along [100], [110], and [111] (Fig.4.6a-c). These graphs
exhibit the variations in vibrational behaviour in the frequency regions mentioned
previously, but also allow better interpretation of the 200-500 cm\(^{-1}\) region which is
difficult to analyze from the dense dispersion relations. In particular, the density of
states derived for the [100] direction of pyrope (Fig.4.6a) demonstrates that there is a
significantly lower contribution from vibrational modes at approximately 400 cm\(^{-1}\),
compared to the [110] and [111] directions.

Hofmeister and Chopelas (1991b) constructed a Kieffer density of states model
(Kieffer, 1979, 1980) of pyrope from the observed IR- and Raman-active modes of this
phase (Hofmeister and Chopelas, 1991a), in order to calculate heat capacity and entropy.
The observed highest frequency internal modes were modelled with 4 Einstein
oscillators, with an optic continuum formed of 6 sections derived from the frequencies
associated with the \(v_2\) and \(v_4\) SiO\(_4\) internal modes, SiO\(_4\)-translations and rotations, Al-
and Mg-cation translations (Fig.4.7); the 3 acoustic branches were treated as Debye
oscillators, described by the acoustic velocities determined by O'Neill \textit{et al.} (1989). The
density of states model constructed by Hofmeister and Chopelas (1991b) shows
reasonable agreement with those obtained from our calculations, particularly in the 150-
400 cm\(^{-1}\) energy range. In the 0-150 and 400-1060 cm\(^{-1}\) regions, our calculations show
that there is a greater contribution from inactive zone centre vibrational modes and
frequencies associated with phonon dispersion not included in the model of Hofmeister
and Chopelas (1991b), which provide a continuous contribution in these energy ranges,
suggesting that these regions cannot be modelled by a small number of discrete
oscillators.
Figure 4.3a: Structure of pyrope projected along the [100] x-axis, showing the 4-fold rotation axes centred on the SiO$_4$ tetrahedra (orange), with 2-fold rotation axes centred on the AlO$_6$ sites (green), and mirror planes parallel to [110], [T10], and the y- and z-axes. The Mg-cations are obscured by the SiO$_4$ tetrahedra (constructed using Cerius$^2$, Molecular Simulations, Inc.).
Figure 4.3b: Calculated reduced-wavevector phonon dispersion relations of pyrope along the [100] direction. Note the significant anti-crossing behaviour at [0.225, 0, 0] where two modes with frequencies of approximately 540 cm$^{-1}$ appear to repel each other as they approach each other in frequency, indicating that they have the same symmetry (IR-active F$_{1u}$ modes).
Figure 4.4a: Structure of pyrope projected along [110], showing the 2-fold rotation axes centred on the MgO₆ (pink), AlO₆ (green) and SiO₄ (orange) cation sites, with mirror planes parallel to the z-axis and [110] (constructed using Cerius², Molecular Simulations, Inc.).
Figure 4.4b: Calculated reduced-wavevector phonon dispersion relations of pyrope along the [110] direction.
Figure 4.5a: Structure of pyrope projected along [111], showing the 3-fold rotation and 3-fold roto-inversion axes centred on the AlO$_6$ sites (green) (constructed using Cerius$^2$, Molecular Simulations, Inc.).
Figure 4.5b: Calculated reduced-wavevector phonon dispersion relations of pyrope along the [111] direction.
Figure 4.6: Calculated vibrational density of states of pyrope along a) [100], b) [110], and c) [111].
4.4.2 Experimental Procedure

Three euhedral translucent rhombic-dodecahedral single-crystals of pyrope, red-pink in colour, approximately 1-1.5 cm in diameter and obtained from high-grade metamorphic rocks in Zimbabwe, were cut into slices approximately 1.5 mm thick. A separate single-crystal was used to obtain crystal slices containing the [100], [110] or [111] crystallographic directions. Euhedral pale-green single-crystals of grossular, approximately 1 cm in diameter and obtained from metamorphosed calcic rocks in Mexico, were ground to a powder with particle size of 50-60 μm. The compositions of these garnets were determined using the electron microprobe at UCL (Table 4.1).
The powdered grossular sample (approximately 20 g), and a set of 3 vertically-stacked crystal slices from each pyrope sample were placed into individual aluminium foil envelopes, covering an area of approximately 4.5 cm², in order to fill as much of the neutron beam as possible. Al-foil is extremely malleable and has a low neutron absorption cross-section (0.231 per 2200 m/s neutrons), making it effectively transparent to neutrons, thus forming an ideal sample container. The samples were inserted into the ISIS pulsed neutron beam and cooled to below 30K using a Closed Cycle Refrigerator (CCR), in order to reduce multi-phonon contributions and signal intensity loss due to the Debye-Waller effect. The ISIS neutron source at RAL is a pulsed spallation source which produces pulses of neutrons with a time width of 0.4 μs every 50 ms. At this is installation, a pulse of H⁺ ions is accelerated to 665 keV in a pre-injector column before passing through 4 cavities in the linear accelerator (LINAC) to reach an energy of 70 MeV (Fig.4.8). At injection into the synchrotron, the electrons are stripped from the ions by very thin (0.25 mm) alumina foil, producing a circulating beam of protons. The synchrotron accelerates the protons to 800 MeV, before they are extracted and sent to the depleted uranium spallation target, typically producing about 25 neutrons per proton impact. This process is repeated 50 times a
second to produce the ISIS pulsed beam. The resultant white spectrum neutrons are subsequently directed to the moderators (ambient water, liquid methane at 100K, or liquid hydrogen at 20K), before being transmitted to the instruments set radially around the spallation target (Fig.4.8).

The neutrons scattered inelastically by the garnet samples were measured using the TFXA (Time Focused Xtal Analyser) spectrometer (Penfold and Tomkinson, 1986; Parker et al., 1995), as used by Pavese et al. (1998). This instrument has a fixed and indirect geometry set-up, operating in the energy loss mode at approximately 12 m from an ambient water moderator. Neutrons which are backscattered at an angle of 135° with respect to the incident beam, impinge on a pyrolytic graphite analyser crystal which, from Bragg’s Law (equation 4.10) selects neutrons of only one wavelength (and its harmonics), with a final neutron energy, $E_f$, of 3.95 meV; the remainder of the neutrons pass through the graphite crystal to be absorbed by the shielding. The neutrons diffracted by the graphite crystal pass through a beryllium filter to eliminate the higher order Bragg reflections before arriving at a detector assembly, which consists of 14 ‘squashed’ $^3$He-filled detector tubes (Fig.4.9). Several analyser-detector systems are used to collect data simultaneously, and the time-versus-counts spectrum of each detector tube is corrected for the incident flux distribution (measured by the ZnS incident beam monitor), and transformed into the more conventional energy-versus-$S(Q,\omega)$ spectrum by standard programmes, with individual spectra co-added to give the final spectrum.

As the final neutron energy and the distance around the TFXA system are known, the time of arrival at the detector of the scattered neutron uniquely defines the incident neutron energy, and thus the energy transfer at the sample. The design the TFXA is such that there is only one value of $Q$ for each energy (the energy transferred is approximately equal to $2Q^2$). Thus, an INS spectrum derived from this instrument is weighted by $Q^2$ (and also by the neutron scattering cross-sections, $\sigma$, for each atom species). In addition to the inelastic detectors, there are also two sets of $^3$He-filled detector tubes either side of the incident beam on the TFXA (Fig.4.9). These measure the elastically scattered neutrons and enable diffraction patterns to be recorded simultaneously with the inelastic spectrum, so that the crystal phase of the material may be verified, and phase changes which occur as an experimental variable is changed may be monitored.
Figure 4.8: The layout of the ISIS spallation pulsed neutron source and position of the instruments at the Rutherford-Appleton Laboratory, Oxford.
Figure 4.9: Schematic layout of the TFXA spectrometer at the Rutherford-Appleton Laboratory, Oxford.
4.5: Presentation and Analysis of Experimental and Simulated INS Spectra

4.5.1 Experimentally-Determined INS Spectra of Pyrope

The INS spectra obtained for the different orientations of pyrope using the TFXA spectrometer are shown in Figures 4.10-4.12, in which the raw spectra have been corrected for the background contribution from the sample container. The measurements from each of the 28 detectors are shown, resulting in spectra with high noise levels but high accuracy. The noise levels are greater in the low-energy transfer range (<20 meV) due to difficulties in measuring very small changes in neutron energies. Comparison of the raw spectra for the 3 orientations of pyrope (Figs.4.10a, 4.11a, 4.12a) demonstrates that the spectrum for the [111] direction is dominated by an intense peak centred at approximately 15 meV (120 cm⁻¹). Thus, it is similar in profile to the INS spectrum recorded by Pavese et al. (1998) for a powder sample of pyrope (Fig.4.13), which has an intense peak at approximately 16 meV. The INS spectra recorded for the [100] and [110] directions in pyrope also contain peaks in the 12-20 meV (100-160 cm⁻¹) range, but these features do not dominate the spectra.

The calculated phonon dispersion relations of pyrope (Figs.4.3b-4.5b) demonstrate that the peaks observed in this energy region (Table 4.2) are attributable to the acoustic modes and lowest frequency optic modes (also IR-active), whereas the smaller peaks in the 10-12 meV (80-100 cm⁻¹) range are solely attributable to acoustic modes (the spectra are not reported for energy transfers of <10 meV because the 0-10 meV region is dominated by peaks associated with elastic scattering). The calculated dispersion relations also demonstrate that the acoustic and lowest energy optic modes (150-155 cm⁻¹) show considerable variation in frequency away from the Brillouin zone centre in comparison with other low-frequency (≤500 cm⁻¹) optic modes. The dispersion of the 150-155 cm⁻¹ modes is greatest along the [110] direction (Fig.4.4b), with a decrease in frequency of approximately 50 cm⁻¹ away from the zone centre. This dispersion results in the lowest frequency optic modes being clearly separable from and lower in frequency than the TO acoustic modes towards the Brillouin zone boundary. The separation of these modes results in the degeneration of the single intense peak observed in the 12-20 meV region by Pavese et al. (1998) and in our spectrum for the [111] direction, into 2 peaks of similar intensity centred at 13 and
Figure 4.10: INS spectra for the [100] direction in pyrope with a) the experimentally-determined spectrum, corrected for background contributions, b) the smoothed experimental spectrum, and c) the simulated spectrum.
Figure 4.11: INS spectra for the [110] direction in pyrope with a) the experimentally-determined spectrum, corrected for background contributions, b) the smoothed experimental spectrum, and c) the simulated spectrum.
Figure 4.12: INS spectra for the [111] direction in pyrope with a) the experimentally-determined spectrum, corrected for background contributions, b) the smoothed experimental spectrum, and c) the simulated spectrum.
Figure 4.13: INS spectrum of pyrope determined from a powder sample by Pavese et al. (1998).

17.5 meV, respectively. This is illustrated more clearly in the smoothed spectrum for the [110] direction (Fig.4.11b), derived using 2 Fourier filter processes from the routine TFXA software. The smaller calculated dispersion of the low-frequency optic modes along the [100] direction in pyrope (Fig.4.3b) results in the mixing of these modes with the acoustic vibrations towards the Brillouin zone boundary, so that separation of the individual modes is more difficult. This causes a smaller splitting of the peak in the 12-20 meV range into 2 peaks centred at approximately 14 and 16.5 meV, which is more clearly illustrated in the smoothed spectrum for this wavevector (Fig.4.10b). The calculated phonon dispersion relations for the [111] direction in pyrope (Fig.4.5b) demonstrate that the lowest frequency optic modes also show
significant dispersion away from the Brillouin zone centre, approaching the frequency of the TO acoustic modes towards the zone boundary. This results in the single intense peak at 15 meV in the INS spectrum, with smaller peaks at approximately 17.5 and 19 meV, which are related to the crossing of the low-frequency optic modes and the LO acoustic mode. These observations show that the contribution from phonon dispersion, which cannot be measured by IR or Raman spectroscopies, has been recorded in our INS spectra.

<table>
<thead>
<tr>
<th>Pyrope [100]</th>
<th>Pyrope [110]</th>
<th>Pyrope [111]</th>
</tr>
</thead>
<tbody>
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<td>8</td>
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<td>6, 7</td>
</tr>
<tr>
<td>11</td>
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<td>-</td>
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<td>17.5</td>
</tr>
<tr>
<td>-</td>
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<td>20</td>
</tr>
<tr>
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<td>-</td>
</tr>
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<tr>
<td>128.5</td>
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Table 4.2: Approximate peaks positions (in meV) in the INS spectra of pyrope (1 meV = 8.065 cm⁻¹).

The results of our mode assignments reported in Chapter 3 and previous spectroscopic studies of garnet (e.g. Hofmeister and Chopelas, 1991a; Hofmeister et al., 1996; Kolesov and Geiger, 1998) indicate that the vibrational frequencies in the 10-20 meV region of the INS spectra are attributable to motions of the Mg- and Si-cations. This is in agreement with the partial density of states calculations by Pavese et al. (1998), which show the contribution from each chemical species to the INS spectrum. The compositions of our pyrope samples (Table 4.1) suggest that the
dodecahedral sites also contain Fe, Mn and Ca atoms, the motions of which will also contribute to this region of the spectrum. The addition of Fe into the pyrope structure results in a small decrease in energy (5-10 cm\(^{-1}\)) of the vibrational frequencies (Kolesov and Geiger, 1998; Hofmeister et al. 1996; Gillet et al., 1992; Hofmeister and Chopelas, 1991a; Geiger et al., 1989; Moore et al., 1971) but in contrast, the addition of Ca or Mn results in a more significant decrease of 30-50 cm\(^{-1}\) between pyrope and the Ca- and Mn-garnet end-members. However, the effect of such substitutions is reported to be minor for impurity contents of <10 mol\% (Hofmeister et al., 1996). Although the addition of impurities is expected to have little effect on the true vibrational density of states of pyrope, the density of states obtained via INS is weighted by the neutron scattering cross-sections for the chemical species involved in each vibration (and a \(Q^2\)-weighting for each energy transfer), and this results in changes in the profile of the density of states. Comparison of the coherent neutron scattering lengths and cross-sections for the atoms present in our pyrope samples (Table 4.3), shows that the neutron scattering cross-section of Fe is 3-4 times larger than those of the other atoms present, which are in the range 2-4 barns. This property of Fe is therefore expected to increase the intensity of the peaks in the INS spectrum corresponding to vibrations involving Fe-cations. The spectrum reported by Pavese et al. (1998) was derived from a pyrope sample containing approximately 1% Fe - a significantly lower Fe-content than in our samples - but contains a more intense peak in the 12-20 meV range compared with our spectra. Thus, the lower intensity of the peaks in this range in our INS spectra may be due to a relative increase, due to the presence of Fe, in the intensity of the peaks in the 20-60 meV range, in which dodecahedral cations still contribute the vibrational modes, or because the spectrum recorded by Pavese et al. (1998) is a sum over all wavevectors, the majority of which may have INS spectra similar to that recorded for the [111] direction.

The 20-95 meV region of the INS spectra of pyrope corresponds to the main optic continuum (160-760 cm\(^{-1}\)) which, in pyrope, is particularly dense due to the large number of vibrational modes occupied at these energy levels and their lack of dispersion across the Brillouin zone. The calculated phonon dispersion relations for the 3 orientations of pyrope (Figs.4.3b-4.5b) demonstrate that this distribution of the optic modes may be subdivided into 2 regions: 160-560 cm\(^{-1}\) (20-70 meV) - the densest region, with vibrational modes showing little dispersive behaviour; and 560-760 cm\(^{-1}\) (70-95 meV) - a comparatively less dense region, with modes showing
greater dispersion. In the INS spectra of pyrope, the 20-70 meV region is characterized by 6-8 major peaks and is separated from the 70-95 meV region, containing 1-2 broad peaks (Figs.4.10b-4.12b), by a trough in the spectrum profile at approximately 70 meV. This feature may also be identified in the INS spectrum reported by Pavese et al. (1998), although the peak positions cannot be readily compared due to limits in resolution. The peak positions in our INS spectra show small variations of up to 2.5 meV (20 cm\(^{-1}\)) with crystallographic orientation (Table 4.2), with no obvious relationship between frequency and wavevector identifiable, and thus the major differences between the spectra are the intensities and widths of the peaks. The position and profile of the individual peaks in the INS spectra can be directly related to variations in the density of the calculated phonon dispersion relations: the peaks correspond to dense regions of the phonon dispersion relations which contain a high number of vibrational modes, and the degree of density governs the intensity of the peaks (together with the neutron scattering powers of the atoms involved in the vibrations and the \(Q^2\) weighting); the troughs in the spectral profiles correspond to areas of the phonon dispersion relations which are less dense or devoid of any contribution from vibrational modes.

<table>
<thead>
<tr>
<th>Atom</th>
<th>(Z)</th>
<th>(A)</th>
<th>(b_{coh})</th>
<th>(\sigma_{coh})</th>
<th>(\sigma_{total})</th>
<th>(\sigma_a)</th>
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Table 4.3: Bound coherent (\(b_{coh}\)) and incoherent (\(b_{inc}\)) neutron scattering lengths (in femtometers); bound coherent (\(\sigma_{coh}\)), incoherent (\(\sigma_{inc}\)) and total (\(\sigma_{total}\)) neutron scattering cross sections and neutron absorption (\(\sigma_a\)) cross-sections (in barns; 1 barn = 100 fm\(^2\)), for the atoms found in our pyrope samples (from Sears, 1986).
For example, the peak at 63 meV (510 cm\(^{-1}\)) in the INS spectrum for the [111] direction of pyrope (Fig.4.12a,b) is attributable to the dense and continuous distribution of vibrational modes at these energies throughout the wavevector in the phonon dispersion relations (Fig.4.5b). The peak is bound by troughs at approximately 57 (460 cm\(^{-1}\)) and 68 meV (550 cm\(^{-1}\)), the first of which corresponds to small gaps observed in the phonon dispersion relations throughout the wavevector at the 460 cm\(^{-1}\) energy level; the second trough corresponds to the area in the phonon dispersion relations at approximately 550 cm\(^{-1}\) which contains very few vibrational modes and divides the optic continuum into 2 regions, as mentioned previously. Similarly, the peak at 25 meV (200 cm\(^{-1}\)) in the spectrum for the [110] direction (Fig.4.11a,b), bounded by 2 troughs at 23 and 27.5 meV, can be related to the dense area of the phonon dispersion relations (Fig.4.4b) at approximately 200 cm\(^{-1}\). The origin of the 2 troughs can be related to the less dense regions in the phonon dispersion relations at approximately 215-240 cm\(^{-1}\) and 170-190 cm\(^{-1}\). This spectrum also contains an additional peak at approximately 21.5 meV (175 cm\(^{-1}\)) which may be related to the mixing of the LO acoustic mode and the low frequency optic modes at approximately [0.175, 0.175, 0.0]. The spectra for the [100] and [110] directions (Fig.4.10-4.11) each contain a broad peak at approximately 92 meV (750 cm\(^{-1}\)). Analysis of the calculated phonon dispersion relations (Fig.4.3b-4.4b) indicate that these peaks correspond to the frequency gap between the internal and external modes (725-800 cm\(^{-1}\)), and hence, according to the calculations, there should be no features in this region of the INS spectrum. It is therefore likely that these peaks are related to multiphonon processes which are not accounted for in the calculations.

The vibrational modes in the 20-70 meV (160-560 cm\(^{-1}\)) region of the INS spectra of pyrope are attributable to translations of the cations present in the dodecahedral, octahedral and tetrahedral sites and rotations of the Si\(_4\)O\(_4\) tetrahedra (Cahay et al., 1981; Hofmeister et al., 1996; Chaplin et al., 1998; Kolesov and Geiger, 1998), in agreement with the partial density of states calculations by Pavese et al. (1998). The composition of the samples used in our INS experiments (Table 4.1) indicates that there is a minor amount of Cr in octahedral coordination in addition to Al. Although the Cr atom has a larger neutron scattering cross-section than Al (Table 4.2), the presence of this impurity is not expected to alter the profile of the spectrum significantly because Mg and O, which have similar scattering powers to Cr, also contribute to the vibrations at these energy levels. The presence of Fe in the
dodecahedral sites, with its greater neutron scattering powers, is expected to have enhanced the intensity of the peaks in this region, as mentioned previously, resulting in changes in the appearance of the spectrum compared to that reported by Pavese et al. (1998). The vibrational modes in the 70-95 meV region (560-760 cm\(^{-1}\)) of the INS spectra are dominated by the bending motions of the SiO\(_4\)-tetrahedra (Hofmeister and Chopelas, 1991a; Hofmeister et al. 1996; Chaplin et al., 1998; Kolesov and Geiger, 1998).

The 100-145 meV (800-1200 cm\(^{-1}\)) energy range in the INS spectra of pyrope corresponds to the internal stretching modes of the SiO\(_4\) tetrahedra (Kolesov and Geiger, 1998; Chaplin et al., 1998; Hofmeister et al. 1996; Hofmeister and Chopelas, 1991a), and is characterized by 1-2 broad peaks which are generally lower in intensity than the other peaks in the spectrum, caused by the reduction of the inelastic signal due to the Debye-Waller factor and the \(Q^2\) weighting, as observed by Pavese et al. (1998). The spectra for the [100] and [111] directions of pyrope (Figs.4.10, 4.12), contain 2 peaks in this region, at approximately 110 and 128 meV. Analysis of the calculated phonon dispersion relations (Fig.4.3b, 4.5b) suggests that the peaks at 110 meV, which have greater intensity, correspond to the lower and more dense part of the phonon dispersion relations of the internal modes (800-960 cm\(^{-1}\)); the peaks at approximately 128 meV can be related to the less dense and highest energy part of the phonon dispersion relations, which show more significant dispersion. Thus, it is clear that in addition to the Brillouin zone centre frequencies measurable by IR and Raman spectroscopies, phonon frequencies associated with inactive zone centre modes and phonon dispersion have also been measured in our INS experiments, from the continuous profile of the spectra throughout the energy range associated with vibrational frequencies of garnets.

4.5.2 Comparison of Experimental Spectra with Simulated TFXA Profiles

Lattice dynamical simulations of our INS experiments on pyrope were performed using the optimized potentials developed by Pavese et al. (1998) and their computer code NEUTRONS, specifically written to simulate experiments on the TFXA spectrometer (see equations 4.33-4.35). The code was modified from its
original general Brillouin zone sampling procedure, so that sampling could be performed along a specified wavevector. Comparison of our simulated and experimentally-determined INS spectra for the [100], [110] and [111] directions in pyrope (Figs.4.10-4.12) demonstrates that there is generally good agreement between the observed and calculated peak positions, particularly in the higher energy transfer region (>30 meV), with an average difference of 2 meV. In the 10-30 meV energy range, the peak positions in the calculated spectra (Fig.4.10c-4.12c) are shifted to higher energies by approximately 6-10 meV, compared with the experimental spectra. This shift was also observed in the simulated INS spectrum reported by Pavese et al. (1998) and was attributed to: the difficulties in accurately simulating the low-frequency modes of pyrope because these modes involve weak interactions; the use of potentials which have as yet been fully developed; and the significant uncertainties in the experimentally-determined low-energy frequencies due to possible structural defects in the sample.

The intensities of the experimentally-determined peaks are not reproduced as accurately in the simulations as the peak positions, particularly in the 10-25 and 95-140 meV ranges in which the intensities of the observed peaks are underestimated. In the low-frequency region, this may be attributed to the presence of Fe in dodecahedral coordination in the pyrope samples which, due to its greater neutron scattering powers compared to the other 8-fold coordinated cations, increases the intensity of the peaks associated with translations of the dodecahedral sites; the underestimation may also be partially attributable to insufficient sampling or inaccurate simulation of the low-frequency modes. In the high-frequency region, the underestimation is directly attributable to multiphonon processes which become increasingly important at high energies (Sjolander, 1958), and whose additional contribution to the theoretical profiles is not accounted for due to our use of the quasi-harmonic approximation. Underestimation of the high-energy peak intensities in the simulated spectrum of pyrope was also reported by Pavese et al. (1998), and the possibility of underestimation of intensity due to overestimation of the Debye-Waller term was excluded by them because the calculated displacement parameters used to simulate the intensity of each one-phonon inelastic process (equation 4.35) were underestimated by approximately 10% in comparison to those determined via XRD (Pavese et al., 1995), leading Pavese et al. (1998) to conclude that the multiphonon contribution was responsible for the disagreement between the observed and
calculated patterns. We have also designated multiphonon processes as responsible for the broad, low-intensity peaks observed in the 85-95 meV region of the experimental INS spectra for the [100] and [110] directions of pyrope as these peaks are not reproduced in the simulated spectra, nor included in the corresponding energy levels in the calculated phonon dispersion relations.

4.5.3 Comparison of INS Spectra of Pyrope and Grossular

In addition to our INS measurements of pyrope, we have also recorded the first INS spectrum of grossular garnet from a powder sample. This spectrum (Fig. 4.14) shows some similarities to the INS spectrum reported by Pavese et al. (1998) for pyrope powder (Fig. 4.13), with a strong peak in the 10-20 meV region which has a greater intensity than the other features in the spectrum. However, this peak in the spectrum of grossular (centred at approximately 12.5 meV) has a lower intensity than the peak observed in the same region of the pyrope spectrum by Pavese et al. (1998). This may be due to the smaller neutron scattering cross-section of Ca (Table 4.3) which effectively lowers the intensity of peaks in the INS spectrum attributable to motions of the Ca-cations in comparison with peaks associated with Mg-cation motions. The presence of a small amount of Fe in our grossular sample, which may have enhanced the intensities of the peaks in the 10-70 meV region, and differences in data collection time (72 hours for the pyrope powder sample (Pavese et al., 1998); 40 hours for our grossular powder sample) may also be contributory factors to the observed differences in the profiles. The INS spectrum of grossular may be analyzed in terms of 11 peaks, centred at approximately 7.5, 12.5, 14.5, 21, 25, 31.5, 41, 63, 78, 104 and 122 meV, in a smoothed spectrum (Fig. 4.14b) obtained using the same Fourier filters employed to derive the smoothed pyrope spectra. This analysis provides a higher resolution than that reported in the spectrum of pyrope by Pavese et al. (1998), and results in additional differences between the spectra. The grossular spectrum shows similarities with our spectra of pyrope, and this is expected from consideration of the garnet samples, which differ mainly in dodecahedral cation chemistry and sample size, and the similarities in instrument set-up and experimental
Comparison of the observed peak positions in our INS spectra of grossular and pyrope demonstrates that the peaks are shifted to lower energies in the grossular spectrum, by an average of 3 meV (25 cm$^{-1}$) for the low-frequency modes (<65 meV), and 6 meV (50 cm$^{-1}$) for the high-frequency modes. This is in agreement with the observed variations in the frequencies of the IR- and Raman-active modes between the pyrope and grossular end-members (Kolesov and Geiger, 1998; Bosenick et al., 1995; Gillet et al., 1992; Hofmeister and Chopelas, 1991a; Geiger et al., 1989; Moore et al., 1971), variations which can be directly attributed to the larger mass of the Ca atom.
4.6 Summary and Conclusions

Thermal neutrons are powerful probes of condensed matter as they have energies comparable to those associated with atomic vibrations, and at 300K, their mass is such that they have wavelengths similar to the interatomic spacings in solids. This is in contrast to other probes which have either the appropriate wavelength (x-rays) or energy (photons). Coherent inelastic neutron scattering (INS) can be used to study the internal dynamics of a solid by measuring the change in energy and momentum of incident neutrons scattered inelastically by a sample, in which the energy lost or gained by a neutron corresponds to a phonon frequency in the sample. This technique is the only method of determining the full vibrational density of states of a solid, in contrast to IR and Raman spectroscopies which yield only the long-wavelength zone centre phonons permissible by selection rules. We have used coherent INS to determine the vibrational density of states of pyrope along crystallographic directions, [100], [110] and [111], and powdered grossular, thus extending the work of Pavese et al. (1998). The observed differences between our INS spectra of pyrope are small but significant, and the peak positions have been interpreted on the basis of calculated phonon dispersion relations. The spectra have also been compared with lattice dynamical calculations which employed the optimized potentials of pyrope (Pavese et al., 1998). The calculated peak positions generally show good agreement with the experimental spectra except in the low-energy range (<25 meV), where the observed peak positions are underestimated. This is attributed to difficulties in simulating the low-energy vibrational modes which are derived from weak interactions and insufficiently described by potentials which are not yet fully-optimized. Also, this region of the spectra is particularly noisy, resulting in poorly constrained peak positions which may uncertain due to structural defects in the samples. The simulated intensities of the peaks are underestimated throughout the spectra and in the mid-low frequency region (<70 meV), this is considered to be due to the presence of Fe in the garnet samples which, with its larger neutron scattering cross-section, has enhanced the intensities of the peaks. In the high-frequency range (70-140 meV), the underestimation of peak intensities by the simulated profiles is attributed to the neglect of the multiphonon contribution, which becomes important at these energy levels, by our quasi-harmonic lattice dynamical calculations. Comparison of the INS recorded spectra for pyrope and grossular demonstrates that
the profiles are generally similar, but the peak positions in the grossular spectrum are shifted to lower energies due to the addition of the less massive Ca-cation, as observed in IR and Raman spectroscopic studies. In future experiments, the noise levels observed in the experimental spectra may be reduced by collecting the inelastic signal for longer than the average 25 hour period used for each pyrope sample; the disagreement between the observed and simulated spectra may be reduced by using pyrope samples with lower Fe-contents, more intense Brillouin zone sampling of the low-frequency modes at low-wavevectors, simulations including Fe in dodecahedral coordination and full optimization of the interatomic potentials in order to describe the vibrational behaviour of pyrope more accurately. It may also be possible in future studies to deconvolute the experimental spectra by removal of the $Q^2$ and neutron scattering cross-sections weightings, to obtain the true vibrational density of states. To date, this procedure has only been reported for the INS spectrum of vitreous silica (Taraskin and Elliot, 1997), in which a correction function was constructed using molecular dynamics calculations of the partial density of states for this phase.
CHAPTER 5: A Raman Spectroscopic Investigation of CaGeO₃ Garnet: An Analogue for Majorite.

5.1 Introduction

Majorite garnet is characterized as a silicon-enriched phase with pyroxene (MgSiO₃) stoichiometry, with Mg- and Si-cations occupying the octahedral sites, thus replacing the Al-cations in aluminosilicate garnets. It was first identified with cubic symmetry (Ia₃d) in the Coorara meteorite (Smith and Mason, 1970), and has since only been found naturally occurring in three other chondrites: the Tenham, Coolaman and Catherwood meteorites (Price et al., 1979; Dodd, 1981; Coleman, 1977). A high-pressure (shock metamorphic) process was proposed for its origin from pyroxene, due to its association with diaplectic glass, maskelynite and ringwoodite. From an investigation of phase relations in the enstatite-ferrosilite system (MgSiO₃-FeSiO₃), Kato (1986) suggested that the shock event reached, at least locally, pressure and temperature conditions exceeding 20 GPa and 2000 °C, and experimental shock-loading of enstatite has indicated that cubic majorite formation occurs in the pressure range 35-50 GPa (Jakubith and Hornemann, 1981; Ahrens and Gaffney, 1971).

Attempts at synthesizing MgSiO₃ garnet in phase equilibria studies of enstatite at conditions in excess of 17 GPa and 1700 °C, have yielded a garnet-structured phase with non-cubic symmetry (e.g. Kato and Kumazawa, 1985; Sawamoto, 1987; Presnall and Gasparik, 1990; Matsubara et al., 1990; Ohtani et al., 1991). Analysis of this phase by XRD has shown that this garnet has tetragonal symmetry, with space group I4₁/a (point group C₄h). The reduction of symmetry is caused by ordering of the Mg- and Si-cations on the octahedral sites (Fig.5.1), and splitting of the single octahedral site in cubic garnets (equipoint 16a) into two distinct positions, equipoints 8d and 8e (Kato and Kumazawa, 1985; Sawamoto, 1987; Angel et al., 1989; Hatch and Ghose, 1989). Garnet-like phases with tetragonal symmetry have also been identified in compounds such as MnSiO₃ (Fujino et al., 1986), CaGeO₃ and CdGeO₃ (Prewitt and Sleight, 1969; Tarte and
Figure 5.1: Physical structure of MgSiO₃ garnet with tetragonal symmetry projected along [110], with independent SiO₄ tetrahedra (orange) linked to octahedra containing ordered Mg- (green) and Si-cations (yellow), with intervening dodecahedral sites also containing Mg-cations (red) (constructed using WebLab ViewerLite, Molecular Simulations, Inc.).
Previous high-pressure and high-temperature experiments to synthesize cubic majorite had required a certain concentration of Al (20-25% - e.g. Ringwood and Major, 1971; Akaogi and Akimoto, 1977; Kanzaki and Ito, 1984; Kraft and Knittle, 1990; Parise et al., 1996) or Fe (20% - Kato, 1986) to stabilize the cubic structure. Detailed analyses of tetragonal majorites have, however, demonstrated that partial octahedral cation disorder may exist (8% - Howell et al., 1990; 20% - Angel et al., 1989; Phillips et al., 1992), although it may be attributable to synthesis conditions and quench rate (Wang et al., 1993), and Yusa et al. (1993) have demonstrated that the effect of cation disorder in majorite is to shift the boundaries of the stability field of tetragonal garnet with pyroxene, wadsleyite + stishovite, ilmenite and perovskite, to lower pressures and temperatures.

Angel et al. (1989) reported the presence of merohedral and pseudomerohedral twinning, with twin lamellae parallel to {110}, in tetragonal majorite synthesized at 17 GPa and 1800 °C. Group theory indicates that order-disorder transformations result in the formation of microdomains in the ordered phase due to the symmetry loss, when the point group of the ordered daughter phase is a subgroup of the disordered parent phase, and that the crystallographic orientation of the domains of the ordered phase are related by the symmetry elements that are absent in the ordered phase but present in the disordered one (e.g. Hammermesh, 1962; Fateley et al., 1972). From Group theoretical analysis of the $Ia\bar{3}d$ to $I4_1/a$ phase transition (in which the diagonal mirror plane on (110) is lost) and the observed twinning, Hatch and Ghose (1989) demonstrated that the cubic-tetragonal phase transformation is an improper ferroelastic transition driven by the onset of a primary order parameter (Mg-Si ordering on the octahedral sites) at the transition temperature. Heinemann et al. (1997) also concluded that the merohedral and pseudomerohedral twins in a majorite synthesized at 2000 °C and 19 GPa, formed as the product of the phase transition during isobaric temperature quench, and from consideration of the synthesis conditions reported by Angel et al. (1989), that the cubic-tetragonal phase transition occurs at temperatures below 1800 °C at 17 GPa. However, Wang et al. (1993) suggested that the boundary of the cubic-tetragonal phase transformation is between 2300 and 2350 °C at 22 GPa, from analysis of modulated ("tweed") microstructures observed parallel to the {101} twin planes in majorite crystals quenched from above 2400 °C and 22 GPa. Improper ferroelastic phase transitions
commonly result in softening of elastic properties at temperatures well below, and in excess of, the transition temperature (e.g. Poirier, 1982; Salje, 1990), with the softening generally greater on the lower symmetry side of the transition. This was observed in the Young's Modulus for the \( Ia\bar{3}d \) to \( I4_{1}/a \) transition in \( \text{Ca}_3\text{Mn}_2\text{Ge}_3\text{O}_{12} \) garnet by Kazey et al. (1982). However, elasticity studies of garnets along the pyrope-majorite join suggest that the bulk and shear moduli show little variation (approximately 8% and 2%, respectively) with increasing majorite content (Bass and Kanzaki, 1990; Yeganeh-Haeri et al., 1990; Yagi et al., 1987, 1992; Rigden et al., 1994; Pacalo and Weidner, 1997). In contrast, Jeanloz (1981) determined an extremely large bulk modulus of 221±15GPa from static compression measurements of a natural majorite from the Catherwood meteorite, with composition \((\text{Mg}_{0.79}\text{Fe}_{0.21})\text{SiO}_3\). The elastic constant data for cubic phases along the pyrope-majorite join at room temperature therefore do not show a softening effect. However, this may be because the data does not extend to high enough majorite contents, or because the elasticity was measured at temperatures below where the transition is kinetically possible.

Significant quantities of pyroxene and garnet are included in the most widely discussed models of mantle mineralogy (e.g. Ringwood, 1975; Anderson, 1984; Anderson and Bass, 1986; Duffy and Anderson, 1989). The dissolution of pyroxene into the garnet structure with increasing pressure (e.g. Ringwood and Major, 1966; Ringwood, 1967; Akaogi and Akimoto, 1977; Sawamoto, 1987; Irifune, 1987; Gasparik, 1989, 1990), and the solid-solution series between pyrope and majorite (Akaogi and Akimoto, 1977; Akaogi et al., 1987; Kanzaki, 1987; McMillan et al., 1989; Rigden et al., 1994; Sinogeikin et al., 1997; Irifune et al., 1996; Parise et al., 1996; Heinemann et al., 1997), suggests that majorite may comprise approximately 40% of the transition zone by volume for peridotitic compositions, and as much as 60% for basaltic or eclogitic compositions (e.g. Irifune and Ringwood, 1987; Weidner and Ito, 1987; Ita and Stixrude, 1992). Studies of majorite have emphasized the dominant role of Mg and Si, and to a lesser extent Fe-components, that together may account for as much as 94 mol% of the mantle (Ringwood, 1975). The role of calcium oxide, which represents perhaps 3 mol% of the mantle, has been treated as relatively unimportant. As the \( \text{Ca}^{2+} \) cation is significantly larger than other common divalent cations proposed to exist in the mantle, Ca may play an influential role in high-pressure silicates by helping to stabilize structures with
appropriately large cation sites, such as garnet. Indeed, Akaogi and Akimoto (1979) have demonstrated that the stability field of garnet expands with Ca-content at pressure. The presence of Ca-rich pyroxene (diopside) and grossular as upper mantle phases, also suggests that Ca-bearing majorites will be important in the transition zone (Akaogi and Akimoto, 1979; Akaogi et al., 1987; Irifune et al., 1989; Gasparik, 1989, 1990; Canil, 1994; Hazen et al., 1994). Thus, knowledge of the physical, elastic, vibrational and hence, thermodynamic properties of majorites of all compositions is essential in interpreting geophysical models of the transition zone. The distribution of the octahedral cations in majorite will affect its vibrational properties and thus its thermodynamic properties resulting, for example, in an increase in configurational entropy with increasing disorder. Only 5 vibrational spectroscopic studies of (Mg,Fe)SiO$_3$ majorite have been reported: the 3 IR spectroscopic studies, performed at ambient conditions (Jeanloz, 1981; Kato and Kumazawa, 1985; McMillan et al., 1989), have yielded 8, 15 and 22 IR-active bands, respectively, out of the 65 modes predicted by FGA of the tetragonal C$_{4h}$ structure (McMillan et al., 1989). The observed peak positions and peak widths were reported to be very similar to those of pyrope, except for additional bands due to the lower symmetry. The Raman spectrum of tetragonal majorite has been recorded by McMillan et al. (1989) at ambient conditions, and by Rauch et al. (1996) to 200 kbar. The two studies yielded a maximum of 34 and 25 bands, respectively, out of the 80 modes predicted by FGA, and again the spectra were reported to be similar to those obtained for pyrope except that many more peaks were apparent. Thus, the existing IR and Raman vibrational spectra of majorite are incomplete and further characterization of the vibrational properties of majorite is required.

Germanate systems have been widely used as analogues for major silicate phases (e.g. CaGeO$_3$ perovskite - Liebermann et al., 1977; Ross et al., 1986; Andrault and Poirier, 1991; MgGeO$_3$ pyroxene - Tarte and Ringwood, 1964; Liebermann, 1974; Andrault et al., 1992; GeO$_2$ - Jorgensen, 1978; Houser et al., 1988; Madon et al., 1991; Yamanaka et al., 1992; Mg$_2$GeO$_4$ olivine - Dachille and Roy, 1960; Hensen, 1977; Weidner and Hamaya, 1983; Fiquet et al., 1992; Reynard et al., 1994; Petit et al., 1996), including analogues for the cubic alumino-silicate garnets (e.g. Ca$_3$Fe$_2$Ge$_3$O$_{12}$ - Tarte, 1965; Ca$_3$Mn$_2$Ge$_3$O$_{12}$ - Kazey et al., 1982) and tetragonal majorite garnets (e.g CaGeO$_3$ - Prewitt and Sleight, 1968; Liebermann, 1974; Ross et al., 1986; CdGeO$_3$ - Ringwood and
Seabrook, 1963). Such analogue systems, in which Ge\(^{4+}\) replaces Si\(^{4+}\), provide a means of determining which properties are directly related to the Si-cations by comparison of isostructural Si and Ge systems (e.g. vibrational spectroscopy to identify modes arising from Si-cation motions), or may provide model systems which are accessible at lower pressures and temperatures than their silicate isomorphs. This is the case for the CaGeO\(_3\) polymorphs which provide a model system for transition zone phase transformations, because pyroxenoid (wollastonite-like), garnet and perovskite structures are accessible at pressures below approximately 7 GPa (Ross et al., 1986), in comparison with the pressures in excess of 17 GPa required for the corresponding silicate system. Ross et al. (1986) recorded the IR and Raman spectra of CaGeO\(_3\) tetragonal garnet at ambient conditions for use in vibrational model calculations of heat capacity. In this chapter, we present Raman spectra of CaGeO\(_3\) tetragonal garnet at temperature and pressure, and investigate possible intrinsic anharmonic behaviour in this majorite analogue, detectable from the variation of Raman peak positions with temperature and pressure (e.g. Mammone and Sharma, 1979-1980; Samara and Peercy, 1981; Gillet et al., 1989, 1992).

### 5.2 Experimental Procedure

Single-crystals of CaGeO\(_3\) tetragonal garnet were synthesized by Dr. N. L. Ross from a starting material of CaGeO\(_3\) wollastonite. The powder was loaded into a Rhenium capsule and held at 5.5 GPa and 1100 °C for 10 hours using a multi-anvil press. The high-pressure and high-temperature Raman spectra of the synthetic CaGeO\(_3\) garnet were recorded using a multichannel DILOR® XY spectrometer at the University of Rennes, France. The microprobe is equipped with a confocal system (e.g. Dhamelincourt et al., 1993) which enhances the signal-to-noise ratio by eliminating the majority of the parasitic light due to thermal emission from heated samples during high-temperature experiments, or background fluorescence from diamonds during measurements at high-pressure. The Raman signal was excited using the 514.5 nm line of a Spectra Physics® Ar-laser, focused on to the sample or pressure calibrant through the objective lens of an optical microscope to a spot <5 μm in diameter (Fig.5.2). The Raman light was collected in the 180° backscattering geometry (Adams et al., 1973) through the same objective, and
focused into the double-subtractive spectrometer equipped with a 1200 lin/mm grating. The backscattered Raman light was analyzed using a Charged-Couple Device (CCD) EGG®-Ortec nitrogen-cooled detector, which significantly lowers both the signal-to-noise ratio and the recording time. Typical slit widths were 100 μm, defining a spectral resolution of approximately 10 μm and giving a bandpass of approximately 2.5 cm\(^{-1}\).

For the high-temperature experiments, a Leitz 1350 heating stage was used, with temperatures measured to within a few Kelvins using a Pt-PtRh10% thermocouple calibrated against known melting-points of certain compounds. The laser light was focused through an Olympus ULWD 50 objective (working distance 8 mm, numerical aperture 0.63). Each high-temperature spectrum was collected from a single accumulation lasting between 250 and 600 seconds, and spectra up to 1225K were obtained. A laser power of 150 mW was used for measurements to 550K, and was increased to 240 mW thereafter.

For the high-pressure experiments, a diamond-anvil cell (DAC) equipped with IIa-type diamonds (700 μm cutlets), selected for their low fluorescence and high transparency to the laser wavelength, was used. Single-crystals of the sample, approximately 5-10 μm in size, were placed in the 200 μm-hole of a stainless-steel gasket, with ruby grains (approximately 5 μm in diameter) whose fluorescence was used for pressure calibration (e.g. Forman et al., 1972; Barnett et al., 1973). The ruby chips were dispersed throughout the gasket hole in order to measure pressure in the vicinity of the sample crystals, and to check for possible pressure gradients. A 4:1 methanol-ethanol mix was used as the pressure-transmitting medium, and is considered to provide hydrostatic conditions to approximately 115 kbar at room temperature (Piermarini et al., 1973). The laser light was focused through a Leitz UTK 40 objective (focal distance 14 mm, numerical aperture 0.32), and low laser power of 12 mW was used to prevent heating of the sample. Each high-pressure Raman spectrum was collected from 3 individual accumulations lasting 100 seconds. Peak positions were estimated to within ±2 cm\(^{-1}\), and spectra were obtained to 115 kbar.
Figure 5.2: Schematic representation of the confocal set-up used on the DILOR® XY micro-Raman spectrometer. The incident laser beam (green) is focused on to the sample via two optically conjugated diaphragms ($D_1$, $D_2$) and the microscope objective lens, placed within the optical train. $D_1$ is a variable confocal aperture allowing the collection of the Raman backscattered light (blue). A diamond-anvil cell or heating stage may be inserted at the laser focal point (after Gillet, 1996).
5.3 Experimentally-Determined Raman Spectra of CaGeO$_3$ Garnet

5.3.1 Raman Spectrum at Ambient Conditions

The Raman spectrum of CaGeO$_3$ tetragonal garnet recorded at ambient conditions (Fig.5.3) is dominated by 2 intense peaks positioned at 804 and 507 cm$^{-1}$, with 12 strong peaks at 779, 726, 650, 615, 375, 326, 291, 267, 245, 206, 182 and 150 cm$^{-1}$, 7 weak peaks at 636, 548, 421, 400, 309, 227 and 135 cm$^{-1}$, and 3 shoulders at 826, 495 and 336 cm$^{-1}$. Thus, a total of 24 fundamental modes could be identified in the spectrum. The positions of these peaks show excellent agreement with those determined by Ross et al. (1986) in their Raman spectroscopic investigation of CaGeO$_3$ garnet. According to McMillan et al. (1989), factor group analysis of XYO$_3$ garnet with tetragonal structure and $I4_1/a$ ($C_{4h}$) symmetry, predicts the total number of symmetry species to be:

$$\Gamma_{\text{vib}} = 25A_g + 27B_g + 28E_g + 32A_u + 31B_u + 33E_u$$

(5.1)
of which the $A_g$, $B_g$ and $E_g$ symmetry species are Raman-active (A$_u$ and E$_u$ modes are IR-active; B$_u$ modes are inactive). Thus, a total of 80 bands is expected to be present in the Raman spectrum. This is significantly greater than the 25 Raman-active modes predicted for the cubic aluminosilicate garnets (Moore et al., 1971; Fateley et al., 1972), as expected from consideration of the reduced symmetry of the Al-poor tetragonal garnets. We were unable to identify all 80 of the predicted modes, primarily because a fully-polarized study was not undertaken. However, it remains unlikely that all modes could be determined from such a study due to the high-probability of peak overlap and limitations in resolution. Previous Raman studies of polycrystalline MgSiO$_3$ tetragonal garnet have similarly only been able to identify 25 (Rauch et al., 1996) and 34 (McMillan et al., 1989) peaks in the spectrum.

The Raman spectrum of CaGeO$_3$ garnet has a similar profile to that of the cubic aluminosilicate garnet end-members (McMillan et al., 1989; Mernagh and Liu, 1990; Hofmeister and Chopelas, 1991a; Gillet et al., 1992; Kolesov and Geiger, 1998), except that it contains more features particularly in the 150-250 and 600-800 cm$^{-1}$ regions, as expected from the distortion to tetragonal symmetry. The bands
Figure 5.3: Raman spectrum of CaGeO$_3$ tetragonal garnet at ambient conditions, with peak positions indicated.
observed in the spectrum may be subdivided into three distinct regions: 135-430, 480-660, and 720-850 cm\(^{-1}\), each containing one intense peak (at 326, 507 and 804 cm\(^{-1}\)). These groupings are similar to those observed in the Raman spectra of the aluminosilicate garnets (Hofmeister and Chopelas, 1991a; Gillet et al., 1992), except for the grouping of the high-energy modes, which extends to 1065 cm\(^{-1}\) for these cubic garnets; no fundamental modes were observed at frequencies in excess of 850 cm\(^{-1}\) in the spectrum of CaGeO\(_3\) garnet at ambient conditions. Our observed spectrum is also similar in profile to the Raman spectra of MgSiO\(_3\) tetragonal garnet determined by McMillan et al. (1989) and Rauch et al. (1996), except that the high-energy peaks reported in the 800-1065 cm\(^{-1}\) range, are shifted to lower wavenumbers (700-850 cm\(^{-1}\)) in CaGeO\(_3\) garnet. The highest energy fundamental Raman modes of garnets are attributable to the internal motions of the tetrahedral sites (Moore et al., 1971; Hofmeister and Chopelas, 1991a, Kolesov and Geiger, 1998; Chaplin et al., 1998). Thus, the observed shift in frequency of the high-energy peaks between the Si- and Ge-bearing garnets is related to the relative masses of the Ge- and Si-cations (72.59 and 28.09 amu, respectively). The larger mass of the Ge-cations results in the GeO\(_4\) internal motions being lower in frequency than the SiO\(_4\) internal modes. Thus, the high-energy modes of the independent GeO\(_4\) tetrahedral groups in orthogermanates are commonly observed in the range 700-900 cm\(^{-1}\) (e.g. Tarte, 1963; Piriou and McMillan 1983; Ross et al., 1986; Gillet et al., 1989; Reynard et al., 1994).

5.3.2 High-Temperature Raman Spectra

The peaks in the Raman spectra of CaGeO\(_3\) tetragonal garnet recorded at high-temperature to 1225K (Fig.5.4) all shift to lower frequencies with increasing temperature, and exhibit typical band-broadening, with the peak-widths showing an approximately linear trend as temperature increases. Above approximately 1230K, the Raman spectrum indicated that the sample had transformed back to wollastonite, as the two major peaks observed at 804 and 507 cm\(^{-1}\) in the spectrum of CaGeO\(_3\) garnet at ambient conditions had both degenerated into doublets (Fig.5.5), with peaks at 836 and 817 cm\(^{-1}\), and 534 and 508 cm\(^{-1}\), respectively. This high-temperature spectrum has
Figure 5.4: Raman spectrum of CaGeO₅ tetragonal garnet at temperature. The scale of the low-frequency data (<550 cm⁻¹) has been doubled so that the peaks in this region are shown with greater clarity.
Figure 5.5: Raman spectrum of CaGeO$_3$ tetragonal garnet at ambient conditions, and at temperatures in excess of 1230K, at which the sample has transformed back to the triclinic wollastonite structure.
the same profile as that obtained for \( \text{CaGeO}_3 \) wollastonite by Ross et al. (1986). Wollastonite has a triclinic structure and belongs to the pyroxenoid group of minerals, in which the \( \text{GeO}_4 \) tetrahedra form chains arranged parallel to the \( y \)-axis.

A total of 12 peaks out of the 24 observed at ambient conditions could be traced over the temperature range studied (300-1225K). The positions of these peaks at each temperature stage (Table 5.1) show a linear trend with increasing temperature (Fig. 5.6). The gradients of the linear regression lines fitted to the data, which yield \((\delta v/\delta T)_P\), demonstrate that the Raman peaks above 300\( \text{cm}^{-1} \) show the greatest rate of change in position with increasing temperature, with a mean frequency shift (MFS) of 0.020 \( \text{cm}^{-1}/\text{K} \). The Raman peaks at energies between 200 and 300\( \text{cm}^{-1} \), have a lower MFS of 0.015 \( \text{cm}^{-1}/\text{K} \), while the lowest energy peaks (100-200\( \text{cm}^{-1} \)) show the smallest frequency shift, of 0.008 \( \text{cm}^{-1}/\text{K} \). These temperature-induced mode shifts show good agreement with those reported by Gillet et al. (1992) for andradite and grossular in the temperature range 300-1300K, and demonstrate that in general, the MFS of Raman modes with temperature decreases with decreasing wavenumber for garnet.

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Table 5.1: Position of the observed Raman peaks of \( \text{CaGeO}_3 \) tetragonal garnet at temperature (units: \( \text{cm}^{-1} \); error: \( \pm 1 \text{ cm}^{-1} \)).
Table 5.1 (continued): Position of the Raman peaks of CaGeO$_3$ tetragonal garnet at temperature (units: cm$^{-1}$; error: ±1 cm$^{-1}$).

<table>
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<tr>
<th></th>
<th>848K</th>
<th>900K</th>
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</tr>
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</table>

5.3.3 High-Pressure Raman Spectra

The peaks in the Raman spectra of CaGeO$_3$ tetragonal garnet recorded at high-pressure to 115 kbar (Fig. 5.7) all shift to higher frequencies with increasing pressure, with no pressure-induced phase transformations observed. The high-pressure spectra suffer from a poor signal-to-noise ratio and diamond fluorescence effects, particularly above 60 kbar, resulting in spectra exhibiting higher noise levels than the high-temperature data. A maximum of 10 peaks out of the 24 observed in the spectrum at ambient conditions could be observed throughout the pressure range studied. The peak positioned at approximately 803 cm$^{-1}$ in the spectrum at ambient conditions again dominates the high-frequency region of the high-pressure spectra. However, the shoulder of this peak (positioned at approximately 777 cm$^{-1}$ at ambient conditions), could also be traced throughout the high-pressure spectra, although it was not clearly observable in the high-temperature spectra. Similarly, the peak at approximately 548 cm$^{-1}$ at ambient conditions could also be observed throughout the high-pressure...
Figure 5.6: Linear variation of 12 Raman peak positions of CaGeO$_3$ tetragonal garnet with temperature.
Figure 5.7: High-pressure Raman spectra of CaGeO$_3$ tetragonal garnet to 115 kbar, corrected for background effects. The scale of the low-frequency data (<600 cm$^{-1}$) has been doubled to assist clarification of peak positions.
regime. In contrast, the peaks at 615, 266, 206 and 150 cm$^{-1}$, clearly observable in the spectra recorded at temperature, could not be traced in the high-pressure spectra. The position of the 10 Raman peaks observable at each pressure stage (Table 5.2) also show a linear trend with increasing pressure (Fig.5.8).

<table>
<thead>
<tr>
<th>Pressure (kbar)</th>
<th>0 kbar</th>
<th>8 kbar</th>
<th>13 kbar</th>
<th>22 kbar</th>
<th>35 kbar</th>
<th>43 kbar</th>
<th>50 kbar</th>
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<td>184.9</td>
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</table>

Table 5.2: Position of the observed Raman peaks of CaGeO$_3$ tetragonal garnet at pressure (units: cm$^{-1}$; error: ±3 cm$^{-1}$).
Figure 5.8: Linear variation of 10 Raman peak positions in CaGeO$_3$ tetragonal garnet with pressure.
The gradients of the linear regression equations describing the pressure-variation of the peak positions, which yield \((\delta v_i / \delta P)_T\), demonstrate that the high-frequency internal stretching modes of the GeO\textsubscript{4} tetrahedra (>700 cm\textsuperscript{-1}) show the greatest rate of change in peak position with increasing pressure, with a MFS of 0.508 cm\textsuperscript{-1}/kbar (Table 5.3). The observed pressure-induced shifts for these modes show good agreement with those reported for grossular by Gillet \textit{et al.} (1992), who determined a MFS of 0.45 cm\textsuperscript{-1}/kbar for this phase over a pressure range of 0-220 kbar. The MFS of the high-frequency modes of pyrope and andradite were reported to be slightly lower, at 0.30 cm\textsuperscript{-1}/kbar and 0.35 cm\textsuperscript{-1}/kbar, respectively. These values are similar to those reported by Rauch \textit{et al.} (1996) for the high-frequency Raman modes of MgSiO\textsubscript{3} tetragonal garnet over the pressure range 0-215 kbar, from whose data MFS of 0.39 cm\textsuperscript{-1}/kbar may be determined. Memagh and Liu (1990), who reported a MFS of approximately 0.42 cm\textsuperscript{-1}/kbar for the high-frequency Raman modes of pyrope, grossular and almandine, also observed that the modes of these garnets recorded at approximately 840 cm\textsuperscript{-1} showed no change in frequency with increasing pressure. The insensitivity of these modes to pressure was suggested to indicate that these vibrations were mainly associated with translations of the Si-cations as opposed to the oxygen atoms, which are expected to be more sensitive to pressure-induced structural distortions. No such pressure-insensitive modes were recorded in the Raman spectra of CaGeO\textsubscript{3} garnet, and Gillet \textit{et al.} (1992) have suggested that the bands observed by Memagh and Liu (1990) are experimental artifacts caused by a strong first-order absorption by the objective lenses used in their experimental set-up, as bands of these energies were not observed in the spectra of aluminosilicate garnets recorded by Gillet \textit{et al.} (1992) or Hofmeister and Chopelas (1991a).

The lower frequency Raman modes of CaGeO\textsubscript{3} garnet (<550 cm\textsuperscript{-1}) exhibit a smaller rate of change in peak position with pressure (Fig.5.8), with a MFS of 0.328 cm\textsuperscript{-1}/kbar; the lowest frequency modes (<250 cm\textsuperscript{-1}) exhibit the smallest changes, with a MFS of 0.211 cm\textsuperscript{-1}/kbar (Table 5.3). Gillet \textit{et al.} (1992) and Rauch \textit{et al.} (1996) also reported that the lower frequency modes (<650 cm\textsuperscript{-1}) of the cubic aluminosilicate garnets and MgSiO\textsubscript{3} majorite garnet have smaller absolute pressure shifts (0.22 and 0.19 cm\textsuperscript{-1}/kbar, respectively) compared with those determined for the high-frequency modes (800-1000 cm\textsuperscript{-1}). As observed in the low-frequency mode shifts for CaGeO\textsubscript{3} garnet, the pressure-induced shifts reported by Gillet \textit{et al.} (1992) and Rauch \textit{et al.} (1996) do not show a simple relationship between decreasing wavenumber and
frequency shift: in the central frequency range of CaGeO₃ garnet (300-500 cm⁻¹), there is a slight increase in frequency shift with decreasing wavenumber, from 0.32 cm⁻¹/kbar at approximately 500 cm⁻¹, to 0.41 cm⁻¹/kbar at approximately 325 cm⁻¹. Similar increases in pressure-induced frequency shifts were observed by Gillet *et al.* (1992) and Rauch *et al.* (1996) in the central frequency regions of the cubic aluminosilicate garnets and MgSiO₃ majorite garnet (300-600 cm⁻¹), from approximately 0.19 cm⁻¹/kbar at 630 cm⁻¹ to 0.36 cm⁻¹/kbar at 370 cm⁻¹ for the cubic garnets, and from 0.161 cm⁻¹/kbar at 515 cm⁻¹ to 0.21 cm⁻¹/kbar at 330 cm⁻¹ for tetragonal majorite. Thus, although the trends observed in the pressure-induced frequency shifts are similar for both the cubic and tetragonal garnets, the observed shifts for CaGeO₃ garnet over the entire frequency range are slightly larger than observed for other garnets. These differences may lie within the experimental uncertainties or may be related to the smaller bulk modulus of this phase (1240 kbar - Liebermann, 1974) compared to that of the aluminosilicate garnets (1379-1779 kbar - Babuška *et al.* 1978), which allows for greater compressibility of the interatomic bonds.

5.4 Intrinsic Anharmonicity Determined from Raman Spectra

5.4.1 Intrinsic Anharmonic Parameters

Anharmonic effects in crystalline systems are important because they influence the high-temperature (>1000K) thermodynamic properties such as specific heat and entropy, and are responsible for crystal properties such as thermal expansivity and the temperature-induced shifts of normal mode frequencies. However, direct measurement of anharmonic effects on the thermodynamic properties is difficult because these effects only become noticeable at high-temperatures, and accurate calorimetric measurements at these temperatures can only be achieved with very small samples. Thus, other investigative methods must be used. The temperature- and pressure-induced shifts of normal mode frequencies observed using Raman spectroscopy is an alternative viable method from which intrinsic mode anharmonic parameters may be calculated. These effects may then be introduced into quasi-harmonic vibrational models of heat capacity to account for anharmonic behaviour.
and observed departures from the Dulong-Petit high-temperature limit. The temperature- and pressure-dependency of a given frequency arises from two contributions (Mammone and Sharma, 1979-1980; Samara and Peercy, 1981):

1) a pure volume contribution due to compressibility and thermal expansion;
2) a volume-dependent (pure temperature and pressure) contribution arising from higher-order anharmonic interactions.

With knowledge of the compressibility and thermal expansion of a phase, it is possible to separate the pure volume contribution from other contributions by performing measurements of both the pressure- and temperature-dependencies of the vibrational modes. Using the observed Raman frequency shifts with temperature, \( (\delta v_i/\delta T)_p \), the isobaric mode Grüneisen parameters are defined as:

\[
\gamma_{ip} = (\delta \ln v_i / \delta \ln \rho)_p = (1/\alpha)(\delta \ln \nu_i / \delta T)_p
\]

where \( v_i \) is the frequency of the \( i \)th mode, \( \rho \) is the density, and \( \alpha \) is the thermal expansion coefficient. Similarly, the pressure-dependencies of the Raman modes, \( (\delta v_i/\delta P)_T \), may be used to determine the isothermal mode Grüneisen parameters, described by:

\[
\gamma_{it} = -(\delta \ln v_i / \delta \ln P)_T = K_T (\delta \ln v_i / \delta P)_T
\]

where \( K_T \) is the isothermal bulk modulus. The mode Grüneisen parameters may subsequently be used to calculate the intrinsic anharmonic mode parameters (Mammone and Sharma, 1979-1980; Samara and Peercy, 1981; Gillet et al., 1989), via the relationship:

\[
a_i = (\delta \ln v_i / \delta T)_v = \alpha(\gamma_{it} - \gamma_{ip})
\]

Thus, an intrinsic anharmonic parameter, \( a_i \), expresses a change in frequency resulting from a change in temperature at constant volume, induced by modifications of the electronic structure of the chemical bond. In the quasi-harmonic approximation, all bonds in a crystalline system behave harmonically, although their equilibrium length
can change. Thus for such a system, $\gamma_{vp} = \gamma_{vp}$, and the calculated anharmonic parameters will be zero. However in real systems, the anharmonic parameters may be non-zero (usually negative), indicative of significant intrinsic anharmonic behaviour. This behaviour can be accounted for in the expression for the constant-volume heat capacity at high-temperatures by perturbing the harmonic potential to introduce the measured intrinsic anharmonic mode parameters, yielding (e.g. Gillet et al., 1989, 1990, 1991; Fiquet et al., 1992):

$$C_v^a = \sum_i \{C_v^h(1 - a_i T)^2 - T U_i^h [a_i^2 + (\partial a_i / \partial T)_v]\}$$  \hspace{1cm} (5.5)

where the superscripts $h$ and $a$ refer to the harmonic and corrected anharmonic heat capacities, respectively. Negative anharmonic parameters will increase $C_v$ values compared to those obtained via quasi-harmonic modelling and thus, the observed departure of the measured $C_v$ from the Dulong-Petit harmonic limit is accounted for. Equation (5.5) may be approximated by the simpler form:

$$C_v^a = \sum_i C_v^h (1 - 2a_i T) = C_v^h - 2T \sum_i a_i C_v^h$$  \hspace{1cm} (5.6)

which yields nearly identical results. At the high-temperature limit ($C_v^h = kT$) where anharmonic effects become most significant, equation (5.6) becomes:

$$C_v^a = C_v^h (1 - 2\bar{a} T)$$  \hspace{1cm} (5.7)

where $\bar{a}$ is the arithmetic mean of the anharmonic parameters. The mode Grüneisen parameters and intrinsic anharmonic parameters of several geologically relevant phases and their analogues have been determined via Raman spectroscopy (e.g. olivine - Gillet et al., 1989; Fiquet et al., 1992; $\beta$-Mg$_2$SiO$_4$ - Reynard et al., 1996; aluminosilicate garnets - Mernagh and Liu, 1990; Gillet et al., 1992; perovskite - Gillet et al., 1993a,b; rutile-structured oxides - Mammone and Sharma, 1979-1980; quartz - Gillet et al., 1990; Castex and Madon, 1995). These studies show that silicate minerals and their germanate analogues typically have negative intrinsic anharmonic parameters (in the range $-1 \times 10^{-5} \text{ K}^{-1}$ to $-10 \times 10^{-5} \text{ K}^{-1}$), and that these parameters are
generally higher in absolute value for the low-frequency modes (lattice modes) than
for the high-frequency internal modes of the SiO$_4$ and GeO$_4$ tetrahedra. In contrast,
Reynard and Guyot (1994), and Reynard and Rubie (1996) reported that the pressure-
and temperature-induced shifts of the Raman modes in MgTiO$_3$-ilmenite (geikielite)
and MgSiO$_3$-ilmenite yielded intrinsic anharmonic parameters close to zero for 6 of
the 10 observed modes, suggesting that the average behaviour of these two phases at
low-temperature is close to that of a quasi-harmonic solid. Thus, determination of the
intrinsic anharmonic parameters of CaGeO$_3$ garnet is of interest in order to ascertain
whether this phase has significant anharmonic behaviour, particularly in comparison
with the cubic aluminosilicate garnets, and to quantify the effect of this behaviour on
the thermodynamic properties and the implications this may have for silicate majorite.

5.4.2 Calculation of the Intrinsic Anharmonic Parameters of CaGeO$_3$ Garnet

From the temperature- and pressure-induced frequency shifts obtained from
our Raman spectroscopic investigation of CaGeO$_3$ garnet, the isothermal and isobaric
mode Grüneisen parameters, $\gamma_{IT}$ and $\gamma_{IP}$, were determined via equations (5.2) and
(5.3), with the intrinsic anharmonic parameters subsequently calculated using
equation (5.4) (Table 5.3). The thermal expansion coefficient determined by Isaak $et$
al. (1992) for grossular (1.92x10$^{-5}$ K$^{-1}$) was used in these calculations, as no thermal
expansivity data currently exists for CaGeO$_3$ garnet. The thermal expansion
coefficient of MgSiO$_3$ tetragonal garnet has been estimated by Sawamoto (1987) as
2.4x10$^{-5}$ K$^{-1}$ at ambient conditions, from a simultaneous high-pressure and high-
temperature investigation of the phase relations of majorite. This value is in good
agreement with the thermal expansion coefficient of 2.36x10$^{-5}$ K$^{-1}$ reported by
Anderson $et$ $al.$ (1992) for pyrope, and lies within the range of all values determined
for pyrope (2.03-2.70x10$^{-5}$ K$^{-1}$ - e.g. Thieblot $et$ $al.$, 1998; Hazen and Finger, 1978).
Thus, the thermal expansion measured for grossular is expected to be similar to that of
CaGeO$_3$ garnet. For the calculation of $\gamma_{IT}$ (equation 5.3), the isothermal bulk modulus
determined by Liebermann (1974) from a study of the elasticity of the pyroxene-
garnet transformation in germanates was used (1240 kbar).
Table 5.3: Pressure and temperature dependencies of the Raman modes of CaGeO₃ tetragonal garnet, and their isothermal and isobaric Grüneisen parameters, used for calculation of the intrinsic anharmonic parameters, $a_i$.

<table>
<thead>
<tr>
<th>Ambient peak position (cm⁻¹)</th>
<th>$(\delta \nu_p/\delta T)_P$ (cm⁻¹ K⁻¹)</th>
<th>$\gamma_{IP}$</th>
<th>$(\delta \nu_p/\delta P)_T$ (cm⁻¹ kbar⁻¹)</th>
<th>$\gamma_{IT}$</th>
<th>$a_i$ (x10⁻² K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>804</td>
<td>-0.02075(4)</td>
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<td>-</td>
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<td>-0.00891(2)</td>
<td>3.17(5)</td>
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</tbody>
</table>

The $\gamma_{IP}$ and $\gamma_{IT}$ parameters determined for CaGeO₃ garnet (Table 5.3) show that the high-frequency modes (>500 cm⁻¹) have smaller absolute values (with average values of $\gamma_{IP} = 1.74(2)$ and $\gamma_{IT} = 0.79(1)$) by a factor of approximately 1.7, than the lower frequency modes, which have average values of $\gamma_{IP} = 3.05(4)$ and $\gamma_{IT} = 1.30(1)$. These trends have also been observed in other studies of silicate and germanate minerals (e.g. Gillet et al., 1989-1993c; Fiquet et al., 1992; Reynard et al., 1996), and can be explained qualitatively within the framework of the harmonic approximation: an oscillator, $i$, can be represented by a spring with a force constant $k_i$, an equilibrium length $r_i$, and a reduced mass $\mu_i$. Thus, the mode frequency of the oscillator may be approximated as:
\[ v_i \approx \mu_i^{-\frac{3}{2}} r_i^{-\frac{3}{2}} \quad \text{(5.8)} \]

and,

\[ (\partial v_i / \partial P)_T \approx \mu_i^{-\frac{3}{2}} r_i^{-\frac{3}{2}} (\partial r_i / \partial P)_T \approx \mu_i^{-\frac{3}{2}} r_i^{-\frac{3}{2}} \beta_i \quad \text{(5.9)} \]

The linear bond compressibility \( \beta_i \) is proportional to \( r_i^3 \) (Hazen and Finger, 1982). Therefore equation (5.9) may be written as:

\[ (\partial v_i / \partial P)_T \approx \mu_i^{-\frac{3}{2}} r_i^{-\frac{3}{2}} \quad \text{(5.10)} \]

It follows that:

\[ \gamma_{\sigma} = (K_T / v_i)(\partial v_i / \partial P)_T \approx K_T r_i^3 \quad \text{(5.11)} \]

which demonstrates that high-frequency modes involving stretching motions of the Ge-O bonds (\( r_i = 1.7 \) Å) have smaller \( \gamma_{\sigma} \) values than the lower frequency modes, which mainly represent oscillators with larger equivalent length values (>2 Å). The same approach applied to the effect of temperature yields:

\[ (\partial v_i / \partial T)_p \approx \mu_i^{-\frac{3}{2}} r_i^{-\frac{3}{2}} (\partial r_i / \partial T)_p \approx \mu_i^{-\frac{3}{2}} r_i^{-\frac{3}{2}} \alpha_i \quad \text{(5.12)} \]

where \( \alpha_i \) is the mean thermal expansion coefficient of the considered bond. Using equation (5.12), it may be shown that:

\[ \gamma_{\varphi} = (1 / \alpha v_i)(\partial v_i / \partial T)_p \approx \alpha_i / \alpha \quad \text{(5.13)} \]

which demonstrates that for the high-frequency modes, low-coordination and higher charged atoms lead to smaller \( \alpha_i \) and thus to small \( \gamma_{\varphi} \) values. For the low-frequency modes, lower charged atoms and higher coordination account for the larger \( \gamma_{\varphi} \) values (Gillet et al., 1989). Thus, the isothermal and isobaric mode Grüneisen parameters are smaller for vibrations involving GeO4 tetrahedra, reflecting the relative incompressibility and weak expansivity of the Ge-O bonds. Volume changes in the structure are incorporated by the weaker bonds, in particular the dodecahedral site.
which is the most sensitive of the constituent polyhedra to temperature and pressure variations (Meagher, 1975). It is this site which contributes significantly to the low-frequency vibrations (e.g. Hofmeister and Chopelas, 1991a; Kolesov and Geiger, 1998; Chaplin et al., 1998), resulting in the higher absolute isothermal and isobaric mode Grüneisen parameters for these modes.

Our calculated isothermal mode Grüneisen parameters, $\gamma_{IT}$, for CaGeO$_3$ garnet, which range from 0.70(2) to 1.60(2), show good agreement with those determined for grossular by Gillet et al. (1992) and Mernagh and Liu (1990), which lie in the ranges 0.51(5)-1.64(17) and 0.81-1.33, respectively. The dataset of Gillet et al. (1992) also shows a general increase in $\gamma_{IT}$ with decreasing wavenumber and yields an average $\gamma_{IT}$ value for the high-frequency modes of 0.83(8), in good agreement with our value for the high-frequency modes of CaGeO$_3$ garnet (0.79(1)), suggesting that the SiO$_4$ and GeO$_4$ tetrahedra in these phases behave similarly in response to pressure variations. An average $\gamma_{IT}$ value of 0.94(14) for the low-frequency modes of grossular may be determined from the dataset of Gillet et al. (1992), which is slightly lower than the average value of 1.30(1) obtained for the low-frequency modes of CaGeO$_3$ garnet. As a similar number of modes of comparable frequency were examined in both datasets, the less favourable agreement between the values must reflect differences in the pressure-induced shifts of the lower frequency modes. The higher average $\gamma_{IT}$ value for CaGeO$_3$ garnet indicates that the modes of this phase shift to higher wavenumbers with increasing pressure at a greater rate than those of grossular, reflecting a more compressible structure as suggested by the smaller bulk modulus of this phase (1240 kbar - Liebermann, 1974) compared to that of grossular (1691(8) kbar - Babuška et al., 1978). The $\gamma_{IT}$ parameters determined by Gillet et al. (1992) for pyrope and andradite were reported to be generally slightly smaller than those determined for grossular, with average $\gamma_{IT}$ values for the high-frequency modes of 0.55(16) and 0.63(7), respectively, and 1.01(13) and 0.96(10), respectively, for the low-frequency modes.

The isobaric mode Grüneisen parameters, $\gamma_{IP}$, of CaGeO$_3$ garnet range from 1.36(2) to 3.33(5), and again show good agreement with those reported for grossular by Gillet et al. (1992), which lie in the range 1.23(5)-3.04(1.07). The dataset of Gillet et al. (1992) yields an average $\gamma_{IP}$ value of 1.29(45) for the high-frequency modes, which is slightly lower than our value for CaGeO$_3$ garnet of 1.74(2), but agrees within
experimental error. The temperature-induced shifts of the high-frequency modes in both pyrope and andradite yield an average $\gamma_{ip}$ value of 1.50(35) (Gillet et al., 1992), which is also in agreement with our value for CaGeO$_3$ garnet within the experimental uncertainties, suggesting that the temperature behaviour of the SiO$_4$ and GeO$_4$ tetrahedra in both garnet structures is similar. The low-frequency mode shifts of grossular, pyrope and andradite yield average $\gamma_{ip}$ values of 2.24(61), 2.36(70) and 1.80(51), respectively, which are generally lower than the average $\gamma_{ip}$ determined for the low-frequency modes of CaGeO$_3$ garnet (3.05(4)), and reflects a more rapid response of the CaGeO$_3$ bonds to temperature-induced variations.

In CaGeO$_3$ garnet, the isobaric mode Grüneisen parameters are consistently larger than the corresponding isothermal parameters (Table 5.3), resulting in intrinsic anharmonic parameters $a_n$ which are non-zero, ranging in value from $-1.2(1)x10^{-5}$ K$^{-1}$ to $-3.8(1)x10^{-5}$ K$^{-1}$, and indicate that there is significant intrinsic anharmonic behaviour in this phase. The absolute intrinsic anharmonic parameters are larger for the low-frequency modes than for the high-frequency modes, as observed in the majority of previous studies of silicate and germanate minerals (e.g. Mammone and Sharma, 1979-1980; Gillet et al., 1989-1993c, Fiquet et al., 1992; Reynard et al., 1996). The intrinsic anharmonic parameters determined for grossular, andradite and pyrope by Gillet et al. (1992) lie in the ranges $-0.74x10^{-5}$ K$^{-1}$ to $-4.36x10^{-5}$ K$^{-1}$, $-0.54x10^{-5}$ K$^{-1}$ to $-3.02x10^{-5}$ K$^{-1}$ and $-0.43x10^{-5}$ K$^{-1}$ to $-5.77x10^{-5}$ K$^{-1}$, respectively, with reported errors of between 30 and 50%. This data suggests that pyrope shows the greatest degree of anharmonic behaviour of the garnets studied via this method. Significant anharmonic behaviour has already been observed for the Mg-cations in the dodecahedral sites in pyrope from low-temperature single-crystal XRD studies (Armbruster et al., 1992; Armbruster and Geiger, 1993; Pavese et al., 1995). Although anisotropic behaviour of the X-cations was also reported for grossular and andradite from the low-temperature investigations, the effects were less pronounced due to the larger size of the Ca-cations filling the dodecahedral sites. Thus, the intrinsic anharmonic parameters for MgSiO$_3$ majorite are expected to have larger absolute values compared to those determined for CaGeO$_3$ majorite.
5.5 Summary and Conclusions

Majorite garnet is considered to form 40-60% of the transition zone (e.g. Irifune and Ringwood, 1987; Weidner and Ito, 1987; Ita and Stixrude, 1992). Naturally occurring majorite, found only in chondrites (e.g. Smith and Mason, 1970; Coleman, 1977; Price et al., 1979), has cubic (Ia3d) symmetry, whereas majorite synthesized in the laboratory has tetragonal (I41/a) symmetry, due to ordering of the octahedral cations (e.g. Kato and Kumazawa, 1985; Sawamoto, 1987; Angel et al., 1989). We have used Raman spectroscopy to investigate the effects of temperature and pressure on the vibrational modes of CaGeO₃ garnet, an analogue for Ca-bearing tetragonal majorite accessible at lower pressures than its equivalent silicate system, in order to study the anharmonic behaviour of this phase. The pressure- and temperature-induced shifts of the Raman frequencies of CaGeO₃ garnet were observed to be greater for the high-energy modes, yielding isothermal and isobaric mode Grüneisen parameters, \( \gamma_{IT} \) and \( \gamma_{IP} \), with smaller absolute values than those determined for the low-frequency modes, and these show good agreement with those reported for the high-frequency modes of andradite and grossular (Gillet et al., 1992). The low-frequency modes (<550 cm⁻¹) of CaGeO₃ garnet show larger pressure-induced shifts and thus larger \( \gamma_{IT} \) and \( \gamma_{IP} \) values than the corresponding modes in grossular, and we conclude that this is related to the smaller bulk modulus of CaGeO₃ garnet, which allows more rapid compressibility of the constituent bonds.

The negative intrinsic anharmonic parameters, \( a_i \), calculated for CaGeO₃ garnet from \( \gamma_{IP} \) and \( \gamma_{IT} \), indicate that this phase shows significant anharmonic behaviour, similar to that reported for grossular. As the \( a_i \) values determined for pyrope are larger than those in grossular (Gillet et al., 1992), we suggest that MgSiO₃ garnet will display greater anharmonicity than CaGeO₃ garnet, and that this behaviour must be included in thermodynamic modelling of the transition zone. Our \( a_i \) values may be used to correct quasi-harmonic calculations of CaGeO₃ thermodynamic properties (e.g Ross et al., 1986). However, our values are only strictly valid for ambient conditions and measurement of their evolution with temperature will require future simultaneous high-pressure and high-temperature spectroscopic experiments. Also, as only 25 of the predicted 80 Raman modes were observed for CaGeO₃ garnet, the intrinsic anharmonic parameters presented here represent the minimum values, and any correction calculated from them must be considered as a minimum correction.
6.1 Summary and Conclusions

The most widely accepted petrological models of the Earth's interior (e.g. Ringwood, 1971; Bass and Anderson, 1984) suggest that the garnet group of minerals comprise a significant proportion of the upper mantle (13-15%) and transition zone (40-60%). Consequently, a full characterization of the structural, elastic, vibrational and thermodynamic properties of these minerals is essential in facilitating accurate geophysical interpretations of seismic profiles of the Earth. For this reason, considerable experimental work has been performed on the more accessible cubic aluminosilicate garnets, $X_3Y_2Si_3O_{12}$, and their solid-solutions in order to determine the structural (e.g. Zemann, 1962; Gibbs and Smith, 1965; Novak and Gibbs, 1971), elastic (e.g. Bonczar et al., 1977; Babuška et al., 1978; Leitner et al., 1980; O'Neill et al., 1991), vibrational (e.g. Moore et al., 1971; Hofmeister and Chopelas, 1991; Hofmeister et al., 1996; Kolesov and Geiger, 1998) and thermodynamic (e.g. Skinner, 1956; Téqui et al., 1991; Richet and Fiquet, 1991; Anderson et al., 1992; Thiéblot et al., 1998) properties of this mineral group.

As simultaneous high-pressure and high-temperature experiments are generally difficult to perform accurately, computational mineral physics has become an important tool in predicting these properties and hence, the relative stabilities of such geologically relevant phases. We have used atomistic modelling based on the classical Born model of solids (Born and Huang, 1954), in which potential functions are used to describe the net effective interatomic forces, to study the properties of the Mg-rich garnet end-member pyrope, $Mg_3Al_2Si_3O_{12}$ (Chapter 2). Using the interatomic potentials developed empirically for simple binary oxides by Lewis and Catlow (1985), Sanders et al. (1984) and Catlow et al. (1982) (Table 2.2), lattice dynamical simulations of pyrope have been performed at upper mantle conditions using the computer code PARAPOCS (Parker and Price, 1989), thus extending the previous work of Patel et al. (1991). Our simulations of pyrope were initially performed using different methods of Brillouin zone sampling (uneven grid sampling - Filippini et al., 1976; special point set - Chadi and Cohen, 1973; mean value point - Baldereschi, 1973), due to the impracticality of calculating the phonon frequency distribution over the entire Brillouin zone. The use of these different sampling procedures in the primitive (80 atoms) and body-centred cubic (160 atoms) unit cells of
pyrope resulted in very little variation in the calculated properties at ambient conditions, and at pressure and temperature. This is concluded to be due to the dense phonon dispersion relations of pyrope which, with 240 vibrational modes showing little dispersive behaviour (Figs.4.3b-4.5b), will produce similar datasets from any point selected in the Brillouin zone. Using a single sampling point in the primitive unit cell, which yields datasets representative of all other sampling methods tested and is most economic in terms of CPU time, the structural, elastic and thermodynamic properties of pyrope were calculated at ambient conditions, to pressures of 100 kbars, and temperatures of 2000K. Comparison of the calculated properties with the extensive experimental data demonstrated that structural and thermodynamic properties, such as lattice parameter, density and heat capacity, were reproduced to within <1%. However, the elastic moduli were poorly reproduced, being overestimated by an average of 18%, indicating that the set of potentials used does not fully describe the atomic interactions of pyrope. The overestimation of elastic moduli appears to have been a common result in previous lattice dynamical (e.g. Winkler et al., 1991; Patel et al., 1991), molecular dynamical (Matsui, 1996) and quantum mechanical (D'Arco et al., 1996) calculations of pyrope, and has been attributed to difficulties in accurately simulating the anomalously large dodecahedral sites within the garnet structure, which contain the highest-coordinated cations with lowest charge, and control the compressional (and thermal expansion) behaviour of the garnet structure (Meagher, 1975; Pavese et al., 1995). Significant anharmonic behaviour has also been ascribed to the cations in these sites from low-temperature XRD investigations (Pavese et al., 1995; Armbruster and Geiger, 1993; Armbruster et al., 1992), behaviour which is not incorporated in our quasi-harmonic calculations.

Recently, Pavese et al. (1998) have refined a set of potentials specifically for pyrope (Table 2.6), through simultaneous fitting to the observed room temperature structural, elastic and vibrational data. The fundamental difference between the empirical potentials developed for the simple oxides comprising pyrope and the optimized potentials is the use of fractional charges for Al, O and in particular Mg, indicating that these atoms deviate significantly from ideal ions in the garnet structure. The optimized potential set of Pavese et al. (1998) is currently only valid for static lattice or low-temperature simulations with negligible thermal contribution. It is therefore anticipated that these potentials will be further refined for use in dynamical simulations of pyrope, so that the structural, elastic, and thermodynamic properties of this garnet, and its stability relations can be simulated more accurately at pressure and
temperature. However, the optimization of interatomic potentials for a specific phase drastically reduces the transferability of the potential set to model other phases of similar chemistry. It may therefore be of interest to concentrate on the \textit{ab initio} approach to modelling garnets \textit{(e.g. D'Arco \textit{et al.}, 1993)}, so that the properties of these minerals can be calculated via quantum mechanics.

Although the set of interatomic potentials employed in our simulations of pyrope do not fully describe the elastic behaviour of this phase, they do provide a good description of its optic mode vibrational properties, as shown by the good agreement between the calculated and experimentally-determined thermodynamic properties (Table 2.3). Hence, this potential set was further employed in a simulation of the 240 vibrational frequencies of pyrope and the displacements of the atoms during each vibration (eigenvectors), in order to study the optic vibrational properties of this phase in more detail \textit{(Chapter 3)}. Selected Brillouin zone centre vibrations of a crystalline solid may be measured experimentally using vibrational spectroscopy, of which Raman and infrared (IR) spectroscopies are the most widely used techniques. Using Group theoretical analysis of the pyrope structure (which predicts 25 Raman- and 17 IR-active modes) and symmetry analysis of the calculated eigenvectors, the symmetry species of each vibrational mode was identified, and thus its Raman- or IR-activity (or inactivity) determined (Tables 3.4 and 3.5). The symmetry species assignment of each mode showed excellent agreement with the number and type of symmetry species predicted by factor group analysis (FGA) of the garnet structure \textit{(e.g. Moore \textit{et al.}, 1971; Fateley \textit{et al.}, 1972)}. Analysis of the previous IR and Raman experimental investigations of pyrope demonstrated that only 3 of the 17 studies \textit{(Hofmeister and Chopelas, 1991a; Hofmeister \textit{et al.}, 1996; Kolesov and Geiger, 1998)} have presented a full set of Raman or IR modes. Comparison of the calculated and experimentally-determined IR and Raman modes shows that there is generally very good agreement between the datasets, again indicating that the interatomic potentials employed in the simulations successfully reproduce the optic vibrational behaviour of pyrope. However, the lowest frequency observed IR mode \textit{(at approximately 134 cm}^{-1} \text{, Hofmeister \textit{et al.}, 1996)}\text{), and the frequencies of the 3 Raman-active modes with A_{1g} symmetry were not accurately reproduced. These modes are all related to SiO$_4$ tetrahedral motions and suggest that the Si-O and O-Si-O potentials employed do not fully describe the vibrational behaviour of this cation site. It is therefore considered that when the optimized potential parameters developed by Pavese \textit{et al.} (1998) are further refined for dynamical simulations, these problems will be resolved. The
LO-TO reversals reported by Hofmeister and Chopelas (1991a) for selected IR modes, in which the TO component is higher in frequency than its corresponding LO mode, were not reproduced in our simulations of pyrope. We consider such reversals to be unphysical and have concluded that these are artifacts of the experimental procedure or the analysis used by Hofmeister and Chopelas (1991a) to determine the position of the IR bands.

Further analysis of the calculated eigenvectors for each vibration, together with additional calculations of the vibrational frequencies of pyrope with simulated isotopic substitution of $^{26}$Mg and $^{30}$Si (Tables 3.15 and 3.16), enabled the dominant atomic motions contributing to each mode to be identified (Tables 3.17 and 3.18). The assignment of the calculated modes to specific site or atomic motions demonstrated that there was excellent agreement with the number of $v_1$-$v_4$ tetrahedral vibrations predicted by the site group to factor group analysis, and with the assignments of the observed modes made by Hofmeister and Chopelas (1991a), Hofmeister et al. (1996) and Kolesov and Geiger (1998). However, our assignments of the calculated lower frequency modes (<450 cm$^{-1}$) have indicated that there is substantial mixing of modes at these energy levels, with translatory motions of the Mg- and Si-cations dominating these vibrations. Although mixing of the low-frequency modes in garnet has previously been suggested (e.g. Hofmeister and Chopelas, 1991a; Hofmeister et al., 1996), our simulation study has demonstrated the extent to which the mode-mixing occurs and also provides an accurate determination of the origin of each vibration. Our study has also provided a dataset that is of use in interpreting poorly resolved regions of the experimental spectra, and has yielded the first presentation of the calculated inactive modes of pyrope which are useful for analyzing the origin of the underestimation of the heat capacity of pyrope determined via Kieffer-type density of states models constructed from spectroscopic data (Hofmeister and Chopelas, 1991b).

IR and Raman spectroscopies provide data on a limited number of zone centre frequencies only, although these experimental techniques are readily accessible. The entire phonon frequency spectrum may be measured experimentally using coherent inelastic neutron scattering (Chapter 4). However, this method requires highly specialized facilities, which are only available at a limited number of installations world-wide. Neutrons produced via nuclear fission or spallation and retarded by a moderating material to energies of 25meV, have both wavelengths and energies at 300K comparable to the interatomic distances and excitations, respectively, in solids, making them highly effective probes of the microscopic structure and dynamics of condensed matter. Analysis
of the change in energy and momentum of thermal neutrons scattered via inelastic collision with the nuclei of a sample, enables measurements of the phonon frequencies of the sample to be made. We have used this method to obtain the vibrational density of states, \( g(\omega) \), of natural pyrope-rich garnet along three specific crystallographic directions: [100], [110] and [111], in order to determine the variation of the phonon frequencies with wavevector, and to extend the previous work of Pavese et al. (1998). The experiments were performed using the inverse-geometry TFXA (Time-Focused Xtal Analyser) spectrometer at the Rutherford-Appleton Laboratory, with the sample temperature retained below 30K in order to reduce multi-phonon and Debye-Waller effects. The origins of the peaks in the INS spectra and their variation with wavevector have been successfully interpreted using calculated phonon dispersion relations of pyrope. We have also performed lattice dynamical simulations of the TFXA experiments using the optimized interatomic potentials and simulation programs devised by Pavese et al. (1998), which are suitable for simulations at 30K. Comparison of the simulated and experimental spectral profiles demonstrated that there was good agreement between the datasets, with the major peaks in the experimental spectra successfully reproduced by the simulations. However, the intensities of the experimentally-determined peaks were generally underestimated and in the 10-50 meV range, this was concluded to be due to the presence of Fe in dodecahedral coordination which, with its larger neutron scattering cross-section compared to the other atoms present in garnet, effectively enhanced the intensities of peaks in this region; the peaks at energies >70 meV were concluded to be underestimated due to multiphonon effects whose contribution was not accounted for in our simulations. We have also presented the results of the first coherent INS density of states measurements of grossular garnet (Ca$_2$Al$_2$Si$_3$O$_{12}$), the profile of which was observed to be very similar to the \( g(\omega) \) spectra of pyrope, although the peak positions were shifted to lower frequencies. The observed frequency shift has been attributed to the lower mass of the Ca atom, and has also been observed in IR and Raman spectroscopic studies of pyrope and grossular end-members (e.g. Kolesov and Geiger, 1998; Bosenick et al., 1995; Gillet et al., 1992; Moore et al., 1971).

Majorite garnet, Mg$_4$Si$_4$O$_{12}$, is considered to comprise 40-60% of the transition zone (e.g. Akaogi and Akimoto, 1977; Irifune and Ringwood, 1987; Ita and Stixrude, 1992) and hence, a full knowledge of its physical, vibrational and thermodynamic properties is crucial for understanding this region of the Earth. Majorite differs from the aluminosilicate garnets in the replacement of Al by Mg$^+$-Si on the octahedral sites, and its
properties are poorly constrained in comparison to the Al-rich garnets due to limited sample availability. Naturally occurring majorite, to date found only in chondritic meteorites (e.g. Smith and Mason, 1971; Dodd, 1981; Price et al., 1979), is cubic in symmetry. However, majorite synthesized in the laboratory is tetragonal in symmetry, with ordering of the Mg- and Si-cations on the octahedral sites (e.g. Angel et al., 1989; Hatch and Ghose, 1989). The phase transformation between the cubic and tetragonal end-members has not been observed in situ, but has been inferred as an improper ferroelastic transition from analysis of microstructures observed in quenched tetragonal phases (Heinemann et al., 1997; Wang et al., 1993) and from Group theoretical analysis (Hatch and Ghose, 1989). Previous studies of mantle minerals have emphasized the dominant roles of Mg and Si oxides, and to a lesser extent Fe oxides - components that together may account for as much as 94 mol% of the mantle (Ringwood, 1975). The role of calcium oxide, which represents perhaps 3 mol% of the mantle's mass, has been less extensively studied. The presence of diopside and grossular as upper mantle phases suggests that Ca-majorite will also be an important phase in the transition zone and hence, full characterization of its properties is essential in order to constrain mantle models further. Germanate analogues, in which Ge$^{4+}$ replaces Si$^{4+}$, provide more accessible models of silicate phases as they are stable at lower temperatures and pressures. The germanate analogue for Ca-majorite is accessible at approximately 7 GPa and 1000K, and has been the subject of previous structural, elastic, vibrational and thermodynamic studies (e.g. Prewitt and Sleight, 1969; Tarte, 1965; Liebermann, 1974; Ross et al., 1986). We have studied the vibrational behaviour of CaGeO$_3$ garnet using Raman spectroscopy (Chapter 5) in order to quantify its intrinsic anharmonic behaviour and constrain heat capacity models of this phase (Ross et al., 1986). We identified a total of 25 of the 80 modes predicted by FGA (McMillan et al., 1989) in the Raman spectrum at ambient conditions of CaGeO$_3$ garnet. The Raman modes of this phase were observed to vary linearly with pressure and temperature to 115 kbars and 1225K, as reported for MgSiO$_3$ majorite (Rauch et al., 1996) and aluminosilicate garnets (Gillet et al., 1992; Memagh and Liu, 1990). From the pressure- and temperature-induced shifts of the Raman modes, the intrinsic anharmonic mode parameters (Mammone and Sharma, 1979-1980; Samara and Peercy, 1981; Gillet et al., 1989) of CaGeO$_3$ garnet were determined and these indicated significant anharmonic behaviour for this phase. The low-frequency modes were observed to have larger absolute anharmonic parameters compared to the high-frequency modes of the GeO$_4$ tetrahedra, a trend which has previously been
observed in other silicate minerals and their germanate analogues (e.g. Gillet et al., 1989, 1990, 1992; Fiquet et al., 1992; Castex and Madon, 1995; Mammone and Sharma, 1979-1980). The anharmonic behaviour of CaGeO$_3$ garnet was also observed to be similar to that reported for grossular, and by analogy with the larger anharmonic parameters reported for pyrope (Gillet et al., 1992), we suggest that MgSiO$_3$ tetragonal majorite will have larger absolute intrinsic anharmonic parameters, and thus exhibit greater anharmonic behaviour than CaGeO$_3$ garnet. It is therefore essential that such behaviour, which effects thermodynamic properties and hence mineral stability, is included in models of mantle mineralogy.

6.2 Future Studies of Garnet Phases

In future studies of garnet, it would be of interest to simulate the profiles of the IR and Raman spectra to provide a more direct and graphical comparison with the experimental data. For the IR spectrum, this will require simulation of the magnitude of the electric dipole caused by each vibration, determined from the charges of the atoms involved and their separation distance from adjacent atoms obtained using the calculated eigenvectors. The intensity of the IR absorption in the vibrational spectrum may be modelled from the relative magnitudes of the dipole changes for each vibration, with small dipole changes generally associated with weak IR bands, and asymmetric vibrations associated with stronger IR absorption. For the Raman spectrum, the magnitude of the instantaneous dipole moment induced by the incident photon and the change in polarizability of the atoms associated with each vibration must be calculated. Raman-active vibrations always involve a change in polarizability, and thus have the same symmetry as one or more of the elements of the polarizability tensor (equation 3.19). The intensity of the scattering may be determined from the power spectrum of the time-dependent polarizability (equation 3.17), and the observation that vibrations with the same symmetry as the diagonal components of the polarizability tensor are associated with the most intense bands in the spectrum, and those associated with off-diagonal components generally have lower intensities; the symmetry species associated with the components of the polarizability tensor may also be found in point group character tables (e.g. Cotton, 1971; Fateley et al., 1972). The profile of the individual peaks in the spectra may subsequently be modelled by the use of Gaussian functions.
It would also be of interest to deconvolute the experimental spectra obtained by coherent INS by removing the $Q^2$ and $\sigma^2$ weightings in order to obtain the more familiar $g(\omega)$ profiles, thus allowing comparison with the density of states obtained from lattice dynamical calculations using PARAPCos (Parker and Price, 1989) and from Kieffer-type models (e.g. Hofmeister and Chopelas, 1991b). For the $\sigma^2$ weighting, this may be achieved using the mode assignments determined in Chapter 3 and calculated partial density of states to identify the atomic species contributing to each frequency. Thus, as $\sigma$ is known for each atom species (e.g. Sears, 1986), the $\sigma^2$ weighting on each frequency can be determined and removed. It would also be of interest to measure $g(\omega)$ of the remaining cubic aluminosilicate garnet end-members using coherent INS, to complement the existing IR and Raman spectroscopic data, and aid constrainment of effective pair potentials for these phases.

In future studies of majorite garnet, it will be essential to have direct observation of the cubic-tetragonal phase transition in order to establish the relative stabilities of the two polymorphs, and hence the symmetry and stability of majorite in the transition zone. As majorite also forms an important solid-solution series with pyrope (e.g. Akaogi et al., 1987; Parise et al., 1996; Sinogeikin et al., 1997; Heinemann et al., 1997), the elastic, vibrational and thermodynamic properties of the garnets along this binary join are important for constraining geophysical and geochemical models of the upper mantle and transition zone. Little variation in elasticity has been reported across the pyrope-majorite (tetragonal) join (e.g. Yagi et al., 1987, 1992; Bass and Kanzaki, 1990; Yeganeh-Haeri et al., 1990; Pacalo and Weidner, 1997), although Jeanloz (1981) determined a significantly higher bulk modulus (221 GPa) for a natural cubic majorite sample (containing approximately 2% Fe). Thus, it is essential to obtain pure samples of cubic majorite of sufficient size in order to determine the elasticity (and also the vibrational and thermodynamic properties), and to quantify the effect of Fe on the bulk moduli of (Mg,Fe)-majorites.

Future work should also include a more detailed polarized Raman study of tetragonal majorite in order to identify all 80 modes predicted for this phase (McMillan et al., 1989). A simulation study (c.f. Chapter 3) could augment this investigation by providing an additional method of identifying all 80 Raman modes; such a study could simultaneously be used to identify all 65 predicted IR-active modes. However, an interatomic potential for Ge$^{4+}$ in tetrahedral coordination is not currently available, and it would therefore be necessary to develop such a potential prior to this study. It would also
be of interest to perform coherent INS experiments on majorite to experimentally determine the full extent of the phonon frequency spectrum.

In future studies of anharmonicity in CaGeO$_3$ garnet, the intrinsic anharmonic parameters calculated in the present study may be used to correct Kieffer-model calculations of the vibrational heat capacity of CaGeO$_3$ garnet (Ross et al., 1986). However, the anharmonic parameters determined for this garnet by us are only valid for ambient conditions, and as only 30% of the expected Raman modes were identified, any correction made using the current data must be considered as a minimum correction. It would therefore be of interest to determine the evolution of the anharmonic parameters with temperature, a procedure which would require simultaneous high-pressure and high-temperature Raman experiments. With the pressure-induced Raman mode shifts of MgSiO$_3$ tetragonal garnet already documented (Rauch et al., 1996), it would also be of considerable interest to determine the temperature-induced mode shifts to complement the high-pressure work and permit calculation of the intrinsic anharmonic parameters of this phase directly. A similar Raman spectroscopic investigation of the disordered cubic majorite could also be performed, which may be easier due to the higher symmetry of the structure and thus the fewer number (25) of Raman modes to be identified, and would provide a good comparison with tetragonal majorite.

Thus, although over the past 30 years considerable advances have been made in our understanding of both the microscopic and macroscopic properties and relative stabilities of geologically relevant phases, considerable gaps still exist in our knowledge of the mineralogy (including the garnet group of minerals) of the Earth, which must be filled before we can fully understand the true composition and dynamics of the Earth's interior.
APPENDIX A

Tables A1-A11: Results of PARAPOCS Simulations of Pyrope Garnet Ambient Conditions, and at Temperature and Pressure.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>300K</th>
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<th>Body-Centred Cubic Unit Cell</th>
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<td>113.7990</td>
<td>113.7990</td>
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<td>2.3998</td>
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<td>1.3800</td>
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Table A1: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 300K using the uneven Brillouin zone sampling method of Filippini et al. (1976), with 1, 8, 27 and 64 sampling points.
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<th>$\left( \frac{2\pi}{a} \right)$</th>
<th>$\left( \frac{2\pi}{a} \right)$</th>
<th>Special Point Set</th>
<th>Maximum Difference</th>
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<td>$\left( \frac{1}{3} \frac{1}{3} \frac{1}{3} \right)$</td>
<td>$\left( \frac{1}{16} \frac{1}{16} \frac{1}{4} \right)$</td>
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<td>323.3788</td>
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<td>321.5418</td>
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<tr>
<td>S (J/mol K)</td>
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<td>250.7174</td>
<td>252.1716</td>
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<tr>
<td>C\textsubscript{11} (GPa)</td>
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<td>379.1949</td>
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<td>C\textsubscript{12} (GPa)</td>
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<td>118.8753</td>
<td>118.8435</td>
<td>118.8743</td>
<td>0.0102</td>
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<td>C\textsubscript{44} (GPa)</td>
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<td>103.9920</td>
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<td>3.6675</td>
<td>3.6676</td>
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<td>V\textsubscript{T} (km/s)</td>
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<td>9.8709</td>
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<td>5.5696</td>
<td>5.5698</td>
<td>5.5696</td>
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<tr>
<td>$\alpha \times 10^3$ (K\textsuperscript{-1})</td>
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<td>1.5691</td>
<td>1.5586</td>
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<td>1.0966</td>
<td>1.0897</td>
<td>1.09729</td>
<td>0.00759</td>
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<td>9.6138</td>
<td>9.6129</td>
<td>9.6139</td>
<td>0.001</td>
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<td>Dielectric (hf)</td>
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<td>2.3997</td>
<td>2.3998</td>
<td>2.3997</td>
<td>0.0001</td>
</tr>
<tr>
<td>Time (hrs)</td>
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<td>0.8200</td>
<td>0.7663</td>
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<td>1.4056</td>
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Table A2: Calculated thermodynamic and elastic properties of the body-centred cubic unit cell of pyrope at 300K using Baldereschi’s (1973) mean value point in the Brillouin zone at (1/6, 1/6, 1/2), and theoretical mean value points at (1/3, 1/3, 1) and (1/16, 1/16, 1/4), in units of 2\pi/a. Results of calculations using the special point set of Chadi and Cohen (1973) are also shown.
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<th>Parameters</th>
<th>1 Point</th>
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<th>27 Points</th>
<th>64 Points</th>
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<th>8 Points</th>
<th>27 Points</th>
<th>64 Points</th>
<th>Maximum Difference</th>
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<td>11.33443</td>
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<td>11.33451</td>
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<td>C(_{11}) (GPa)</td>
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<td>K (GPa)</td>
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<tr>
<td>Hill µ (GPa)</td>
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<td>(\rho) (g/cm(^3))</td>
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<td>3.6769</td>
<td>3.6769</td>
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<td>3.6768</td>
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<td>(V_p) (km/s)</td>
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<td>9.8957</td>
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<td>(V_s) (km/s)</td>
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<td>2.4031</td>
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Table A3: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 50K using the uneven Brillouin zone sampling method of Filippini et al. (1976), with 1, 8, 27 and 64 sampling points.
Table A4: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 100K using the uneven Brillouin zone sampling method of Filippini et al. (1976), with 1, 8, 27 and 64 sampling points.
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<tr>
<td>Cv (J/mol·K)</td>
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<td>0.1574</td>
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<tr>
<td>S (J/mol·K)</td>
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<td>64 Points</td>
<td>Maximum Difference</td>
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<td>8 Points</td>
<td>27 Points</td>
<td>64 Points</td>
<td>Maximum Difference</td>
</tr>
<tr>
<td>G (eV)</td>
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<tr>
<td>Cp (J/mol·K)</td>
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<td>0.1574</td>
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<td>0.0002</td>
<td>0.1574</td>
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<tr>
<td>Cv (J/mol·K)</td>
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<td>0.0002</td>
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<td></td>
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<td>0.0001</td>
<td>0.0002</td>
<td>0.1574</td>
<td></td>
</tr>
<tr>
<td>S (J/mol·K)</td>
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<td>1.1052</td>
<td></td>
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</tbody>
</table>

Table A5: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 200K using the uneven Brillouin zone sampling method of Filippini et al. (1976), with 1, 8, 27 and 64 sampling points.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>500K</th>
<th>Primitive Unit Cell</th>
<th>Body-Centred Cubic Unit Cell</th>
<th>Maximum Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 Point</td>
<td>8 Points</td>
<td>27 Points</td>
<td>64 Points</td>
</tr>
<tr>
<td>G (eV)</td>
<td>-5387.5834</td>
<td>-5387.5414</td>
<td>-5387.5382</td>
<td>-5387.5376</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.35753</td>
<td>11.35754</td>
<td>11.35754</td>
<td>11.35753</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>1465.0457</td>
<td>1465.0511</td>
<td>1465.0497</td>
<td>1465.0489</td>
</tr>
<tr>
<td>Cp (J/mol.K)</td>
<td>416.9430</td>
<td>416.8414</td>
<td>416.9374</td>
<td>416.9270</td>
</tr>
<tr>
<td>Cv (J/mol.K)</td>
<td>412.9952</td>
<td>412.8924</td>
<td>412.9876</td>
<td>412.9776</td>
</tr>
<tr>
<td>S (J/mol.K)</td>
<td>444.1310</td>
<td>443.1148</td>
<td>443.0360</td>
<td>443.0330</td>
</tr>
<tr>
<td>C_{11} (GPa)</td>
<td>374.7144</td>
<td>374.7097</td>
<td>374.7109</td>
<td>374.7116</td>
</tr>
<tr>
<td>C_{22} (GPa)</td>
<td>117.7784</td>
<td>117.7772</td>
<td>117.7775</td>
<td>117.7777</td>
</tr>
<tr>
<td>C_{33} (GPa)</td>
<td>103.3400</td>
<td>103.3393</td>
<td>103.3395</td>
<td>103.3396</td>
</tr>
<tr>
<td>K (GPa)</td>
<td>201.4889</td>
<td>201.4851</td>
<td>201.4861</td>
<td>201.4867</td>
</tr>
<tr>
<td>V_p (km/s)</td>
<td>9.8388</td>
<td>9.8387</td>
<td>9.8387</td>
<td>9.8387</td>
</tr>
<tr>
<td>V_s (km/s)</td>
<td>5.5545</td>
<td>5.5545</td>
<td>5.5545</td>
<td>5.5545</td>
</tr>
<tr>
<td>V_0 (x10^9 K^-1)</td>
<td>1.8850</td>
<td>1.8852</td>
<td>1.8855</td>
<td>1.8853</td>
</tr>
<tr>
<td>Gruneisen, γ</td>
<td>1.01425</td>
<td>1.01464</td>
<td>1.01453</td>
<td>1.01447</td>
</tr>
<tr>
<td>Dielectric (st)</td>
<td>9.7332</td>
<td>9.7334</td>
<td>9.7333</td>
<td>9.7333</td>
</tr>
<tr>
<td>Dielectric (hf)</td>
<td>2.3950</td>
<td>2.3950</td>
<td>2.3950</td>
<td>2.3950</td>
</tr>
<tr>
<td>Time (hrs)</td>
<td>0.1542</td>
<td>0.3104</td>
<td>0.7125</td>
<td>1.5256</td>
</tr>
</tbody>
</table>

Table A6: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 500K using the uneven Brillouin zone sampling method of Filippini et al. (1976), with 1, 8, 27 and 64 sampling points.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>1 Point</th>
<th>8 Points</th>
<th>27 Points</th>
<th>64 Points</th>
<th>Maximum Difference</th>
<th>1 Point</th>
<th>8 Points</th>
<th>27 Points</th>
<th>64 Points</th>
<th>Maximum Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>G (eV)</td>
<td>-5401.3988</td>
<td>-5401.3314</td>
<td>-5401.3262</td>
<td>-5401.3254</td>
<td>0.0734</td>
<td>-5401.2902</td>
<td>-5401.2926</td>
<td>-5401.2939</td>
<td>-5401.2945</td>
<td>0.0043</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.38097</td>
<td>11.38099</td>
<td>11.38098</td>
<td>11.38098</td>
<td>0.0002</td>
<td>11.38101</td>
<td>11.38099</td>
<td>11.38098</td>
<td>11.38098</td>
<td>0.0003</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>1474.1372</td>
<td>1474.1445</td>
<td>1474.1420</td>
<td>1474.1406</td>
<td>0.0073</td>
<td>1474.1533</td>
<td>1474.1431</td>
<td>1474.1409</td>
<td>1474.1401</td>
<td>0.0132</td>
</tr>
<tr>
<td>C_G (J/mol.K)</td>
<td>467.5096</td>
<td>467.5116</td>
<td>467.5864</td>
<td>467.5722</td>
<td>0.0768</td>
<td>467.4914</td>
<td>467.5690</td>
<td>467.5544</td>
<td>467.5440</td>
<td>0.0776</td>
</tr>
<tr>
<td>C_v (J/mol.K)</td>
<td>459.8604</td>
<td>459.8580</td>
<td>459.9318</td>
<td>459.9190</td>
<td>0.0738</td>
<td>459.8514</td>
<td>459.9328</td>
<td>459.9200</td>
<td>459.9106</td>
<td>0.0814</td>
</tr>
<tr>
<td>S (J/mol.K)</td>
<td>652.4792</td>
<td>653.1742</td>
<td>653.0950</td>
<td>653.0814</td>
<td>0.695</td>
<td>652.4792</td>
<td>652.5120</td>
<td>652.5312</td>
<td>652.5398</td>
<td>0.0606</td>
</tr>
<tr>
<td>C_{11} (GPa)</td>
<td>366.8717</td>
<td>366.8634</td>
<td>366.8676</td>
<td>366.8688</td>
<td>0.0063</td>
<td>366.7973</td>
<td>366.8059</td>
<td>366.8078</td>
<td>366.8085</td>
<td>0.0112</td>
</tr>
<tr>
<td>C_{22} (GPa)</td>
<td>115.8812</td>
<td>115.8797</td>
<td>115.8802</td>
<td>115.8805</td>
<td>0.0015</td>
<td>115.8504</td>
<td>115.8525</td>
<td>115.8529</td>
<td>115.8531</td>
<td>0.0027</td>
</tr>
<tr>
<td>C_{33} (GPa)</td>
<td>102.1507</td>
<td>102.1498</td>
<td>102.1501</td>
<td>102.1503</td>
<td>0.0009</td>
<td>102.1190</td>
<td>102.1203</td>
<td>102.1206</td>
<td>102.1207</td>
<td>0.0017</td>
</tr>
<tr>
<td>K (GPa)</td>
<td>196.2649</td>
<td>196.2599</td>
<td>196.2617</td>
<td>196.2626</td>
<td>0.005</td>
<td>196.2204</td>
<td>196.2310</td>
<td>196.2325</td>
<td>196.2331</td>
<td>0.0127</td>
</tr>
<tr>
<td>Hill (GPa)</td>
<td>110.9260</td>
<td>110.9240</td>
<td>110.9250</td>
<td>110.9250</td>
<td>0.002</td>
<td>110.8970</td>
<td>110.8990</td>
<td>110.9000</td>
<td>110.9000</td>
<td>0.003</td>
</tr>
<tr>
<td>ρ (g/cm³)</td>
<td>3.6320</td>
<td>3.6319</td>
<td>3.6319</td>
<td>3.6319</td>
<td>0.001</td>
<td>3.6319</td>
<td>3.6319</td>
<td>3.6319</td>
<td>3.6319</td>
<td>0.00</td>
</tr>
<tr>
<td>V_p (km/s)</td>
<td>9.7808</td>
<td>9.7807</td>
<td>9.7807</td>
<td>9.7808</td>
<td>0.001</td>
<td>9.7797</td>
<td>9.7797</td>
<td>9.7797</td>
<td>9.7797</td>
<td>0.00</td>
</tr>
<tr>
<td>V_s (km/s)</td>
<td>5.5264</td>
<td>5.5264</td>
<td>5.5264</td>
<td>5.5264</td>
<td>0.00</td>
<td>5.5258</td>
<td>5.5258</td>
<td>5.5258</td>
<td>5.5258</td>
<td>0.00</td>
</tr>
<tr>
<td>α (x10³ K⁻¹)</td>
<td>2.0952</td>
<td>2.0958</td>
<td>2.0959</td>
<td>2.0958</td>
<td>0.0007</td>
<td>2.0941</td>
<td>2.0936</td>
<td>2.0933</td>
<td>2.0932</td>
<td>0.0009</td>
</tr>
<tr>
<td>Gruneisen, γ</td>
<td>0.99237</td>
<td>0.99266</td>
<td>0.99256</td>
<td>0.9925</td>
<td>0.0002</td>
<td>0.99170</td>
<td>0.99129</td>
<td>0.99120</td>
<td>0.99116</td>
<td>0.00054</td>
</tr>
<tr>
<td>Dielectric (hf)</td>
<td>2.3869</td>
<td>2.3869</td>
<td>2.3869</td>
<td>2.3869</td>
<td>0.00</td>
<td>2.3869</td>
<td>2.3869</td>
<td>2.3869</td>
<td>2.3869</td>
<td>0.00</td>
</tr>
<tr>
<td>Time (hrs)</td>
<td>0.1818</td>
<td>0.3662</td>
<td>0.8651</td>
<td>1.9830</td>
<td>1.8012</td>
<td>0.9344</td>
<td>2.2947</td>
<td>6.7707</td>
<td>14.5300</td>
<td>13.5956</td>
</tr>
</tbody>
</table>

Table A7: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 800K using the uneven Brillouin zone sampling method of Filippini et al. (1976), with 1, 8, 27 and 64 sampling points.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>1 Point</th>
<th>8 Points</th>
<th>27 Points</th>
<th>64 Points</th>
<th>Maximum Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>α (Å)</td>
<td>11.4160</td>
<td>11.4160</td>
<td>11.4160</td>
<td>11.4160</td>
<td>0.0001</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>1487.8135</td>
<td>1487.8198</td>
<td>1487.8153</td>
<td>1487.8131</td>
<td>0.0067</td>
</tr>
<tr>
<td>G (eV)</td>
<td>-5426.5400</td>
<td>-5426.4390</td>
<td>-5426.4310</td>
<td>-5426.4298</td>
<td>0.1090</td>
</tr>
<tr>
<td>Cₐ (GPa)</td>
<td>113.1983</td>
<td>113.1972</td>
<td>113.1980</td>
<td>113.1984</td>
<td>0.0012</td>
</tr>
<tr>
<td>Cₚ (GPa)</td>
<td>100.3554</td>
<td>100.3546</td>
<td>100.3552</td>
<td>100.3555</td>
<td>0.0009</td>
</tr>
<tr>
<td>K (GPa)</td>
<td>188.6799</td>
<td>188.6757</td>
<td>188.6787</td>
<td>188.6802</td>
<td>0.0045</td>
</tr>
<tr>
<td>[ρ (g/cm³)]</td>
<td>3.5986</td>
<td>3.5986</td>
<td>3.5986</td>
<td>3.5986</td>
<td>0.00</td>
</tr>
<tr>
<td>Vₚ (km/s)</td>
<td>9.6938</td>
<td>9.6938</td>
<td>9.6938</td>
<td>9.6938</td>
<td>0.00</td>
</tr>
<tr>
<td>Vₛ (km/s)</td>
<td>5.4830</td>
<td>5.4830</td>
<td>5.4830</td>
<td>5.4830</td>
<td>0.00</td>
</tr>
<tr>
<td>α (x10⁻⁵ K⁻¹)</td>
<td>2.2850</td>
<td>2.2849</td>
<td>2.2850</td>
<td>2.2848</td>
<td>0.0002</td>
</tr>
<tr>
<td>Gruneisen, γ</td>
<td>1.00672</td>
<td>1.00687</td>
<td>1.00676</td>
<td>1.00760</td>
<td>0.00088</td>
</tr>
<tr>
<td>μ (μm/°C)</td>
<td>10.3254</td>
<td>10.3256</td>
<td>10.3254</td>
<td>10.3254</td>
<td>0.0002</td>
</tr>
<tr>
<td>Dielectric (st)</td>
<td>2.3748</td>
<td>2.3748</td>
<td>2.3748</td>
<td>2.3748</td>
<td>0.00</td>
</tr>
<tr>
<td>Time (hrs)</td>
<td>0.1845</td>
<td>0.3848</td>
<td>0.9137</td>
<td>1.9614</td>
<td>1.7769</td>
</tr>
</tbody>
</table>

Table A8: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 1200K using the uneven Brillouin zone sampling method of Filippini et al. (1976), with 1, 8, 27 and 64 sampling points.
Table A9: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 1500K using the uneven Brillouin zone sampling method of Filippini et al. (1976), with 1, 8, 27 and 64 sampling points.
<table>
<thead>
<tr>
<th>Parameters</th>
<th>2000K</th>
<th>Primitive Unit Cell</th>
<th>Body-Centred Cubic Unit Cell</th>
<th>Maximum Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 Point</td>
<td>8 Points</td>
<td>27 Points</td>
<td>64 Points</td>
</tr>
<tr>
<td>G (eV)</td>
<td>-5492.2444</td>
<td>-5492.0760</td>
<td>-5492.0626</td>
<td>-5492.0604</td>
</tr>
<tr>
<td>a (Å)</td>
<td>11.50187</td>
<td>11.50179</td>
<td>11.50175</td>
<td>11.50174</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>1521.6268</td>
<td>1521.5852</td>
<td>1521.5716</td>
<td>1521.5661</td>
</tr>
<tr>
<td>C_p (J/mol.K)</td>
<td>519.8358</td>
<td>519.6092</td>
<td>519.7514</td>
<td>519.7338</td>
</tr>
<tr>
<td>C_v (J/mol.K)</td>
<td>490.5590</td>
<td>490.3884</td>
<td>490.5250</td>
<td>490.5138</td>
</tr>
<tr>
<td>S (J/mol.K)</td>
<td>1111.1914</td>
<td>1110.1498</td>
<td>1110.0752</td>
<td>1110.0594</td>
</tr>
<tr>
<td>C_{11} (GPa)</td>
<td>328.0857</td>
<td>328.1181</td>
<td>328.1287</td>
<td>328.1331</td>
</tr>
<tr>
<td>C_{12} (GPa)</td>
<td>107.3742</td>
<td>107.3801</td>
<td>107.3828</td>
<td>107.3836</td>
</tr>
<tr>
<td>C_{44} (GPa)</td>
<td>95.8729</td>
<td>95.8784</td>
<td>95.8802</td>
<td>95.8810</td>
</tr>
<tr>
<td>K (GPa)</td>
<td>170.8312</td>
<td>170.8570</td>
<td>170.8654</td>
<td>170.8689</td>
</tr>
<tr>
<td>Hill (GPa)</td>
<td>101.4250</td>
<td>101.4340</td>
<td>101.4360</td>
<td>101.4370</td>
</tr>
<tr>
<td>ρ (g/cm³)</td>
<td>3.5186</td>
<td>3.5187</td>
<td>3.5187</td>
<td>3.5187</td>
</tr>
<tr>
<td>V_s (km/s)</td>
<td>5.3689</td>
<td>5.3691</td>
<td>5.3691</td>
<td>5.3692</td>
</tr>
<tr>
<td>α (x10⁵ K⁻¹)</td>
<td>2.7358</td>
<td>2.7329</td>
<td>2.7332</td>
<td>2.7329</td>
</tr>
<tr>
<td>Gruneisen, γ</td>
<td>1.09075</td>
<td>1.09017</td>
<td>1.08998</td>
<td>1.08990</td>
</tr>
<tr>
<td>Dielectric (st)</td>
<td>11.4721</td>
<td>11.4704</td>
<td>11.4699</td>
<td>11.4696</td>
</tr>
<tr>
<td>Dielectric (hf)</td>
<td>2.3458</td>
<td>2.3458</td>
<td>2.3458</td>
<td>2.3458</td>
</tr>
<tr>
<td>Time (hrs)</td>
<td>0.2079</td>
<td>0.4542</td>
<td>1.0664</td>
<td>2.2071</td>
</tr>
</tbody>
</table>

Table A10: Calculated thermodynamic and elastic properties of the primitive and full body-centred cubic unit cells of pyrope at 2000K using the uneven Brillouin zone sampling method of Filippini *et al.* (1976), with 1, 8, 27 and 64 sampling points.
Table A11: Calculated thermodynamic and elastic properties of the primitive unit cell of pyrope at pressure using a single Brillouin zone sampling point, according to the sampling method of Filippini 	extit{et al.} (1976).
List of References


-(1977) Pyroxene-garnet solid-solution equilibria in the systems Mg$_4$Si$_4$O$_{12}$-Mg$_2$Al$_2$Si$_3$O$_{12}$ and Fe$_4$Si$_4$O$_{12}$-Fe$_3$Al$_2$Si$_3$O$_{12}$ at high-pressures and temperatures. Physics of the Earth and Planetary Interiors 15, 90-106.


PRESNALL, D.C. and GASPARIK, T. (1990) Melting of enstatite (MgSiO$_3$) from 10 to 16.5 GPa and the forsterite (Mg$_2$SiO$_4$)-majorite (MgSiO$_3$) eutectic at 16.5 GPa: Implications for the origin of the mantle. *Journal of Geophysical Research* 95, 15771-15777.


SAWAMOTO, H. (1987) Phase diagram of MgSiO$_3$ at pressures up to 24 GPa and temperatures up to 2200 °C: Phase stability and properties of tetragonal garnet. In *High-Pressure Research in Mineral Physics* (Editors: M.H. Manghnani and Y. 276


SINOGEIKIN, S.V., BASS, J.D., ONEILL, B., AND GASPARIK, T. (1997) Elasticity of tetragonal end-member majorite and solid-solutions in the system Mg_{4}Si_{4}O_{12}-Mg_{3}Al_{2}Si_{3}O_{12}. *Physics and Chemistry of Minerals*, 24, 115–121.


