

The theory of the spin-lattice relaxation of copper in a Tutton salt crystal

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Abstract. A calculation of the relaxation of Cu^{2+} in potassium zinc Tutton salt has been made on a crystal field model. The magnitude and anisotropy predicted are in good agreement with experiment. The results imply that the tetragonal field splitting δ is about 7700 cm^{-1} and the cubic field splitting Δ_0 about 8700 cm^{-1} .

1. Introduction

Experimental and theoretical studies of the spin-lattice relaxation of magnetically dilute systems of transition series ions in non-magnetic host lattices suggest that the processes involved are not yet fully understood. One of the purposes of the present calculation was to see how well the commonly accepted relaxation mechanisms worked in one particular situation.

Cupric ions enter substitutionally for zinc in potassium zinc Tutton salt, and the experimental advantages of this system will be discussed in the following paper (Gill 1964). There is a further advantage that Cu^{2+} , having an isolated Kramers doublet lowest, may shed some light on the two similar systems Ti^{3+} and Co^{2+} , which relax at helium temperatures between three and five orders of magnitude faster than expected (Van Vleck 1940, Foglio and Pryce, to be published).

The Hamiltonian of Cu^{2+} in a static crystal field may be written

$$\mathcal{H}_{\text{Cu}} = \mathcal{H}_0 + \mathcal{H}_{\text{Cr}} + \mathcal{H}_{\text{so}} + \mathcal{H}_{\text{Z}} + \mathcal{H}_{\text{I}}$$

where the terms are in order of importance. The free-ion Hamiltonian \mathcal{H}_0 gives rise to a ^2D ground state. \mathcal{H}_{Cr} describes the interaction of the crystal with the ion, and will be taken to the crystal field approximation. It is assumed that \mathcal{H}_{Cr} is entirely due to the distorted octahedron of water molecules surrounding the ion, whose effect is represented by an appropriate electrostatic potential. Overlap of the 3d electron wave functions of the Cu^{2+} ion and the ligands will be neglected, as is the possibility of electron transfer between the ion and the ligands. The spin-orbit interaction \mathcal{H}_{so} is $\lambda \mathbf{L} \cdot \mathbf{S}$ within the 3d configuration for a hole in the 3d shell described by \mathbf{L} , \mathbf{S} . \mathcal{H}_{Z} is the electronic Zeeman energy. The nuclear Zeeman energy, together with terms arising from the interaction of the nuclear magnetic moment with the electronic moment, the anomalous s-electron contribution and quadripolar interactions, are contained in \mathcal{H}_{I} . Although \mathcal{H}_{I} introduces extra terms in the relaxation rate, these prove to be small and will not be discussed.

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2. The $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ complex

The cupric 3d shell contains nine electrons, and can be treated as a hole in a closed $3d^{10}$ shell. The orbitals for the hole are labelled ϵ , θ , ξ , η , ζ , and transform under the cubic group as x^2-y^2 , $2z^2-x^2-y^2$, yz , xz and xy respectively. In a static strictly cubic field, ξ , η , ζ are degenerate, as are ϵ , θ which form the degenerate ground state. A lower energy configuration may be obtained by a tetragonal distortion of the complex of the six ligands and the Cu^{2+} ion. This follows from the theorem of Jahn and Teller, and is illustrated in figures 1 and 2. The terms quadratic in the distortion arise from the usual forces which maintain the equilibrium of the crystal, and are the same for all the energy levels. The terms linear in the distortion are seen most clearly by subtracting off the common quadratic terms as in figure 2(b) and are the terms whose existence follows from the theorem cited.

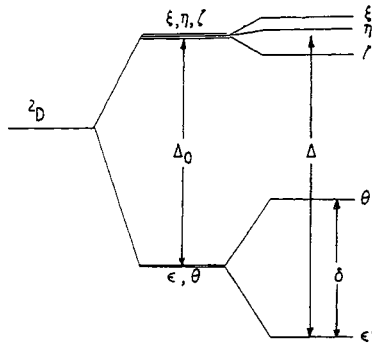


Figure 1. The energy levels of Cu^{2+} in crystal fields of cubic and lower symmetry.

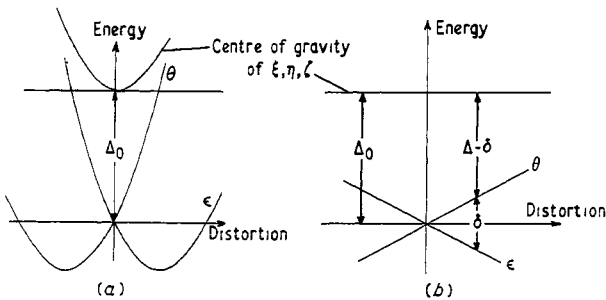


Figure 2. The effect of a tetragonal distortion on the energy levels of Cu^{2+} . The distortion from an octahedral arrangement of ligands is positive when two ligands move away from and four towards the Cu^{2+} ion. The curves for ξ , η , ζ lie close to that of their centre of gravity. In (b) a common quadratic term has been subtracted from all energy levels.

In a rhombic field all degeneracy except Kramers' degeneracy is lost. The members of the orbital triplet (ξ , η , ζ) are still nearly degenerate in the case of dilute deuterated potassium copper Tutton salt (Bleaney, Bowers and Pryce 1955) and their splitting will be neglected in this calculation. The splitting of the orbital doublet (ϵ , θ) by the tetragonal field is not altered by small rhombic components, so the result

$$\Delta = \Delta_0 + \frac{1}{2}\delta \quad \text{or} \quad \Delta_0 = \Delta \left(1 - \frac{1}{2d}\right) \quad (1)$$

which can be seen from figure 2(b) for the tetragonal case, is still valid. Δ , Δ_0 and δ are defined in the figure and $d = \Delta/\delta$. The rhombic term alters the wave functions of the doublet ϵ , θ , giving

$$\begin{aligned} |\epsilon\rangle \rightarrow |\epsilon'\rangle &= |\epsilon\rangle \cos \alpha + |\theta\rangle \sin \alpha \\ |\theta\rangle \rightarrow |\theta'\rangle &= |\theta\rangle \cos \alpha - |\epsilon\rangle \sin \alpha. \end{aligned}$$

α can be estimated from the g values, as

$$\begin{aligned} g_x - 2 &\simeq -\frac{2\lambda}{\Delta} (\cos \alpha + \sqrt{3} \sin \alpha)^2 \\ g_y - 2 &\simeq -\frac{2\lambda}{\Delta} (\cos \alpha - \sqrt{3} \sin \alpha)^2 \\ g_z - 2 &\simeq -\frac{8\lambda}{\Delta} \cos^2 \alpha. \end{aligned} \quad (2)$$

(Abragam and Pryce 1951)

Using $g_x = 2.16$, $g_y = 2.04$ and $g_z = 2.42$, we find $\alpha = 9^\circ 22'$ and $\lambda/\Delta \simeq 0.054$. The average over all angles of g is 2.21. The matrix elements of orbital angular momentum, given in table 1, are zero within the sub-space ϵ , θ . Thus, as λ/Δ is so small, it is adequate to treat \mathcal{H}_{so} and smaller terms to an appropriate order of perturbation theory, whereas \mathcal{H}_0 and \mathcal{H}_{Cr}^0 must be diagonalized to the extent indicated above. \mathcal{H}_{Cr}^0 is the value of \mathcal{H}_{Cr} for the ligands in their static equilibrium positions.

\mathcal{H}_{Cr} is modulated by thermal and zero point vibrations, giving the spin-lattice interaction

$$\mathcal{H}' = \mathcal{H}_{Cr}(\mathbf{r}, \mathbf{R}) - \mathcal{H}_{Cr}(\mathbf{r}, \mathbf{R}_0)$$

where \mathbf{R} represents the nuclear coordinates of the complex, \mathbf{R}_0 their static equilibrium values and \mathbf{r} the coordinates of all the electrons of the Cu^{2+} ion. As $\mathbf{R} - \mathbf{R}_0$ will be small compared with R , an appropriate $\text{Cu}^{2+} - \text{H}_2\text{O}$ separation, a Taylor expansion can be made:

$$\mathcal{H}' = \sum_{\text{Cu}^{2+} \text{ electrons}} \left\{ \sum_{\alpha} W_{\alpha}(\mathbf{r}_j) \frac{Q_{\alpha}}{R} + \sum_{\alpha, \beta} W_{\alpha\beta}(\mathbf{r}_j) \frac{Q_{\alpha} Q_{\beta}}{R^2} + \dots \right\}$$

where the Q_{α} are the normal coordinates of the complex. \mathcal{H}' is invariant under operations of the symmetry group of the complex, including the inversion operator. Thus W_{α} has the same parity as Q_{α} , and will have non-zero matrix elements within $3d^9$ only if Q_{α} has even parity. The Q_{α} of odd parity can contribute pairwise in the second term of \mathcal{H}' , but are negligible as the intermediate states are about $70\,000 \text{ cm}^{-1}$ away.

The W_{α} and Q_{α} will be taken to be those for a complex with complete cubic symmetry. The W_{α}/R are then the V_{α} defined by Van Vleck (1939), and the Q_{α} are linear combinations of distortions of the complex which transform according to irreducible representations under the cubic group. The neglect of non-cubicity may be excused in several ways. Firstly, it is hard to improve on the approximation with the available information, for the environment of the Cu^{2+} ion is not well known; probably it consists of a rhombically distorted octahedron of water molecules whose dipole moments are not necessarily parallel to the octahedron axes. Secondly, other simplifications are needed in this calculation, such as the use later of the approximation of plane waves for the normal coordinates of the crystal. An exact solution for these for a crystal as complex as a Tutton salt is extremely difficult, yet it would be unrealistic to include non-cubicity

Table 1. Matrix of the components of L in units of \hbar

	$ \xi\rangle$	$ \eta\rangle$	$ \zeta\rangle$	$ \theta'\rangle$	$ \epsilon'\rangle$
$\langle\xi $	—	$-i(x)$	$i(y)$	$i(\sqrt{3} \cos \alpha - \sin \alpha)(x)$	$i(\cos \alpha + \sqrt{3} \sin \alpha)(x)$
$\langle\eta $	$i(x)$	—	$-i(x)$	$-i(\sqrt{3} \cos \alpha + \sin \alpha)(y)$	$i(\cos \alpha - \sqrt{3} \sin \alpha)(y)$
$\langle\zeta $	$-i(y)$	$i(x)$	—	$2i \sin \alpha(x)$	$-2i \cos \alpha(x)$
$\langle\theta' $	$-i(\sqrt{3} \cos \alpha - \sin \alpha)(x)$	$i(\sqrt{3} \cos \alpha + \sin \alpha)(y)$	$-2i \sin \alpha(x)$	—	—
$\langle\epsilon' $	$-i(\cos \alpha + \sqrt{3} \sin \alpha)(x)$	$-i(\cos \alpha - \sqrt{3} \sin \alpha)(y)$	$2i \cos \alpha(x)$	—	—

(x), (y), (z) label the components of L , for example, $i(x)$ means L_x has a matrix element i .

Table 2. Matrix elements of distortions of the crystal field

	$ \xi\rangle$	$ \eta\rangle$	$ \zeta\rangle$	$ \theta'\rangle$	$ \epsilon'\rangle$
$\langle\xi $	$G_4(\sqrt{3}\epsilon - \theta) + G_{7a}$	$G_3\zeta$	$G_3\eta$	$-G_{2\xi}(\cos \alpha + \sqrt{3} \sin \alpha)$ $-G_{6\theta}(\sqrt{3} \cos \alpha - \sin \alpha)$	$+G_{2\xi}(\sqrt{3} \cos \alpha - \sin \alpha)$ $-G_{6\theta}(\cos \alpha + \sqrt{3} \sin \alpha)$
$\langle\eta $	$G_3\zeta$	$-G_4(\sqrt{3}\epsilon + \theta) + G_{7a}$	$G_3\xi$	$-G_{2\eta}(\cos \alpha - \sqrt{3} \sin \alpha)$ $+G_{6\theta}(\sqrt{3} \cos \alpha + \sin \alpha)$	$-G_{2\eta}(\sqrt{3} \cos \alpha + \sin \alpha)$ $-G_{6\theta}(\cos \alpha - \sqrt{3} \sin \alpha)$
$\langle\zeta $	$G_3\eta$	$G_3\xi$	$2G_4\theta + G_{7a}$	$2G_{2\xi} \cos \alpha - 2G_{6\theta} \sin \alpha$	$2G_{2\xi} \zeta \sin \alpha + 2G_{6\theta} \cos \alpha$
$\langle\theta' $	$-G_{2\xi}(\cos \alpha + \sqrt{3} \sin \alpha)$ $-G_{6\theta}(\sqrt{3} \cos \alpha - \sin \alpha)$	$-G_{2\eta}(\cos \alpha - \sqrt{3} \sin \alpha)$ $+G_{6\theta}(3 \cos \alpha + \sin \alpha)$	$2G_{2\xi} \zeta \cos \alpha$ $-2G_{6\theta} \sin \alpha$	$G_7(-\theta \cos 2\alpha + \epsilon \sin 2\alpha)$ $+G_{8d}$	$G_7(\epsilon \cos 2\alpha - \theta \sin 2\alpha)$
$\langle\epsilon' $	$+G_{2\xi}(\sqrt{3} \cos \alpha - \sin \alpha)$ $-G_{6\theta}(\cos \alpha + \sqrt{3} \sin \alpha)$	$-G_{2\eta}(\sqrt{3} \cos \alpha + \sin \alpha)$ $-G_{6\theta}(\cos \alpha - \sqrt{3} \sin \alpha)$	$2G_{2\xi} \zeta \sin \alpha$ $+2G_{6\theta} \cos \alpha$	$G_7(\epsilon \cos 2\alpha - \theta \sin 2\alpha)$	$G_7(\theta \cos 2\alpha + \epsilon \sin 2\alpha)$ $+G_{8d}$

but to use this simplification. Thirdly, it will appear later that Q_2 is largely responsible for the relaxation. This only involves motion of the ligands in the plane normal to the tetragonal axis, and the configuration of these molecules is altered only in size by the static tetragonal distortion. The correct W_2 is that for the cubic case, using a value of R appropriate to the ligands involved. As the way the W_α transforms under operations of the cubic group is known, their matrix elements between the orbitals $\epsilon, \theta, \xi, \eta, \zeta$, whose wave functions transform like those of d orbitals, are proportional to the elements of known matrices (Griffith 1961, § 8.7 and A.20). The proportionality constants can be calculated and a transformation made to the orbitals which diagonalize $\mathcal{H}_0 + \mathcal{H}_{\text{Cr}}$. The result appears as table 2.

The W_α form bases for the representations A_1 ($\alpha = 1$, breathing mode), E ($\alpha = 2, 3$, pumping mode), T_1 ($\alpha = 19, 20, 21$, rotations) and T_2 ($\alpha = 4, 5, 6$, shearing mode) of the cubic group. There are seven non-zero proportionality constants G_α corresponding to the elements of $\alpha = 1$ and $\alpha = 2, 3$ in the (ϵ, θ) sub-space of $\alpha = 1$, $\alpha = 2, 3$ and $\alpha = 4, 5, 6$ within the (ξ, η, ζ) sub-space, and of $\alpha = 4, 5, 6$ and $\alpha = 19, 20, 21$ between the two sub-spaces. They can be expressed, in the approximation that the ligands give an isotropic field of force μ/x^2 at distance x from the ligand, in terms of μ, R, e (the magnitude of the electronic charge) and $\langle r^n \rangle$, the expectation value of the n th power of the mean distance of a 3d electron from the nucleus. $\langle r^n \rangle$ is assumed to be the same for all d orbitals. To this approximation,

$$\Delta_0 = \Delta \left(1 - \frac{\delta}{2\Delta} \right) = \frac{25 e \mu}{3 R^2} \rho_4$$

where

$$\rho_n = \langle r^n \rangle / R^n, \quad \text{and if } \gamma_i = G_i / G_1$$

$$G_1 = -\frac{3\sqrt{3}}{7} \Delta_0 \left(1 + \frac{24\rho_2}{25\rho_4} \right)$$

$$\gamma_2 = -\frac{1}{5} \left(1 + \frac{8\rho_2}{5\rho_4} \right) \left(1 + \frac{24\rho_2}{25\rho_4} \right)^{-1}$$

$$\gamma_3 = -\frac{4}{5\sqrt{3}} \left(1 - \frac{6\rho_2}{5\rho_4} \right) \left(1 + \frac{24\rho_2}{25\rho_4} \right)^{-1}$$

$$\gamma_4 = -\frac{2}{3} \left(1 - \frac{18\rho_2}{25\rho_4} \right) \left(1 + \frac{24\rho_2}{25\rho_4} \right)^{-1}$$

$$\gamma_5 = -\frac{21}{25\sqrt{3}} \left(1 + \frac{24\rho_2}{25\rho_4} \right)^{-1}$$

$$\gamma_6 = \frac{7}{15\sqrt{2}} \left(1 + \frac{24\rho_2}{25\rho_4} \right)^{-1}$$

$$\gamma_7 = -\frac{14}{45\sqrt{2}} \left(1 + \frac{24\rho_2}{25\rho_4} \right)^{-1}.$$

Using a value for ρ_2/ρ_4 obtained from the calculation for Cu^{1+} by Hartree and Hartree (1936) and $R = 2.05 \text{ \AA}$,

$$\begin{aligned} G_1 &= -3.40\Delta_0 \\ \gamma_2 &= -0.304 & \gamma_5 &= -0.106 \\ \gamma_3 &= +0.350 & \gamma_6 &= +0.072 \\ \gamma_4 &= +0.318 & \gamma_7 &= -0.048. \end{aligned} \tag{3}$$

γ_6, γ_7 will be dropped from now on. Their contribution to the relaxation rate is a further order of magnitude smaller than (3) suggests, for equation (4) shows that this contribution is reduced by the fifth power of the ratio of the velocities of transverse to longitudinal waves.

The distortions Q_α of the complex can be related to the normal coordinates of the crystal. It is necessary to make a number of approximations, in particular that the crystal may be assumed isotropic, that the mean square displacements are independent of the site in the unit cell and that the long wave limit may be used. These should be reasonable at temperatures much less than the Debye temperature. The isotropy assumption means that the acoustic phonons (which are almost exclusively responsible for relaxation at low temperatures) can be described in terms of one longitudinal and two transverse modes, and together with the homogeneity assumption means that the normal coordinates of the crystal can be taken as standing plane waves. From the long wave limit it follows that, for phonons of wave vector \mathbf{f} and polarization s , $|\mathbf{f}|R \ll 1$ and that $\omega_{\mathbf{f}s} = |\mathbf{f}|v_s$. Here $\omega_{\mathbf{f}s}$ is the corresponding angular frequency and v_s the relevant velocity of sound. Then

$$\frac{Q_\alpha}{R} = \sum_{\mathbf{f},s} \left(\frac{\hbar\omega_{\mathbf{f}s}}{2M_c v_s^2} \right)^{1/2} \psi_\alpha(\mathbf{f}, s) (a_{\mathbf{f}s} + a_{\mathbf{f}s}^+) \sin \phi_{\mathbf{f}s}$$

where M_c is the crystal mass, and $a_{\mathbf{f}s}, a_{\mathbf{f}s}^+$ phonon annihilation and creation operators, with matrix elements

$$\langle n_{\mathbf{f}s} | a_{\mathbf{f}s} | n_{\mathbf{f}s} + 1 \rangle = \langle n_{\mathbf{f}s} + 1 | a_{\mathbf{f}s}^+ | n_{\mathbf{f}s} \rangle = (n_{\mathbf{f}s} + 1)^{1/2}.$$

$n_{\mathbf{f}s}$ is the phonon occupation number of the mode \mathbf{f}, s in thermal equilibrium and is $\{\exp(\hbar\omega_{\mathbf{f}s}/kT) - 1\}^{-1}$. $\phi_{\mathbf{f}s}$ is a phase which appears because the nodes of (\mathbf{f}, s) have some distribution with respect to the Cu^{2+} ion. For a random distribution the expectation value of $\sin^2 \phi_{\mathbf{f}s}$ is $\frac{1}{2}$. The ψ_α transform under the cubic group in the same way as the Q_α and are functions of the phonon polarization vector with components $(X_{\mathbf{f}s}, Y_{\mathbf{f}s}, Z_{\mathbf{f}s})$ and the unit wave vector $\mathbf{f}/|\mathbf{f}|$ with components (L, M, N) . For each phonon (\mathbf{f}, s)

$$\begin{aligned} \psi_2 &= XL - MY & \psi_3 &= \frac{1}{\sqrt{3}} (2ZN - XL - YM) \\ \psi_4 &= YN + ZM & \psi_{19} &= YN - ZM \\ \psi_5 &= ZL + XN & \psi_{20} &= ZL - XN \\ \psi_6 &= XM + YL & \psi_{21} &= XM - YL. \end{aligned}$$

For later use we need the two summations

$$\begin{aligned} \sum_{\text{I}} (\alpha, \beta) &= \sum_{s, \mathbf{f}/\mathbf{f}} \frac{\psi_\alpha^* \psi_\beta}{v_s^5} \\ \sum_{\text{II}} (\alpha, \beta, \gamma, \delta) &= \sum_{\substack{s, s' \\ \mathbf{f}'/\mathbf{f}', \mathbf{f}/\mathbf{f}}} \frac{(\psi_\alpha \psi_\beta' - \psi_\alpha' \psi_\beta)^* (\psi_\gamma \psi_\delta' - \psi_\gamma' \psi_\delta)}{v_s^5 v_{s'}^5} \end{aligned}$$

where

$$|\mathbf{f}| = f \text{ and } \psi_\alpha = \psi_\alpha(\mathbf{f}, s), \psi_\alpha' = \psi_\alpha(\mathbf{f}', s').$$

By transforming $\sum_{\mathbf{f}/\mathbf{f}}$ into an integral $\int_{4\pi} d\Omega_{\mathbf{f}}$ and using the transformation properties

of the ψ_α under the cubic group, we obtain

$$\left. \begin{aligned} \sum_{\mathbf{I}} (\alpha, \beta) &= \delta_{\alpha\beta} \frac{4\pi}{15} \left(\frac{4}{v_1^5} + \frac{6}{v_t^5} \right), \quad \alpha = 2, 3, 4, 5, 6 \\ \delta_{\alpha\beta} \frac{4\pi}{15} \left(\frac{10}{v_t^5} \right), \quad &\alpha = 19, 20, 21 \\ \delta_{\alpha\beta} \frac{4\pi}{15} \left(\frac{10}{v_1^5} \right), \quad &\alpha = 1 \end{aligned} \right\} \quad (4)$$

$$\sum_{\mathbf{II}} (\alpha, \beta, \alpha, \beta) = 2(1 - \delta_{\alpha\beta}) \sum_{\mathbf{I}} (\alpha, \alpha) \sum_{\mathbf{I}} (\beta, \beta)$$

Apart from some obvious permutations, all other $\sum_{\mathbf{II}} (\alpha, \beta, \gamma, \delta)$ are zero.

The different velocity factor for rotations can be simply included by multiplying G_5 by $(5/v_t^5) (2/v_1^5 + 3/v_t^5)^{-1}$. For $v_1/v_t = 1.5$, γ_5 becomes -0.131 , and it is this which is used in all subsequent stages. As the contribution from rotations is not large, the estimate of v_1/v_t is not of critical importance.

3. Transition probabilities

We write the Hamiltonian for a crystal containing a single Cu^{2+} ion

$$\mathcal{H} = \mathcal{H}_{\text{Cu}} + \mathcal{H}_{\text{lattice}} + \mathcal{H}'$$

where

$$\mathcal{H}_{\text{lattice}} = \sum_{f,s} \hbar\omega_{fs} (a_{fs}^+ a_{fs} + \frac{1}{2})$$

in the harmonic approximation, and, omitting $\mathcal{H}_{\mathbf{I}}$ which proves to be unimportant,

$$\mathcal{H}_{\text{Cu}} = (\mathcal{H}_0 + \mathcal{H}_{\text{Cr}}^0 + 2\beta\mathbf{S} \cdot \mathbf{H}) + (\lambda\mathbf{L} \cdot \mathbf{S} + \beta\mathbf{L} \cdot \mathbf{H}) = \mathcal{H}^A + P.$$

Mattuck and Strandberg's method (1960, to be referred to as MS) is adopted. Like the method of Van Vleck (1940), $\mathcal{H}_{\text{lattice}}$ and \mathcal{H}^A are treated exactly, and \mathcal{H}' as a perturbation, but whereas Van Vleck also treats P as a perturbation, P is diagonalized in MS to an appropriate order by Löwdin's method. These two cases differ least when P (which has no diagonal elements between eigenstates of \mathcal{H}^A) is small compared with the separation of the ground states from the nearest excited states to which P connects it. Here $P \sim \lambda < 1000 \text{ cm}^{-1}$ is much less than $\Delta > 10^4 \text{ cm}^{-1}$. For the Raman process, the important terms are easier to pick out in the Van Vleck case, and this helps the selection of the important terms for the approach of MS.

The excited electronic states of the complex are 10^3 to 10^4 cm^{-1} above the ground state, so at most temperatures only the ground (ϵ') Kramers doublet is populated. It is therefore convenient to write a Hamiltonian which gives the transition probability for the direct or the Raman process in terms of a_{fs} , a_{fs}^+ and spin operators which operate between the eigenstates of a spin Hamiltonian of effective spin $\frac{1}{2}$ describing the behaviour of the lowest Kramers doublet.

Let the doublet be $|+\rangle$, $|-\rangle$ and $E_+ - E_- = \hbar\omega_0$. Then

$$\mathcal{H}_{\text{direct}} = \sum_{\substack{f,s \\ i>j}} \left(\frac{\hbar\omega_{fs}}{2M_c v_s^2} \right)^{1/2} \psi_\alpha(\mathbf{fs}) (a_{fs} + a_{fs}^+) \sin(\phi_{fs}) 2\lambda\beta H \\ \times \{ \mathcal{L}_i^\alpha g_{ik} S_i + \mathcal{L}_{i,j}^\alpha (S_i l_{jz} + S_j l_{iz}) \}$$

$$\mathcal{H}_{\text{Raman}} = \sum_{\substack{f \\ f's'}} \left(\frac{\hbar\omega_{fs}}{2M_c v_s^2} \right)^{1/2} \left(\frac{\hbar\omega_{f's'}}{2M_c v_{s'}^2} \right)^{1/2} \psi_\alpha \psi_\beta' \sin \phi_{fs} \\ \times \sin \phi_{f's'} (a_{fs} + a_{fs}^+) (a_{f's'} + a_{f's'}^+) \mathcal{G}_{\alpha\beta}^{ff's's'} S_i.$$

The tensors \mathcal{L}_i^α and $\mathcal{L}_{i'}^\alpha$ are defined in equation (45) of MS, and $\mathcal{G}_{i,\alpha\beta}$ is the first term in MS, equation (57). The Raman process has contributions from the first term in \mathcal{H}' taken to second order, or the second term to first order. These terms are proportional to factors of order $(W^2/\delta)f_1$, Wf_2 , where $W \sim W_\alpha \sim W_{\alpha\beta}$ and $f_1 \sim \hbar T$, $f_2 \sim \hbar\omega_0 = g\beta H$ appear because the contributions to the Raman process vanish in the limit of zero f_1 , f_2 respectively. At all temperatures of interest the first term dominates, and the other will not be discussed further. The spin components S_i , referred to the axes of the complex, are related to the spin components σ_i , referred to axes in which the z axis is parallel to the applied magnetic field of magnitude H , by

$$S_i = \sum_j l_{ij} \sigma_j$$

which also defines the l_{ij} . For simplicity we can write

$$\mathcal{H}_{\text{direct}} = F_x S_x + F_y S_y + F_z S_z = \Phi_x \sigma_x + \Phi_y \sigma_y + \Phi_z \sigma_z \\ \mathcal{H}_{\text{Raman}} = P_x S_x + P_y S_y + P_z S_z = \left\{ \frac{1}{2} \sum_j P_j (l_{jx} - il_{jy}) \right\} \sigma_+ \\ + \left\{ \frac{1}{2} \sum_j P_j (l_{jx} + il_{jy}) \right\} \sigma_- + \left\{ \sum_j P_j l_{jz} \right\} \sigma_z.$$

The transformation of coordinates is simpler in the Raman case as the P_j , unlike the F_j , do not involve the l_{ij} . Replacing the summations over phonons by integrals over a sphere containing the same number of phonons as the first Brillouin zone, the direct process transition probability is

$$W_{\rightarrow\rightarrow-}^{\text{direct}} = \frac{1}{4} \frac{2\pi}{\hbar^2} \frac{V}{8\pi^3} \sum_s \int df f^2 \int d\Omega_f \langle n_{fs} + 1 | \Phi_x - i\Phi_y | n_{fs} \rangle^2 \delta(\omega_0 - \omega_{fs})$$

where V is the volume of the crystal. In detail, the relevant integrals over angles are given in (4). The relaxation time τ_{direct} is equal to $(W_{\rightarrow\rightarrow-}^{\text{direct}} + W_{-\rightarrow+}^{\text{direct}})^{-1}$ and is given by

$$\frac{1}{\tau_{\text{direct}}} = \frac{1}{3\pi} \frac{\omega_0^4}{g^2} kT \frac{1}{\rho} \left(\frac{2}{5v_1^5} + \frac{3}{5v_2^5} \right) \left(\frac{\lambda}{\Delta} \right)^2 \left(\frac{G_1}{\Delta} \right)^2 \sum_\alpha \theta_\alpha. \quad (5)$$

The θ_α are complicated functions of the l_{ij} , Δ/δ , the rhombicity and the γ_i . The approximation

$$2n_{\omega_0} + 1 = \coth \frac{\hbar\omega_0}{2kT} \simeq \frac{2kT}{\hbar\omega_0}$$

has been used, as $\hbar\omega_0/2kT < 1/8$ for all the experiments. As $\omega_0 = g\beta H/\hbar$, the direct process relaxation time is proportional to $H^{-4} T^{-1}$. Similarly

$$W_{\rightarrow\rightarrow-}^{\text{Raman}} = \frac{1}{4} \frac{2\pi}{\hbar^2} \left(\frac{V}{8\pi^3} \right)^2 \sum_{s,s'} \int \int df df' f^2 f'^2 \delta(\omega' - \omega + \omega_0) \int d\Omega_f d\Omega_{f'} \\ \times \left| \left\langle \begin{matrix} n_{fs} - 1 \\ n_{f's'} + 1 \end{matrix} \right| \frac{1}{2} \sum_j P_j (l_{jx} - il_{jy}) \begin{matrix} n_{fs} \\ n_{f's'} \end{matrix} \right\rangle \right|^2.$$

There are no cross terms in $P_i P_{j \neq i}$, because none of the factors $\psi_\alpha' \psi_\beta - \psi_\alpha \psi_\beta'$ occurs for more than one value of i . Ultimately

$$\frac{1}{\tau_{\text{Raman}}} = 2 \frac{\hbar^2}{2\pi^3} \left(\frac{G_1}{\Delta}\right)^4 \left(\frac{\lambda}{\Delta}\right)^2 \frac{1}{\rho^2} \left(\frac{2}{5v_1^5} + \frac{3}{5v_t^5}\right)^2 8! \left(\frac{\hbar T}{\hbar}\right)^9 \Gamma\left(\frac{\Theta_D}{T}\right) \times \{(W_y + W_z) - (W_y - W_x)m^2 + (W_x - W_z)n^2\} \quad (6)$$

where

$$\Gamma(x_D) = \frac{1}{8!} \int_0^{x_D} \frac{dx (x^8 e^x)}{(e^x - 1)^2}$$

tends to unity as x_D tends to infinity. Θ_D is the Debye temperature and $\Gamma(x_D)$ has been given by Ziman (1954). The W_i represent the contribution of the corresponding P_i , and (l, m, n) are the direction cosines of the magnetic field with respect to the axes of the complex. In this case $W_x \neq W_y \neq W_z$ so that the relaxation is anisotropic, but independent of the magnitude of the applied field. This contrasts with the case of a cubic environment when $W_x = W_y = W_z$, and the Raman process is independent of the direction of the applied field. The W_i are complicated functions of Δ/δ , the γ_i , and the rhombicity. Hill and Smith (1953) have measured the specific heat of $(\text{NH}_4)\text{Zn}$ Tutton salt, from which one can derive v_N , where $v_N^{-3} = (\frac{1}{3}v_1^{-3} + \frac{2}{3}v_t^{-3})$. In calculating $\bar{v}_K^{-5} = \frac{2}{5}v_1^{-5} + \frac{3}{5}v_t^{-5}$ for $(\text{K})\text{Zn}$ Tutton salt, it is assumed that $\bar{v}_K = v_N$. This should not lead to a large error and gives $\bar{v}_K^5 = 1.0 \times 10^{27} \text{ cm}^5 \text{ sec}^{-5}$. Tutton (1916) quotes $\rho_{\text{KZn}} = 2.246$. The remaining factors in (5) and (6) are λ/Δ which was derived from the g values in (2), and $G_1/\Delta = (G_1/\Delta_0)(1 - 1/2d)$ which is given in (3). It is not necessary to know λ , Δ_0 or G_1 separately at any stage, which is very convenient in view of the lack of optical data. The one unknown parameter is $d = \Delta/\delta$, and both relaxation rates can be written in terms of this. ω_0 is $0.9455 \times 2\pi \times 10^{10} \text{ rad sec}^{-1}$.

$$\frac{1}{T\tau_{\text{direct}}} = 0.72 \times 10^{-3} \left(\frac{2.21}{g}\right)^2 \left(1 - \frac{1}{2d}\right)^2 \{A + Bn^2 + Cn^4 + D(l^4 + m^4 + n^4) + E(l^2 - m^2) + Fn^2(l^2 - m^2)\} \text{ deg}^{-1} \text{ sec}^{-1}.$$

$$\left. \begin{array}{ll} A = 9.95d^2 + 7.90d + 31.24 & B = -(8.62d^2 + 6.90d + 80.02) \\ C = 8.62d^2 + 6.90d + 79.91 & D = -(9.95d^2 + 7.90d + 0.99) \\ E = +7.72 & F = 15.82d^2 + 10.86d - 35.0 \end{array} \right\} (7)$$

$$\left. \begin{array}{l} \frac{1}{T^9 \tau_{\text{Raman}}} = 2.15 \times 10^{-8} (T - Um^2 + Vn^2) \left(1 - \frac{1}{2d}\right)^4 \Gamma(x_D) \\ T = 3.017d^4 + 2.677d^3 + 1.783d^2 + 0.512d + 0.981 \\ U = 0.200d^4 + 0.863d^3 + 0.411d^2 + 0.048d - 0.181 \\ V = 0.247d^4 + 1.946d^3 + 1.118d^2 + 0.378d - 0.532. \end{array} \right\} (8)$$

When the magnetic field is parallel to one of the axes of the complex (one of $l, m, n = 1$), the dependence of the direct process on d disappears except for $(1 - 1/2d)^2$, where the terms in d correspond to energy denominators $\delta = E_{g'} - E_{e'}$ rather than Δ . In the sub-space $|\epsilon'\rangle, |\theta'\rangle$ \mathbf{L} has zero elements and there are only non-zero elements of Q_2 and Q_3 , which transform under the cubic group like $x^2 - y^2$, $2xz - x^2 - y^2$. As \mathcal{H}' , which is linear in spin and magnetic field components, is invariant under these transformations, it will contain terms

$$A_e Q_2 (S_x H_x - S_y H_y) + A_\theta Q_3 (2S_z H_z - S_x H_x - S_y H_y)$$

where the axes are those of the complex. When \mathbf{H} is parallel to one of these axes, the only non-zero terms are proportional to $HS_i \equiv H\sigma_z$. This has no off-diagonal elements, so the contributions of Q_2 , Q_3 , and hence the terms in d , will vanish for these orientations.

4. Discussion of experimental results

A detailed comparison of equations (7) and (8) with experiment is given in the following paper. The Tutton salts contain two types of Cu^{2+} site, which are related by a translation plus a reflection and whose tetragonal axes are nearly perpendicular. As, for most of the orientations considered their magnetic resonance lines overlap, it is expected that cross relaxation will be important. By assuming that the cross relaxation occurs much more rapidly than the spin-lattice relaxation and conserves the total Zeeman energy, rather good agreement results. The direct process relaxation rate when the magnetic field is parallel to the axes of the complex enables one to estimate the accuracy of the terms in (7) which involve d only in the factor $(1-1/2d)^2$. The predicted rate is about $0.67(1-1/2d)^2$ of that observed, which is very reasonable considering the assumptions made, particularly those concerning the lattice system. A change in velocity of sound of about 25% would correct the terms, and would probably correspond to the inhomogeneity of the lattice. Correspondingly, the Raman process was corrected by a factor $(0.67)^2 \times (1-1/2d)^4$ before being used to estimate d . The question of cross relaxation is not so clear-cut here, as the cross-relaxation rate is temperature independent and will be more important at low temperatures. It appears that the estimate of $d = 1.64$ is not sensitive to the extent of the cross relaxation, and so this value was used to predict the orientation dependence of the direct process.

This estimate of d is compatible with optical data given by Griffith (1961). In aqueous solution Δ appears to be $12\,600\text{ cm}^{-1}$, which, with $d = 1.64$ and equation (1), gives $\delta \sim 7700\text{ cm}^{-1}$ and $\Delta_0 \sim 8700\text{ cm}^{-1}$. This is consistent with the values for hexaquo-complexes of adjacent divalent ions as $\Delta_0 \sim 7900\text{ cm}^{-1}$ for Co^{2+} ($3d^7$) and $\Delta_0 \sim 8500\text{ cm}^{-1}$ for Ni^{2+} ($3d^8$).

Measurements of the relaxation time above 90°K were made by Bagguley and Griffiths (1952) and by Bleaney *et al.* (1951). The most important phonons will be those with energies near to $k\Theta_D$, where $\Theta_D \simeq 105^\circ$. For these very few of the assumptions made are valid—in particular the neglect of optical modes. Simply using an appropriate value of $\Gamma(x_D)$ gives a rate slower than that observed by about an order of magnitude. Further reasons for the discrepancy lie in the change in g values with temperature, and the interpretation of this phenomenon by Abragam and Pryce (1950). There was evidence before starting this calculation that the Van Vleck mechanism was responsible for the relaxation, as in the dilute specimens the observed relaxation times were long, independent of concentration, and had the temperature dependence expected. The only significant feature which has not yet been confirmed in detail is the frequency dependence. This situation contrasts with that of Co^{2+} in MgO at liquid helium temperatures (Foglio and Pryce 1964) for which the Co^{2+} relaxation time depends strongly on the concentrations of Co^{2+} and other iron group impurities, and the relaxation rate is inconsistent with a calculation similar to the one described here, and with acoustic and uniaxial stress measurements. It is, of course, considerably harder to prepare impurity-free crystals of MgO, which must be grown from the melt, than to prepare pure crystals of the water soluble Tutton salts. One feature of spin-lattice relaxation phenomena is that systems so dilute as to be essentially free from the effects of pairs or larger clusters of paramagnetic ions can be greatly influenced by low concentrations of impurities.

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