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MINERAL INCLUSIONS IN DIAMOND AND THEIR

GEOLOGICAL SIGNIFICANCE

by

J. W. Harris, B.Sc., M.Sc.

A thesis submitted to the University of London

for the degree of

Doctor of Philosophy in the Faculty of Science.

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ABSTRACT

A study of the solid mineral inclusions which occur in diamonds was undertaken (a) in the hope of defining more precisely the pressure and temperature conditions prevailing during the genesis of natural diamonds, and (b) to obtain greater understanding of the mineralogy of the Earth's upper mantle.

Fourteen mineral species, two of which had not previously been reported in diamond, were identified from X-ray diffraction patterns. Where possible the relative crystallographic orientation of host and inclusion for monocystals, (or preferred orientation for powders) was determined. In particular, a check was made to see whether the actual contact faces were those expected from considerations of epitaxy.

Measurements of thermal expansion of garnets while enclosed in diamond and after removal have been made to provide data for estimates of the pressure/temperature conditions prevailing when the garnets were enclosed. The variation between the two specimens is outside the range of experimental error, and indicates that several factors must be taken into account when formulating a theory.

A non-destructive method of chemical analysis of these inclusions is virtually essential for comparative geochemical studies. Garnet should be extremely favourable for X-ray site occupation analysis.
experiments, because different X-ray reflections can be associated with separate components of the structure. Data has been collected from one such inclusion in order to compare the accuracy attainable in this way with that possible by other techniques.
ACKNOWLEDGEMENTS

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I also wish to thank Mr. E. Nave for technical assistance; Mr. R. Reed for constructing the supplementary apparatus used in this work; Miss J. Bedney for assistance in the preparation of photographic prints; and Mrs. A. Graeme-Barber for measuring X-ray photograph intensities with the Isodensitracer.

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My thanks are also due to Professor M. Blackman, Dr. T. H. K. Barron, Dr. A. Clark, Dr. M. K. Wells, Dr. H. O. A. Meyer, and Mr. R. C. Henriques with whom I had much stimulating discussion, and to Mr. D. Wally for help with computer programmes.

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CONTENTS

ABSTRACT ......................................................................................... 2

ACKNOWLEDGEMENTS ..................................................................... 4

GENERAL INTRODUCTION .................................................................. 8

CHAPTER I: A STUDY OF DIAMOND INCLUSIONS .......................... 12

Introduction ..................................................................................... 12
Historical Review of Diamond Inclusions ........................................ 13
Apparatus ......................................................................................... 23
The Quantitative Analysis of Diamond Inclusions .............................. 24
Results ............................................................................................ 31
Detailed Discussion of the Results .................................................. 33
Introduction ..................................................................................... 33
Syngenetic Inclusions .................................................................... 34
Epigenetic Inclusions ..................................................................... 47
The Morphology of the Inclusions .................................................. 54

CHAPTER II: RELATIVE CRYSTALLOGRAPHIC ORIENTATION OF
INCLUSIONS TO DIAMOND ............................................................. 58

Introduction ..................................................................................... 58
Experimental Procedure ................................................................... 59
Results ............................................................................................ 62
Discussion ......................................................................................... 62
Comparison with Similar Russian Investigations .............................. 85
Conclusion ......................................................................................... 87

CHAPTER III: THERMAL EXPANSION OF GARNET INCLUSIONS ....... 89

Introduction ..................................................................................... 89
Previous Work ................................................................................ 90
Apparatus and Experimental ......................................................... 93
Estimates of Errors ......................................................................... 98
Discussion ......................................................................................... 113
Conclusion ......................................................................................... 122

CHAPTER IV: X-RAY SITE OCCUPATION OF ANALYSIS OF GARNET ... 123

Introduction ..................................................................................... 123
X-ray Site Occupation Analysis ....................................................... 124
Introduction ..................................................................................... 124
Atomic Scattering Factors .............................................................. 129
CHAPTER IV (Contd)

The Garnet Series .......................... 134
Experimental Procedure .................... 138
    Introduction ................................ 138
    General X-ray Procedure ................. 143
Computational Procedure for X-ray Site Occupation Analysis 148
Results ........................................ 155
Discussion and Conclusions .................. 164

REFERENCES .................................... 174

APPENDIX I

Tabulated Experimental Data .................. 183

APPENDIX II

Details of the Space Group of Garnet ............. 247

APPENDIX III

Publications .................................... 250
GENERAL INTRODUCTION

It has long been known that diamonds are found either in alluvial or eluvial deposits, or in a kimberlite material of igneous origin. The kimberlite is considered to be the source rock and this might be taken to indicate that the diamonds crystallised in situ after the igneous eruption, but it is equally possible that the diamonds originated at deeper levels in the mantle and were carried to their present position by the eruption. Since the successful synthesis of diamonds with hydrostatic pressures of 50 kbs and temperatures around 1500°C, it has generally been assumed that if pressures and temperatures of this order are required, diamonds could not have been formed where they are now found, and hence the deep level origin must be preferred.

It is of interest to see whether these two possibilities are susceptible to experimental test. One possibility is suggested by the fact that many diamonds contain inclusions of minerals also present in kimberlite. While these are often of variable composition laws relating such variations to condition of formation are now established. One might therefore expect that inclusions within diamond could differ from similar minerals found in the kimberlite, either because of initial chemical differences, or subsequent alteration of kimberlite minerals not enclosed by the diamond. This possibility is discussed in Chapter I.
A second possibility is that if diamonds were formed at pressures and temperatures well above those expected in the pipes, minerals included will actually be high pressure/high temperature phases perhaps unrecorded elsewhere. This possibility is supported by the mineral coesite found as an inclusion. However, as no further examples have so far been found, this aspect was not pursued in the present work. Also if the inclusions had undergone phase changes, their morphology would not be expected to be that of a normal crystal of the lower pressure phase. Accordingly a detailed study of the morphology of these inclusions is given in Chapter I.

The converse situation is that low pressure/low temperature minerals ought not to be found in diamond if a high pressure/high temperature origin is correct. But in fact minerals such as quartz and kaolinite have been encountered in the present study. This problem is discussed in Chapter I.

Another question that arises is why so many diamonds do in fact contain inclusions. Do they act as seeds for diamond growth, or are they deposited sometimes on diamond surfaces available at some stage in the demonstrably complex growth history of many specimens and subsequently occluded? A similar situation would be expected if the inclusions have been included as liquids which subsequently crystallised out within the diamond.

If they act as seeds, epitaxial relationships might be expected,
as also in the case where the inclusions formed on existing diamond surfaces. Epitaxial relationships between diamond and garnet and olivine are discussed in Chapter II.

One curious feature of completely general occurrence is strain birefringence in diamond which, being cubic, should be optically isotropic. One possibility is that the thermal expansion of the relatively pure (Type II) diamond differs slightly from that of impure (nitrogen doped?) Type I. Experimental data available prior to this work showed variations of the same order of magnitude as the experimental error, and this question is still unresolved. However, many diamonds show very strong localised birefringence in the neighbourhood of inclusions, indicating that there is considerable strain present at room pressure and temperature. This is to be expected if the inclusion was reduced in volume by the high pressure occurring at the time it was enclosed. Measurement of the thermal expansion of inclusions while still restricted by the diamond as compared with the value for the free inclusion after removal have been made to provide data for a theoretical estimate of the pressure and temperature of formation. The experimental results for two garnets are given in Chapter III.

The fact that these mineral inclusions have been preserved unaltered gives them considerable interest in their own right, so that a detailed investigation of these specimens is of general interest in the context of Upper Mantle geology. Accurate non-destructive
chemical analysis is extremely difficult for specimens of this size, and an attempt to achieve this by means of site-occupation analysis for garnet by X-ray diffraction is described in Chapter IV.

Granville-Wells (Thesis 1951) noted that inclusions seemed to be more numerous in Type II diamonds. It is of interest that 10 out of the 15 specimens here considered are classified as Type II, though this is considered the rare type of diamond, especially in large sizes. The significance of this observation is not yet clear.
CHAPTER I

A STUDY OF DIAMOND INCLUSIONS

Introduction

In the present work, a systematic examination was made on a quantity of African diamonds using X-ray diffraction techniques. At first, it was decided to attempt a mineralogical study on one type of inclusion rather than a general survey. The mineral garnet was chosen partly because it was expected that garnet could easily be identified by colour, and being cubic, it could be characterised more rapidly. However, colour proved an unsuccessful method of identifying garnets as the first five red-coloured inclusions were identified as garnet (2), calcite, spinel, and kaolinite, and it was also found that the range of chemical composition of garnets encountered in kimberlite made it difficult to characterise the garnets accurately. Hence it was felt that a more general examination of such diamond inclusions as were available would be more informative.

Fifteen diamond specimens have so far been examined in detail. These contain both syngenetic and epigenetic mineral inclusions. The places of origin of these diamonds are not known exactly, but the information gained from this study will provide a basis for subsequent investigations on diamond inclusions and kimberlite from known regions, from which similar specimens can generally be recognised.
It is largely on the results of these studies, presented as Appendix I, that the subsequent discussion in Chapter I is based. A final section discusses the morphology of the inclusions and some suggestions are put forward to account for the observations.

**A Historical Review of Diamond Inclusions**

Any observations that were made on diamonds up to the beginning of the 18th century, were undoubtedly made on diamonds of Indian origin, as India was then the only known source, but in 1727 the Brazilian deposits were discovered, and these diamonds soon became the centre of early research. This situation changed however, when the much larger South African diamond fields were discovered and quickly developed towards the end of the 19th century. Some further research into foreign material in diamonds was carried out up to the present time, but the first systematic study was completed on inclusions in Ural and Siberian diamonds after the development of the Russian diamond fields in the early 1950's.

The early history of diamond inclusions is essentially told in a series of books published between 1676 and 1932. However, an attempt has been made to trace and investigate the claims made by the authors referred to in these books, so that an evaluation could be made of the rather heterogeneous mineralogy that was found in the later literature.

The diarist John Evelyn was perhaps the first to observe a
diamond inclusion. On September 29th 1645 he wrote, "I went .... to see the Collection of a Noble Venetian Signor Rugini: he has a stately Palace richly furnish'd, .... but above all was a Diamond which had growing in it a faire Rubie."

It is not surprising that the inclusion was identified as ruby, for this mineral was one of the few red gems well known from ancient times, but the mineral was probably a garnet.

In 1676, John Baptiste Tavernier published a book on his voyages to India to purchase diamonds for Louis XIV, and makes reference to "knots" and black spots enclosed within some of the diamonds. However, no identifications were offered.

In Boutan's book of 1886 are summarised the names of some of the early investigators into diamond inclusions, and in the following table are listed the various scientists and the inclusions with which they are accredited.

(1) Brewster 1835 (gas)  (8) Damour 1856 (gold)
(2) Dumas 1840 (rutile)  (9) Brewster 1861 (gas/liquid)
(3) Petzold 1842 (quartz) (10) Göppert 1862 (plant remains)
(4) Wohler 1842 (a resume) (11) Cohen 1873 (haematite)
(5) Harting 1850 (pyrite)  (12) Cohen 1876 (ilmenite)
(6) Damour 1853 (topaz)  (13) Chatto 1886 (pyrite)
(7) Des Cloiseaux 1855 (plant remains)
Little evidence is given by Brewster (1835) for the gas inclusions which he observed, other than the ellipsoidal shape of the inclusion and the strain birefringence effects in the adjacent diamond, and both these phenomena can be characteristic of anhedral olivine inclusions (Orlov 1959, and this Thesis).

In Dumas's paper no reference was found to "l'acide titanique" (rutile) so that this attribution may be in error, but topaz was mentioned as being the cause of a discrepancy of 9 milligrams between the real and calculated weight of a diamond at the end of an experiment.

The book by Fetzold and references 4, and 6, were not reviewed as they are not held in libraries in this country, and reference number 5 is simply a note giving information on a memoir by Haring, and makes no mention of the mineral pyrite. Another contribution by this author in 1858 was not traced, but Haring and Boim (1859) do refer to the recovery of pyrite from a diamond and its subsequent decomposition and analysis, although no procedures are given.

Des Cloiseaux (1855) affirms the presence of gold and fuliginous material in regular layers in the diamond, and Damour (1856) refers to flakes of gold in fractures in carbonado from Brazil. Neither author however, presents evidence for the recognition of these substances.

In 1861 Brewster further discussed the possibility of gas or liquid inclusions in diamond. While the observations seem accurate,
the conclusions are largely inferred from a study of similar cavities in topaz.

The most detailed work completed at this time was by Göppert, who in a beautifully illustrated memoir, presents arguments from which he concludes that the enclosures observed in diamond are of definite vegetable origin. It seems probable that what he actually noted, was foreign material lying in cleavage or other fracture planes in the diamond. Such substances can have a mesh-like distribution in these planes which appear similar to cell structures (Diamond D7 Appendix I). His ideas were also probably influenced by the biogenic theory for the origin of the carbon in diamonds, first proposed by Brewster (1835).

The evidence for the presence of haematite (ironglance) and ilmenite as diamond inclusions proposed by Cohen, is based on two observations: (1) the rhombohedral and tabular habit of the included crystals with prominent faces lying parallel to octahedral faces of the diamond, and (2), a comparison of similar crystal morphology from the haematite deposits of St. Gotthard. To account for some green material observed in diamond Cohen suggested this to be a copper compound.

No reference to Chatrion's paper of 1886 was found, but according to Boutan, this author recognised pyrites in a diamond. Boutan makes reference also to a diamond in which he observed a number of fissures filled with an unknown red-coloured material, and in his book, several of the diagrams of Göppert are presented as well as one from Chatrion's 1886 paper.
In 1897, Bonney edited and presented as a book the works of Professor Carvill Lewis, and this publication mentions most of the investigators quoted by Boutan, but several new names appear and these are given below.

(1) Kengott 1853 (diamond)    (3) Schauf 1873 (diamond)
(2) Zirkel 1873 (a resume)    (4) Jannettaz 1879 (gas)

The journals containing references 2 and 3 are not held by English libraries, but according to Lewis, Zirkel gives a full resume of the inclusions found prior to the discovery of South African diamonds. Kengott (1853), noted an oriented wine-yellow coloured octahedral diamond enclosed by a colourless octahedron and Jannettaz (1879) accounts for the yellow colour of some diamonds by suggesting that compressed gas is responsible.

The latter paper also mentions that Petzold observed quartz crystals in diamond on which a brown material was present, and Wöhler apparently concluded that plant remains existed in diamond.

Friedel (1879, 1883, 1884) and Moissan (1896), both investigated black grains in diamond, and as such material was consumed with the diamond when burnt, concluded that it must consist of carbonaceous material. This seems the first evidence for the presence of graphite as an inclusion in diamond.

Bauer's book on Precious Stones was translated from the German
by Spencer in 1904, and like previous publications the earlier work is similarly reviewed. However, the discovery accredited to Des Cloiseaux of chlorite as an inclusion in diamond as veriform aggregates of green scales, is noted for the first time. Also discussed are fluid enclosures in the diamond, and from their behaviour when heated Bauer concludes that the liquid consists of either carbon dioxide and water, or a saline solution. Red enclosures he considered were generally rare, although limonite was occasionally found in diamond cracks.

In 1907 Sutton made the first identification of garnet as an inclusion, and in a series of books Crookes (1909), Catelle (1911), Escard (1914), and Wagner (1914) refer to the earlier work in varying degrees of detail. However, Escard (p 102) mentions topaz as an inclusion, and Wagner (p 145) a reddish-brown garnet for which a refractive index is given, and a diopside as enclosures from South African diamonds.

In 1921 Sutton to some extent reviewed the inclusions found in South African diamonds and mentions olivine for the first time as a definite inclusion. He suggests that the common mineral inclusions are garnet, ilmenite, and iron pyrites, with graphite as a common cognate inclusion, and cites as epigenetic minerals calcite, apophyllite, and pectolite occurring in diamond fractures. Also in 1921 Sutton further discusses calcite as an overgrowth on diamonds.

Friedel (1923) then oxidised some black inclusions in diamond
and concluded it was graphite, and in the same year, Colony describes an intergrowth of quartz in a diamond of Brazilian origin. Spencer (1924) from a diamond specimen given by Sutton, then seems certainly to have identified magnetite as an inclusion.

Sutton's book on diamonds in 1928 refers to some of his earlier work, and the minerals chromite, picotite, and zircon are remarked on as possible diamond inclusions. Gas and liquid inclusions, however, are dismissed as being "favourite myths". A further example of quartz from a Brazilian diamond was noted by Correns (1931), and this author considered the quartz to be of epigenetic origin derived from late solutions associated with the mother rock.

Williams (1932) gives a resume of inclusions found in diamonds from 1904, and mentions as new inclusions original magma, an unspecified pyroxene, and a mica (biotite); the latter two being identified by F. E. Wright. The mica was brown in colour, its shape was determined by the octahedral plane of the diamond, and the specimen was examined as a powder. While no evidence of the amount or character of the powder is given, a certain reserve is placed on this identification, as primary biotite would considerably restrict the temperature and pressure range for the initial conditions of the formation of diamond. However, the presence of a powdered mineral in the cleavage plane of diamond is one of the common occurrences of epigenetic mineral inclusions.
In 1948 and 1952 Gubelin completed some detailed microscopic work on diamond inclusions. In the latter paper is presented several photographs of most of the inclusions mentioned by the more recent investigators. However, two photographs of quartz inclusions from Brazilian diamonds look very similar in morphology to the mineral olivine, the commonest included mineral, which is omitted from the list of photographic identifications. Reference is also made to the presence of original magma in the diamond. This type of phenomenon, also mentioned by Williams (1932), has often been noted during this present examination of diamond, but as yet has not been studied in detail. It seems that such material consists of very fine crystallites of some mineral or minerals, rather than part of the original magma. However an olivine powder in an African diamond was identified by Gnevushev and Futergendler (1963) who accounted for this occurrence by suggesting that an ultrabasic olivine glass representing original magmatic material was enclosed by a rapidly growing diamond.

In 1953 Mitchell and Giardini identified for the first time a colourless olivine inclusion in a diamond by X-ray diffraction techniques, and this has now developed into the chief means by which an unambiguous identification can be made of a diamond inclusion.

Using this technique, investigations into inclusions in Russian diamonds were made by Futergendler (1956, 1958, 1960) and the minerals enstatite and chromospinel were identified for the first time. The
minerals olivine, chrome diopside, and garnet were also found, and some physical properties of the inclusions are presented.

Part of a paper by Maertenson (1957) discusses the presence of a corroded zircon in diamond but the mineral was identified by optical means.

In 1959 Orlov completed a further but more detailed X-ray study on 35 diamonds principally from the Urals and Siberia, although some were of African origin. The three chief inclusions found were olivine, pyrope garnet and chromaspinel, and details of cell parameters and refractive indices are given together with diagrams of the morphology of the inclusions. The epigenetic minerals identified by Orlov were some serpentine as a pseudomorph after an olivine inclusion in an African diamond, red quartz, and a red iron hydroxide which filled a diamond fracture plane. The final section of the paper deals with a discussion of diamond inclusions.

Eppler (1961) in listing the inclusions from earlier literature, shows many photographs of the more common ones, and apatite is identified for the first time. A paper by Gnevushev and Nikolaeva also in 1961 on Yakutia diamond inclusions, was only read in abstract as it is not held by English libraries, but this indicated that while such minerals as olivine, pyrope, magnetite, and graphite were found, brookite and anatase were inclusions although no identification procedures for these minerals are given in the abstract.
In 1961 Milledge using X-ray diffraction techniques found the mineral coesite in natural diamond, and Shah and Lang (1963) in studying inclusions in the 1\(\mu\) to 5\(\mu\) size range by X-ray topography, were able to show that they were precipitates formed after the stones had grown. However, the chemistry of the precipitates was not determined.

Sharp (1966) in studying batches of South African diamonds found as a common black inclusion pyrrhotite, with other intergrown phases as pentlandite and pyrite. Identifications were made by X-ray techniques. According to Sharp, these minerals resulted from exsolution of a former high-temperature phase included at the time of formation, but the pyrite was certainly not a syngenetic inclusion. In the same year, observations made on diamonds from the Kimberley area by Seal, revealed the presence of spherical inclusions of approximately 1-3\(\mu\) diameter, and microprobe analysis showed the elements of Al, Si, Fe, Ca, and Mg in these inclusions. The same author also showed by the use of gas chromatography and electron microprobe analysis that Si, K, Ca, nitrogen and oxygen were present in specimens of diamond "coat", (a green/grey/yellowish opaque layer present on many specimens, especially from the Congo (Polinard 1931)).

An infra-red spectra of a diamond coat from the Congo was completed by Chrenko et al in 1967, and they give evidence from which is concluded that the coat consists of calcium carbonate, water, and diamond which have grown syngenetically.
At the Diamond Conference (Cambridge 1967) Seal further discussed the minute enclosures in diamond and gave a microprobe analysis of an olivine inclusion, and the present author outlined some means by which epigenetic minerals in diamond could be recognised.

Finally, from 1957 onwards several papers dealing with inclusions in diamonds which are of interest to gemmologists have been published, and most of these are given in Bibliography No. 44 issued by the Industrial Diamond Bureau Ltd, London.

Apparatus

The identification of all the minerals found as inclusions was principally determined on an ordinary 3.00 cm radius Unicam X-ray camera using Cu K radiation. In some cases however, it was necessary to use the electron microprobe to give a unique identification of a specimen, either because the sample was too small to be identified by X-rays, or the specimen formed part of an isomorphous series. In such events, the Cameca low-angle take off electron microprobe was used, and in order to facilitate such investigations a piece of apparatus was designed which enabled qualitative analyses to be made while the unknown was attached to a diamond fragment.

The appliance shown in Fig. I(a), consisted of a small brass cylinder whose width and depth was governed by the Cameca holder into which it fitted, Fig. I(b). Within the cylinder were three adjustable screws over which lay compression springs, and these permitted a
copper circular disc to be adjusted so that the specimen was level before it was placed into the holder. Copper was chosen for the disc in view of its electrical and thermal properties.

In Fig. II is shown another piece of apparatus ("the squeezer") used in this study. This was designed to facilitate the release of the inclusions from the diamonds. The instrument comprised a short brass cylinder with recesses in each end in which observation windows were fitted. Sectionally east-west were located two adjustable screws to hold the specimen in position, but these were not found necessary. Pressure was applied across the specimen by means of one fixed plunger and one that was adjustable. The adjustable plunger of hardened steel, worked through a guide system in which a ball-bearing prevented the plunger from rotating when the screw was tightened.

The specimen is placed between the plungers and the observation windows fitted. When the diamond has broken, the pieces are retained in the cylinder between the observation windows and can be easily removed for further examination.

The Quantitative Analysis of Diamond Inclusions

The importance of quantitative studies particularly of the syngenetic inclusion in diamond was realised soon after the commencement of this study, and steps were taken to find a suitable analytical apparatus and to perfect a method of specimen preparation. A non-destructive quantitative analysis was desired to allow for the possibility
Figure I(a)

(x5)

Figure I(b)
Figure II

(x1.5)
of further studies being conducted on the inclusions, and because of this, three techniques of analysis were considered bearing in mind the minute size of the samples.

(a) Neutron Activation Analysis

Physical as opposed to chemical neutron activation analysis, is a non-destructive technique in which a standard and unknown sample are irradiated with neutrons and responses from the now radioactive elements are measured using a scintillation counter.

The use of the standard eliminates the necessity for corrections of the gamma emissions for the various elements.

However, the radioactive half-lives of several of the principal elements likely to be found in the silicates are short, (e.g. Al $t^{1/2} = 2.3$ mins., Mg $t^{1/2} = 9.5$ mins., Si $t^{1/2} = 2.6$ hrs. and Mn $t^{1/2} = 2.6$ hrs., Bowen and Gibbons (1963)), and thus this technique was not considered suitable in the present case.

(b) Ordered Site Occupation Analysis using X-rays

In some of the common isomorphous silicate systems the principal cations such as Mg, Fe, Ca, Si, and Al lie on special positions in the crystal lattice. Because of this condition some atoms contribute to certain X-ray intensities and not to others, and the intensity of these reflections will be in part a measure of the amounts of those atoms in the lattice. If enough of these reflections
are obtained, a chemical composition for the specimen can be determined. The systems of olivine and garnet are particularly favourable to this type of analysis, and the development of this technique for the garnet series is the subject of Chapter IV.

(c) **Electron Microprobe Analysis**

The instrument comprises an electron optic system which focuses a beam of electrons to a diameter of 0.1 to 3μ on a polished specimen. Where the electrons strike the specimen they generate characteristic X-ray spectra of the chemical elements contained in the area irradiated. An X-ray optic system analyses the emitted X-rays according to wavelength and intensity and the analysis is determined after correcting the intensities for absorption, fluorescence, and electron back-scatter.

Because of the nature of the beam and the smallness of the sample, this method of analysis was most useful for the present study, and various methods of sample preparation were investigated.

(i) **Sample Preparation for Microprobe Analysis**

The problem of sample preparation was approached in two ways. Firstly the possibility was considered of preparing the inclusions for microprobe analysis while still enclosed by the diamond. In Fig. III is shown the diamond surface produced after grinding on a diamond impregnated lap, but before polishing using diamond powders. It was found that during the polishing stage of the preparation, the
Figure III

(x50)
difference in relative hardness between the inclusion and the diamond resulted in the silicate specimen being plucked from the diamond, and so this approach was abandoned.

The second preparative technique however proved successful. The inclusion was separated from the diamond and then mounted in a standard microprobe holder using cold-mix araldite as a matrix. The polishing was effected on rouge paper.

While this technique did fulfil the requirements of the microprobe some disadvantages were noted.

(a) There was a tendency, in spite of a coating of graphite, for electron build-up and heating to occur in the araldite.

(b) It was virtually impossible to release the inclusion from the araldite once the examination had been completed.

(c) From the point of view of convenience, it was necessary to produce a technique of preparation in which several different samples could be examined in the same holder rather than just a single specimen.

Recently these disadvantages have been overcome by using a matrix of low-melting solder in a multiple brass holder. The inclusions are easily polished and readily released from the matrix once the analyses have been completed.
The preparation of samples for microprobe analysis is still in the development stage although raw data has been obtained from an olivine mounted in cold-mix araldite, and a garnet mounted in solder.

**Results**

The detailed study completed on fifteen diamonds containing inclusions is given in Appendix I, but a summary of these results is presented in Fig. IV.

This chart lists some of the characteristics of the diamond and gives information about the numbers of inclusions contained by each diamond specimen. The chart has also been designed so that future work can be added conveniently.

While the chart is essentially self-explanatory, three special points are worth making.

(i) There appears to be no systematic relationship between the morphology of the diamond and the type classification for these gems as octahedral, dodecahedral, broken, and flats are of Type I and Type II.

(ii) Syngenetic inclusions seem not to be dependent on the diamond type since olivines, and garnets occur in both groups.

(iii) There is ample evidence to show that the syngenetic minerals co-exist as inclusions in the same diamond. For instance, garnet, olivine and enstatite in D6;
### SUMMARY CHART OF WORK COMPLETED ON 15 DIAMONDS

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**Figure IV**

**Inclusion Details**

- **OG**: Stretched
- **CT**: Etched
- **SP**: Stepped
- **EP**: Edged
- **MN**: Mineral
- **AG**: Aggregate
- **NR**: Number

**Orientation**

- **GTR**: Graphite
- **GRN**: Garnet
- **GYR**: Garnet

**Refractive Index**

- **1.695-1.700 garnet**

**Cell Size**

- **11.52-11.534 garnet**

**Chemical Analysis**

- **Garnet**
- **Enstatite**
- **Diopside**

**Envelope**

- **Diopside**
- **Garnet**

**Garnet**

- **Diopside**
- **Garnet**

**Inclusion Details**

- **OG**: Stretched
- **CT**: Etched
- **SP**: Stepped
- **EP**: Edged
- **MN**: Mineral
- **AG**: Aggregate
- **NR**: Number
diopside and olivine in DI1; and garnet and enstatite in DI5.

(iv) Type II diamonds predominate, which is not the case for diamonds as a whole, especially large ones.

Detailed Discussion of the Results

Introduction

The minerals found as inclusions have been divided into syngenetic and epigenetic groups, the division being based on the following definitions.

For syngenetic minerals:

(i) The included mineral is a constituent of rocks considered to be associated with the initial environment of diamond formation; i.e. the olivines, garnets, enstatites, and diopsides of such rocks as garnet peridotites, pyroxenites, eclogites, and kimberlites.

(ii) The mineral is known to have a stable phase at pressures and temperatures envisaged for the formation of natural diamond.

(iii) The mineral forms discrete crystals within the diamond, and commonly the crystals are bounded by their own faces.

(iv) The minerals give single crystal photographs when X-rayed.

For epigenetic minerals:

(i) The included mineral is one which does not have a stable pressure/temperature field at the conditions envisaged for diamond synthesis (e.g. kaolinite).
(ii) Some of the minerals are associated with known secondary alteration processes in the kimberlite (e.g. calcite, haematite).

(iii) The minerals are observed to be distributed over diamond fractures, cleavage planes, or other discontinuities, which may or may not be connected with surface features of the diamond.

(iv) The minerals give unoriented powders when X-rayed.

These definitions cover most, but not all, of the possibilities, as observations of such rare occurrences as an olivine powder in a diamond (Gnowushev and Putergondler 1963) have not been incorporated into the division.

The syngenetic minerals are garnet, olivine, enstatite, diopside, spinel and rutile. Minerals considered to be epigenetic are calcite, haematite, kaolinite, xenotime, quartz, graphite, and pentlandite.

**Syngenic Mineral Inclusions**

**Introduction**

Beginning in the late 1950's detailed studies were conducted principally at the Carnegie Institute of Washington into synthetic and natural mineral systems known to exist in the region of the Earth's upper mantle. As most of these results are of considerable interest to the present study, they will be presented and briefly discussed,
for they indicate the pressure temperature range likely for the formation of natural diamond, and direct attention to the importance of quantitative chemical analysis of the diamond silicate inclusions.

In 1955 diamond was successfully synthesised by the General Electric Company, and details of the diamond graphite equilibrium curve were published by Bundy, Bovenkirk, et al in 1961. Boyd and England (1960) presented the phase boundaries for the SiO₂ system, and of particular interest is the quartz-coesite transition, as coesite has been noted as a diamond inclusion (Milledge 1961). The same authors in 1962 gave results for the stability field of pyrope, an important mineral satellite of diamond, in the range 15 to 50 kbars and temperatures up to about 1900°C, and this was followed by the stability curve for the reaction (enstatite + spinel) in equilibrium with (pyrope + forsterite) at elevated pressures and temperatures (Macgregor 1964).

In a series of papers Ringwood (1962a and b), and Clarke and Ringwood (1964) proposed temperature depth curves for the oceanic, orogenic, and PreCambrian Shield areas of the crust, based on the amount of heat likely to be produced from radioactive constituents in eclogite, the thermal conductivity of the rocks making up the outer part of the Earth, and the gravity flux of these rocks. As kimberlites are associated with PreCambrian Shield areas, the curve places a general restriction on the upper limit of melting beneath such areas.
Experimental evidence further suggests that use can be made of two solid solution series involving kimberlite minerals which vary continuously depending on the pressure and/or temperature.

Boyd and England (1964) showed that the Al$_2$O$_3$ content in enstatite co-existing with pyrope was sensitive to the pressure and the temperature; the Al$_2$O$_3$ content tending to increase with temperature at constant pressure, but decreasing with pressure at constant temperature. Thus it was possible to determine the approximate pressure and temperature of formation for an enstatite once the Al$_2$O$_3$ content was known. It would obviously be of interest to analyse enstatites found as diamond inclusions.

In the system diopside-enstatite Boyd and Scheirer (1964), and Davis and Boyd (1966) completed the diopside solvus in that system at 1 atmosphere and 30kbs respectively. The results showed that the two curves were very close, indicating that the equilibrium was relatively independent of temperature. Chemical analyses of diopsides from kimberlites given by Boyd (1967), lie very close to this diopside-enstatite join, so that an equilibrium temperature could be given to the analysed diopside.

The analyses so far completed are of diopside found in kimberlite, and it would be of considerable use to have similar analyses of the diopsides found as diamond inclusions.

In Fig. V is plotted all the results discussed above, except for
FIGURE V

(CARNEGIE YEAR BOOK 63)

wt % Al$_2$O$_3$ in En

En + Sp at Py + Fo

G = D

Qtz at Co

Co = COESITE
D = DIAMOND
En = ENSTATITE
Fo = FORSTERITE
G = GRAPHITE
Py = PYROPE
Qtz = QUARTZ
Sp = SPINEL
B = PRECAMBRIAN SHIELD GEOTHERM

DEPTH, KILOMETERS

PRESSURE, KILOBARS
the diopside-enstatite equilibrium. The various curves help to
give a clearer understanding of the conditions prevailing in the
Earth's upper mantle. For instance, (i) the maximum Al$_2$O$_3$ content
for a Kimberlite enstatite would be just over 2 per cent, and this
agrees well with present chemical analyses, and (ii) the data indicates
that the temperature range in which primary minerals form in Kimberlite
is 1000°-1300°C with a pressure of 45-55 kbars.

In the absence of chemical analyses of the syngenic inclusions
it has only been possible to compare the physical properties of the
diamond inclusions found in this study with other results from African
and Russian sources, and then to compare these properties with those
of the similar properties of the satellite minerals in Kimberlite.

**Garnet**

Garnet may be abundant or virtually absent in a Kimberlite pipe,
but this satellite mineral of diamond has received the most detailed
investigation. Most work has been confined to the determination of
some of the physical properties, particularly the refractive index,
specific gravity, and cell parameter, as the first two properties
could be determined in the field while the prospecting was in progress.
To assist in this work a compilation of the physical properties of
Kimberlite garnets was made by Campbell-Smith in 1957 for Consolidated African
Selection Trust Ltd, and this work was later added to by Granthem (1960).

The report indicated that the refractive index for Kimberlite
garnets varied from 1.725 to 1.780, although the majority lay between 1.74 and 1.76, and this was from determinations as far apart as Zarnitsa in Siberia (Bobrievich 1959; Zveder 1957), Mwadui in Tanganyika (Tremblay 1956), and Basutolend (Stockley 1947). Also the deeper coloured garnets tended to have the higher refractive indices due principally to increases in the \( \text{Cr}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \) content.

Cell parameter determinations up to that time however, were only completed on a few garnet specimens of Russian origin. These ranged from 11.519 to 11.544 Å for 8 specimens (Bobrievich 1959).

A three-fold division of kimberlite garnets, principally from South Africa, based on refractive indices and cell parameter, was suggested by Gratten-Bellew (1963). As can be seen from Fig. VI, the division of the garnets into the diamond-bearing and non-diamond bearing kimberlites is very subtle, and analyses by Smirnov (1959), Bobreivich (1959), and Nixon (1963), indicate that a two-fold division into eclogite and kimberlite garnets is more feasible. This is further borne out by the work on kimberlite garnets and garnet peridotites by O'Hara and Mercy (1963) and Okhapkin et al (1961) respectively.

With the new data the refractive index range slightly increased from 1.722 to 1.796 and the cell parameter from 11.479 to 11.641. Nevertheless, the bulk of the refractive indices lay between 1.74 and 1.76 and the cell parameter between 11.520 and 11.560 (Fig. VI).
Also in Fig. VI is plotted the data from garnets found as inclusions in diamond.

All the garnet inclusions fall into the eclogite rather than the kimberlite field. This is principally due to the higher refractive index of the garnet inclusions relative to their counterparts found in the kimberlite matrix. Sobolov (1949), showed that the refractive index of pyrope and almandine garnets increased with the \( \text{Cr}_2\text{O}_3 \) and \( \text{Fe}_2\text{O}_3 \) content, and more recently, Nixon (1963) has demonstrated that the refractive index of garnets from kimberlite increase with the \( \text{Cr}_2\text{O}_3 \) content. Thus the evidence suggests that the garnets found as inclusions in diamond are pyrope-almandine in type, and the one garnet inclusion qualitatively examined on the microprobe during the course of this work, gave strong responses for Cr and Fe.

Spectral analysis of Russian garnet inclusions by Orlov (1959) indicated the presence of Mg, Fe, Al, and Si, but no mention was made of the elements Cr, Ti and Mn, the principal trace elements found in free garnets by Bobrievich (1959) and Nixon (1963).

**Olivine**

The composition of the olivines found as inclusions was determined by measuring the cell parameters, using the data of Yoder and Sahama (1957).

Most investigators considering the free olivines in kimberlite
and its nodules (Bobrevich 1959, Nixon 1963, O'Hara and Mercy 1963), determined the composition by wet analyses and from a study of the optical properties of the mineral, in particular the variation of optic axial angle (2V), (cf Bowen and Schairer 1935). The chemical analyses indicate that impurities in the olivines of this environment rarely exceed 2 per cent. This suggests that the X-ray method used in this study, which is based on data for pure magnesium and iron olivines, should give reliable results with an estimated error of 1 per cent.

The four determinations made indicate a composition range between 91.0 and 92.8 molecular per cent of the forsterite and member. This compares favourably with Rovsha (1962) who quotes a composition varying between 86 and 100 molecular per cent forsterite for olivines included in Russian diamonds, from the work of Futergerdler (1958) and Orlov 1959).

The forsterite composition of the olivines found in garnet peridotites varies between 92 - 95 mol. per cent Fo. in South Africa, O'Hara and Mercy (1963); 89 - 92 mol. per cent Fo. in Basutoland, Nixon (1963); and 86 - 92 mol. per cent Fo. in Siberia, Bobrevich (1959). Also, Rovsha (1962) found a variation of 86 - 94 mol. per cent Fo. for olivines included in chrome spinal grains from Yakutia kimberlites.

A spectral analysis of a single olivine inclusion of Siberian
origin by Orlov (loc. cit.) showed the presence of Ni and Cr, and these two elements reach their greatest abundance as trace elements from free olivines in both Russian and African kimberlite (Bobrievich 1959, Nixon 1963).

**Orthopyroxenes**

Like the olivines, the orthopyroxenes of the garnet peridotites have a high magnesium content. Dawson (1962) gave 92 - 94 mol. per cent enstatite (En) and Nixon (1963) 89 - 92 mol. per cent En. from Basutoland material based on chemical analyses, and from refractive index measurements Bobrievich (1959) determined a composition of 89 - 90 mol. per cent En. for orthopyroxenes of Siberian origin.

In the present study, the enstatite was identified while partially enclosed by the diamond, but gave cell parameters very close to the enstatite end member of that series.

The writer has found records of thirteen chemical analyses of enstatite from kimberlite; 7 by O'Hara and Mercy 1963; 1 by Banno et al 1963; 4 by Nixon 1963; and 1 by Macgregor and Ringwood 1964. The maximum content of $\text{Al}_2\text{O}_3$ is 2.65 per cent (O'Hara and Mercy). However, no chemical analyses of enstatites as diamond inclusions are known, so comparisons at present are not possible.

**Clinopyroxenes**

Details of analyses of diopsides and chrome diopsides from kimberlites are given by Nixon (1963) and Boyd (1967), but no
comparative information is available from Russian sources, although diopside as an inclusion has been noted by Futergendler (1958).

The two diopsides found as inclusions in this study had cell parameters close to the diopside end of the diopside-hedenbergite series.

**Rutile**

Rutile has long been known in the kimberlite environment (Wagner 1914), though Williams (1932) mentioned that the dark-brown coloured mineral was not very common. Since then Bobrievich (1959), Okhapkin (1961) and Nixon (1963) have observed this mineral from their respective areas, and Bobrievich proposed rutile as an inclusion in diamond. This was confirmed by the work of Futergendler and Gnevushev (1963), and the three rutile crystals found in the course of this work exhibit similar cell parameters and colour to those found by Futergendler and Gnevushev.

**The Spinel Group**

According to Orlov (1959) chrome spinels are very common inclusions in Siberian diamonds. They are brown to cherry-brown in colour with a variable morphology and have an average cell edge of 8.287 Å. A spectral analysis indicated the elements Fe, Cr, Al, and they were identified as chrome picotite.

The same mineral was examined in detail by Rovsha (1962) in a
study of minerals associated with diamond, and both Wagner (1914) and Williams (1932) mention chromite in the Kimberlite. Dobrievich (1959) and Nixon (1963) identified chromian spinels consisting principally of the elements Cr and Fe, with Mg, Ti, and Al occurring as minor elements.

The eight inclusions that the writer found in a single diamond compare in shape and colour to those discussed by Ozlov, and from the cell parameter they could be chrome spinels. However, the specimens were too small for chemical analysis.

[Recently acquired specimens from Sierra Leone also appear to contain spinels as common inclusions, but these have not yet been studied in detail.]

Conclusions

The present evidence indicates that the varieties of syngenetic minerals occurring as inclusions in diamond and the minerals found in Kimberlite can be correlated, for similar assemblages have been found in both Russian and African diamonds and their respective Kimberlite pipes. There appears also to be a similarity between the chemical composition of the inclusions and similar minerals in the diamond matrix. The refractive indices and cell parameters of the garnets for instance, lie within the range found for garnets in Kimberlites, and the chemical composition of the olivines show a close correlation. Unfortunately, there is not at present sufficient
evidence to allow chemical comparison to be made for the other inclusions.

In order to examine more closely the apparent similarity in the mineralogy and chemistry of diamond inclusions and minerals found in the kimberlite matrix, it is of importance to know from which kimberlite pipe the diamond specimens originated.

Russian work by Orolva (1960) on diamond concentrates and inclusions from Siberia and the Urals, found that the chromium content was absent in the garnet inclusions from Ural stones, but was considerable in garnet inclusions found in Siberian diamonds. Also Ilupin (1963) noted characteristic mineral differences between kimberlites from various diamond provinces in Western Yakutia.

So far, no similar comparative studies have been completed from South African diamond regions largely because the mining operation merges the output from the pipes currently being mined. It has long been known (Sutton 1928), that there is a colour variation in the diamonds from near neighbour kimberlite pipes in South Africa, but how far this reflects a difference in mineralogy needs detailed investigation.

This type of study may also answer the question of when the diamonds formed. For instance, it would be of interest to see whether the inclusions found in diamonds are independent of kimberlite rock type, or if there is any variation in the diamond morphology in a
specific pipe. If this proved to be the case, it would indicate a
diamond origin in the Upper Mantle rather than the kimberlite pipe.

In a recent visit to Sierra Leone, samples of diamonds and
matrix rock from the same levels in two composite kimberlite pipes
were obtained in order to answer some of these questions.

Epigenetic Mineral Inclusions

Introduction

Included minerals which have formed subsequently to the diamond
occur in at least five different ways. The mode of occurrence of
these minerals in the diamond which has so far been found are:-

(A) As veneers on fracture or cleavage planes in diamond.
(B) As veneers on disc-shaped fractures around olivine crystals in
diamond.
(C) As aggregates within the diamond.
(D) As pseudomorphs after primary (?) minerals in diamond.
(E) As a precipitate on primary mineral inclusions in diamond.

Veneers on Fractures

Sutton (1921) noted that several diamonds were fractured while
still in the kimberlite pipe, and his observations show that stresses
can develop, possibly during the injection of the pipe, but more
probably just after, which cause the diamond to crack. The fractures
observed are not necessarily governed by diamond cleavage directions.
In the present work, specimens D5 and D8 for example, possessed cracks
containing epigenetic material which were not in any specific
diamond direction. In D7 however, a fracture was developed parallel
to a [110] diamond direction. Generally, the material found as
veneers existed in diamonds which were either considerably cracked or
showed fractures which clearly intersected the diamond surface (e.g.
diamond D7, and specimens D3, D5 and D8 respectively). The minerals
found in this form were calcite, haematite, kaolinite, and xenotime,
and they are considered to have diffused along the fracture planes
of the diamond subsequently to diamond formation.

On the other hand, the specimen of graphite in D14 was taken
from a cleavage surface which was entirely contained within the
diamond. Bowden and Tabor (1965) using room temperature
compressibilities and densities of graphite and diamond, concluded
that the pressure necessary for internal graphitisation of diamond
would be of the order of $10^5$ atm, and at this pressure, diamond would
be the thermodynamically stable form and thereby inhibit any incipient
graphitisation. The spontaneous reaction diamond to graphite is
exothermic, and therefore it is difficult to see why the process once
started would not consume the diamond. However if one supposes that
the diamond was internally fractured, graphitisation could then occur
in vacuo at about 1800°C (Lonsdale and Milledge 1965). Nevertheless,
a high pressure must be exerted on the interior of the diamond as
graphite has a density ranging from 2 - 2.3 which is some 63 per cent
less than that of diamond, and it is also of interest that the pressure
necessary to produce an area of approximately 0.71 sq mm of graphite containing at least two single graphite crystals, was accommodated in a diamond whose cross-sectional area parallel to the plane of graphitisation was only 5.30 sq mm and whose thickness was 1 mm.

One other possibility is that the graphite acted as a nucleus to the diamond, but the irregular nature of the zone of graphitisation and the two single crystals adjacent to veneers of powdered graphite suggest a development of an internal fracture followed by a process of graphitisation.

**Veneers on Disc-shaped Fractures**

Disc-shaped fractures were observed around olivine inclusions from several diamonds, e.g. D14 and D10, but only in one case was any mineral material observed in a fracture plane. Three olivines caused quite a large fracture to develop and pentlandite was found not only in the fracture plane, but also coating all visible facets of a small olivine inclusion.

In 1966 Sharp found pentlandite as an associate of pyrrhotite as an inclusion in diamonds, and considered it to be the probable exsolution from a former, unspecified high temperature phase, included at the time of formation. During the present study several diamonds have been observed in which black disc-shaped fractures exist deep within the diamond with no surface contact. If such fractures prove to contain pentlandite or pyrrhotite, it would be
difficult to explain such occurrences except by a process of exsolution such as proposed by Sharp.

However, in the present case, it is thought that the material penetrated along the fracture produced when a series of olivine inclusions expanded and caused a fracture to develop which intersected the diamond surface. The coating of the smallest olivine probably occurred as it lay in the centre of the principal disc-fracture zones of neighbouring olivines.

**Aggregates within Diamond**

It is more difficult to account for the examples of calcite and kaolinite which are found as anhedral aggregates within diamonds D3 and D7 respectively. In the case of diamond D7, this specimen was badly fractured, and there is a strong possibility that at the intersection of several of these cracks within the diamond, a situation existed which permitted a concentration of kaolinite to develop.

With the calcite however, there is much more uncertainty. There is relatively little fracturing in the specimen, and yet the calcite seems to have aggregated just beneath the diamond surface, and with access to the surface. Possibly, the calcite aggregated in some small cavity resulting from the imperfect growth of the diamond. A process involving the occlusion of calcite and then regrowth of the diamond is considered to be remote in view of the access that the calcite has to the surface.
Pseudomorphs

The specimen of quartz found as an inclusion lay close to the surface of an unfractured diamond. Since the quartz had a distinctly crystalline morphology, yet X-rays showed the specimen to be an unoriented powder, it is considered that the occurrence of quartz is pseudomorphic. The original mineral is not known, and the means by which replacement occurred in the absence of fractures can not easily be explained.

One method to account for such observations would be the removal or alteration of some primary mineral from the surface of a diamond to leave a cavity in which quartz precipitated and was then covered by a period of diamond regrowth.

It is thought unlikely that the quartz was once a higher temperature crystalline polymorph of SiO₂ as the presence of crystalline coesite found by Milledge (1961), suggests that once a mineral has been included it is frozen in that form, and protected from further change by the enclosing diamond.

Orlov (1959) in discussing the presence of serpentine pseudomorphing an olivine crystal from an African diamond, suggests that microcracks not normally seen under the microscope are responsible for the intrusion of the foreign material. The present specimen has been kept intact so that this possibility can be investigated.
Precipitates

The presence of kaolinite associated with the two diopside inclusions in diamond Dil poses some interesting questions. It is unlikely that diopside would normally decompose to form kaolinite as the small amount of aluminium in diopside would be insufficient to form a discrete mineral with a considerable amount of alumina such as kaolinite. Further, there is no evidence of any crystallographic association other than coincidence between the diopside and the kaolinite from the pole figures determined in Appendix I, and the general strain of the diopsides as shown by X-rays is probably the result of the highly fractured state of the host diamond. Kaolinite is a low temperature and pressure polymorph in the Kaolinite Group of minerals, and its association with diopside can perhaps be explained in one of two ways.

(i) The kaolinite was intruded along the numerous fractures in the diamond and finely precipitated on the diopsides
(ii) Acid and oxidising reagents used during the course of cleaning the diamond altered the surface of the diopsides.

The latter is suggested as a possibility in view of some recent observations made on surface material found on some Premier diamonds. The material had resisted acid treatment but consisted essentially of diopside which was coated with kaolinite.
Conclusions

In order to account for the epigenetic mineral specimens found in kimberlite, it will be of use to briefly consider processes of alteration which are known to exist in kimberlite pipes subsequent to their injection into the Earth's crust.

According to Williams (1932), one of the most notable features of the groundmass of kimberlite is the extent to which the olivines, and sometimes the enstatites and diopside, have been serpentinised. While the mechanism of this process is not fully understood, the concensus of opinion is that it probably involves the reagents of water and carbon dioxide in some form, which produces the mineral serpentine from the silicate as a breakdown product. Also often found interstitially or disseminated through the kimberlite matrix are several minerals including calcite, zeolites, and quartz, which are closely associated with the serpentine and are considered to be the result of highly mineralised solutions of magmatic origin percolating through the kimberlite. There is further Russian evidence (C.F. Davidson, private communication, 1966) that iron oxides as well as a selection of metallic sulphides such as pyrite, pyrrhotite, sphalerite, wurtzite, galena, and molybdenite occur in Yakutia diamond kimberlite.

Thus it seems likely that some of these minerals become included in diamond fractures and cracks during this stage of alteration in
the history of the kimberlite pipe, and it is suggested that the
minerals kaolinite and xenotime which do not appear to have been
noted in kimberlite pipes also formed as a result of these solutions.

The possible types of condition favourable to the formation
of graphite as an inclusion in diamond has been discussed above.
However, Orlov (1960) accounts for the presence of graphite inclusions
by suggesting that they occur as a result of internal stresses at
temperatures of 900° - 1000°C. While the kimberlite shows evidence
of shearing, the answer to this question must await further
experimental evidence.

The Morphology of the Inclusions

Detailed observations on included minerals in diamond were
undertaken (i) to see if a morphological pattern emerged in the same
way as was observed during the production of synthetic diamonds
(Bovenkirk et al 1959), (ii) to check on the possibility that the
inclusion had undergone a phase change after inclusion, and (iii) to
ascertain whether any additional information could be obtained about
the initial environment of the diamond.

Sufficient goniometric studies have not yet been completed on
each mineral type to permit conclusions to be drawn about distinct
morphological patterns. The type of morphology found may reflect
specific temperature and pressure ranges for their formation, but
unfortunately, very little other work concerning detailed morphological
studies on ultrabasic minerals has been completed, as there are few environments either natural or synthetic in which these minerals develop singly.

However, the euhedral morphologies of the olivines, garnets, and enstatites while quite complex with numerous small facets some of relatively high hkl values, belong nevertheless to their respective crystal systems and exhibit a habit consistent with that system. None show evidence of having undergone phase changes after inclusion. Further, the diopside has an unusual, but simpler crystal form, being comprised of pinacoid and (111) faces only, and a relatively simple morphology is also presented by the rutile crystal. The spinels on the other hand appear to be characterised by an absence of any crystal form.

Apart from unblemished crystal faces, several of the inclusions possessed distinct facets which were etched, striated, or stepped. The garnet crystal on diamond D1 exhibited three types of surface marking on adjacent faces, and individual faces of some of the olivines showed striations and stepped features. On the other hand, a garnet in D15 and an olivine in D12 showed very poor morphology, and recently from a Ghanaian diamond not yet studied in detail, it was established that an ellipsoidal inclusion was olivine.

The processes which produced the surface features observed are not well understood, but may be similar to those suggested in other
fields. For instance, Ueda (1961) grew germanium crystals with surface striations and suggested that they were the result of supercooling in the melt followed by an evolution of latent heat which produced a rapid growth thereby relieving the supercooling. Muller and Wilhelm (1964) studied striations on InSb crystals and drew the conclusion that these features were the result of temperature fluctuations due to convective instabilities in the melt. Verma (1953) p 163, considered that etch phenomena were a feature of dissolution in an undersaturated solution, and step features were essentially due to growth (p 10 - 14).

Thus surface blemishes may indicate that the initial environment of diamond formation was a changing one, and if the diamond at some stage partially covered the inclusion, this would result in only individual or groups of facets being subjected to change when conditions varied. The range of morphologies shown by some of the inclusions also further suggest a changing environment, although this may indicate a rapid diamond growth. For example, the diamond engulfed the inclusion before a morphology was developed, rather than the inclusion being in the process of dissolving when it was incorporated by the diamond. This process may be linked to some temperature instability in the initial environment.

It is well known that some diamonds grow intermittently (Frank and Lang 1965), and to note the relationship of inclusion to the
diamond growth patterns would be of considerable help in evaluating the earlier stages in the history of a diamond.
Chapter II

The relative crystallographic orientation
of inclusions to diamond

Introduction

As part of the work, the relative crystallographic orientation of the various types of inclusion and the host diamonds was studied using X-ray diffraction techniques. The diamonds considered were all of African origin, and this investigation enables a preliminary comparison to be made, with similar work completed in Russia on Siberian and Ural diamonds from 1956 - 64.

During an investigation of inclusions in diamond made by Mitchell and Giardini (1953) at least one of the olivine inclusions was preferentially oriented with respect to the diamond structure. More recently, Futergendler (1956), (1958); Futergendler and Frank-Kamenetsky (1961); and Frank-Kamenetsky (1964) have found that several minerals, olivine, garnet and chrome-spinel, show preferential orientations.

In the present work, the crystallographic relationship has been determined for thirteen olivines, two garnets, two enstatites, one diopside, and a graphite specimen in sixteen diamonds. A discussion of these results is presented and a preliminary comparison is made with similar Russian investigations.
**Experimental Procedure**

When two or more inclusions were observed in the same diamond, the relative orientations of these minerals were often best achieved by first breaking the diamond in order to separate the inclusions. This procedure not only reduces the possibility of misinterpreting complex Laue photographs, but also removes any difficulties which might arise due to centring the inclusion in the X-ray beam, for generally, some surface of the inclusion has become exposed.

The inclusion contained by the diamond, or diamond fragment, is oriented using Laue photographs so that one major crystallographic axis is parallel to the rotation axis of the X-ray camera, and a second axis lies at a known position relative to the X-ray beam. **Fig. 1** shows a Laue photograph of a diamond containing a garnet, with the four-fold axis of the garnet lying parallel to the X-ray beam, and mounted about a [110] garnet direction.

The relative orientation of the two minerals is determined by the method described in the International Tables for X-ray Crystallography, Vol. II, P 164-74, (1959). A $\theta - \phi$ chart (loc. cit. p 174) is used to obtain the co-ordinates of a major zone of the diamond, usually [110], which is then plotted on a stereographic net, and the principal axes of the diamond are determined.

To represent the obtained information in the clearest way, it is replotted giving the principal axes of the inclusion relative to
a "set" diamond. During this procedure care should be taken to ensure that right-handed sets of axes are used for both diamond and its inclusion.

Another method that was used to investigate possible crystallographic relationships between diamond and the inclusion, involved computing the information obtained from the stereogram. The computer programme related the orientation of the inclusion structure relative to the diamond structure in such a way that one could, by inspection, see if any poles of faces of either the diamond or the inclusion lay parallel to one another. The programme gave all possible poles for (hkl) planes where the maximum value of h, k or l was 3, but this maximum could be varied. The spacings of the planes were also recorded, and the computer programme was tested using a known orientation of an olivine inclusion in diamond.

However, whilst this technique does quickly present relative orientations, the format of the results is not very clear, and because of this, the stereographic procedure for presenting the results is adopted.

In view of the two graphical methods which are employed in order to obtain the required information, a maximum error of about 2° may result.

Finally, the use of accurate scale models of diamond and the minerals found as inclusions has proved to be of considerable value
in determining possible epitaxial relationships once the common zones have been found.

**Results**

The result of the relative orientations between the diamonds and the inclusions are presented as a series of stereograms. Except for the garnet orientations, only the principal directions of the inclusions relative to the diamonds are plotted on the stereograms. However, the coincidence of the 110 and 111 poles of the inclusions to the poles in the diamond was only found in the garnet cases. The olivine results have been divided so that on Fig. III are plotted orientations of multiple inclusions of olivine found in diamond (Nos. 1, 2, 3, 5, 6) and an olivine (No. 4), whose three principal pole directions are parallel to three poles in the diamond. Fig. IV shows the remaining seven orientations numbered 7 to 13. Of the thirteen olivines summarised in these results, nine were oriented by R. Henriques during the course of his study of olivine (Thesis in preparation), but interpretation of these results are the author's.

The orientations to the diamond of enstatite, diopside, and garnet are shown in Figs. VI, VII and VIII, whilst the result for graphite is to be found towards the end of the section.

**Discussion**

Before discussing the results, the principal factors which determine epitaxial growth of one mineral on another will briefly be
considered, as this has relevance to certain arguments which are to be proposed in evaluating the results obtained.

The first essential in oriented overgrowth is to have at least one plane in the overgrowth parallel to a plane of the substrate. Royer (1928); Bunn (1933); Neuhaus (1943); Hartman (1953) have all suggested as the result of experimental evidence, that the chance of epitaxy is then enhanced if there is a similarity in the dimensions between the planes that are parallel. A third factor is that a geometrical similarity on the two planes should exist, but it appears that the dimensional correspondence is often more important (Royer 1928). Coupled with the geometric factor is the charge distribution of the atoms in the two planes. Another factor suggested by Perroni and Cocchi (1958) is that the symmetry in the two planes is more important than dimensional similarity.

The olivine orientations will now be considered.

**Olivine Orientations**

If one considers in detail the relative orientation of the olivine whose principal directions parallel pole directions in the diamond (No. 4, Fig. III) then some interesting features emerge. In Table I is given the parallel zones for this mineral pair, and further information such as the interfacial angles between the zones.
### Table I

<table>
<thead>
<tr>
<th>PARALLEL ZONES</th>
<th>INTERFACIAL ANGLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>Diamond</td>
</tr>
<tr>
<td>[001]</td>
<td>[011]</td>
</tr>
<tr>
<td></td>
<td>[001] - [010] = 90°</td>
</tr>
<tr>
<td>[010]</td>
<td>[111]</td>
</tr>
<tr>
<td></td>
<td>[010] - [100] = 90°</td>
</tr>
<tr>
<td>[100]</td>
<td>[211]</td>
</tr>
<tr>
<td></td>
<td>[100] - [001] = 90°</td>
</tr>
</tbody>
</table>

The parallelism of the [010] and [111] poles of olivine and diamond respectively was first observed by Mitchell and Giardini (1953) and also by Putergendler and Kamenetsky (1961). The latter authors suggested that the similarity of the SiO₄ tetrahedra and carbon tetrahedra (CC₄) of these structures governed the oriented overgrowth between these two minerals.

In Fig. II are shown the relative projections for the parallel planes in the olivine and diamond. It can be seen that there is exact geometrical orientation between the SiO₄ tetrahedra and carbon tetrahedra on the planes [001] of olivine and [011] of diamond, when the other zones in the crystal are parallel. In order to assess the possibility of an interchange taking place between the SiO₄ and CC₄ units, these tetrahedra will be considered more closely.

The principal differences between the two units are as follows:
FIGURE 11

PROJECTIONS OF THE SILICA TETRAHEDRA OF OLIVINE ON THE PLANES 100, 001, And 010, AND THE CARBON TETRAHEDRA ON THE PLANES 211, 011, AND 111 OF DIAMOND.

OLIVINE
- Mg atoms
- Oxygen atoms
- Si atoms
- Si + O atoms
- O + O atoms

DIAMOND
- Carbon atoms
- C + C atoms

Scale $\frac{1''}{2} = 1$ Å
(i) The average length of an Si-O bond in the silicates for which a relative orientation has been determined is 1.62 Å. The C-C bond length for diamond is 1.54 Å.

(ii) The attraction of the cations in the silicate influences the SiO$_4$ tetrahedra in such a way as to cause distortion of this unit. The degree of distortion depends on the number of different cations in the silicate. No such distortion exists for the CC$_4$ unit.

(iii) The lower electronegativity of silica relative to oxygen causes the negative charge for the silica tetrahedra to concentrate more on the peripheral oxygens, but in the carbon tetrahedra, the negative charge is distributed more towards the central carbon atom in view of the uniform electronegativity of the molecule.

(iv) There is also a large difference between the covalent radii of these elements: Si = 1.17 Å, C = 0.77 Å, O = 0.66 Å (Pauling 1960).

These differences, which are quite considerable, are differences, however, which have been determined at room temperature and pressure, and not at those conditions at which natural diamond most probably formed. Experiments on silicates at elevated temperatures and pressures to examine changes which occur in the SiO$_4$ tetrahedra, have only involved the temperature parameter, but indicated, that the SiO$_4$ unit should be considered quite differently under such conditions.
In 1962 Glasser et al discussed the topotactic* reaction of several silicate compounds at temperatures between 500° - 600°C and drew some tentative generalisations from their work. They suggested that the size and electronegativity of the cation partly decide which ions migrate in the structure, and which do not during a reaction. With small cations such as Mg$^{2+}$, Al$^{3+}$, Fe$^{3+}$, Si$^{4+}$ the oxygen framework tends to stay relatively unchanged while cations migrate, although the oxygen packing may change. If large electronegative cations are involved (e.g. U$^{4+}$ or Pb$^{4+}$) these probably remained fixed while the oxygen atoms move. Thus they conclude, that SiO$_4$ rarely behave as units in high temperature reactions and point out that ".... the Si-O bonds are often less stable than the cation-oxygen bonds. The concept of the silicate anion as the most important element of structure is not a good starting point for an understanding of these reactions. The packing of the oxygen atoms, and of any large cation present, is more important than silicon".

Lacy (1965) also presents a similar result for the SiO$_4$ unit, and suggests that the Si-O bond is not a strong one at high temperatures.

Evidence for the behaviour of the CG$_4$ tetrahedra at elevated temperatures and pressure is again confined to experiments involving

* A reaction involving the conversion of a substance to a pseudomorph governed by some three dimensional correspondence between the structures of the product and the host.
only temperature. The thermal expansion measurements on diamond which reflects the expansion of the covalent C-C bond, by Thewlis and Davey (1956); Skinner (1956) and Wright (1966), all show that the expansion rate is very small. Also, attempts to dope diamonds with foreign atoms such as boron and aluminium, Wentorf and Bovenkirk (1962), only occurred just below the oxidation point of the mineral. These results suggest that the C-C bond is relatively stable at elevated temperatures, but migration of foreign ions through the structure can take place.

The extent to which pressure will influence these situations at high temperatures is unfortunately not known. However, if the oxygen positions in the silicate are still the important feature and form relatively stable platforms, then the silicon and carbon atoms can distribute themselves in the hollows of the charge distribution between the oxygens. The Si-O and C-O bond energies given by Pauling (1960) are similar; 88.2 Kcal/mole and 84.0 Kcal/mole respectively, suggesting that oxygen can change its allegiance from silica to carbon or vice versa.

In Table II is given the percentage misfits with respect to the olivine for the relevant repeat distances in, and perpendicular to the planes under discussion. The percentage misfits lie within the proposed limits of Royer (1928) at 15 per cent and Yanulow (1948) at 17 per cent.
### Table II

<table>
<thead>
<tr>
<th>PROJECTIONS</th>
<th>PARAMETERS</th>
<th>( \theta )</th>
<th>Percentage Misfit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olivine</td>
<td>Diamond</td>
<td>Olivine</td>
<td>Diamond</td>
</tr>
<tr>
<td>100</td>
<td>211</td>
<td>(i) 5.981</td>
<td>5.044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) 10.195</td>
<td>3.092x3</td>
</tr>
<tr>
<td>001</td>
<td>0( \overline{1} )</td>
<td>(i) 10.195</td>
<td>5.824x2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) 4.756</td>
<td>6.178</td>
</tr>
<tr>
<td>010</td>
<td>1( \overline{1} )</td>
<td>(i) 5.981</td>
<td>5.044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) 4.756</td>
<td>4.368</td>
</tr>
</tbody>
</table>

**Parallel Zones**

| [001] | [0\( \overline{1} \)] | 5.981 | 2.522x2 | 15.7 |
| [010] | [1\( \overline{1} \)]  | 10.195| 2.059x5 | -1.0 |
| [100] | [211]            | 4.756 | 1.456x3 | 8.2  |

Thus there is dimensional similarity between the olivine and the diamond, which would favour oriented overgrowth.

It seems therefore, that the relationship found between this olivine and the diamond could be epitaxial, involving an oxygen framework to which carbon can attach, or possibly a carbon framework to which oxygens can be secured.

The olivine orientation which has just been considered, was the only one of that silicate, whose principal poles paralleled poles in
the diamond. It can be seen from Figs. III and IV, that the poles for the a-axes of the remaining olivines are distributed in the vicinity of the [110] [211] and [111] poles of diamond. The b and c axes of the olivines on the other hand, give the appearance of being twisted about the a axis direction producing a much broader distribution for these poles across the remaining three quadrants of the stereogram.

To see if the distributions of the a axes of the olivine with respect to the [110] [211] and [111] poles of diamond was statistically significant, the angles between the two were determined.

In the cases of the [110] and [211] poles of diamond, the nearest pole to the olivine axis was chosen. Thirteen random poles were then plotted on a stereogram by normalising three random numbers to uniquely define one pole. Points falling outside the sphere were rejected in order to give a uniform spherical distribution. The angles from these poles to the nearest [110], [211] and [111] of the diamond was then determined, and experimental and random poles compared using the "Student's" t-test. The results indicated that for all three poles of diamond considered, the poles were randomly situated. The angles between the two sets of poles and other details are given in Table III. In Fig. V(a) are the a-axes of olivine and in Fig. V(b) are the thirteen random points.
STEREOGRAPHIC PLOT OF THE PRINCIPAL POLES OF OLIVINE RELATIVE TO THE DIAMOND
FIG. IV

STEREOGRAPHIC PLOT OF THE PRINCIPAL POLES OF
OLIVINE RELATIVE TO THE DIAMOND
Table III

Test of Significance Between a-axes of Olivine and Random Poles

**a-axes of olivine:**

<table>
<thead>
<tr>
<th>Olivines</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
<th>10</th>
<th>11</th>
<th>12</th>
<th>13</th>
</tr>
</thead>
</table>

Angular deviation

<table>
<thead>
<tr>
<th>from</th>
<th>(i) 110</th>
<th>20</th>
<th>26</th>
<th>6</th>
<th>19</th>
<th>3</th>
<th>24</th>
<th>30</th>
<th>17</th>
<th>25</th>
<th>20</th>
<th>18</th>
<th>7</th>
<th>18</th>
</tr>
</thead>
<tbody>
<tr>
<td>(ii) 211</td>
<td>10</td>
<td>12</td>
<td>24</td>
<td>11</td>
<td>29</td>
<td>7</td>
<td>nil</td>
<td>20</td>
<td>8</td>
<td>15</td>
<td>14</td>
<td>23</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>(iii) 111</td>
<td>22</td>
<td>11</td>
<td>29</td>
<td>22</td>
<td>36</td>
<td>16</td>
<td>19</td>
<td>34</td>
<td>15</td>
<td>15</td>
<td>18</td>
<td>29</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

Mean (\(\bar{x}\))

<table>
<thead>
<tr>
<th></th>
<th>17.923</th>
<th>14.385</th>
<th>21.846</th>
</tr>
</thead>
</table>

St. deviation (\(s\))

<table>
<thead>
<tr>
<th></th>
<th>8.127</th>
<th>6.825</th>
<th>7.822</th>
</tr>
</thead>
</table>

**Random poles:**

Angular deviation

<table>
<thead>
<tr>
<th>from</th>
<th>(i) 110</th>
<th>4</th>
<th>15</th>
<th>27</th>
<th>29</th>
<th>21</th>
<th>27</th>
<th>29</th>
<th>23</th>
<th>12</th>
<th>13</th>
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<th>38</th>
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<tbody>
<tr>
<td>(ii) 211</td>
<td>27</td>
<td>16</td>
<td>13</td>
<td>11</td>
<td>18</td>
<td>8</td>
<td>14</td>
<td>11</td>
<td>20</td>
<td>20</td>
<td>14</td>
<td>27</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>(iii) 111</td>
<td>31</td>
<td>26</td>
<td>32</td>
<td>9</td>
<td>15</td>
<td>14</td>
<td>6</td>
<td>14</td>
<td>24</td>
<td>23</td>
<td>16</td>
<td>46</td>
<td>29</td>
<td></td>
</tr>
</tbody>
</table>

Mean (\(\bar{x}\))

<table>
<thead>
<tr>
<th></th>
<th>21.615</th>
<th>16.154</th>
<th>21.923</th>
</tr>
</thead>
</table>

St. deviation (\(\sigma\))

|------------|--------|--------|--------|

"Student's" t-test defined by

\[
t = \frac{|\bar{x} - \bar{z}| \sqrt{n - 2}}{s}
\]

**Results:**

for [110] \(t = 1.019\); [211] \(t = 1.391\); [111] \(t = 0.281\)

For 12 degrees of freedom none are significant.
FIG. V

(a) OLIVINE POLES

- OLIVINE a axis
- TWO POLES
+ DIAMOND POLES

(b) RANDOM POLES

- RANDOM POLES
+ DIAMOND POLES

STEREOGRAPHIC COMPARISON BETWEEN 13 a-AXES OF OLIVINE
WITH 13 RANDOM POLES
Whilst it is appreciated that the population of points is not very large, it does suggest that the misalignments observed are probably just chance situations.

The question then arose as to whether or not the first olivine was only fortuitously related to the diamond. From the evidence, a case for an epitaxial relationship between this inclusion and its host can be argued, and a similar orientation has been found by Mitchell and Giardini, and Futergendler (loc. cit.). A final conclusion on this matter, however, must await the determination of many more olivine orientations.

**Orientations of Multiple Olivine Inclusions**

In one diamond it was possible to determine the orientation of three out of the four olivine inclusions relative to the diamond (D 10, Appendix I), and in another diamond, a pair of olivine inclusions were oriented. These were shown in Fig. III and numbered 1, 2, 3, 5, 6.

The distribution of the principal axes for the olivines relative to the diamond, indicate that no specific orientation exists either between the two diamond specimens, or between the individual inclusions in each diamond. In the case of diamond D 10 (Nos. 1, 2, 3 above) two of the olivines [110] directions lay close to [111] directions in the diamond.
Enstatite, Diopside and Garnet Inclusions

The factors mentioned during the discussion of the olivine results can now be applied to some extent in a consideration of the enstatite, diopside and garnet orientations relative to the diamond.

**Enstatite:** In Fig. VI are shown the two enstatite orientations. Although the poles of the principal directions of the enstatites lie close to diamond poles, there is no specific reason to suppose that the relationship is anything but random.

**Diopside:** The single diopside orientation given in Fig. VII (D 11, Appendix I) also shows no common pole direction with the diamond, but the a-axis of the diopside lies close to a [111] direction in the diamond.

**Garnet:** As can be seen from Fig. VIII, the garnet from D 1 possesses common zone axes with the host diamond. In Table IV are given the dimensional correspondence in, and perpendicular to the parallel planes with respect to the garnet. Apart from the poor dimensional relationship between the projections [111] and [110] of garnet and diamond respectively, other values fall within the proposed limits. Similarly Fig. IX and Table V illustrate the equivalent data for the garnet from diamond D 2.

It is interesting that the garnet orientations do not involve principal directions in the garnet, and one reason for this may be the position of the oxygen atoms in the garnet structure. Oxygen is
STEREOREOGRAPHIC PLOT OF THE PRINCIPAL POLES OF
ENSTATITE RELATIVE TO THE DIAMOND

FIG. VI

DIAMOND POLES

a axis enstatite
b
x
FIG. VII

STEREOGRAHIC PLOT OF THE PRINCIPAL POLES OF A DIOPSIDE RELATIVE TO THE DIAMOND
FIG. VIII

STEREOGRAPHIC PLOT OF THE PRINCIPAL, 111, 110 AND 211 POLES RELATIVE TO THE DIAMOND FOR GARNET (D1)
### Table IV

**Dimensional Correspondence for Garnet (D1) and Diamond**

<table>
<thead>
<tr>
<th>Projections</th>
<th>Parameters ( \theta )</th>
<th>Percentage Misfit</th>
</tr>
</thead>
<tbody>
<tr>
<td>garnet</td>
<td>diamond</td>
<td>garnet</td>
</tr>
<tr>
<td>110</td>
<td>11(^\text{I})</td>
<td>116.88</td>
</tr>
<tr>
<td></td>
<td>(i)</td>
<td>17.35</td>
</tr>
<tr>
<td>111</td>
<td>11(\text{I})</td>
<td>16.31</td>
</tr>
<tr>
<td></td>
<td>(i)</td>
<td>14.12</td>
</tr>
<tr>
<td>211</td>
<td>112</td>
<td>10.09</td>
</tr>
<tr>
<td></td>
<td>(i)</td>
<td>16.31</td>
</tr>
</tbody>
</table>

**Parallel Zones**

| [110]       | [11\(\text{I}\)]         | 6.650             | 2.059 x 3        | 7.1              |
| [111]       | [11\(\text{I}\)0]         | 8.147             | 2.522 x 3        | 7.1              |
| 211         | [112]                     | 4.702             | 1.456 x 3        | 7.1              |
FIG. IX

DIAMOND POLES
• Diamond poles

COINCIDENT POLES
• a axis garnet
+ b " "
× c " "
□ 110 poles of garnet
Δ 111 " "
□ 211 " "

STEREOGRAPHIC PLOT OF THE 100, 111, 110, AND 211 POLES OF GARNET (D2) RELATIVE TO THE DIAMOND
Table V

**Dimensional Correspondence for Garnet (D2) and Diamond**

<table>
<thead>
<tr>
<th>Projections</th>
<th>Parameters 0</th>
<th>Percentage Misfit</th>
</tr>
</thead>
<tbody>
<tr>
<td>garnet</td>
<td>diamond</td>
<td>garnet</td>
</tr>
<tr>
<td>111</td>
<td>211</td>
<td>(i) 16.31</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) 14.12</td>
</tr>
<tr>
<td>211</td>
<td>011</td>
<td>(i) 10.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) 16.31</td>
</tr>
<tr>
<td>011</td>
<td>111</td>
<td>(i) 21.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(ii) 17.35</td>
</tr>
</tbody>
</table>

**Parallel Zones**

<table>
<thead>
<tr>
<th>Parallel Zones</th>
<th>011</th>
<th>111</th>
<th>8.147</th>
<th>1.456 x 6</th>
<th>- 10.7</th>
</tr>
</thead>
<tbody>
<tr>
<td>[111]</td>
<td>[211]</td>
<td></td>
<td>4.702</td>
<td>2.522 x 2</td>
<td>10.7</td>
</tr>
<tr>
<td>[211]</td>
<td>[011]</td>
<td></td>
<td>6.650</td>
<td>2.059 x 3</td>
<td>7.1</td>
</tr>
<tr>
<td>[011]</td>
<td>[111]</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
the only atom which does not lie on a special position, and with the high symmetry of the mineral, space group $Ia\overline{3}d$, the result is an absence at right angles to the principal directions of planes in which oxygens predominate. If the oxygens are the important atoms in a possible epitaxy with diamond, then the planes [110], [111] and [211] of the garnet may be more favourable. However, this point has yet to be determined by plotting the necessary projections of the garnet.

Graphite Inclusion

An optical study of diamond D 14 revealed that the flakes of graphite contained in the diamond, lay parallel to a [111] plane of the diamond (Appendix I). Whilst it was not possible to determine the orientation of the graphite in the plane [111] of diamond, the orientation most probably corresponds to the situation proposed by Mosh (1935) and demonstrated by Grenville-Wells (1952) for oriented overgrowth involving these two minerals. The energy necessary for the transformation at $25^\circ C$ of graphite to diamond is $453 \text{ cal} \text{s mole}^{-1}$ (Frosen et al 1944). This energy is necessary because a trigonal tetrahedral distribution of carbon is forced to a hexagonal planar distribution, or vice versa. In Fig. X is shown the dimensional and geometric similarity of the two planes involved.
FIG. X

DIAMOND (111)

GRAPHITE (0001)

--- normal bonds
--- foreshortened bonds

○ carbon atoms
○ C + C atoms

Scale in Å
% Misfit = 2.5%
A Comparison with Similar Russian Investigations

In 1961 and 1964 Putergendlor and Frank-Kamenetsky and Frank-Kamenetsky (loc. cit.) suggested that an epitaxial relationship existed between some of the olivines, garnets, and chrome spinels that they found as inclusions in diamonds from the Urals and Siberia. In Table VI is given the relative crystallographic orientations of their olivines and garnets. No results were given for the other silicates although Putergendlor (loc. cit.) noted diopside as an inclusion in diamond, and since it was not possible in view of the numbers to orient the spinels found as inclusions in an African diamond, this too can not be compared.

As can be seen from Table VI one orientation for olivine and three for garnet were found and in all, twelve diamonds were studied. The olivine orientation is the same as that found in the present work, but the garnet orientations are different. The curious feature about the garnet orientation is that a principal direction of the garnet is parallel to three different diamond poles, and yet, there appears to be no coincidence of other zone directions in the planes that are parallel (see Table VI). In the two instances of oriented garnets described in this work, three sets of planes are coincident (see Tables III and V).

The Russian authors suggest that epitaxy in the case of garnet takes place in the directions [110] of diamond and [001] of garnet and involves the edges of the two tetrahedral units of SiO$_4$ and C$_4$.
Table VI

Specific Orientations of Inclusions in Russian Diamonds

Garnet

(i) [001] garnet parallels the [111] diamond. In the planes the 100 direction of garnet is 5° from the 110 direction of diamond.

(ii) [001] garnet parallels the [211] diamond. In the planes the 100 direction of garnet is 10° from the 011 direction of diamond.

(iii) [001] garnet parallels the [311] diamond. In the planes, the 100 direction of garnet is 8° from the 011 direction of diamond.

Clivine

(i) [010] olivine parallels the [111] diamond. In the planes, the [101] zone axis of olivine is parallel to the [101] zone axis of diamond.
This proposal seems to be incorrect as these directions in the two crystals are not parallel (see above) and hence the edges of the tetrahedra will not be parallel. However, no firm conclusion can be made as to the validity of this suggestion at present.

Since the publication of these papers Putergendler and Frank-Kamenetsky (private communication 1965) have found two further specific orientations for olivine in diamond, and the common planes involved are given below:

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Olivine</th>
</tr>
</thead>
<tbody>
<tr>
<td>[001]</td>
<td>parallel to [001]</td>
</tr>
<tr>
<td>[001]</td>
<td>parallel to [100]</td>
</tr>
</tbody>
</table>

It is interesting that a similar orientation of an inclusion has been found in an African and Russian diamond. However, at this stage it would be premature to suggest that this implied a similarity in the conditions of formation of the diamonds in these two regions. A conclusion such as this can only be assessed after several more orientations have been compared.

**Conclusion**

The orientation studies particularly of olivine, suggest that generally the inclusion is occluded by the growth of the diamond, rather than their existing an epitaxial or topotaxial relationship between the two minerals. In the case of different minerals co-existing in the same diamond, as for example the olivine and enstatite
(D6, Appendix I), no specific orientation was found, and this also seems to apply to the multiple inclusions of olivine found in diamond D10. However, if epitaxy does occur between the inclusions and the diamond, it appears to be governed by the similarity between the geometric and dimensional parameters in the two planes that are parallel, which in turn will produce only small differences in the surface energy of the two planes. The continued orientation of the silicates found as inclusions will enable more definite conclusions to be presented in the future.

It is also hoped to consider the proportion of inclusions which act as nuclei to the diamond. This can be achieved by determining the diamond growth fronts in the surface regions of the inclusion by using X-ray topography. This work might also reveal that a greater percentage of specifically oriented inclusions act as nuclei to diamond growth.
CHAPTER XIII

THE THERMAL EXPANSION OF GARNET INCLUSIONS

Introduction

It is of considerable petrological and geophysical interest to try and determine the pressure and temperature of formation of natural diamond, as its presence at surface levels in the earth's crust appear to be far removed from those of its initial environment. One approach to determine these conditions exactly has been that of the experimental petrologist, who has in recent years completed work on the phase diagrams of simplified multiple silicate mineral systems known to be associated with diamond; this has lead to a narrowing of the possible temperature and pressure ranges for natural diamond formation (Chapter I). Another approach, which is more theoretical, has involved the determination of certain physical parameters of the individual minerals associated with diamond, in an attempt to fit these determined properties into some thermodynamic equations in order to obtain the pressure-temperature ranges. In the following work the latter line of approach has been pursued.

In the course of discussion, it became clear that no simple theory would suffice for the many factors involved in a study of this sort. However, it was considered that a knowledge of the difference between the thermal expansion rates of inclusions, whilst still
enclosed by the diamond, and when free from it, would provide a basis from which a theory could be developed by adapting already known thermodynamic equations. Thus the present study involves the experimental determination of these required parameters for the mineral garnet, and estimates the degree to which the values obtained are in error at particular temperatures. The two garnet specimens give widely differing results, those for the Type II diamond appearing anomalous, but the result for the Type I diamond has been used by Dr. T. H. K. Barron and Mr. R. W. Munn of Bristol University to estimate the temperature and pressure of formation of this diamond. (R. W. Munn: Thesis in preparation).

**Previous Work**

The diamond in Fig. I shows a strain birefringence effect, under crossed polarisers, in the region directly adjacent to an olivine inclusion, and Fig. II shows a diamond which has fractured around an olivine inclusion. These types of phenomena were first interpreted by Brewster (1835) and later by Sorby and Butler (1869) who both suggested that this represented the result of pressure exerted by the inclusion on its host. Since then, several workers have observed and described similar occurrences in diamond-bearing rocks of South Africa and Russia (Sutton 1918, 1921, 1928; Williams 1932; Orlov 1960).

Now (a) if these strain effects can be considered as elastic over geological time, then they represent stored information about the pressure and temperature of origin of the minerals and (b), if at the
point of deposition an equilibrium into a thermodynamic equilibrium existed between the solidus and its liquid. Therefore, that the metastable state of the transition occurred in the transition from the gas to the solid state.

In this laboratory, it is observed that the absorption of the dry ice is increased at the rate of two to three liters per hour. As this process continues, the color of the liquid changes from deep blue to light green, and the temperature of the liquid drops sharply. In addition, the expansion of the observed liquid is not corrected and a phase of deposition is observed in the liquid.
point of formation an approximation to a thermodynamic equilibrium existed between the inclusion and its host, then the anisotropic strain effects observed around inclusions resulted from the differences in the coefficients of expansion ($\alpha$) and compressibility ($\beta$) between the two minerals.

In 1961 Rosenfeld and Chase considered this situation and found it possible to determine a thermodynamic equation which represented the absence of anisotropic strain around an inclusion. The equation involved the expansion and compressibility coefficients, and related these to temperature and pressure, but was designed specifically for two isotropic minerals, one lying inside the other. The proposed parameters for measurement were a series of pressures and temperatures at which no piezobirefringence was observed between the host and its inclusion, and a piece of apparatus was described and designed to do this. Once these parameters had been determined, it would then be possible to construct graphs of pressure-temperature equilibrium for a mineral pair, and completed for several different but associated mineral pairs, should result in a zone where all the minerals were in P.T equilibrium, representing, most probably, the region of formation.

However, no experimental results were offered using this apparatus, and none have appeared subsequently in the literature, (J. L. Rosenfield private communication 1967) which suggests that perhaps some experimental factor was found which prevented, or limited, the application of this technique.
Another approach, on similar but more mathematical lines, to the physical relationships between an inclusion of one material in a different matrix, has been given by Eshelby in a series of papers 1957 - 1962. The author discusses the general conditions when a region, or an inclusion, within an isotropic elastic solid undergoes a spontaneous change of form, and equations are presented from which one can determine the amount of stress in the inclusion, or the matrix, if the elastic constants of the materials are known. At present the application of the equations to the present study is under discussion.

In 1965, Henriques reported some preliminary results for the thermal expansion of an olivine crystal whilst still constrained by its diamond host, and further work of this type is in progress. (Henriques, to be published.)

**Apparatus and Experimental**

The thermal expansion measurements were made on thermocouples fitted on to a standard goniometer head in a 3.00 cm radius Unicam X-ray camera. A simple attachment, coupled to a hot-stage microscope with a reference junction at 20°C, was adapted from apparatus developed by Welch (1954) and the prototype has been described by Meyer (1965). A photograph of the apparatus is shown in Fig. III.

A Pt/Pt + 10% Rh thermocouple, 0.2 mms in diameter, is attached to the goniometer by replacing the normal specimen dovetail with an enlarged dovetail, holding the thermocouple and connecting wires. It was found that the cell parameters of the garnets could be obtained
from oscillation photographs, so the basal part of the apparatus (required for complete rotations) described by Meyer was not used. The connecting wires passed through the base of the camera to the heating equipment. The temperature of the thermocouple was measured as an E.M.F. on either a normal potentiometer or an automatic digital voltmeter.

An adhesive was employed to unite either the diamond or the garnet to the thermocouple, and in the experiments a dental cement called Kalsogen P 705 was used as it was found that this had adhesive properties up to about 500°C and could easily be dissolved by concentrated acid from the specimen and the thermocouple after an expansion experiment.

It was also found worthwhile, particularly for runs involving the diamond, to shape the bulb at the thermocouple junction point, usually about 0.75 mm in diameter, as this allowed the diamond to be held more firmly by the cement.

Finally, the Straumanis method of loading film into X-ray cameras as described by Henry et al., (1961), page 170, was followed in all the investigations and the films were measured on a travelling microscope with a screw of accuracy 0.001 cm.

For the constrained expansions the diamond containing the garnet was mounted on the thermocouple with adhesive and the garnet oriented about some crystallographic axis, usually [100] or [110].
For the free expansions, the garnets were broken out of the diamond using the "Squeezer" apparatus (Chapter I), and were then mounted about some crystallographic axis on the thermocouple. Using Cu K radiation, oscillation ranges were then selected to record the high-angle reflections (12,66) and/or (10,10A) \((0 = 80^\circ)\) which were used in the determinations of the cell constants at the various temperatures. At five minute intervals the thermocouple voltage was recorded to check the constancy of the temperature, and generally, the value was uniform to within \(\pm 1^\circ\)C.

This experimental procedure did not vary except that in the expansion of the garnets inside the diamond, two additional problems arose.

Ordinarily, no special technique would be needed to centre a garnet on the rotation axis of the camera, even if on a thermocouple, whilst still maintaining the crystal in the centre of the X-ray beam. Also, the expansion of the whole of the thermocouple with increase in temperature would not usually alter this orientation of the small garnet freed from the diamond. However, in expansions involving the garnet in the diamond, these two factors become important and had to be considered.

The large refractive index of the diamond has the effect of giving only the apparent position of an inclusion, rather than the true position, unless viewed at right angles to a diamond facet. Thus,
The inclusion has to be made coincident with the rotation axis of the camera, by X-ray methods for accurate cell parameters to be determined. This alignment is achieved with X-rays by taking Laue photographs 180° apart. If a duplicated set of reflections for the inclusion is observed (see Fig. IV), then the crystal is not properly centred, and after making slight adjustments to the sliders of the arcs, the experiment is repeated until no duplication of reflections is observed; (Davis 1967).

The heating of a thermocouple carrying a relatively large diamond can soon cause the crystal to mis-set and this then necessitates re-centring the crystal at any given temperature before carrying on with the expansion experiment. In these experiments it was only occasionally necessary to re-centre the crystal during an expansion test.

The two diamonds and the garnets they contained used in the thermal expansion investigation have been described in Chapter I (diamonds D1 and D2; garnets D1 and D2). In Table I are the temperatures to which each specimen was taken.

<table>
<thead>
<tr>
<th>Table I</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) D1</td>
</tr>
<tr>
<td>(b) D1</td>
</tr>
<tr>
<td>(c) D2</td>
</tr>
<tr>
<td>(d) D2</td>
</tr>
</tbody>
</table>
In the case of (a) the diamond split when attempting to obtain results for 800°C, a point which will be discussed later, and with (c) the thermocouple was not able to support the diamond at a temperature above 700°C. For the runs (b) and (d) the upper temperature limit of 1000°C was chosen so as not to strain the thermocouple (M.P. 1760°C).

No attempt was made to obtain a second set of results for (c) because of the possibility that the first expansion developed fractures in the diamond around the inclusion which would cause a freer expansion of the garnet if reheated a second time.

In Tables II, III, IV and V are shown the cell parameters of the garnets measured at specific temperatures, for the four expansion experiments. (An error correction has been applied to the values of the cell parameters, which is discussed in detail in the next section, and a reference junction correction has been made for the abscissa.) Figure V graphically represents these details.

Estimation of Errors

The probable errors of the cell parameter and temperature were determined for all the expansion experiments. However, in the case of the expansion runs completed for the garnets before removal from the diamond, tests showed that further temperature errors existed, and these were then estimated. It will be convenient to discuss first the expected errors, before considering those which were found subsequently to the work.
### Table II

Garnet Dl Expansions

**Expansion Inside the Diamond**

<table>
<thead>
<tr>
<th>Temperature (°C)*</th>
<th>Cell Parameter (Å)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td></td>
<td>(K_{\alpha 1})</td>
<td>(K_{\alpha 1})</td>
</tr>
<tr>
<td>24</td>
<td>11.515</td>
<td>11.515</td>
</tr>
<tr>
<td>110</td>
<td>11.518</td>
<td>11.519</td>
</tr>
<tr>
<td>220</td>
<td>11.524</td>
<td>11.526</td>
</tr>
<tr>
<td>356</td>
<td>11.530</td>
<td>11.531</td>
</tr>
<tr>
<td>620</td>
<td>11.542</td>
<td>11.540</td>
</tr>
</tbody>
</table>

Cell parameter error = \(\pm 0.0015\) Å.

*Corrected for reference junction.

### Table III

Garnet Dl Expansions

**Free Expansion of Garnet**

<table>
<thead>
<tr>
<th>Temp (°C)*</th>
<th>Cell Parameter (Å)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a)</td>
<td>(b)</td>
</tr>
<tr>
<td></td>
<td>(K_{\alpha 1})</td>
<td>(K_{\alpha 2})</td>
</tr>
<tr>
<td>126</td>
<td>11.533</td>
<td>11.531</td>
</tr>
<tr>
<td>318</td>
<td>11.553</td>
<td>11.555</td>
</tr>
<tr>
<td>532</td>
<td>11.576</td>
<td>11.576</td>
</tr>
<tr>
<td>818</td>
<td>11.608</td>
<td>11.610</td>
</tr>
<tr>
<td>1012</td>
<td>11.630</td>
<td>11.630</td>
</tr>
</tbody>
</table>

Cell parameter error = \(\pm 0.0015\) Å.

*Corrected for reference junction.
### Table IV

**Garnet D2 Expansions**

**Expansion Inside the Diamond**

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)*</th>
<th>Cell Parameter ($A^\circ$)</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a) $K_{\alpha 1}$</td>
<td>(b) $K_{\alpha 1}$</td>
</tr>
<tr>
<td>24</td>
<td>11.531</td>
<td>11.530</td>
</tr>
<tr>
<td>128</td>
<td>11.539</td>
<td>11.541</td>
</tr>
<tr>
<td>356</td>
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<td>11.555</td>
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<tr>
<td>539</td>
<td>11.571</td>
<td>11.570</td>
</tr>
<tr>
<td>710</td>
<td>11.577</td>
<td>11.579</td>
</tr>
</tbody>
</table>

Cell Parameter error = ±0.0015 $A$.

*Corrected for reference junction.

---

### Table V

**Garnet D2 Expansions**

**Free Expansions of Garnet**

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)*</th>
<th>Cell Parameter</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(a) $K_{\alpha 1}$</td>
<td>(b) $K_{\alpha 1}$</td>
</tr>
<tr>
<td>24</td>
<td>11.535</td>
<td>11.535</td>
</tr>
<tr>
<td>126</td>
<td>11.544</td>
<td>11.546</td>
</tr>
<tr>
<td>218</td>
<td>11.555</td>
<td>11.553</td>
</tr>
<tr>
<td>324</td>
<td>11.566</td>
<td>11.566</td>
</tr>
<tr>
<td>422</td>
<td>11.576</td>
<td>11.577</td>
</tr>
<tr>
<td>520</td>
<td>11.586</td>
<td>11.587</td>
</tr>
<tr>
<td>620</td>
<td>11.597</td>
<td>11.598</td>
</tr>
<tr>
<td>718</td>
<td>11.609</td>
<td>11.610</td>
</tr>
<tr>
<td>817</td>
<td>11.620</td>
<td>11.619</td>
</tr>
<tr>
<td>920</td>
<td>11.633</td>
<td>11.632</td>
</tr>
<tr>
<td>1028</td>
<td>11.646</td>
<td>11.644</td>
</tr>
</tbody>
</table>

Cell Parameter error = ±0.0015 $A$.

*Corrected for reference junction.*
Cell Parameter Errors

The principal factors that give rise to systematic errors in the values of cell parameters are (i) miscentring of the specimen on the rotation axis of the camera, and (ii) the measurement of the X-ray film. The experimental procedure took account of, and corrected for the first of these two causes, and thus the actual measurement of the film was left as the main source of error. In this respect, the Straumanis film loading technique minimises this error, as it allows high-angle reflections to be measured accurately. Nevertheless, the actual film measurement has a reproducibility error, and to estimate this value, some films were measured several times. This resulted in an error of $\pm 0.0015 \, \text{Å}$ being placed on all the measurements for the cell parameter, and as the variation of points when plotted (see Fig. V) fell within this error range, no point distribution error was added to the initial value.

Temperature Errors

To determine the temperature for any one of the experiments, the EMF from the thermocouple was converted into a temperature by considering the calibration curve for the thermocouple. To check the accuracy of this curve, one of the batch of thermocouples employed in this work (two only were used) was chosen to test the calibration curve, first published for a Pt/Pt + 10%Rh thermocouple by Shenker et al (1955). This experiment, involving temperatures up to 900°C and using pure chemicals of known melting-points as temperature
indicators, also provided useful information about the steadiness of the hot-stage microscope and recording apparatus. Table VI shows the results obtained in this experiment using a normal potentiometer and a digital voltmeter. From this data, it can be seen, that there is almost exact agreement between the measured temperature values and those of the known chemicals, indicating that the EMF from the thermocouple junction was reliable. Probably, the thermocouple was accurate to ±1° to 2°C for the whole range considered. The calibration curve with reference junction at 20°C is plotted as part of Fig. VI (page 108). These results also suggest that both the hot-stage microscope and the potentiometer were dependable instruments.

It seemed therefore, that the temperature of the thermocouple junction could be recorded and determined very exactly, and a maximum error was placed at ±2°C for any temperature.

Further Temperature Errors

The further temperature errors which were found involved the experiments determining the constrained expansions of the two garnets. Tests showed that when the diamond was heated on the thermocouple, the temperature reading at the uppermost point of the diamond was not that recorded by the thermocouple. It was obviously important to try and determine these variations, for they would result in changes being made to the expansion curves of the garnets inside the diamonds. Thus, an attempt was made to determine the temperature gradient across a diamond specimen, under the present experimental conditions, and to
### Table VI

**Pt/Pt + 10% Rh Thermocouple Calibration Data**

**Comparative Temperature Details**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide .......</td>
<td>115°C</td>
<td>0.61</td>
<td>115</td>
<td>0.64</td>
<td>117°C</td>
</tr>
<tr>
<td>Benzanilide .......</td>
<td>163°C</td>
<td>1.005</td>
<td>164</td>
<td>1.004</td>
<td>165°C</td>
</tr>
<tr>
<td>Saccharin .........</td>
<td>228°C</td>
<td>1.485</td>
<td>227</td>
<td>1.53</td>
<td>230°C</td>
</tr>
<tr>
<td>Sod. Nitrate .......</td>
<td>307°C</td>
<td>2.212</td>
<td>306</td>
<td>2.24</td>
<td>307°C</td>
</tr>
<tr>
<td>Lithium Hydroxide</td>
<td>450°C</td>
<td>3.540</td>
<td>449</td>
<td>3.56</td>
<td>450°C</td>
</tr>
<tr>
<td>Sod. Iodide .......</td>
<td>651°C</td>
<td>5.526</td>
<td>650</td>
<td>5.54</td>
<td>652°C</td>
</tr>
<tr>
<td>Pot. Chloride .....</td>
<td>790°C</td>
<td>6.990</td>
<td>788</td>
<td>7.00</td>
<td>790°C</td>
</tr>
<tr>
<td>Pot. Fluoride .....</td>
<td>880°C</td>
<td>7.940</td>
<td>878</td>
<td>7.97</td>
<td>880°C</td>
</tr>
</tbody>
</table>

*The temperatures have been corrected for a reference junction at 20°C.*
see to what extent, the adhesive acted as an insulator between the diamond and the thermocouple.

It was considered unlikely, however, that such effects were observable in the case of the expansion of the freed garnets, for the following two reasons.

(a) The relative large size of the thermocouple to the garnet, a ratio of approximately 8 : 1, would ensure that the garnet was of uniform temperature.

(b) The minute amount of adhesive, necessary to hold the garnet in position, would not act as an insulator between the garnet and the thermocouple.

In the case of the constrained expansions the two points outlined above are somewhat different as, (i) the diamonds containing the inclusions, are relatively large when compared with the thermocouple (at least 2 : 1), and (ii) an amount of adhesive is used which covers the upper surface of the thermocouple, and could act as an insulator between the diamond and the thermocouple.

**Insulation Effect of Dental Cement**

To check this effect, an amount of adhesive equivalent to that used in the original experiments, was placed on the thermocouple, and a pure chemical of known melting-point placed on dental cement. The temperature at which the crystal melted was then compared with its true melting-point. This was then repeated for a series of chemicals,
renewing the dental cement before each new determination. Table VII shows the results obtained for two investigations, and the graph of Figure VI compares the calibration curve of the thermocouple with the details given in columns 1 and 6 of Table VII.

From Figure VI it can be seen that the adhesive does act as an insulator, and the extent to which this varies as a function of temperature is given in Table VIII. The temperature error shown in that table is made up of a reproducibility error and a point distribution error taken from the graph.

**Temperature Gradient Across the Diamond**

To estimate heat loss across a diamond, two diamond specimens of different sizes were chosen, and these can be seen in Figure VII (Diamond A and B). Similar experiments were completed as before, except that the crystals of known melting-point were placed on the top of the diamond. The results of the separate runs for Diamond A and Diamond B are given in Table IX. Columns 1, 2 and 4 of Table IX are plotted on Figure VIII with the dental cement curve for comparison.

This graph clearly shows that a temperature gradient exists across the diamonds, and further indicates that the gradient is not only a function of the temperature, but is also dependent upon the size of the diamond. The estimated errors, made up of reproducibility and point distribution errors, are given as a function of temperature in Table X.
### Table VII

Dental Cement Calibration Details

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>M.P.</th>
<th>EMP*</th>
<th>Final Temp.</th>
<th>EMP*</th>
<th>Final Temp.</th>
<th>Average</th>
<th>TEMP.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide .......</td>
<td>115°C</td>
<td>0.67</td>
<td>123</td>
<td>0.72</td>
<td>127</td>
<td>0.70</td>
<td>125°C</td>
</tr>
<tr>
<td>Benzamidine .......</td>
<td>163°C</td>
<td>1.06</td>
<td>171</td>
<td>1.10</td>
<td>176</td>
<td>1.13</td>
<td>173°C</td>
</tr>
<tr>
<td>Saccharin ...........</td>
<td>220°C</td>
<td>1.59</td>
<td>239</td>
<td>1.61</td>
<td>241</td>
<td>1.60</td>
<td>240°C</td>
</tr>
<tr>
<td>Sod. Nitrate .......</td>
<td>307°C</td>
<td>2.76</td>
<td>366</td>
<td>2.74</td>
<td>364</td>
<td>2.75</td>
<td>365°C</td>
</tr>
<tr>
<td>Lithium Hydroxide ....</td>
<td>450°C</td>
<td>4.10</td>
<td>510</td>
<td>4.10</td>
<td>510</td>
<td>4.10</td>
<td>510°C</td>
</tr>
<tr>
<td>Sod. Iodide .......</td>
<td>650°C</td>
<td>6.02</td>
<td>696</td>
<td>5.98</td>
<td>694</td>
<td>6.00</td>
<td>695°C</td>
</tr>
<tr>
<td>Pot. Chloride ......</td>
<td>790°C</td>
<td>7.48</td>
<td>832</td>
<td>7.60</td>
<td>844</td>
<td>7.54</td>
<td>838°C</td>
</tr>
</tbody>
</table>

*The temperatures have been corrected for a reference junction at 20°C.

### Table VIII

Insulation Effect of the Dental Cement as a Function of Temperature

<table>
<thead>
<tr>
<th>Temp. ........... (°C)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>600</th>
<th>650</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. Reduction (°C)</td>
<td>12</td>
<td>16</td>
<td>20</td>
<td>28</td>
<td>34</td>
<td>40</td>
<td>48</td>
<td>52</td>
<td>55</td>
</tr>
<tr>
<td>Total Error (°C)</td>
<td>±4</td>
<td>±4</td>
<td>±8</td>
<td>±12</td>
<td>±12</td>
<td>±12</td>
<td>±12</td>
<td>±12</td>
<td>±12</td>
</tr>
</tbody>
</table>
Figure VII

Diamonds A and B

(x25)
### Table IX

**Temperature Differences Across Diamonds A and B**

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>M.P.</th>
<th>EMF</th>
<th>TEMP.</th>
<th>EMF</th>
<th>TEMP.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetanilide</td>
<td>115°C</td>
<td>0.72</td>
<td>130°C</td>
<td>0.73</td>
<td>130°C</td>
</tr>
<tr>
<td>Benzalanilide</td>
<td>163°C</td>
<td>1.16</td>
<td>185°C</td>
<td>1.17</td>
<td>185°C</td>
</tr>
<tr>
<td>Saccharin</td>
<td>228°C</td>
<td>1.72</td>
<td>250°C</td>
<td>1.70</td>
<td>250°C</td>
</tr>
<tr>
<td>Sod. Nitrate</td>
<td>307°C</td>
<td>2.83</td>
<td>375°C</td>
<td>2.83</td>
<td>375°C</td>
</tr>
<tr>
<td>Lithium Hydroxide</td>
<td>450°C</td>
<td>4.47</td>
<td>546°C</td>
<td>4.89</td>
<td>584°C</td>
</tr>
<tr>
<td>Sod. Iodide</td>
<td>651°C</td>
<td>7.02</td>
<td>794°C</td>
<td>7.64</td>
<td>847°C</td>
</tr>
</tbody>
</table>

---

Average of 3 sets of readings

* Average of 4 sets of readings

* The temperatures have been corrected for a reference junction at 20°C.
Table X

The Temperature Differences Across Diamond as a Function of Temperature

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>600</th>
<th>650</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Temp Reduction for</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Diamond A</td>
<td>6</td>
<td>8</td>
<td>20</td>
<td>32</td>
<td>40</td>
<td>52</td>
<td>68</td>
<td>76</td>
<td>84</td>
</tr>
<tr>
<td>(ii) Diamond B</td>
<td>6</td>
<td>8</td>
<td>24</td>
<td>44</td>
<td>56</td>
<td>70</td>
<td>92</td>
<td>106</td>
<td>120</td>
</tr>
<tr>
<td>Maximum Errors for</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) A</td>
<td>±4</td>
<td>±4</td>
<td>±6</td>
<td>±6</td>
<td>±12</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii) B</td>
<td>±3</td>
<td>±4</td>
<td>±13</td>
<td>±16</td>
<td>±16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table XI

Total Temperature Differences as a Function of Temperature

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>450</th>
<th>500</th>
<th>600</th>
<th>650</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. Reduction for</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Diamond A</td>
<td>18</td>
<td>24</td>
<td>38</td>
<td>60</td>
<td>74</td>
<td>92</td>
<td>116</td>
<td>128</td>
<td>139</td>
</tr>
<tr>
<td>(ii) Diamond B</td>
<td>18</td>
<td>24</td>
<td>44</td>
<td>72</td>
<td>90</td>
<td>110</td>
<td>140</td>
<td>158</td>
<td></td>
</tr>
<tr>
<td>Total MAX. Error for</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) A</td>
<td>±8</td>
<td>±8</td>
<td>±14</td>
<td>±18</td>
<td>±24</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ii) B</td>
<td>±7</td>
<td>±8</td>
<td>±21</td>
<td>±28</td>
<td>±28</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Underlined temperatures were used to construct the new curves of Fig. IX.
It was clear therefore that there existed quite drastic differences in temperature between the thermocouple and the uppermost point of the diamond, particularly at high temperatures. The total difference made up of the insulation effect of the dental cement, and temperature gradient across the diamond is given in Table XI, with the total errors at specific temperatures.

It was now possible to make some corrections to the constrained expansion curves of Fig. V. It was decided to apply the corrections given by the larger diamond B, as this specimen approximated more closely in size to the original diamonds used, and the corrected curves are plotted in Figure IX. In both the original diamonds, the garnets lay fairly close to the centre of the specimen, and this is why the curves have been plotted through the centre of the temperature gradient.

Finally, in Figure X, these two curves are plotted with the linear expansions of the garnets. An error of ± 0.0015 Å still applies for the ordinate of all the lines, but where the estimated temperature error is not marked it is to be regarded as ± 2°C.

In subsequent experiments an optical pyrometer confirmed that the temperature of a diamond of this size was appreciably lower than that of the thermocouple.

Discussion

Thermal Expansion Measurements

The results of figure X enable the coefficients of thermal
expansion to be determined for the constrained and linear expansions of the garnets. The constrained expansion coefficients were found by determining the slopes of the curves at several temperatures. The linear expansions were obtained by fitting the results given in Tables II and IV to a straight line by the method of least-squares, and then by determining the slopes of the lines. These values were then used in the following standard equation

$$\alpha_L = \frac{1}{\Delta t} \cdot \frac{\Delta a}{\Delta t}$$

$$a_t = \text{cell parameter at temperature (t).}$$

$$\frac{\Delta a}{\Delta t} = \text{slope of the line at temperature (t).}$$

$$\alpha_L = \text{coefficient of linear expansion.}$$

The results are given in Table XII.

The Constrained Expansions

The diamonds have caused quite a marked constraint on the expansion rates of the garnets; yet the constraint on D1 is much greater than that of D2. To account for this expansion difference, information about the diamonds and the garnets they contain was examined, and is outlined below.

Garnet D1
(1) larger inclusion; size ratio 1:5.
(2) chemical composition.
(3) possessed an inclusion.
### TABLE XII

**Garnet Thermal Expansion Results**

#### Free Expansions

<table>
<thead>
<tr>
<th>Material</th>
<th>( \alpha_L )</th>
<th>( \alpha_V )</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1 Garnet</td>
<td>9.647 (10^{-6})</td>
<td>28.94 (10^{-6})</td>
</tr>
<tr>
<td></td>
<td>9.456 (10^{-6})</td>
<td>28.37 (10^{-6})</td>
</tr>
</tbody>
</table>

**Temperature Range** = 1000°C.

#### Constrained Expansions

<table>
<thead>
<tr>
<th>Material</th>
<th>Temp. (°C)</th>
<th>100</th>
<th>200</th>
<th>300</th>
<th>400</th>
<th>500</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1 Garnet</td>
<td>( \alpha_L(10^{-6}) )</td>
<td>4.95</td>
<td>4.86</td>
<td>4.77</td>
<td>4.10</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>( \alpha_V(10^{-6}) )</td>
<td>14.85</td>
<td>14.58</td>
<td>14.31</td>
<td>12.30</td>
<td>10.62</td>
</tr>
<tr>
<td>D2 Garnet</td>
<td>( \alpha_L(10^{-6}) )</td>
<td>8.27</td>
<td>8.26</td>
<td>8.17</td>
<td>7.75</td>
<td>5.18</td>
</tr>
<tr>
<td></td>
<td>( \alpha_V(10^{-6}) )</td>
<td>24.81</td>
<td>24.78</td>
<td>24.51</td>
<td>23.25</td>
<td>15.54</td>
</tr>
</tbody>
</table>

\( \alpha_V = (3 \alpha_L) \) = Coefficient of the volume expansion.
Garnet D2  

(1) size ratio 1:12.

(2) chemical composition.

(3) no inclusion

Diamond D1  
Type I diamond.

Diamond D2  
Type II diamond.

Apart from these differences, there are two other possibilities which may be important.

(a) The expansions did not follow an elastic deformation.

(b) The differences in the curves genuinely reflect a different initial pressure of the inclusion in the diamond.

The thermal expansion of a substance is a function of the material, the temperature, and the external pressure; it is not dependent on the size. Thus it is probable that the size of the inclusion in the diamond will not give rise to the differences between the two constrained expansion curves. However, the smaller size ratio of the D1 specimen may account for the splitting of that diamond at about 800°C. The fracture occurred when the strain-field in the confining diamond reached the surface. The D2 diamond, on the other hand, having a smaller inclusion was able to withstand the strain created at comparable temperatures. (R. W. Munn, to be published.)

The chemical differences between the two garnets as indicated by the refractive index and cell parameters (Chapter I) are considered
not to be significant. Table XI shows the similarity of the thermal expansion coefficients for the freed garnets, and it is unlikely that chemical differences would account for the observed effects during the constrained expansions.

The presence of the minute crystalline substance included in part of garnet Di is also thought not to be important. That part of the garnet was not used in the free expansion of the mineral, and most probably had no measurable influence on the constrained expansion rate.

The principal differences between Type I and Type II diamonds is that the former contain some impurity, generally considered to be a small proportion of nitrogen. Some of the nitrogen may be disseminated through the lattice, but seems largely to be concentrated in the form of platelets, (Evans 1965). Thus the Type I diamond may have different deformation properties compared with the purer Type II diamond, in the same way that steel or duraluminium has different deformation properties compared with pure iron or aluminium. The constrained expansion curves, therefore, may represent this condition, with the Type I diamond not deforming as readily as that of the Type II, resulting in a much more constrained expansion of an included mineral.

The possibility of a non-elastic deformation occurring in the diamond could produce different expansion rates for the inclusions. However, the general shape of the two curves is similar, and further, an olivine inclusion measured before and after an expansion, (Henriques, thesis 1968), gave the same cell parameter.
The final contingency, that the curves do reflect a different origin for the diamond, is extremely interesting, for several workers, du Toit, Rogers, and Wagner as described by Williams (1932), in discussing the origin of diamonds consider at least two depths of formation; either in the Upper Mantle, or the kimberlite pipe.

**The Free Expansions**

The free expansion coefficient for the garnets given in Table I, suggests either that the chemistry of the two crystals is very similar, or that the cumulative effect of chemical difference on the expansion rates is small.

In 1956 Skinner determined the thermal expansion coefficients of five synthetic end-members of the garnet series. In Figure XI are plotted the expansions of the end-members, and as can be seen from the graph, the points lie on shallow curves.

According to Skinner (private communication Freidel 1967), it is improbable that the curves of the graphs are significant, as errors due to experimental uncertainty in temperature measurement and control did arise. Skinner also mentioned that there was a larger chance for temperature differences to exist near room temperature between the specimen and the thermocouple in the apparatus.

While it seems that the present results reflect more accurately the expansion curve of garnet, there is still a necessity for further experiments to be completed in this field.
FIG XI

CHANGE OF GARNET CELL CONSTANT WITH TEMPERATURE (SKINNER 1956)

$a_t = \text{cell edge at temp. } t$
$a_i = \text{cell edge at initial temp.}$

TEMP. (°C)
Conclusion

It is fortunate that the two garnets chosen for the expansion experiments were contained in different diamond types, as this draws attention to the possible importance of this factor. The possible extent of this effect on the expansion rates of the garnets is not certain, but this could perhaps be estimated by X-ray topography. Type I and Type II diamonds when strained to the same extent may show significant differences in their strain pattern on a topograph. With the Type I diamond, however, the distribution of the nitrogen in the diamond, may influence the resultant strain field.

If the constrained expansions are independent of the diamond type, then these curves may reflect the different conditions under which diamond has formed. By collecting more data, this possibility can be evaluated and may prove significant in studying the genesis of the diamond.
CHAPTER IV

X-RAY SITE OCCUPATION ANALYSIS OF GARNET

Introduction

In Chapter I, it was pointed out that chemical analysis of the inclusions in diamond would greatly assist in determining the chemistry of the initial environment before and during diamond formation, and that a favourable non-destructive quantitative technique of analysis was the electron microprobe. In this chapter, a second possible non-destructive analytical method using X-ray diffraction techniques will be outlined using the mineral garnet as an example.

X-ray site occupation analysis can be completed in the course of a crystal structure determination and the major part of this work so far has been in evaluating the potentialities of this technique as a quantitative method of analysis, using computer programmes and facilities currently available in this laboratory.

The X-ray basis for the analysis is set out in detail, and certain specialised techniques discussed by taking as examples garnets of known chemical compositions. The results take the form of a series of comparisons between the X-ray data obtained from a kimberlite and a garnet inclusion from a diamond, and already published garnet analyses from the same environment. This is a realistic example in that one of the primary objectives of this research is to establish
the similarity or otherwise of inclusions and kimberlite minerals. As a result of these tests some conclusions about the possible usefulness of this method of analysis are presented.

X-Ray Site Occupation Analysis

Introduction

The observed integrated intensity of an X-ray reflection, \( I \), is given in equation 1, taken from International Tables for X-ray Crystallography, Vol. II, chapter 5, (1959).

\[
I_{(hkl)} = \text{const.} \cdot V \cdot I_o \cdot A \cdot E \cdot L \cdot p \cdot |F_r(hkl) e^{-\beta \sin^2 \theta \over \lambda^2}|^2
\]  

(1)

const. includes efficiency of detector, and other factors.

\( V \) = volume of crystal.

\( I_o \) = intensity of incident beam.

\( A \) = absorption.

\( E \) = extinction.

\( L \) = Lorenz effect.

\( p \) = polarisation effect.

\( F_r(hkl) \) = structure amplitude for atoms at rest.

\[ e^{-\beta \sin^2 \theta \over \lambda^2} \]  

= temperature factor.

The nature of each factor is considered in turn.

Absorption reduces the resultant intensity of the diffracted beam according to the formula
\[ I = I_0 e^{-\frac{\mu}{p}} (\mu_t) \]

where \( \frac{\mu}{p} \) = mass absorption coefficient for the appropriate wavelength and chemical composition.

\[ t = \text{thickness of the specimen.} \]

and \( p \) = density of the specimen.

For specimen of mixed composition, as in the case of garnet, the mass absorption coefficient for the sample is given by the expression

\[ \frac{\mu}{p} = \sum \left( \frac{\mu}{p} \right)_i x_i \]

where \( \rho \) = the mean density of the specimen, and \( x_i \) = proportion by weight of a constituent element of mass absorption coefficient \( \left( \frac{\mu}{p} \right)_i \).

The mass absorption coefficients used in this work were taken from International Tables, Vol. III, p 175-192 (1962), assuming the crystal to be a sphere.

The factor \( E \), is an extinction correction which is often found to be necessary in practice. This is an extremely complicated phenomenon, but in fact an empirical extinction correction of the form

\[ I_{\text{true}} = \alpha I_{\text{obs}} + \beta I_{\text{obs}}^2 \]

which is frequently used, and which only introduces one extinction parameter, \( \beta \), gives satisfactory results for most purposes, and a correction of this form was applied.
The Lorenz and polarisation factors are usually combined in one correction, as they arise solely from the geometry of the incident and diffracted X-ray beams, and are dependent on $\theta$, and the Bragg angle. The nature of the correction factors varies depending on the type of X-ray examination being undertaken (e.g. single crystal, rotation, or powder X-ray photographs), and the polarisation of the incident beam, (here assumed to be unpolarised).

The structure factor $F_r(hkl)$ may be expressed in exponential form as shown in equation II, (International Tables, Vol. II, p 241, 1959).

$$F_r(hkl) = \sum_r f_r(hkl) e^{2\pi i (hx_r + ky_r + lz_r)} \quad (II)$$

The value $f_r(hkl)$ is the atomic scattering factor $f_r$ for the atoms $r$, for the planes of spacing $d(hkl)$. The $e^{2\pi i (hx_r + ky_r + lz_r)}$ takes account of the positional parameter $(x_r, y_r, z_r)$ of the atom $r$, and the summation is taken over all the atoms in the unit cell where $x$, $y$, $z$, are the fractional coordinates of an atom.

Since $e^{i\theta} = \cos \theta + i \sin \theta$

Then

$$F_r(hkl) = \sum_r f_r(hkl) \left[ \cos 2\pi (hx_r + ky_r + lz_r) 
+ i\sin 2\pi (hx_r + ky_r + lz_r) \right] \quad (III)$$

If crystals are centrosymmetric and the origin is taken at a centre of symmetry, then for every atom at a position $xyz$ in the
lattice, there is a corresponding atom at $\bar{x} \bar{y} \bar{z}$, and since
\[ \sin(-A) = -\sin(A), \] and \[ \cos(-A) = \cos A, \] then equation (III) reduces to
\[ F_r(hkl) = 2\sum f_r(hkl) \cos 2\pi(hx_r + ky_r + lz_r) \] (IV)

The arrangement of atoms in the unit cell, gives rise to
symmetry elements which constitute one of the 230 space groups. If
the various symmetry operations are applied to a point xyz in a
general position in the unit cell, then an array of equivalent points
will be generated by the existing symmetry elements. However, if
a point xyz lies on certain types of symmetry elements (e.g. a mirror
plane), then these points are in special positions and will be fewer
in number than the points in the general positions, but the space
group symmetry will be maintained over all equivalent points.

Hence the summation in equation (IV) may be simplified for atoms
in special positions, as certain of the coordinates of the atoms will
be a simple fraction of the unit cell, or be zero. For instance,
the special positions for the trivalent ions in garnet have the xyz
coordinates as shown in Table I, assuming the origin of the unit cell
to be the $\bar{3}$ position, (see Appendix II). When the hkl reflection 420
is summed over these points (see Table I), the structure amplitude
$F(420)$ becomes zero.
<table>
<thead>
<tr>
<th>Equivalent points for the ( \frac{1}{3} ) position in garnet.</th>
<th>( \cos 2\pi (hx + ky + lz) ) for the hkl reflection 420</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0 0</td>
<td>( 2\cos 2\pi(0) = 2 )</td>
</tr>
<tr>
<td>0 1/2 1/2</td>
<td>( 2\cos 2\pi(1) = 2 )</td>
</tr>
<tr>
<td>1/2 0 1/2</td>
<td>( 2\cos 2\pi(2) = 2 )</td>
</tr>
<tr>
<td>1/2 1/2 0</td>
<td>( 2\cos 2\pi(3) = 2 )</td>
</tr>
<tr>
<td>1/4 1/4 1/4</td>
<td>( 2\cos 2\pi(3/2) = -2 )</td>
</tr>
<tr>
<td>1/4 3/4 3/4</td>
<td>( 2\cos 2\pi(5/2) = -2 )</td>
</tr>
<tr>
<td>3/4 1/4 3/4</td>
<td>( 2\cos 2\pi(7/2) = -2 )</td>
</tr>
<tr>
<td>3/4 3/4 1/4</td>
<td>( 2\cos 2\pi(9/2) = -2 )</td>
</tr>
</tbody>
</table>

Therefore \( \sum \cos 2\pi (hx + ky + lz) = 0 \)

and \( F(420) = 0 \).

The last term of equation (I) p. 124, namely \( e^{-\frac{8\sin^2 \Theta}{\lambda^2}} \),

where \( \Theta = 8\pi^2 \mu^2 \), and \( \mu^2 \) is the mean squared displacement amplitude perpendicular to any given plane, is the Debye-Waller temperature factor, which takes account of the thermal vibrations of the atoms in the crystal. These vibrations increase with temperature and generally cause a reduction in the intensity of a particular reflection.

Assuming that the data can be put on an absolute scale, and that corrections can be made for absorption, extinction, temperature, and experimental geometric factors, then the \( F_r(hkl) \) values can be
shown to be dependent on the relative positions \((x, y, z)\) of the atoms in the unit cell, and on their atomic scattering factors.

If the atoms occupy special positions in the unit cell in which \(x, y,\) and \(z,\) are all fixed, then their geometrical factors are known exactly, and hence the observed \(F_{\text{r}}(hkl)\) values can be related directly to the atomic scattering factor.

It is the atomic scattering factors which are involved in X-ray site-occupation analysis, and therefore will be considered in some detail.

**Atomic Scattering Factors**

The atomic scattering factors are dependent on the electron density distribution of an atom, and the scattering efficiency of an atom when at rest for X-rays varies with the glancing angle \(\theta,\) as can be seen in [Fig. I](#), curve \(f_{\text{o}}\), for the case of iron, (International Tables, Vol. III, p. 213, 1962). The decrease of the scattering with angle is due to the fact that the electrons in different parts of the atom will not scatter X-rays in phase, and the partial interference reduces the net amplitude of scattering from the single atom. This phenomenon is illustrated in [Fig. II](#) taken from Bueger, fig. 32, (1953).

Several other factors, however, will influence the shape of the curve as derived from the experimental data. For instance, a rise in temperature causes an increase in the thermal motion and hence in
FIG. I

Curve of iron modified for absorption and temperature factors.
the effective volume of an atom, and the partial interference effect mentioned above is enhanced, so that at higher \( \sin \theta/\lambda \) values there is a further decrease in the atomic scattering factor. This is illustrated in Fig. I for an isotropic temperature correction by curve \( f_o e^{-B} \) where \( B = 1 \). If, however, the atom is not thermally isotropic a much more complicated temperature correction is necessary, in which the thermal motion is usually represented by a vibration ellipsoid. The temperature correction for all atoms in garnet were found to be small, with \( B's \) less than 1.0 \( \AA^2 \), and as reasonable anisotropy would give \( B \) values in different directions which would be comparable with experimental error, only isotropic values were applied to the data. Furthermore, thermal anisotropy of atoms in special positions is constrained to exhibit the symmetry of the special position. As some
of the atoms in which we are interested (those in the 4 positions) are in fact constrained to have isotropic B factors, (see below), these corrections would in any case only be applicable to silicon and oxygen atoms, and the atoms in the divalent sites.

Another factor which influences the observed data, and hence in this instance the atomic scattering curves (principally at low Sinθ/λ values) is absorption. The X-ray reflections occurring at low angles are heavily absorbed in passing through the crystal, but at high angles less absorption occurs. The curve f_{o}^0(abs) for a spherical crystal of iron using Cu Kα radiation where t = 1.5, illustrates this effect in Fig. 1, (p. 130).

The extinction factor has the effect of reducing the value of the strong reflections which generally occur at low angles, and extinction is sometimes considered as an enhanced absorption factor. As it is specimen dependent, a value must be determined from internal evidence for each crystal studied.

One other correction which will critically influence the overall experimental atomic scattering factor, even after the absorption, extinction, and temperature factors have been taken into account, is the scaling factor necessary to put the observed X-ray data onto an absolute scale. The f curves are absolute quantities derived from wave functions for the atoms concerned, but the X-ray data is a set of relative intensities not related to the intensity of the X-ray source. Determination of the absolute scale would involve time, mass
of crystal, efficiency of film, processing, and is not feasible in work of this kind. Thus the scaling factor influences the experimentally derived curves by raising or lowering them. A reliable scaling factor is absolutely vital, however, when there are more than one species of atom lying in a crystal site, as it is this ratio which is to be determined. In such cases a number of electrons is assigned in the structure amplitude formula, but a different result would be obtained if an incorrect scaling factor had been applied to the data.

However, in the case of garnet, those reflections for which the additional special reflection conditions required for the \( \bar{3}, \bar{4} \) and 222 positions are not obeyed, (See Appendix II) contain contributions only from oxygen, and if each cell is assumed to contain 96 oxygen atoms, these can be used to fix the absolute scale. Unfortunately, these reflections are generally weak, and hence in these tests not as accurately determined as would be desirable, but this is true in principle, and is one reason why garnet is a very favourable crystal for such site occupation studies.

In the calculation of the \( f \) curves, the assumption is made that the binding energy of the electron is small compared with the energy of the X-ray photon, and that the bound electron has the same scattering power as the free electron. However, bound electrons in atoms are excited by various select ranges of X-ray wavelengths, in the region of the absorption edges of the atoms, and this modifies the scattered radiation. A dispersion correction must then be applied
to the atomic scattering curve, and Fig. III illustrates this point
for the element Chromium with Mo, Cr, and Cu radiations.

It is possible by the use of selected X-ray wavelengths either
side of the absorption edges, to determine the amount of that atom
present in a substance. For instance, James (1948, p. 183), discussed
the work of Wyckoff (1930) who determined experimentally the f curves
of nickel and oxygen in the compound NiO using this technique.

In principle, however, garnets which appear, for example, to
have similar intensities when using MoKα radiation might differ for
Cu Kα, which lies near to the K absorption edge of Fe. Careful
inspection of Fig. Va and Vb (p. 147) does show some intensity
differences which did not appear so marked in the analysis carried
out with MoKα radiation, but at this stage of the present work, the
use of dispersion effects as a means of chemical analysis has not
been attempted.

The Garnet Series

The minerals in the garnet group comprise six principal
orthosilicate end-members in an isomorphous series. These are
pyrope (Mg$_3$Al$_2$Si$_3$O$_{12}$), almandine (Fe$_3^+$Al$_2$Si$_3$O$_{12}$), andradite
(Ca$_3$(Fe$^{+3}$,Ti)$_2$Si$_3$O$_{12}$), grossularite (Ca$_3$Al$_2$Si$_3$O$_{12}$), spessartine
(Mn$_3$Al$_2$Si$_3$O$_{12}$), and uvarovite (Ca$_3$Cr$_2$Si$_3$O$_{12}$).

A garnet corresponding to an end-member is rare, and the name
is assigned according to the dominant molecular type present.
Fig. III

Dispersion corrections to the $f$ curve of chromium for Mo, Cu, and Cr radiations.

$\Sigma N$, $f_0 + \Delta f$ only.

$\sin \theta / \lambda$ (Å$^{-1}$)

Number of electrons

25 20 15 10 5 0
Generally the minerals are divided into the "pyraepite" and "ugrandite" series in which there is fairly complete and continuous variation in composition, but between which no continuous variation seems to exist. The garnets from the kimberlite environment consist of about 70 mol. per cent of the pyrope molecule, 15 mol. per cent of the almandine molecule, with the four other end-member molecules making up the remainder.

The crystal structure of garnet was first completed by Menzer (1928) on natural powdered specimens of pyrope, grossularite, andradite, almandine, and spessartine. A refinement of synthetic grossularite was completed by Abrahams and Geller (1958), and a two dimensional refinement of synthetic pyrope was obtained by Zemann and Zemann (1961). Gibbs and Smith (1965) then completed a three dimensional least-squared refinement on another crystal of pure synthetic pyrope.

An attempt at X-ray site occupation analysis of powdered rare earth garnets by Miller (1960) proved inconclusive as only two of the observed reflections proved sensitive to ionic distribution.

The unit cell of garnet contains eight formula units and the space group of the crystal is Ia3d. The \( R_3' \), \( R_2' \) and silicon atoms lie on special positions in the crystal lattice, the oxygen atoms having the only positional parameters to be determined. The 24 \( R_3'' \) atoms (e.g. Ca, Mg, Mn, Fe\(^{2+} \)) lie on the \( 4 \) symmetry points; the 16 \( R_2'' \) atoms (e.g. Al, Cr\(_2\), Ti, Fe\(^{3+} \)) are at the \( 3 \) positions, and the
24 silicons are to be found at the 222 positions, (see Appendix II). If the origin of the cell is taken at \( \frac{3}{2} \) then the atomic coordinates of the atoms on special positions in the unit cell are \((1/8, 0, 1/4), (0,0,0), \) and \((3/8, 0, 1/4)\) respectively. The coordinates of the oxygen atom have been determined by several workers and the more recent ones are listed below.

**Coordinates in \( \tilde{a} \)**

<table>
<thead>
<tr>
<th></th>
<th>( x )</th>
<th>( y )</th>
<th>( z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) Abraham and Geller (1958) ((\text{Ca}_2\text{Al}_2\text{Si}_3\text{O}_12))</td>
<td>-0.0389</td>
<td>0.0456</td>
<td>0.1524</td>
</tr>
<tr>
<td>(ii) Zemann and Zemann (1961) ((\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_12))</td>
<td>0.034±0.001</td>
<td>0.050±0.001</td>
<td>0.654±0.001</td>
</tr>
<tr>
<td>(iii) Smith and Gibbs (1965) ((\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_12))</td>
<td>0.0329±0.004</td>
<td>0.0508±0.004</td>
<td>0.6531±0.004</td>
</tr>
</tbody>
</table>

It was necessary in order to simplify the calculations to make certain assumptions about the garnets.

(i) It was assumed that there was an absence of chemical zoning in such small crystals of garnet from the kimberlite environment. This assumption was supported by the sharp high angle reflections observed on X-ray photographs, which might have been expected to show broadening if appreciable variation in lattice parameter occurred. Absence of birefringence might also set an upper limit on permissible inhomogeneity.
(ii) It was assumed that if substitution of one element with another took place in the garnet isomorphous series, it occurred at definite sites in the crystal lattice and was governed by the similarity of the electronegativities of the elements involved.

(iii) It was assumed that the amount of substitution in the silicon position in the garnet lattice was negligible. This was assessed from an examination of garnet analyses recalculated on the basis of 24 oxygens, (Deer, Howie, and Zussman 1962).

(iv) So little titanium was observed that it was assumed that only the ferric ion existed in the trivalent site of the andradite garnet end-member.

Experimental Procedure

Introduction

In order to see to what extent chemical variation in the garnet series could be detected by X-ray diffraction techniques, natural specimens of pyrope, grossularite, almandine, and uvarovite were kindly supplied by the British Museum (Natural History). The specimens were selected by the British Museum as being reasonably near the end-members required, although no chemical analyses of the specimens were given. However, random rotation X-ray photographs using CoKα radiation clearly showed considerable differences between the crystals, in the intensity of comparable groups of reflections and also in the cell parameters, (see Fig. IV). The Straumanis method of loading X-ray film into a camera was used in order that cell dimensions could be
FIG. IV

RANDOM ROTATION STRAUMANIS PHOTOGRAPHS OF

BRITISH MUSEUM GARNETS.

GROSSULAR. UFF 1917 261

ALMANDINE PYROPE. 1959 230

ALMANDINE. BM 62870

Co Kα Kβ

Co Kα Kβ

Co Kα Kβ
determined if required, (see Henry et al 1961, p. 170).

To determine whether any similar variation existed in a more restricted field of the garnet series, four garnets from the concentrate of kimberlite material from South Africa were chosen, on the basis of the colour variation observed in a large quantity of such garnets. An inspection of rotation and oscillation photographs using CoKα radiation, however, indicated that great care to make the specimens strictly comparable would be necessary in order to detect useful differences in the intensities of corresponding reflections, although small changes in lattice parameter could be readily seen. Nevertheless large variations in lattice parameter certainly do exist within the group of garnets with which we are concerned and Fig. V shows the very large difference in lattice parameter between the orange inclusion from diamond (Fig. Va) and the claret coloured kimberlite chip (Fig. Vb) as compared with the variation between the latter and a ground sphere of a similar claret coloured kimberlite garnet, (Fig. Vc).

In order to estimate the possible accuracy of site occupation analysis, a garnet for which a set of X-ray data had been obtained was also quantitatively analysed on an electron microprobe. The garnet for this work was chosen from the kimberlite concentrates used before, and care was taken to avoid a garnet with any obvious contaminant. The garnet was divided into a number of pieces, a polished specimen prepared for the electron microprobe, and another smaller piece of approximate size 0.47 mm x 0.37 mm x 0.34 mm, was used for the crystal
FIG. V

STAUANIS ROTATION PHOTOGRAPHS OF GARNETS USING Cu RADIATION.

a) INCLUSION GARNET. (ORANGE) $d = 11.652\,\text{Å}$, 111 $\uparrow$ CuK$\alpha$, K$\beta$

b) KIMBERLITE GARNET CHIP. (CLARET) $d = 11.529\,\text{Å}$, 111 $\uparrow$ CuK$\alpha$, K$\beta$

c) KIMBERLITE GARNET GROUND SPHERE. (CLARET) $d = 11.535\,\text{Å}$, 111 $\uparrow$ CuK$\alpha$
structure determination.

The microprobe analysis was kindly completed by members of the Geology Department of Imperial College, on a Geoscan Electron Microprobe, and corrections for absorption, atomic number effect, fluorescence, and dead-time, were incorporated in the computer programme used by them to process the data.

Knowing the extent of likely errors it was now of interest to see whether comparisons and distinctions could be made between chemically analysed garnets from the kimberlite environment, and garnet inclusions from diamond for which the chemistry was not known, but for which X-ray data could be obtained.

The garnet inclusion chosen for this purpose was taken from Diamond D15, described in Appendix I, and the garnet measured 0.28 mm x 0.06 mm x 0.15 mm, and the chemical analyses with which the X-ray data was compared were as follows.

(i) The microprobe analysis of the kimberlite garnet referred to above.

(ii) A microprobe analysis of a garnet inclusion from a diamond of unknown origin by Meyer (1968). The analysis, 15s, was chosen because of the relatively high weight percentage of Cr₂O₃, as Meyer (1968) has shown that Cr₂O₃ is an important constituent in some garnet inclusions in diamond.
General X-ray Procedure

The X-ray intensity data of the garnet inclusion were obtained in the first instance on a 6.00 cms diameter Unicam camera using CuK radiation by setting the crystal about the [111] crystallographic axis. Although the original choice of this axis was accidental, it soon proved a most useful one, as it was shown in the computation of the data that there was not the severe duplication of reflections due to the high symmetry of garnet, that would have occurred if either the [100] or [110] directions had been used. In order to obtain a complete set of data the crystal was progressively oscillated through three sets of 15° of arc commencing from the (110) mirror plane position. The X-ray intensities were obtained on two sets of film packs containing three films each for each oscillation range, and the films covered the time interval 24 hours to approximately 7 minutes.

The photographs showed poor spot shape and quite severe absorption effects, and it became clear in processing the Cu data, that considerable internal inconsistencies existed, (attributed largely to absorption effects because of the irregular crystal shape). Examples of isodensitracr records are shown in Fig. VIII, (see below).

A further set of data was therefore collected for both crystals using MoK radiation. This data, obtained on a Leeds Weissenberg camera of 5.73 cms diameter, consisted of three rotation photographs over the time range 9 hours to approximately 1 hour, again taken about the [111] crystallographic axis of the garnet crystals.
It was found that considerable benefit was gained by using MoKα radiation, partly because of decreased absorption, and partly because rotation photographs taken about axes of high symmetry result in the averaging of many equivalent reflections. For a full rotation photograph, the [111] axis is especially favourable for a cubic crystal, because reflections which are equivalent by definition (hkl C) are superposed, (see Appendix II), and some averaging to offset irregularities automatically occurs. This effect can also be seen in Fig. Vb (p. 141) which shows almost as good spot shapes as those obtained from a ground sphere, (Fig. Vc). Fig. VI shows two typical rotation photographs for the kimberlite and inclusion garnets, taken with MoKα radiation.

The intensities of both sets of reflections were measured on a Joyce-Loebl Isodensitracer and the principles of operation, taken from page 10 of the Operation Manual for the instrument are shown in Fig. VII. The type of patterns obtained for some of the actual garnet reflections is presented in Fig. VIII.

Fig. VIIIa shows some of the very irregular spot shapes due to absorption effects which generally prevailed throughout the Cu data, and Figs. VIIIb and VIIIc show the typical rounded shapes of reflections obtained from the Mo data. The differences in the size of the spots is due to the initial crystal size, and is not a consequence of different instrumental magnification. The peak heights were measured from the isodensitracer records by counting contours, not the integrated intensities.
FIG. VI

SPECIMEN KIMBERLITE AND INCLUSION GARNET

ROTATION PHOTOGRAPHS.

KIMBERLITE GARNET.  [111] axis.  Mo Kα

INCLUSION GARNET.  [111] axis.  Mo Kα

ENLARGEMENTS FROM FILM RADIUS 2.87 cms.
4.1. Write-Out Method

4.2. Conventional microdensitometers scan along a single line and present a graph of optical density (or transmission) versus the displacement of the probing light beam. The Isodensitracer successively scans along several lines, using the "dropped line" technique common in making contour maps from elevation information in stereo pairs of aerial photographs. (See Figure 6.)

4.3. The write-out pen changes its mode of writing whenever the density (or object brightness) changes by a small, preselected amount, or discrete density increment. As the density along a scan decreases, the pen writes a solid line until the limit of this discrete density increment is reached. Then it writes a series of equally spaced dots until the next increment limit is reached. The pen lifts up and leaves a blank for the next increment. The pattern, line—dots—blank, is repeated as long as the density is decreasing. When the density is increasing, the pattern is reversed, blank—dots—line. The use of three write-out symbols makes it obvious whether the density is decreasing or increasing as the mode changes. Density increments can be varied from 0.005 to 0.1D to provide accurate plotting of samples of all densities.

Figure 6. Comparison of Conventional and Dropline Write-Outs.
FIG. VIII

Specimen
Isodensitracer
Records.

VIIIa.
INCLUSION OSCILLATION DATA
(Cu Kα)

VIIIb.
INCLUSION ROTATION DATA (Mo Kα)

VIIIc.
KIMBERLITE ROTATION DATA (Mo Kα)
All the experimental data was processed on a Ferranti Pegasus computer, using existing programmes based on those described by Milledge and Milledge (1961).

**Computational Procedure for X-ray Site Occupation Analysis**

With a garnet of known chemical composition it is possible to calculate the contributions from the atoms in the special and general positions in the unit cell to the calculated $F_{hkl}$ values. The method by which this is achieved will now be described using as an example the chemical analysis of garnet El0 (Nixon et al. p. 1104, 1963).

The analysis is presented below.

\[
\begin{align*}
\text{SiO}_2 &= 41.90 \\
\text{TiO}_2 &= 0.11 \\
\text{Al}_2\text{O}_3 &= 16.92 \\
\text{Cr}_2\text{O}_3 &= 7.52 \\
\text{Fe}_2\text{O}_3 &= 1.24 \\
\text{FeO} &= 6.17 \\
\text{MnO} &= 0.59 \\
\text{MgO} &= 19.64 \\
\text{CaO} &= 6.27 \\
\text{Total} &= 100.36
\end{align*}
\]

The weight percentage of the oxides are reduced to atomic fractions on the basis of one oxygen, positional parameters are assigned for oxygen, and temperature factors specified for each atom type. As the latter two groups of parameters are not explicitly known for garnet El0, values were chosen which were consistent with end-member garnet structure analyses, (e.g. Gibbs and Smith 1965).
The resulting data in Table II shows the individual contributions by the various atoms to the overall calculated structure factors. It will be noted that certain atoms do not contribute to certain reflections, and it is this fact which greatly facilitates the extraction of chemical information about the garnet.

If, on the other hand, the chemistry of the garnet is not known, but a set of x-ray data has been obtained and processed in a manner similar to that described earlier, it is theoretically possible to determine the chemical composition from the experimental data. This is done by starting with percentage site occupations corresponding to a plausible chemical composition, and then refining these percentages using the observed data. However, owing to the general similarity of all the atomic scattering factors concerned, as a function of \( \sin \theta / \lambda \), several different combinations will generally lead to similar \( F_{hkl} \) values, so that ambiguous results are possible. A disadvantage from the computational standpoint is that very small (< 5 per cent) concentrations of a particular atom type in one of the variable sites make contributions to \( F_{hkl} \) of magnitude comparable to that of the errors in the data, and this will lead to instabilities in the least squares refinement.

One way in which these problems may be overcome in practice, and information as to the composition of the garnet obtained, is to determine the number of electrons in a single site in terms of an average scattering factor curve. This was done here by refining the
<table>
<thead>
<tr>
<th>AT. FRACTION</th>
<th>0.000</th>
<th>0.250</th>
<th>0.500</th>
<th>0.750</th>
<th>1.000</th>
<th>1.250</th>
<th>1.500</th>
<th>1.750</th>
<th>2.000</th>
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<tr>
<td>Fe&lt;sup&gt;3+&lt;/sup&gt;</td>
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<tr>
<td>Fe&lt;sup&gt;2+&lt;/sup&gt;</td>
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<td>Mn</td>
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<td>Ca</td>
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</tbody>
</table>

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**MAGNITUDE AND SIGN OF INDIVIDUAL CONTRIBUTIONS TO F<sub>HKL</sub>**

**FOR GARNET E10 (NIXON).**

* INCLUSION DATA BEFORE EXTINCTION CORRECTION APPLIED.

(SEEN TABLE IX FOR CORRECTED DATA)
site occupation parameters of only the lightest possible atom (Al or Mg) in a site. In order to demonstrate the admissibility of this procedure, Nixon's garnet El0 will again be used as an example, because the known chemical composition of this garnet approximates to the average composition expected for garnets of unknown chemistry in which we are interested.

Choosing Mg (Z = 12), and Al (Z = 13) for the divalent and trivalent sites respectively, the equivalent site occupations are defined as shown in Table III.

**TABLE III**

**Divalent Site**

<table>
<thead>
<tr>
<th>Element</th>
<th>At. Fraction (1 oxy. atom)</th>
<th>At. No.</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>0.1765</td>
<td>x</td>
<td>12</td>
</tr>
<tr>
<td>Ca</td>
<td>0.0405</td>
<td>x</td>
<td>20</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>0.0311</td>
<td>x</td>
<td>26</td>
</tr>
<tr>
<td>Mn</td>
<td>0.0030</td>
<td>x</td>
<td>25</td>
</tr>
</tbody>
</table>

Reduce in terms of Mg equivalence (i.e. 12 electrons)
Divide by 12 = 0.3176

**Trivalent Site**

<table>
<thead>
<tr>
<th>Element</th>
<th>At. Fraction (1 oxy. atom)</th>
<th>At. No.</th>
<th>Electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>0.1203</td>
<td>x</td>
<td>13</td>
</tr>
<tr>
<td>Cr</td>
<td>0.0359</td>
<td>x</td>
<td>24</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>0.0056</td>
<td>x</td>
<td>26</td>
</tr>
</tbody>
</table>

Reduce in terms of Al equivalence (i.e. 13 electrons)
Divide by 13 = 0.1978
Using the two values obtained from Table III, a list of calculated $F_{hk1}$ values was prepared using just the Mg and Al atomic scattering curves. A further list was then obtained using the same reflections, but this time all the atomic fractions in the divalent and trivalent sites had their own appropriate atomic scattering curves, and the corresponding $F_{hk1}$ values calculated.

A comparison of these results is shown in Table IV for the reflections obtained from the rotation photographs of the garnets set about a [111] crystallographic axis. The same positional and temperature factor parameters were used in each case. As can be seen the agreement between equivalent and total $F_{hk1}$ values for the divalent and trivalent sites is very close, especially in view of the size of the experimental errors, and indicates that it is reasonable to use the equivalent site occupation technique as a means of analysing the X-ray data.

Knowledge of the number of electrons in a particular site leads to a unique solution of the chemistry if the site is considered to be fully occupied by only two types of atom. Full occupation is presumed to be the general rule for divalent and trivalent sites in garnet analyses, the Fe being distributed between the two so as to achieve an overall balance of electrical charge.

As an example consider an experimental result indicating 15 electrons in a site occupied only by Ca ($Z = 20$) and Mg ($Z = 12$).
<table>
<thead>
<tr>
<th></th>
<th>( F_{\text{obs}} )</th>
<th>( \text{EQUV} ) ( \text{Mg}^+ )</th>
<th>Total ( \text{Mg}^+ )</th>
<th>( \text{EQUV} ) ( \text{Al}^3+ )</th>
<th>Total ( \text{Al}^3+ )</th>
<th>( \text{SI} ) ( \text{Oxy} )</th>
<th>(-\Delta^*)</th>
<th>(+\Delta^*)</th>
<th>(-\Delta^{**})</th>
<th>(+\Delta^{**})</th>
<th>(-\Delta^{***})</th>
<th>(+\Delta^{***})</th>
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<td>-</td>
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<td>(1)</td>
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<td>96</td>
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<td>89.67</td>
<td>89.67</td>
<td>100.19</td>
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<td>+20.77</td>
<td>-</td>
<td>+</td>
<td>-</td>
<td>+</td>
<td>(1)</td>
</tr>
</tbody>
</table>

**Legend:**

- \(/\) All atom contributions additive.
- \(\text{F}_{\text{calc}}\) decreases.
- \(\pm\) \(\text{F}_{\text{calc}}\) increases.
- \(\%\) \(\text{F}_{\text{calc}}\) approx. proportional to the component.
- \(\text{NO change}\) in \(\text{F}_{\text{calc}}\).

**Test of the feasibility of using equivalent site occupations and expected changes in relative magnitudes of \(F_{\text{HKL}}\) with composition.**
If the percentage calcium occupation is $\alpha$, then

$$20\alpha + 12(1 - \alpha) = 15$$

in which case $\alpha = 0.375$.

However, in the case of garnet there are more than two atom types substituting in the two variable sites, and hence a unique solution cannot be attained without additional X-ray diffraction data obtained with radiations where anomalous dispersion is operative (see p. 135), or other types of information such as cell parameter, density, or refractive index.

Presentation of the data for garnet E10 in the forms shown in Tables II and IV, provides a convenient means of examining the possible influence of a change in the chemistry of E10 on the calculated $F_{hkl}$ values. In order to do this the oxygen and silicon contributions for particular $F_{hkl}$ values shown in Table II have been added and appear as a single column in Table IV. This addition is not strictly valid as a general rule, as contributions from these two atoms may have slightly different values in different garnets, but it is unlikely to introduce an appreciable error over a small composition range. Table IV, therefore, further shows the effect of a change of occupancy for the atoms in divalent and trivalent sites on the $F_{hkl}$ values, and a detailed discussion of these changes is to be found in the concluding remarks of this chapter (p. 167).

Table IV also illustrates two further points. The $F_{hkl}$ values marked with an asterisk (*), and a dash (/) have not been included in
the examination. Those which are asterisked are $F_{hkI}$ values to which only oxygen contributes (see Table II also), and it is from these values that the absolute scale factor is determined. The remaining calculated $F_{hkI}$ values are those to which positive contributions are made from all the component atoms, (see Table II). The relatively large value for these structure amplitudes will indicate, when compared with the observed $F_{hkI}$ values, whether or not extinction is present in the data.

**Results**

The results will take the form of a series of comparisons between two published chemical analyses of garnets, and the MoKα X-ray data from the kimberlite garnet and the garnet inclusion in diamond. The internal inconsistencies in the CuKα data obtained for the inclusion garnet indicated that this data set were unsatisfactory, so that only the MoKα data will be treated in detail. The results will be considered in the following sections.

**Section I**  
A comparison of the X-ray data from a fragment of a kimberlite garnet with an electron microprobe analysis of another fragment of the same specimen.

**Section II**  
A comparison of the X-ray data of the garnet inclusion with the garnet inclusion analysis of Meyer (1968).

**Section III**  
A comparison of the X-ray data from the garnet inclusion with the microprobe analysis of the kimberlite garnet.
Section I

The Electron Microprobe Results

The garnet analysis received from Imperial College with the various errors for each atomic component is given in Table V. A maximum machine error was given at 5 per cent.

Since the electron probe can only determine total iron, the FeO contents were adjusted to give sufficient Fe₂O₃ to satisfy charge requirements.

The X-ray Results

Following the procedure outlined before, the equivalent site occupations for the divalent and trivalent sites on the basis of one oxygen were chosen to be Mg and Al respectively.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic Per Cent</th>
<th>Recalculated as Wt per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>19.430 ± 0.972</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Ti</td>
<td>0.183 ± 0.009</td>
<td>TiO₂</td>
</tr>
<tr>
<td>Al</td>
<td>11.280 ± 0.564</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td>Cr</td>
<td>0.224 ± 0.011</td>
<td>Cr₂O₃</td>
</tr>
<tr>
<td>Fe</td>
<td>13.672 ± 0.694</td>
<td>Fe₂O₃</td>
</tr>
<tr>
<td>(total)</td>
<td></td>
<td>FeO</td>
</tr>
<tr>
<td>Mn</td>
<td>less than 500 ppm</td>
<td>MnO</td>
</tr>
<tr>
<td>Mg</td>
<td>8.745 ± 0.437</td>
<td>MgO</td>
</tr>
<tr>
<td>Ca</td>
<td>5.290 ± 0.265</td>
<td>CaO</td>
</tr>
<tr>
<td>Oxygen by difference</td>
<td>40.976 ± 2.049</td>
<td>Total</td>
</tr>
</tbody>
</table>

103.25
and the values obtained from the analysis are given below.

\[
\begin{align*}
\text{Oxy.} & = 1.000 \\
\text{Mg.} & = 0.363 \\
\text{Al.} & = 0.185 \\
\text{Si.} & = 0.250
\end{align*}
\]

Using in the first instance the arbitrary isotropic B factors of \(0.60 \, \AA^2\) for all atoms, the oxygen positional parameters determined for pure synthetic pyrope by Gibbs and Smith (1965), and the equivalent site occupation parameters determined from the electron microprobe analysis, the observed \(F_{hkl}\) values (corrected for absorption) were compared with the calculated \(F_{hkl}\) values and extinction corrections derived (\(\alpha = 1.000, \beta = 0.0015\), see p. 125). The oxygen position, B factors, and site occupation parameters were then allowed to refine and the result after three cycles of refinement is shown in Table VI.

It will be seen from Table VI, that with a residual of 7.96 percent the recommended shifts to the variable parameters (\(A\)), lie well within the estimated standard deviations (\(\sigma\)), and a further calculation using the ranges* listed in Table IX (p. 166) gave a value of \(R' = 2.4\) percent. [A value of \(R' = 0\) would indicate \(AF\) always < estimated standard deviation.] A low value of \(R'\) means that there is no appreciable signal from the remaining \(AF\) values, so that further refinement would be unprofitable.

An estimate of the errors involved in the experimentally determined site occupations using this set of data may be made from the standard

*Ranges are derived experimentally from estimated errors in the observed data, and are roughly equivalent to estimated standard deviations for these reflections.
### TABLE VI

**XYZ (FRACTIONS)**

<table>
<thead>
<tr>
<th></th>
<th>OXY (GENERAL POSITION)</th>
<th>'MG' (SPECIAL POSITION)</th>
<th>'AL' (SPECIAL POSITION)</th>
<th>SI (SPECIAL POSITION)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03384</td>
<td>0.05014</td>
<td>0.65330</td>
<td>0.13500</td>
<td>0.00000</td>
</tr>
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</table>

**REFINEMENT OF VARIABLE PARAMETERS**

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<thead>
<tr>
<th>INITIAL</th>
<th>REFINED*</th>
<th>RECON. FROM R = 2.96</th>
<th>RECON. RANGES</th>
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<tr>
<td>SIT. OCC.</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>OX 1.000</td>
<td>1.003</td>
<td>+0.003</td>
<td>0.024</td>
</tr>
<tr>
<td>'MG' 0.363</td>
<td>0.334</td>
<td>+0.002</td>
<td>0.022</td>
</tr>
<tr>
<td>'AL' 0.185</td>
<td>0.188</td>
<td>+0.012</td>
<td>0.027</td>
</tr>
<tr>
<td>SI 0.250</td>
<td>0.243</td>
<td>+0.007</td>
<td>0.026</td>
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</table>

<table>
<thead>
<tr>
<th>B FACTORS</th>
</tr>
</thead>
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<tr>
<td>OX 0.600</td>
</tr>
<tr>
<td>'MG' 0.600</td>
</tr>
<tr>
<td>'AL' 0.600</td>
</tr>
<tr>
<td>SI 0.600</td>
</tr>
</tbody>
</table>

**OXY. POSITIONS**

| X | 0.93284 | 0.0396 | 0.00031 | 0.00103 | 0.00000 |
| Y | 0.00141 | 0.0928 | 0.00000 | 0.00110 | -0.00000 |
| Z | 0.65330 | 0.65207 | 0.00009 | 0.00110 | 0.00000 |

| 1 | 2 | 3 | 4 | 5 |

**SITE OCCUPATION REFINEMENT OF A KIMBERLITE GARNET FOR WHICH A MICROPROBE ANALYSIS IS AVAILABLE FOR COMPARISON.**
deviations of the refinement results (i.e. column 4, Table VI), which indicate that the absolute error is approximately the same for all atoms, and hence the percentage standard deviation is of the order of 7 per cent for the "Mg" position, and some 14 per cent for the "Al" position. It should be noted, however, that the site occupation is strongly negatively correlated with the temperature factor, (see Table XI, p. 171), and this fact must be taken into account when assessing such results. Overall errors of the order of 10 per cent should probably be assumed in these site occupation parameters, which would bring X-ray and microprobe results into approximate agreement.

Section II

A Comparison of the Garnet Inclusion in Diamond with Garnet 15E (Meyer)

The quantitative microprobe analysis of garnet 15E (Meyer 1968) and the determined equivalent site occupancy for the cation sites is set out below.

\[
\begin{align*}
\text{SiO}_2 &= 41.8 \\
\text{FeO} &\quad (\text{Fe as FeO}) = 5.71 \\
\text{TiO}_2 &= 0.02 \\
\text{MnO} &= 0.20 \\
\text{Al}_2\text{O}_3 &= 15.7 \\
\text{MgO} &= 24.2 \\
\text{Cr}_2\text{O}_3 &= 10.9 \\
\text{CaO} &= 2.19 \\
\text{Total} &= 100.72
\end{align*}
\]

Equivalent Site Occupation.

\[
\begin{align*}
\text{Oxy} & \quad \text{Mg} & \quad \text{Al} & \quad \text{Si} \\
1.000 & \quad 0.286 & \quad 0.217 & \quad 0.250
\end{align*}
\]
As a starting point for the comparison with the X-ray data from the garnet inclusion, the oxygen positional parameters, and B factors obtained from one of the refinements of Section I, were used to calculate a new set of $F_{hkl}$ values employing the equivalent site occupancy of garnet 15E.

In Table VII is shown the first cycle of refinement with a residual of 11.25 per cent. The recommended changes in the site occupations were generally large and in the "Mg" case was larger than the standard deviation. No further refinement was carried out as the recommendations were towards the X-ray microprobe result, (see Table VI, p. 158) which suggested that Meyer's garnet inclusion was chemically quite different from the author's garnet inclusion.

Section III

A Comparison of the Garnet Inclusion in Diamond with the Microprobe Result of the Kimberlite Garnet

Using the parameters obtained from the final refinement in Section I, (see Table VI, p. 158) a new set of calculated $F_{hkl}$ values were determined for the kimberlite garnet and refined against the X-ray data of the garnet inclusion. Table VIII shows the final cycle of refinement with a residual of 6.10 per cent, and the recommended shifts for all variable parameters lie well within the estimated standard deviations.
## TABLE VII

XYZ (FRACTIONS)

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<th>O</th>
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<td>0.03482</td>
<td>0.04920</td>
<td>0.65137</td>
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OXY (GENERAL POSITION)

Mg (SPECIAL POSITION)

Al (SPECIAL POSITION)

Si (SPECIAL POSITION)

**REFINEMENT OF VARIABLE PARAMETERS.**

**INITIAL**  \( R = 11.35 \)  **RECON.**  **AFTER ONE CYCLE**

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<td>0.000</td>
</tr>
<tr>
<td>I r</td>
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</tr>
<tr>
<td>Al</td>
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**X FACTORS.**

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<td>si</td>
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**OXY. POSITIONS.**

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<tr>
<th></th>
<th>( \Delta )</th>
<th>( \delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ox</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>y</td>
<td>0.482</td>
<td>0.000</td>
</tr>
<tr>
<td>z</td>
<td>0.65175</td>
<td>0.000</td>
</tr>
</tbody>
</table>

**SITE OCCUPATION REFINEMENT OF THE GARNET INCLUSION IN DIAMOND WITH THE MICROPROBE ANALYSIS**

OF A GARNET INCLUSION FROM DIAMOND (MEYER 1968) FOR COMPARISON.
### TABLE VIII

<table>
<thead>
<tr>
<th>XYZ (FRACTIONS)</th>
<th>OXY (GENERAL POSITION)</th>
<th>Mg (SPECIAL POSITION)</th>
<th>Al (SPECIAL POSITION)</th>
<th>Si (SPECIAL POSITION)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02343 0.04920 0.6537</td>
<td>0.02343 0.04920 0.6537</td>
<td>0.02343 0.04920 0.6537</td>
<td>0.02343 0.04920 0.6537</td>
<td>0.02343 0.04920 0.6537</td>
</tr>
</tbody>
</table>

#### REFINEMENT OF VARIABLE PARAMETERS

<table>
<thead>
<tr>
<th>INITIAL</th>
<th>REFINED</th>
<th>RECON FROM R=6.10</th>
</tr>
</thead>
<tbody>
<tr>
<td>SIT, OCC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OX 1.000</td>
<td>1.000</td>
<td>+0.004 0.018</td>
</tr>
<tr>
<td>Mg 0.337</td>
<td>0.338</td>
<td>-0.004 0.016</td>
</tr>
<tr>
<td>Al 0.179</td>
<td>0.188</td>
<td>-0.013 0.019</td>
</tr>
<tr>
<td>Si 0.350</td>
<td>0.350</td>
<td>-0.004 0.020</td>
</tr>
</tbody>
</table>

#### B FACTORS

| OX 0.512 | 0.417 | -0.003 0.127 |
| Mg 0.343 | 0.265 | 0.038 0.093 |
| Al 0.520 | 0.774 | 0.050 0.123 |
| Si 0.404 | 0.416 | 0.033 0.117 |

#### OXY POSITIONS

| X 0.03433 | 0.03486 | 0.00009 0.00070 |
| Y 0.04920 | 0.04793 | 0.00009 0.00081 |
| Z 0.68137 | 0.65205 | 0.00002 0.00087 |

---

SITE OCCUPATION REFINEMENT OF THE GARNET INCLUSION IN DIAMOND WITH THE MICROPROBE ANALYSIS OF THE KIMBERLITE GARNET FOR COMPARISON.
The similarity between the two sets of site occupations suggests that the chemistry of the garnet inclusion is probably related to the kimberlite garnet, and is not of high Chromium content. However, there is an interesting anomaly here, in that there is a considerable difference between the cell size of the kimberlite garnet \((a = 11.529 \text{ \AA})\) and that of the garnet inclusion \((a = 11.652 \text{ \AA})\). Unfortunately, the cell size of Meyer's chrome-rich garnet is not known, (Meyer: private communication). A garnet analysis El6 by Nixon (1963) which has an almost identical chemistry to that of the kimberlite garnet also has a closely similar cell size, \((11.545 \text{ \AA})\).

Quite drastic chemical differences would appear to be necessary to account for this large change in cell parameter, and this anomaly is at present being investigated further.

Using these parameters it may be possible to determine some broad garnet chemistry which can be reinterpreted in terms of the number of electrons per site, so that a comparison can be made with
the X-ray data and allow a unique chemistry to be determined. However, as this work dealt with the development of the analytical technique, it was of interest to see to what extent chemical distinctions could be gauged between the X-ray data and the published garnet analyses mentioned earlier. The results of the work are discussed in the next section.

**Discussion and Conclusions**

If site occupation analysis were to become another non-destructive quantitative analytical technique comparable with the microprobe, it would be necessary to determine the site occupation in the various crystals to within an accuracy of $\pm 2$ per cent. In practical terms this will mean that the standard deviation on the site occupation at present indicating an error of some 10 per cent will have to be reduced by at least a factor of five. Fortunately, this is only an exploratory analysis, and a number of variations are possible which could improve the accuracy of the observed data.

Collecting the data around the [111] garnet axis using ordinary rotation photographs turned out to be a simple and relatively satisfactory procedure. The data obtained was far from complete, for only 67 independent reflections were observed and no attempt was made to utilise any unresolved reflections, but it was less complicated by severe duplication of reflections than would have been the case for rotations about the [100] or [110] cube axes, and allowed very good
internal scaling factors to be determined, as many reflections were observed independently on several layer lines. The use of rotation photographs also removed the need for spot shape corrections, and the use of MoKα radiation minimised the problem of absorption.

However, in the measurement of the films themselves some improvement can be expected. The X-ray intensities were recorded using an isodensitracer, (see Fig. VIII, p. 147), and the density increment contours for a reflection were fixed by the commutator-wedge combination used. With this arrangement intensities can only be determined to the nearest contour, and hence values for weak reflections are very inaccurate, as is the case with many other measuring methods. These weak reflections therefore exhibit a large error range in the observed data. For instance in Table IX, is shown a full list of the observed $F_{hkl}$ values and many reflections with an $F_{hkl}$ value of less than 10, show considerable error ranges, some of the order of 30 per cent.

Recently, a "vernier contour" attachment has been designed and made in this laboratory for the Joyce-Loebl Isodensitracer, which allows much smaller density increments to be measured, and this attachment has been described by Milledge and Graeme-Barber (1968). A considerable improvement can be expected therefore, in the accuracy of the whole of the data, but especially in the case of weak reflections where improvements of the order of 50 per cent might be expected.
### TABLE IX

<table>
<thead>
<tr>
<th>INCLUSION</th>
<th>KIMBERLITE</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_{\text{S}} )</td>
<td>( F_{\text{S}} )</td>
</tr>
<tr>
<td>range</td>
<td>range</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( F_{\text{C}} )</th>
<th>( -\Delta^{+++} )</th>
<th>( +\Delta^{++} )</th>
<th>( F_{\text{C}} )</th>
<th>( -\Delta^{++} )</th>
<th>( +\Delta^{++} )</th>
<th>( F_{\text{C}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{KIMB} )</td>
<td></td>
<td></td>
<td>( 15 \text{E} )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Legend:**
- \( / / \) ALL ATOM CONTRIBUTIONS ADDITIVE.
- \( / / \) ONLY OXYGEN CONTRIBUTING.
- \( \) F.CALC. DECREASES.
- \( + \) F.CALC. INCREASES.
- \( -2 \) F.CALC. APPROX. PROPORTIONAL TO THE COMPONENT.
- \( \text{ID.C.} \) NO CHANGE IN F.CALC.
- \( < \) OBSERVED, BUT LESS THAN THAT VALUE.

**Site Occupation:**

- \( \text{H.H.} \) 0.316
- \( \text{H.L.} \) 0.317

**Available experimental data and an example of the expected changes in \( F_{\text{HKL}} \) for a given change in the divalent and trivalent site occupation ratio.**
The improvement in measuring the data would then allow a more accurate absolute scale factor to be determined. It has been mentioned before (p. 133), that this factor should be determined from reflections to which only oxygen contributes, and that these reflections are generally of weak intensity and hence not so accurately determined.

One of the main objects of this work has been to assess the changes that might be expected in the relative $F_{hk1}$ values with plausible changes in the chemical composition of the garnets, and in particular, for our problem, the effect of an increase in the chromium content in the trivalent site. In part of Table IX (p. 166) is shown the lists of $F_{calc}$ for the microprobed, E10, and 15E garnets; to make the calculated values virtually independent of everything but the site occupations, mean positional and temperature factor values between the kimberlite garnet and garnet 15E were deliberately chosen, (see top part of Table IX). Also in Table IX is shown the increase or decrease in each calculated $F_{hk1}$ value if a change occurs in the atomic contribution from the divalent ($\pm \Delta^{++}$) and trivalent ($\pm \Delta^{+++}$) sites. For this purpose garnet E10 was used as a standard (see also Table IV, p. 153).

The most useful reflections from which to observe the influence that a change of garnet chemistry has on the calculated $F_{hk1}$ values, are those reflections whose $F$ value simply increases or decreases in spite of opposing changes in the atomic contributions from the divalent and trivalent sites. In Table IX eight reflections fall into this class and these are listed below in Table X.
Taking reflection 10 2 0 as an example, it will be seen that the "Mg" site occupation decreases 14.5 per cent in going from garnet E10 to the kimberlite garnet, and this causes a 15.6 per cent decrease in the calculated F value, which in terms of the intensity on an X-ray film represents a 30 per cent change, (since $I \propto |F|^2$, see equation (1), p. 124). Similarly a 9.8 per cent increase in the "Mg" site from garnet E10 to garnet 15E produces some 40 per cent change in the intensity of the reflection. Thus when slight changes occur in the chemical composition of the garnet, quite drastic intensity changes can be expected in certain reflections.

<table>
<thead>
<tr>
<th></th>
<th>Kimberlite</th>
<th>-Δ+++</th>
<th>+Δ++</th>
<th>E10</th>
<th>-Δ++</th>
<th>+Δ+++</th>
<th>15E</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 2 0</td>
<td>5.51</td>
<td>-</td>
<td>-</td>
<td>6.53</td>
<td>+</td>
<td>+</td>
<td>7.71</td>
</tr>
<tr>
<td>10 2 0</td>
<td>-7.37</td>
<td>+</td>
<td>+</td>
<td>-6.63</td>
<td>-</td>
<td>-</td>
<td>-5.69</td>
</tr>
<tr>
<td>4 4 0</td>
<td>-6.18</td>
<td>+</td>
<td>+</td>
<td>-5.08</td>
<td>-</td>
<td>-</td>
<td>-3.63</td>
</tr>
<tr>
<td>10 6 0</td>
<td>-4.02</td>
<td>+</td>
<td>+</td>
<td>-3.39</td>
<td>-</td>
<td>-</td>
<td>-2.52</td>
</tr>
<tr>
<td>10 10 0</td>
<td>6.21</td>
<td>-</td>
<td>-</td>
<td>6.62</td>
<td>+</td>
<td>+</td>
<td>6.98</td>
</tr>
<tr>
<td>8 6 2</td>
<td>-2.56</td>
<td>+</td>
<td>+</td>
<td>-1.82</td>
<td>-</td>
<td>-</td>
<td>-0.96</td>
</tr>
<tr>
<td>4 4 4</td>
<td>-23.62</td>
<td>+</td>
<td>+</td>
<td>-21.35</td>
<td>-</td>
<td>-</td>
<td>-18.94</td>
</tr>
<tr>
<td>12 4 4</td>
<td>-8.71</td>
<td>+</td>
<td>+</td>
<td>-7.53</td>
<td>-</td>
<td>-</td>
<td>-6.26</td>
</tr>
</tbody>
</table>

Equiv. Site Occ.

"Mg" 0.363 0.317 0.286
"Al" 0.185 0.198 0.217

Percentage Site Occ. change from E10.

"Mg" 14.5 per cent 0 9.8 per cent
"Al" 6.6 per cent 0 9.6 per cent

Percentage Changes in $F_{cal}$ in some reflections.

10 2 0 15.6 per cent decrease

10 10 0 6.2 per cent decrease
With the analysis being completed, for only 61 reflections for the Kimberlite garnet and 67 reflections for the inclusion, some improvement in the standard deviations for the site occupancies might be expected simply by carrying out the analysis using more reflections. However, with a mineral of such high symmetry it might be necessary to set the crystal about some unusual axis in order to obtain more independent reflections and we intend to try to determine the optimum choice of axis. [Under these conditions it is probable that a greater proportion of the reflections are going to be weak, but the new assemblage to the isodensitracer should accurately measure their intensity.]

One further way of attaining greater precision would be to use only those reflections which can be determined with high accuracy as opposed to the present procedure of using all the data. For instance, the error ranges on several of the large observed $F_{hkl}$ values is relatively small (e.g. reflections 10 2 0, 8 4 0, 10 4 0, Table IX). Although this procedure would reduce quite drastically the number of reflections used a smaller standard deviation might in fact be achieved. However, enough reflections must be included to ensure that a realistic absolute scale factor and extinction correction can be found.

One further procedural point in the refinement is to decide from the recommendations to the variable parameters whether further refinement
would be profitable. It has already been shown (p. 129) that once the positional parameters had been fixed, the final values of the atomic scattering factors, and hence the equivalent site occupancies, are dependent on the interaction of the absorption, extinction, absolute scale, and temperature parameters. Since the absorption in the present content is small, and the absolute scale can be determined from the "oxygen" reflections, once an empirical extinction correction has been derived, it is the site occupation and temperature parameters which undergo the major variations during the course of the refinement. However, the overall scale factor and temperature factors are inversely correlated, so that for example a refinement for which the scale factor is lowered may merely result in a corresponding increase in the temperature factors, and scale changes of 1 or 2 per cent, (certainly tolerable in relation to the accuracy of the data used to fix the scale) can produce appreciable changes. This point can be illustrated from the refinement of the inclusion data starting from the microprobe analysis and is shown in Table XI. In refinement A, is a list of calculated $F_{hkl}$ values giving a residual of 5.42 per cent. This cycle of refinement indicated that for the site occupations and temperature factors used, our "absolute" scale factor was 4 per cent too high, but in order to approach it, the site occupations and temperature factors should be changed by the amounts shown. Reducing the absolute scale by 2 per cent when using the recommended changes, [Refinement B, R factor of 6.10 per cent] produces recommendations of the opposite sign. Such oscillations sometimes imply that too large a percentage of the
### TABLE XI

#### INTERACTION OF PARAMETERS DURING REFINEMENT.

**REFINEMENT A.**

<table>
<thead>
<tr>
<th>XYZ (FRACTIONS)</th>
<th></th>
<th>OXY.</th>
<th>MG.</th>
<th>AL</th>
<th>SI.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0268</td>
<td>0.0247</td>
<td>0.0295</td>
<td>0.005</td>
<td>0.000</td>
<td>0.005</td>
</tr>
<tr>
<td>0.0250</td>
<td>0.0250</td>
<td>0.0250</td>
<td>0.005</td>
<td>0.000</td>
<td>0.005</td>
</tr>
<tr>
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<td>0.015</td>
<td>0.015</td>
<td>0.005</td>
<td>0.000</td>
<td>0.005</td>
</tr>
<tr>
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<td>0.0033</td>
<td>0.0033</td>
<td>0.005</td>
<td>0.000</td>
<td>0.005</td>
</tr>
</tbody>
</table>

**ABSOLUTE SCALE FACTOR** = 0.99999

**B FACTORS SITE OCC.**

| OXY. | 0.47 | 1.00 |
| MG.  | 0.35 | 1.00 |
| AL.  | 0.35 | 1.00 |
| SI.  | 0.35 | 1.00 |

<table>
<thead>
<tr>
<th>F(g)</th>
<th>F(c)</th>
<th>DF</th>
<th>W.DF</th>
</tr>
</thead>
<tbody>
<tr>
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<td>20</td>
<td>30</td>
<td>40</td>
</tr>
<tr>
<td>50</td>
<td>60</td>
<td>70</td>
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<tr>
<td>90</td>
<td>100</td>
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<td>160</td>
</tr>
<tr>
<td>170</td>
<td>180</td>
<td>190</td>
<td>200</td>
</tr>
</tbody>
</table>

**REFINEMENT B.**

<table>
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<th>XYZ (FRACTIONS)</th>
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<th>MG.</th>
<th>AL</th>
<th>SI.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0268</td>
<td>0.0247</td>
<td>0.0295</td>
<td>0.005</td>
<td>0.000</td>
<td>0.005</td>
</tr>
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<td>0.0250</td>
<td>0.0250</td>
<td>0.0250</td>
<td>0.005</td>
<td>0.000</td>
<td>0.005</td>
</tr>
<tr>
<td>0.0117</td>
<td>0.015</td>
<td>0.015</td>
<td>0.005</td>
<td>0.000</td>
<td>0.005</td>
</tr>
<tr>
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<td>0.0033</td>
<td>0.0033</td>
<td>0.005</td>
<td>0.000</td>
<td>0.005</td>
</tr>
</tbody>
</table>

**ABSOLUTE SCALE FACTOR** = 0.98800

**B FACTORS SITE OCC.**

| OXY. | 0.47 | 1.00 |
| MG.  | 0.35 | 1.00 |
| AL.  | 0.35 | 1.00 |
| SI.  | 0.35 | 1.00 |

<table>
<thead>
<tr>
<th>F(g)</th>
<th>F(c)</th>
<th>DF</th>
<th>W.DF</th>
</tr>
</thead>
<tbody>
<tr>
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<td>30</td>
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</tr>
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<td>60</td>
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<tr>
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<td>100</td>
<td>110</td>
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<td>130</td>
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<td>160</td>
</tr>
<tr>
<td>170</td>
<td>180</td>
<td>190</td>
<td>200</td>
</tr>
</tbody>
</table>

**REFINEMENT RECOMMENDATIONS.**

**OXYGEN PARAMETER.**

| Δ X | 0.00006 |
| Δ Y | 0.00008 |
| Δ Z | 0.00009 |

<table>
<thead>
<tr>
<th>Δ B FACTORS</th>
<th>Δ SITE OCC.</th>
<th>Δ RESIDUAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>OXY.</td>
<td>0.0005</td>
<td>0.0005</td>
</tr>
<tr>
<td>MG.</td>
<td>0.0006</td>
<td>0.0006</td>
</tr>
<tr>
<td>AL.</td>
<td>0.0007</td>
<td>0.0007</td>
</tr>
<tr>
<td>SI.</td>
<td>0.0008</td>
<td>0.0008</td>
</tr>
</tbody>
</table>

**ABSOLUTE SCALE FACTOR** = 0.9973

**RESIDUAL** = 0.96

**WEIGHTED RESIDUAL** = 0.94
calculated shift has been applied (see for example Sparks p. 170, 1961), but in this context it shows that no improvement can be expected from further cycles of refinement. A further indication is that the recommended changes are less than the estimated standard deviations, though not as small a fraction as would normally be desirable.

Once the equivalent site occupancies of the garnet have been determined as accurately as possible, several other problems still remain. The site occupation parameters for the case of garnet consist of some combination of three elements in the divalent site, (e.g. Ca, Fe, Mg) [really four, but Mn is virtually absent], and three elements in the trivalent site (Cr, Al, Fe). In order to assign the proportion of each element in each site, at least two other parameters must be determined for the garnet, because the number of unknown parameters exceed the determinative equations obtainable solely from the X-ray results. Density, refractive index, magnetic susceptibility, and unit cell size, are four obvious parameters that may assist in defining the garnet chemistry. They will have to be measured to an accuracy of 1 or 2 per cent to be really determinative. In the X-ray work, anomalous dispersion and differential X-ray absorption may also be useful, and this possibility is now being explored in this laboratory, (Henriques. Thesis in preparation).

It would seem that as a quantitative analytical technique X-ray site occupation refinement should be favourable in cases of simple isomorphous mineral groups, such as the olivine series, where only one
ion is substituted by another, and where there is little substitution from elements outside the series, at least in olivines of the kimberlite environment. In these cases a unique chemistry may be determined directly from the X-ray result. However, in the more complicated isomorphous series such as garnet, knowledge of the number of electrons in a given site still leads to a certain degree of chemical ambiguity. The technique can of course always be used, as in this case, to compare the data from the unknown garnet with values calculated for any desirable composition. Known garnet series have not previously been considered in terms of the number of electrons per site, or of the sums or ratios of the electrons in the divalent and trivalent sites. We propose to express some of the established relationships between chemistry and physical properties in these terms to see whether they may in fact suggest interesting correlations.
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In the presence of many smaller fractures, and the presence of a
garnet inclusion, the specimen may explain for the natural origin
erecting (Chapter III).

Hoping the examination of the garnet still unobserved by the
diamond, the fracture splits through the garnet twice, by natural fracture as
shown in Fig. 1, the fracture plane being approximately parallel to
a (100) plane of the diamond and cut a (111) diamond plane. The
fracture can also possibly sometimes between the fracture of the diamond
and in the smaller half of the specimen, a typical split. Dehiscence was
observed (Fig. 1b). This fracture, above largest visible distance were
0.01 cm, and located towards one edge of the garnet, was
APPENDIX I

TABULATED EXPERIMENTAL DATA

DIAMOND D1

The diamond: A dodecahedron of average edge 1.0 mm with no visible fractures and whose faces were etched and slightly rounded. The specimen was classified as a Type I by X-rays, but the Laue reflections indicated that it was somewhat strained.

Included in the diamond was a good single crystal of garnet whose cell edge whilst still enclosed by the diamond measured 11.513 ± 0.002 Å.

In the absence of any obvious fractures and the presence of a garnet inclusion, the specimen was chosen for the thermal expansion experiments. (Chapter III)

During the expansion of the garnet whilst still enclosed by the diamond, the diamond split through the garnet into two unequal halves shown in Fig. 1a; the fracture plane being approximately parallel to a (100) plane of the diamond and not a (111) cleavage plane. The garnet was also unevenly distributed between the halves of the diamond and in the smaller half of the garnet, a very dark red inclusion was observed (Fig. 1b). This inclusion, whose largest visible dimensions were 0.03 x 0.02 mm, was located towards one edge of the garnet, was
roughly octahedral in shape, and lay just beneath the garnet surface. In removing this section of the garnet from the diamond, it broke into several fragments. The deep red inclusion was recovered, but whilst a few faint Laue spots showed it to be crystalline, an identification of the material was not possible. This specimen is still available for further work.

The larger piece of the garnet was also successfully released from the diamond and found to be a well-faceted crystal Fig. 1c and Fig. 1d.

The garnet when laid on the fracture surface consisted of eight faces in all arranged so that one facet, an irregular hexagon, was surrounded by several differently inclined side faces one of which was broken. Whilst facets 1 and 2 gave excellent reflections during goniometric work, the latter exhibited in a number of places near its periphery, surface features in the form of minute stepped faces which accentuated the overall hexagonal outline of this facet (Fig. 1d). Faces 3 and 4 were minutely pitted and as far as could be seen, the minute pits were evenly distributed and had no particular form at magnification of (x 180). The remaining faces 5, 6 and 7 were striated, and the latter was also slightly rounded. In the case of the striations on facets 5 and 6 these were shown to be parallel to a [111] direction in the garnet, but no specific crystallographic direction was determined for those on face 7.
In order to determine the morphology several X-ray photographs were taken to find a zone axis as some of the faces have relatively high indices and no zone axis was initially recognised from goniometric measurements. Six of the seven faces were indexed, the seventh being a rounded striated face, and these together with interfacial angles are given in Table 1a. (See also Fig. 1d.)

A qualitative electron microprobe analysis showed the presence of Mg, Al, Si, Ca, Fe, Cr, with the Cr content being very similar to the Fe content. The refractive index measured in standard liquids was $1.786 \pm 0.005$ which with the cell parameter for the freed garnet of $11.521 \pm 0.002 \overset{\circ}{A}$ indicated the specimen to be a pyrope-almandine.

The relative crystallographic orientation between the inclusion and the diamond was also determined. The parallel directions of the garnet and diamond are given below but discussed in detail in Chapter II.

<table>
<thead>
<tr>
<th>garnet</th>
<th>diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>110</td>
<td>111</td>
</tr>
<tr>
<td>111</td>
<td>110</td>
</tr>
<tr>
<td>211</td>
<td>112</td>
</tr>
</tbody>
</table>

In Figs. 1e, 1f, and 1g are shown the majority of the internal facets of the diamond left when the garnet was removed. The surfaces reproduce exactly (mag. x 180) the features observed in the garnet and this indicates that the surface markings of the garnet were present before enclosure by the diamond.


**TABLE 1a**

Interfacial Angles of Garnet Inclusion in D1.

<table>
<thead>
<tr>
<th>Zone (a)</th>
<th>Faces 1, 2, 3.</th>
<th>Crystal set about [111]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal Face</td>
<td>Goniometer Reading</td>
<td>Interfacial Angle</td>
</tr>
<tr>
<td>1</td>
<td>351° 45'</td>
<td>69° 45'</td>
</tr>
<tr>
<td>2</td>
<td>282° 00'</td>
<td>51° 30'</td>
</tr>
<tr>
<td>3</td>
<td>230° 30'</td>
<td></td>
</tr>
</tbody>
</table>

Average of two sets of readings

<table>
<thead>
<tr>
<th>Zone (b)</th>
<th>Faces 4, 5, 6.</th>
<th>Crystal set about [111]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>320° 00'</td>
<td>54° 00'</td>
</tr>
<tr>
<td>2</td>
<td>14° 00'</td>
<td>38° 30'</td>
</tr>
<tr>
<td>5</td>
<td>52° 30'</td>
<td>27° 00'</td>
</tr>
<tr>
<td>6</td>
<td>79° 30'</td>
<td></td>
</tr>
</tbody>
</table>

Average of five sets of readings

Deviations from the calculated interfacial angles particularly in Zone (b), arise from the imperfections exhibited by the crystal facets.
Since the garnet faces had been indexed, it was also possible to see if the important crystallographic directions of the diamond and the garnet shown to be parallel by the relative orientation (see above), were normal to mutual crystal faces. There was a (110) face of the garnet parallel to a (111) face on the diamond. This fact was established by X-ray Laue photographs. Thus the structural epitaxy determined was also a morphological one.

**DIAMOND D2**

The diamond: A twinned octahedron of side 1.20 mm, the twin plane being parallel to a (111) face. The faces on both sides of the twin plane were built up by a series of shallow growth sheets of diminishing size which gave a convex curvature to the peripheral region of these faces. (Fig. 2a.) A shallow groove crossed one of the faces. The diamond was classified by X-rays as a strain-free Type II.

In the larger half of the diamond was a faceted deep-red coloured garnet (Fig. 2b). Its cell parameter measured inside the diamond was 11.529 ± 0.002 Å and there were no birefringence effects in the adjacent diamond.

Because this diamond exhibited similar characteristics to specimen DI, it was put aside for thermal expansion measurements (Chapter III).

The relative orientation of the garnet to the diamond was determined and the parallel directions are given below, but discussed
in Chapter II.

<table>
<thead>
<tr>
<th>garnet</th>
<th>diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>211</td>
</tr>
<tr>
<td>211</td>
<td>011</td>
</tr>
<tr>
<td>011</td>
<td>111</td>
</tr>
</tbody>
</table>

The large flat face of the garnet, Fig. 2b, was shown to be parallel to a [111] direction in the diamond and this face was later indexed as a (110) garnet face. Thus the structural epitaxy was again shown to be a morphological one. The size of the garnet specimen (0.2 x 0.06 x 0.06 mm) and the smallness of the smooth facets, prevented the determination of the remaining morphology.

The size of the crystal also prevented the determination of an accurate refractive index. However, the measurement was between 1.78 and 1.80, and with a cell edge of 11.534 ± 0.002 Å measured for the freed silicate, the garnet was of pyrope composition.

**DIAMOND D3**

The diamond: A distorted rhombic dodecahedron of average edge 1.25 mm with striated and considerably curved faces. The striations were parallel to 111 directions and except for one region shown in Fig. 3a, the diamond was free from fractures. The specimen was a strain-free, untwinned Type II diamond.

Two inclusions of calcite were found in the fracture zone; one orange in colour and sheet-like in form, and the other more aggregated
giving a deeper red hue Fig. 3b. The sheet-like calcite covered an area of 0.0025 sq. mm. The form of this inclusion was suggestive of material penetrating along some pre-existing diamond fracture plane.

The second inclusion was not connected to the first (Fig. 3b) and consisted of an irregular shaped aggregate which in part consisted of a series of diminishing triangular steps similar to those on diamond surfaces.

Both the inclusions had openings to the surfaces of the diamond (Fig. 3b).

The calcite was polycrystalline, consisting of unoriented powder in which there were a few larger crystallites (Fig. 3c).
DIAMOND D4

The diamond: A transparent perfectly-formed octahedron of edge 1.0 mm. The major part of all the (111) faces were free from surface markings except near the four fold axes where some imperfections were observed. The regular arrangement of these fractures pointed to them being growth phenomena rather than a product of abrasion. The diamond was classified by X-rays as a Type I.

Clearly visible within the diamond were eight reddish brown inclusions belonging to the spinel series; the colour being darker than that of the garnet inclusions in D1 and D2.

The largest crystal, Fig. 4a, was tabular in habit with an irregular outline. It was elongated approximately parallel to [110] direction in the diamond and the flat part of the crystal appeared to be parallel to a [111] diamond direction. The thickness varied between 0.1 and 0.2 mm and where the thickness was greatest, small crystal facets formed the sides of the mineral, one of which seemed parallel to a [111] direction in the diamond. From the inner edge of this crystal stemmed an arcuate fracture.

An irregular rod-like spinel measuring 0.5 mm in length lay adjacent to the former inclusion (Fig. 4b). It was similarly elongated and had a series of small facets making up the sides.

Of the other inclusions, five were small rounded anhedral crystals about 0.1 mm in size, but the sixth had a most irregular shape shown in
Fig. 4b. It exhibited a series of broad shallow steps lying parallel to the long direction of the crystal (Fig. 4b), and this feature was also observed on a facet of the rod-like spinel and on the flat surface of the largest inclusion.

The X-ray rotation photograph of the spinels shown in Fig. 4c, gave rough cell parameters of 8.30 Å and in the absence of other data, it is not possible to define exactly the specimen within the spinel group. The cell parameter may reflect the stoichiometric composition, but more likely represents a substitution in a particular species resulting in the increase of the cell parameter. The mineral picotite* has been found as a Russian diamond inclusion (Orlov 1960), and the cell parameter of 8.29 Å is similar to that of the present inclusion.

The specimens were too small for further work and the existence of several separate crystals prevented relative orientation studies.

* **picotite**: A mineral of the spinel series resulting from substitution of Cr in the Al position of the mineral hercynite (Fe$^{2+}$Al$_2$O$_4$).
**DIAMOND D5**

The diamond: A dodecahedron of average edge 1.5 mm elongated in a [111] diamond direction (Fig. 5a); the facets being rounded and showing [110] diamond laminations. The specimen was classified as a strain-free Type II diamond.

The only prominent fracture which penetrated the diamond (Figs 5a and 5b), contained a veneer of red haematite or ilmenite. Fig. 5c shows part of the fracture surface when the diamond was broken. The sparseness of the mineral on the plane occurred when the diamond fractured; it does not reflect a poor initial distribution.

A qualitative microprobe analysis showed the presence of only Fe, which strongly suggests that the specimen was haematite.

Like the calcite of D3, the specimen was an unoriented powder with an occasional crystallite giving rise to discrete spots on the powder rings (Fig. 5d).
DIAMOND D6

The diamond: A triangular-shaped macle of edge 2.5 mm and of thickness 1.0 mm. The (111) faces showed [110] laminations which caused the terminating faces to be considerably rounded. The specimen was a strain-free Type II diamond.

At first the only observed feature was a small fracture containing some reddish coloured material (Fig. 6a). On fragmenting the diamond, however, two small inclusions of average size less than 0.1 mm and two relatively large ones of average size 0.15 mm were discovered attached to diamond fragments.

A colourless well faceted crystal of enstatite can be seen in Figs 6a and 6b. The cell parameters of the mineral measured whilst still partly in the diamond were,

\[
\begin{align*}
a & = 18.231 \pm 0.003 \AA \\
b & = 8.828 \pm 0.002 \AA \\
c & = 5.185 \pm 0.025 \AA \\
\end{align*}
\]

The relative crystallographic orientation of the enstatite to the diamond is discussed in Chapter II.

The veneer of brown-yellow material was distributed intermittently along the fracture plane; parallel to a (110) plane in the diamond. The largest visible extent of the smear was 0.023 mm long (Fig. 6a), and other small patches of similar coloured material was observed in directly adjacent areas in the diamond.
Laue photographs of several hours duration revealed the veneer to be in powder form without being preferentially oriented. A prominent doublet was obtained from one photograph Fig. 6e, and from another Fig. 6d, a prominent single powder line with a 3.04 Å spacing. The doublet of the first photograph resembles in X-ray data two strong lines of the mineral xenotime (see also diamond D6), and the spacing of 3.04 Å is the strongest line for the mineral calcite (see diamond D3).

Two further inclusions are shown in Fig. 6e; a garnet and an olivine. The garnet was deep-red in colour, had a euhedral morphology, but was slightly elongated being 0.092 mm long and 0.067 mm wide in the two visible dimensions. No form of surface marking was observed on visible facets and the crystal cell edge was 11.532 ± 0.002 Å, and the refractive index was between 1.76 and 1.78.

The colourless olivine also had a distinct morphology with no surface markings being 0.08 mm wide and 0.17 mm long. The relative orientation of the specimen to the diamond was found (Chapter II), but the cell parameters were not determined as the specimen shattered when attempts were made to release the inclusion from the diamond.

The final small inclusion was roughly rectangular in shape measuring 0.04 x 0.01 x 0.02 mm, Fig. 6f. X-ray Laue photographs established the specimen to be crystalline, but so far the mineral has not been identified. It is, however, available for further study.
DIAMOND E7

The diamond: A dodecahedron of edge 1.5 mm and showing numerous striations parallel to [110] diamond directions, with several fractures cutting across the surface striations. X-ray Laue photographs classified the diamond as a considerably strained Type II.

Within the diamond was observed a red inclusion but an X-ray pattern of this material could only be obtained when the diamond was broken. The red inclusion was an aggregate of kaolinite (Fig. 7a) giving an unoriented X-ray powder (Fig. 7b). The kaolinite measured 0.03 mm by 0.015 mm and associated with it were several smears of brown-yellow material (Fig. 7a), and a further selection are shown in Fig. 7c. From one of these diamond fragments a 7 Å powder spacing was determined which suggested that the smears were kaolinite, although the spacing is common to other minerals in the same group (e.g. dickite).

The material in the fracture planes was generally evenly distributed but in a few places there was a concentration producing a much redder material resembling the kaolinite colour. Also, in certain positions the distribution of the material was mesh-like (Fig. 7d), and probably resulted from the process whereby material penetrated along the fracture.
DIAMOND D8

The diamond: Essentially a dodecahedron with several additional faces which caused the dodecahedral edge to vary in length between 0.5 mm and 1.5 mm. There were no obvious striations on the facets, but the majority were slightly convex. The diamond was strain-free and classified by X-rays as a Type II.

Towards one side of the specimen were two sheet fractures roughly parallel to one another but at different levels near the surface of the diamond. In the lower fracture which intersected the surface at one point shown in Fig. 8a, was some brown coloured material covering the whole of the fracture plane 1 mm x 0.75 mm (Fig. 8b). Laue photographs taken parallel and perpendicular to the plane of the material, identified it as xenotime (YPO₄). The xenotime was in powder form (Fig. 8c), not preferentially oriented, and did not lie in any specific diamond plane.
Figure 8c
DIAMOND D9

The diamond: A very etched and broken octahedron with an edge averaging 1.5 mm. The (111) faces showed growth sheets of diminishing size giving these facets a stepped perspective and several fractures were evident. The diamond was essentially a strain-free Type I.

In one corner of the diamond was identified a cluster of three reddish-brown crystalline rutiles. One of the rutiles lay in a hollow in the surface of the diamond in such a manner that it was trapped, but loose in the cavity. The other two specimens were enclosed by the diamond, and less than 0.2 mm away. The relative orientations of the rutiles to the diamond could not be determined due to the proximity of the three crystals to one another.

When the diamond was fragmented the inclusion in the hollow of the diamond was recovered, but the other inclusions were partially broken. The complete crystal had a distinct morphology (Figs 9a and 9b), and although the facets were etched, the indices of the faces were determined and are given in Table 9a.

The other two larger crystals were similar in colour but had no distinct morphology (Figs 9c and 9d).

The cell parameters of the three unstrained rutile crystals are set out below.
<table>
<thead>
<tr>
<th>Crystal Face</th>
<th>Goniometer Reading</th>
<th>Interfacial Angle</th>
<th>Calculated Angle</th>
<th>Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>88° 30'</td>
<td>52° 30'</td>
<td>56° 00'</td>
<td>100</td>
</tr>
<tr>
<td>B</td>
<td>36° 00'</td>
<td>88° 00'</td>
<td>90° 00'</td>
<td>320</td>
</tr>
<tr>
<td>C</td>
<td>308° 00'</td>
<td>38° 00'</td>
<td>33° 00'</td>
<td>320</td>
</tr>
<tr>
<td>D</td>
<td>270° 00'</td>
<td>57° 00'</td>
<td>56° 00'</td>
<td>100</td>
</tr>
<tr>
<td>E</td>
<td>213° 00'</td>
<td>81° 00'</td>
<td>79° 00'</td>
<td>320</td>
</tr>
<tr>
<td>F</td>
<td>132° 00'</td>
<td>45° 00'</td>
<td>45° 00'</td>
<td>110</td>
</tr>
<tr>
<td>A</td>
<td>89° 00'</td>
<td></td>
<td></td>
<td>100</td>
</tr>
</tbody>
</table>

Average of four sets of readings.

Face (110) was determined by X-rays.

The differences between certain of the determined and calculated interfacial angles arise from the imperfections of those crystal faces.
The cell parameters of the rutiles were computed from several Straumanis X-ray photographs. The relatively high accuracy for the c-axis of rutile No. 2, was obtained when the crystal was set about the [110] crystal direction, because a first layer 233 reflection which was very strong and easy to measure occurred at a very high theta value. The a-axis parameters differ from that determined for rutile by Cromer and Harrington (1955), but the values fall within the 2 per cent variation observed in the Ti-O bond length by Bauer (1956) and given as the cause of the variation in the cell edge.

**DIAMOND D10**

The diamond: A clear octahedron of edge 0.75 mm with rounded corners, and with several faces showing a stepped perspective making them slightly convex (Fig. 10a). The octahedron was shown by X-rays to be a strain-free Type I diamond.

The diamond contained four olivine inclusions, three being approximately at the same level in the specimen. Around two of the largest inclusions were disc-shaped zones which did not extend to the surface of the diamond, but at one point linked three of the inclusions (Fig. 10a). The fracture zones appeared black and their size was proportional to the size of the inclusion; the diameter of the fracture zone being approximately twice the diameter of the crystal inclusion (see Figs. 10a and 10b). Around the fourth inclusion there was no fracture surface and no strain birefringence effects were observed.
On breaking the diamond, the disc-fracture surface was exposed and this is shown in Fig. 10b. Lying in this plane were two olivines partially enclosed by the diamond, and the internal facets of a third olivine which was recovered (Fig. 10c). The large inclusion was colourless and rather tabular in habit although the facet exposed was not a flat one, and on one side and actually touching this mineral, was a much smaller euhedral olivine crystal which was coated on all observed facets by a black metallic substance (Fig. 10d). The cell parameters for these two crystals are given below.

<table>
<thead>
<tr>
<th>Crystal A (Largest)</th>
<th>Crystal B</th>
</tr>
</thead>
<tbody>
<tr>
<td>a 4.769 ± 0.025 Å</td>
<td>4.773 ± 0.025 Å</td>
</tr>
<tr>
<td>b 10.216 ± 0.003 Å</td>
<td>10.214 ± 0.003 Å</td>
</tr>
<tr>
<td>c 5.991 ± 0.002 Å</td>
<td>5.990 ± 0.002 Å</td>
</tr>
</tbody>
</table>

The values of the b and c cell parameters of these minerals correspond, according to Yoder and Sahama (1957), to a chemical composition for the olivines of

\[92.5 \pm 1\] per cent Mg for Crystal A and

\[92.8 \pm 1\] per cent Mg for Crystal B.

The third olivine inclusion was colourless, euhedral, and free from surface markings (Fig. 10c), and the several faces in the [h0l] zone were indexed using a goniometer and universal stage respectively. A panoramic view of the [0kl] zone and the other facet is given in Table 10a. Unfortunately, the remaining faces of the crystal were not indexed, and its cell parameters not determined as the crystal was then lost.
**TABLE 10a**

**PANORAMIC DISPLAY OF FACES IN THE [010] ZONE OF OLIVINE**

![Diagram of faces in the [010] zone of olivine]

<table>
<thead>
<tr>
<th>CRYSTAL FACE</th>
<th>READING</th>
<th>INTERFACIAL ANGLE</th>
<th>CALCULATED ANGLE</th>
<th>INDICES</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>51.9</td>
<td>40° 24'</td>
<td>41° 24'</td>
<td>001</td>
</tr>
<tr>
<td>2</td>
<td>102.3</td>
<td>110° 0'</td>
<td>108° 0'</td>
<td>032</td>
</tr>
<tr>
<td>3</td>
<td>212.3</td>
<td>29° 36'</td>
<td>30° 27'</td>
<td>011</td>
</tr>
<tr>
<td>5</td>
<td>241.9</td>
<td>40° 36'</td>
<td>41° 24'</td>
<td>001</td>
</tr>
<tr>
<td>6</td>
<td>282.5</td>
<td>48° 54'</td>
<td>48° 48'</td>
<td>032</td>
</tr>
<tr>
<td>7</td>
<td>331.4</td>
<td>49° 48'</td>
<td>48° 48'</td>
<td>010</td>
</tr>
<tr>
<td>8</td>
<td>21.2</td>
<td>40° 36'</td>
<td>41° 24'</td>
<td>001</td>
</tr>
</tbody>
</table>

**UNIVERSAL STAGE (h01) FACE**

<table>
<thead>
<tr>
<th>UNIVERSAL STAGE</th>
<th>(h01) FACE</th>
<th>ANGLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>62° 0'</td>
<td>60° 0'</td>
</tr>
<tr>
<td>4</td>
<td>52° 0'</td>
<td>54° 0'</td>
</tr>
<tr>
<td>5</td>
<td>64° 6'</td>
<td>63° 0'</td>
</tr>
</tbody>
</table>

**AVGAGE OF 4 SETS OF READINGS**


The black metallic material lying in the disc-fracture zone and probably also coating one of the olivine crystals proved to be powdered pentlandite \((\text{FeNi})_9 \text{S}_3\). A flake measuring 0.025 x 0.019 mm was removed from the disc-fracture and the identification was made by means of X-ray Laue photographs, and a qualitative microprobe analysis which revealed the presence of Ni, Fe, and S.

The diamond was then further broken down in an attempt to release the inclusions, but the diamond shattered and the largest inclusion and the one coated with pentlandite were destroyed, but the fourth olivine was retrieved in one piece and diagrams of the \([hk0]\) zone of it are shown in Fig. 10e.

The olivine was colourless, and in Table 10b is given the results of goniometric work completed for the \([0kl]\) and \([hk0]\) zones of the mineral. Fig. 10f shows the panoramic display of the faces in the \([0kl]\) zone. No attempt was made to index the few remaining faces in view of their smallness, and all the facets observed exhibited no surface markings.

The cell parameters of the olivine measured when free from the diamond were

\[
\begin{align*}
a & = 4.761 \pm 0.002 \\
b & = 10.218 \pm 0.003 \\
c & = 6.003 \pm 0.030
\end{align*}
\]

This indicates a composition of 91.7 per cent Mg for the olivine.

During the course of this study, the relative orientation of three of the four olivines to the diamond was determined, and these
are discussed in Chapter II as olivines 1, 2, and 3.

**TABLE 10b**

_Interfacial Angles of an Olivine Inclusion from D10_

Zone [hk0] - see Fig. 10e.

<table>
<thead>
<tr>
<th>Crystal Face</th>
<th>Goniometer Reading</th>
<th>Interfacial Angle</th>
<th>Calculated Angle</th>
<th>Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40° 43'</td>
<td>113° 00'</td>
<td>115° 00'</td>
<td>010</td>
</tr>
<tr>
<td>6</td>
<td>153° 43'</td>
<td>157° 00'</td>
<td>155° 00'</td>
<td>110</td>
</tr>
<tr>
<td>7</td>
<td>310° 43'</td>
<td>22° 21'</td>
<td>25° 00'</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>335° 43'</td>
<td>67° 43'</td>
<td>65° 00'</td>
<td>010</td>
</tr>
<tr>
<td>1</td>
<td>40° 43'</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Zone [Okl] - see Fig. 10f.

<table>
<thead>
<tr>
<th>Crystal Face</th>
<th>Goniometer Reading</th>
<th>Interfacial Angle</th>
<th>Calculated Angle</th>
<th>Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>195° 15'</td>
<td>23° 15'</td>
<td>23° 00'</td>
<td>010</td>
</tr>
<tr>
<td>2</td>
<td>218° 30'</td>
<td>180° 15'</td>
<td>180° 00'</td>
<td>041</td>
</tr>
<tr>
<td>3</td>
<td>38° 15'</td>
<td>67° 30'</td>
<td>67° 00'</td>
<td>041</td>
</tr>
<tr>
<td>4</td>
<td>105° 45'</td>
<td>49° 30'</td>
<td>49° 36'</td>
<td>001</td>
</tr>
<tr>
<td>5</td>
<td>155° 15'</td>
<td>40° 00'</td>
<td>40° 24'</td>
<td>010</td>
</tr>
<tr>
<td>1</td>
<td>195° 15'</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average of four sets of readings.

The larger differences between determined and calculated interfacial angles in the [hk0] zone, arise because of the smallness of the crystal faces in that zone (see Fig. 10e).
The diamond: Roughly dome-shaped, a flat cleavage plane forming the base of the dome, and also acting as a "window" through which examination of the specimen could be made. The edges of the dome made a rough octahedron, with the upper part consisting of rounded and etched octahedral faces (Fig. 11a). The diamond was classified by X-rays as an unstrained Type II.

The surface of the cleavage plane exhibited a great deal of pitting, and in particular, two cavities were prominent, one roughly hexagonal and the other tabular in shape, both having growth features on the shoulders (Fig. 11b). Fractures stemming from these cavities penetrated into the diamond, and several of them appeared to reach two light green inclusions.

These inclusions were two diopsides, which were tabular in habit and lay approximately at the same level in the diamond. Also contained by the diamond but more in the dome of the specimen, were two much smaller equidimensional transparent inclusions, surrounded by small disc-shaped fractures (Fig. 11a and 11b). Under polarised light, these transparent crystals gave bright birefringence colours, suggestive of the mineral olivine.

The diamond when broken, released one of the diopsides and partially exposed the other, but the two transparent crystals were not recovered.
The crystal of diopside (Fig. 11c) was slightly broken, but had a distinct rhombic tabular habit and consisted of two relatively large prism faces bordered principally by 111 faces. This information was determined by goniometric work the details of which are given in Table 11a.

Except for face B (Fig. 11c), the diopside facets were evenly etched (x 160), and gave rise to rather large differences between determined and calculated interfacial angles (see Table 11a), and the other prism face E was broken and uneven in one part, showing many striations parallel to a [110] diopside direction. Laue photographs further showed the crystal to be strained and partially twinned. The latter effect could be eliminated from the X-ray photographs by varying the position of the crystal with respect to the X-ray source, and it was considered that the effect resulted from the uneven part of the face B.

The cell parameters for the diopside were

\[
\begin{align*}
\text{Diopside} & : a = 9.708 \pm 0.004 \, \text{Å} \\
b & = 8.910 \pm 0.050 \\
c & = 5.117 \pm 0.002 \\
\end{align*}
\]

\[
\begin{align*}
\theta & = 105^\circ 30' \pm 30' 
\end{align*}
\]

The Laue photographs also revealed the presence of preferentially oriented kaolinite powder associated with the diopside crystal, although no evidence of this was observed optically (x 160).

To investigate whether the kaolinite powder was in some way related to the morphology of the diopside, a series of eighteen 10°
**FIG. 11c**

![Crystal diagram](image)

**TABLE 11a**

<table>
<thead>
<tr>
<th>CRYSTAL FACE</th>
<th>READING</th>
<th>INTERFACIAL ANGLE</th>
<th>CALCULATED ANGLE</th>
<th>INDICES</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>284° 0'</td>
<td>54° 30'</td>
<td>55° 0'</td>
<td>111</td>
</tr>
<tr>
<td>B</td>
<td>230° 30'</td>
<td>70° 30'</td>
<td>76° 0'</td>
<td>000</td>
</tr>
<tr>
<td>C</td>
<td>160° 0' *</td>
<td>70° 30'</td>
<td>49° 0'</td>
<td>111</td>
</tr>
<tr>
<td>D</td>
<td>105° 30'</td>
<td>54° 30'</td>
<td>54° 0'</td>
<td>111</td>
</tr>
<tr>
<td>E</td>
<td>51° 0'</td>
<td>54° 30'</td>
<td>26° 0'</td>
<td>100</td>
</tr>
<tr>
<td>F</td>
<td>23° 0'</td>
<td>28° 0'</td>
<td>99° 0'</td>
<td>311</td>
</tr>
<tr>
<td>A</td>
<td>284° 0'</td>
<td>99° 0'</td>
<td>99° 0'</td>
<td>111</td>
</tr>
</tbody>
</table>

* poor reading.*
X-ray oscillation photographs about the b-axis were taken, so that the pole figure for the (001) and (200) powder lines of kaolinite could be plotted with respect to the diopside, in the manner described by Barrett (1943) (chapter IX, p. 158–162).

In Figs. 11d and 11e are shown the upper halves of these pole figures, the kaolinite being evenly distributed about the meridian, and as the (200) plane of kaolinite has the same spacing as the (131) plane, (Brindley and Robinson (1946)), this has been plotted on Fig. 11c.

The distribution of the (001) pole of kaolinite has approximately two-fold symmetry which may reflect the two-fold axis of the diopside, and the maximum concentrations of the (001) kaolinite pole lie near to the pole (001) and (001) of the diopside.

In Fig. 11e, the only concentration of the (200) pole of kaolinite lies close to the (100) pole of diopside. Unlike the other pole figure, however, there is no obvious symmetry.

There may be therefore, an association between the principal axes of the diopside and the kaolinite; the kaolinite powder being related to the diopside morphology by the (100) plane of diopside and the (200) plane of kaolinite, but not by the other condition.

The second diopside seen in Figs. 11f and 11g was similar in colour to the first one, had etched faces and one irregular facet was
FIG 11d

(001) POLE FIGURE OF KAOLINITE

FIG 11e

(100) and (13\bar{1}) POLE FIGURE OF KAOLINITE
striated Fig. 11g. The specimen also had kaolinite in some way attached to it, but the diamond fragment to which the diopside was attached, prevented the determination of the pole figure.

Facet B, Fig. 11g, was identified by X-rays as (001), and goniometry showed face A to be 181° away and was indexed as (001). The diopside cell parameters measured whilst still in the diamond were:

\[
\begin{align*}
\text{Diopside} & : a = 9.685 \pm 0.010 \text{ Å}, \quad b = 8.910 \pm 0.050 \text{ Å}, \quad c = 5.119 \pm 0.005 \text{ Å} \\
& = 105° 30' \pm 30'
\end{align*}
\]

The relative crystallographic orientation to the diamond of the diopside was also determined and is discussed in Chapter II.

**DIAMOND D12**

The diamond: A very irregular octahedron of edge 1.5 mm with several rounded and block-etched faces (Fig. 12a). The diamond was an unstrained Type II. Apart from broken octahedral corners, the specimen showed no obvious fracturing, but a hollow adjacent to a red-brown inclusion showed internal faceting indicating the former presence of some crystals.

Optically, the red-brown inclusion appeared to have a morphology and only a very small fracture emanated from the inclusion, but did not reach the surface. However, X-ray Laue photographs indicated the mineral to be a powdered aggregate of quartz, although some large
crystallites within the powder were present (Fig. 12b).

In view of the great interest in the presence of quartz as a diamond inclusion, the specimen has been preserved intact.
DIAMOND D13

The diamond: A triangular "flat" of 2.0 mm side and 1.0 mm thickness with one side smooth with sharp edges, and the other consisting of piles of triangular plates of diminishing size Fig. 13a. The diamond was classified by X-rays as an unstrained Type II.

The diamond contained two colourless, but highly birefringent olivine inclusions, both elongated in a [110] diamond direction (Fig. 13a).

The larger inclusion had a tabular habit of length 0.15 mm and a maximum thickness of 0.09 mm. The thickness varied owing to a step feature which ran the length of the c-axis of the crystal, and on the higher side of this feature were several much smaller steps (Fig. 13b). The edges of the crystal were particularly rounded, and a series of striations also ran parallel to the c-axis of the olivine. Surrounding the crystal was a disc-shaped fracture which may have at one point reached the diamond surface, but the attitude of this plane was governed by the inclusion, for it was developed parallel to the tabular habit of the crystal and was inclined to the (111) surface of the diamond (Fig. 13a).

The second crystal was euhedral and clear of surface markings. In the vicinity of this inclusion there were two fractures (Fig. 13c), but these did not intersect the mineral, and may have been fractures not associated with the olivine.
Neither inclusions caused a strain effect in the diamond.

On fragmentation the diamond shattered and only the largest inclusion was recovered, it being split along the step feature parallel to the direction of elongation.

Fig. 13d shows the morphology of the crystal together with the interfacial angles. These angles are not very precise in view of the roundness of the individual facets. The face (010) and (010) were determined by X-rays.

The olivine cell parameters were

\[
\begin{align*}
a & \quad b & \quad c \\
4.761 \pm 0.002 \, \text{Å} & \quad 10.224 \pm 0.003 \, \text{Å} & \quad 6.003 \pm 0.030 \, \text{Å}
\end{align*}
\]

This corresponds to a chemical composition of 91.0 ± 1 per cent Mg for the olivine.
FIG. 13d

INTERFACIAL ANGLES

<table>
<thead>
<tr>
<th>CRYSTAL FACE</th>
<th>READING</th>
<th>INTERFACIAL ANGLE</th>
<th>CALCULATED ANGLE</th>
<th>INDICES</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>275°0'</td>
<td>71°30'</td>
<td>65°0'</td>
<td>010</td>
</tr>
<tr>
<td>B</td>
<td>346°30'</td>
<td>53°30'</td>
<td>55°0'</td>
<td>110</td>
</tr>
<tr>
<td>C</td>
<td>40°0'</td>
<td>55°0'</td>
<td>65°0'</td>
<td>110</td>
</tr>
<tr>
<td>D</td>
<td>95°0'</td>
<td></td>
<td></td>
<td>010</td>
</tr>
</tbody>
</table>

AVERAGE OF 3 SETS OF READINGS
DIAMOND D14

The diamond: A triangular "flat" of edge 3.5 mm and thickness 1.0 mm with sharply defined side faces. The specimen was classified by X-rays as an unstrained Type I. The black area with an irregular outline Fig. 14a, appeared to be contained entirely within the diamond and was most probably a diamond fracture plane as it was optically parallel to a [111] diamond direction.

Outside the fracture area there were several very small clear inclusions with maximum diameters of 0.06 mm, one of which is shown in Fig. 14b. As far as could be observed, all these inclusions were well faceted single crystals of olivine.

The diamond was broken open in such a manner as to expose the fracture zone which is seen in Fig. 14c. The black metallic material proved to be graphite; a fact determined by an X-ray study on two single crystals removed from the diamond. One was irregular in shape but the other had a rough hexagonal outline (Fig. 14d).

Generally, the graphite lay as a veneer on the exposed surface, but where the plane became minutely stepped, the material was located on the (111) cleavage planes and not on surfaces approximately perpendicular to these planes. Further, one graphite crystal when being removed for examination was observed to cleave in the plane of the flake, which strongly suggested that the c-axis of the graphite was perpendicular to the crystal flake and this was later confirmed by X-rays. This orientation of graphite to the diamond is discussed in
detail in Chapter II.

Also lying in the graphite region was a flake of a brown coloured material (Fig. 14c), but so far, no attempt has been made to identify this mineral.

X-ray Laue photographs of both the crystals of graphite showed them to be single crystals, and because of the rarity of monocrystals of graphite, the stacking of one of the specimens was investigated following the procedure suggested by Lipson and Stokes (1942).

In order to determine whether the mineral was a two-layer hexagonal, or a three-layer rhombohedral graphite, the nature of the interlayer spacing was considered. The results showed that the specimen was comprised predominantly of hexagonal graphite, this result being arrived at as follows:-

Oscillation limits about the b-axis of graphite were set to include the $\alpha$ and $\beta$ reflections from the plane (101) and the $\alpha$-reflection from the plane (100) (Fig. 14e). The (1,0,1, 2/3) reflection which denotes the rhombohedral form of graphite, should then occur between the (100) and (101) reflections (Fig. 14e), but after a fifteen hour oscillation this reflection was not observed. As the average reduction in intensity between the same $\alpha$- and $\beta$- reflection is about a factor of five, and since half the intensity of the $\alpha$-reflection of (101) could have been observed, then this indicated that at a maximum only 10 per cent of rhombohedral graphite could be present in this specimen.
FIG. 14e

\( a^*c^* \) RECIPROCAL LATTICE
OF GRAPHITE

\[ \begin{array}{c}
\text{000} \\
\text{001} \\
\text{002} \\
\text{003} \\
\text{004} \\
\text{005} \\
\end{array} \]

\[ \begin{array}{c}
\text{010} \\
\text{011} \\
\text{012} \\
\text{013} \\
\text{100} \\
\text{101} \\
\end{array} \]

\[ \begin{array}{c}
\text{200} \\
\text{201} \\
\text{202} \\
\text{203} \\
\end{array} \]

\[ \begin{array}{c}
\text{110} \\
\text{112} \\
\end{array} \]
This value falls within the range of 4 - 14 per cent for the rhombohedral content of natural graphite, proposed by Lipson and Stokes (loc. cit).

To determine the nature of the hexagonal layers comprising the graphite crystal, the 1120 reflection was considered. The resultant oscillation photograph showed that this reflection was rather diffuse with powder streaks extending on both sides of it, indicating that the layers themselves were not perfect.

**DIAMOND D15**

The study of this diamond is not yet complete.

The diamond: A flat cleavage plane formed one side of this irregular specimen, which had rounded faces some with faint [110] laminations (**Fig. 15a**). The diamond was generally free from fractures and was classified by X-rays as an unstrained Type II. Within the specimen were many inclusions.

Two garnets have been identified, both orange-red in colour, and one is shown in **Fig. 15b**. The crystal was tabular in habit except for a stepped feature at one end, and the facets were rounded. The cell parameter measured free from the diamond was 11.6514 ± 0.002 Å. This crystal was subsequently used in the study of garnet discussed in Section IV.

There were also at least six variously-shaped very pale green transparent crystals, a selection of which are shown in **Figs 15c, 15d,**
and 15e. All the specimens had rounded facets and one was ellipsoidal (Fig. 15e). A single specimen so far identified proved to be enstatite. It was tabular in habit and part of it contained a much darker brownish mineral Fig. 15f, which as yet has not been identified.

On both the garnet and several of the transparent inclusions (Figs. 15a and 15e) were black patches often hexagonal in outline of maximum size 0.013 mm, but generally much smaller 0.007 mm. These patches lay on the interface between the inclusion and the diamond — a fact determined first by optics, and confirmed when the diamond was broken open.

No result was obtained from a qualitative microprobe analysis of some of these patches, and in view of the colour and hexagonal nature of the material, it is suggested that these specks are single crystals of graphite. In Fig. 15g is shown a diamond fracture surface on which are large numbers of these crystals which indicate that the graphite (?) can develop on any subsurface discontinuity.
APPENDIX II.
