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Anisotropy of the Spin-Lattice Relaxation for the Kramers Doublets in Cubic Crystals. II. Analysis of Specific Cases

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Using the expressions derived earlier for the anisotropy of spin-lattice relaxation for Kramers doublets in cubic crystals, numerical estimates have been made of the anisotropies for Co^{2+} in MgO and Yb^{3+} in CaF_2 crystals. The results show that the Γ_{3g} mode of the complex formed by the nearest neighbors around the Co^{2+} ion contribute most significantly to the relaxation rate at low temperature, and the anisotropy varies as $\{1-(l^4+m^4+n^4)\}$, where l, m, n are the direction cosines of the Zeeman field about the crystal axes. On the other hand, for Yb^{3+} in CaF_2, one of the two Γ_{5g} modes is most effective for relaxation processes, and this causes an anisotropy which is given by $(l^4+m^4+n^4)$. The implications of these results for other paramagnetic crystals are discussed.

1. INTRODUCTION

IN previous papers[1,2] it was shown that for Kramers doublets the spin-lattice relaxation should be anisotropic at low temperature where the single-phonon process is important, whereas it is isotropic at higher temperature where a two-phonon process is important. So from the point of view of anisotropy study it is the low-temperature region which is of importance. The relaxation in this region is Zeeman-field-dependent. From the Van Vleck model[3] of relaxation, the symmetry modes of the complex formed around the paramagnetic ion by the nearest ligands are most important for relaxation processes. It has been shown earlier[1] that for Kramers doublets, in cubic crystals, the contribution to the relaxation rate from the Γ_{1g} mode is isotropic, whereas the Γ_{3g} and Γ_{5g} modes give rise to anisotropy, given by $\{1-(l^4+m^4+n^4)\}$ and $(l^4+m^4+n^4)$, respectively. So if all the modes contribute, the general form of the relaxation rate is expected to be of the form $a_1+a_2(l^4+m^4+n^4)$. The importance of the anisotropic contribution depends on the ratio of a_2/a_1. A numerical estimation has been made here of the relative values of a_1 and a_2 for Co^{2+} ions in MgO and for Yb^{3+} ions in CaF_2. The details of the calculations are given in Sec. 2. The results show that for Co^{2+} in MgO, $a_1=-a_2$, i.e., the Γ_{3g} mode makes up the major contribution to the relaxation rate; and for Yb^{3+} in MgO, $a_1 \simeq 0$, i.e., the relaxation is mainly due to one of the two Γ_{5g} modes. The expected range of variations of the relaxation rates is discussed in Sec. 3 for these two specific cases.

2. CALCULATION OF THE RELAXATION RATE

The complexes around Co^{2+} in MgO and Yb^{3+} in CaF_2 are of the XY_6 and XY_8 types, respectively. In the case of XY_6, there are three vibrational symmetry modes, viz., Γ_{1g}, Γ_{3g}, and Γ_{5g}, which are relevant for relaxation calculations; whereas for the XY_8 complex, the four modes which are to be considered are Γ_{1g}, Γ_{3g}, and $2\Gamma_{5g}$. Following the formalism of the dynamical spin Hamiltonian developed in an earlier paper[1] we have:

For Co^{2+} in MgO

$$\begin{aligned}\mathcal{H}_{\mathrm{dyn}} = C_1\beta(S_1H_1)_0(\Gamma_{1g})Q(\Gamma_{1g}) &+ C_2\beta\sum_i (S_1H_1)_2(\Gamma_{3g}{}^i)Q(\Gamma_{3g}{}^i)\\ &+ C_3\beta\sum_i (S_1H_1)_2(\Gamma_{5g}{}^i)Q(\Gamma_{5g}{}^i). \qquad (1)\end{aligned}$$

For Yb^{3+} in CaF_2

$$\begin{aligned}\mathcal{H}_{\mathrm{dyn}} = C_1\beta(S_1H_1)_0(\Gamma_{1g})Q(\Gamma_{1g}) &+ C_2\beta\sum_i (S_1H_1)_2(\Gamma_{3g}{}^i)Q(\Gamma_{3g}{}^i)\\ &+ C_3\beta\sum_i (S_1H_1)_2(\Gamma_{5g}{}^i)Q(\Gamma_{5g,1}{}^i)\\ &+ C_4\beta\sum_i (S_1H_1)_2(\Gamma_{5g}{}^i)Q(\Gamma_{5g,2}{}^i). \qquad (2)\end{aligned}$$

Recently, Tucker[4] has measured the change in g factor for Co^{2+} in MgO under uniaxial stress. He expressed δg_i in terms of the strain components e_j by the relation

$$\delta g_i = F_{ij}e_j \qquad (3)$$

and measured the nonvanishing constants F_{11}, F_{12}, and F_{44}. He has also estimated these parameters theoretically, considering a point-charge model for O^{2-} ions around the Co^{2+} ion. Expressing the symmetry coordinates Q_i in terms of the strain components e_j, we get the following relationships between the dynamical Hamiltonian constants in Eq. (1) and the F_{ij}:

$$\begin{aligned}F_{11}&=(\sqrt{2}/3)(C_1+2C_2)R,\\ F_{12}&=(\sqrt{2}/3)(C_1-C_2)R,\\ F_{44}&=C_3/\sqrt{2}R. \qquad (4)\end{aligned}$$

Using the experimental values[4] of F_{11}, F_{12}, and F_{44}, we thus get

$$\begin{aligned}RC_1&=-5/\sqrt{2},\\ RC_2&=-101/\sqrt{2},\\ RC_3&=10\sqrt{2}, \qquad (5)\end{aligned}$$

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[1] D. K. Ray, T. Ray, and P. Rudra, Proc. Phys. Soc. (London) **87**, 485 (1966).

[2] T. Ray and D. K. Ray, previous paper, Phys. Rev. **164**, 420 (1967).

[3] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[4] E. B. Tucker, Phys. Rev. **143**, 264 (1966).

and from the theoretical values[4] calculated from the point-charge model, we get

$$C_1=0,\quad RC_2=-963/\sqrt{2},\quad RC_3=88\sqrt{2}. \tag{6}$$

It is to be noted that though the absolute magnitudes of the constants in the point-charge model are greater by one order of magnitude than the experimental values, the ratio $C_2^2:C_3^2$, which determines the relative contributions of the Γ_{3g} and Γ_{5g} modes to the relaxation rate, is nearly same for both sets of values. For Yb^{3+} in CaF_2, no experimental results on the g shift under uniaxial stress are available. So we calculate the constants C_i from a model of the F^- charge around the Yb^{3+} ions. For simplicity of calculation we shall use the effective-point-charge model. It has recently been shown[5] that in the case of rare-earth ions, covalency is not very important for the crystal potential terms with $L=2$, whereas for terms with $L=4$ and 6, it is essential to consider the covalency factor. But for the $L=2$ terms, the shielding of the crystal potential by the $5s$ and $5p$ electrons of the rare-earth ion has to be taken into account, which effect will reduce the magnitude of the point charge on the F^- ions. In the estimation of the parameters C_i for the Yb^{3+} ion in CaF_2 we find that the $L=2$ terms in the orbit-lattice interaction predominates over the other terms, and so the effective-point-charge model is expected to be a good approximation. The form of the orbit-lattice interaction for Yb^{3+} in CaF_2 is

$$\begin{aligned}V_{\text{O-L}}=&\{A_1\langle r^0\rangle Y_0(\Gamma_{1g})+A_2\langle r^4\rangle Y_4(\Gamma_{1g})+A_3\langle r^6\rangle Y_6(\Gamma_{1g})\}Q(\Gamma_{1g})+\{A_4\langle r^2\rangle \sum_i Y_2(\Gamma_{3g}{}^i)Q(\Gamma_{3g}{}^i)\\&+A_5\langle r^4\rangle \sum_i Y_4(\Gamma_{3g}{}^i)Q(\Gamma_{3g}{}^i)+A_6\langle r^6\rangle \sum_i Y_6(\Gamma_{3g}{}^i)Q(\Gamma_{3g}{}^i)\}\\&+\{A_7\langle r^2\rangle \sum_i Y_2(\Gamma_{5g,1}{}^i)Q(\Gamma_{5g,1}{}^i)+A_8\langle r^4\rangle \sum_i Y_4(\Gamma_{5g,1}{}^i)Q(\Gamma_{5g,1}{}^i)+A_9\langle r^6\rangle \sum_i Y_6(\Gamma_{5g,1}{}^i)Q(\Gamma_{5g,1}{}^i)\}\\&+\{A_{10}\langle r^2\rangle \sum_i Y_2(\Gamma_{5g,2}{}^i)Q(\Gamma_{5g,2}{}^i)+A_{11}\langle r^4\rangle \sum_i Y_4(\Gamma_{5g,2}{}^i)Q(\Gamma_{5g,2}{}^i)+A_{12}\langle r^6\rangle \sum_i Y_6(\Gamma_{5g,2}{}^i)Q(\Gamma_{5g,2}{}^i)\}\\&+\{A_{13}\langle r^6\rangle \sum_i Y_6(\Gamma_{5g,2}{}^i)Q(\Gamma_{5g,1}{}^i)+A_{14}\langle r^6\rangle \sum_i Y_6(\Gamma_{5g,1}{}^i)Q(\Gamma_{5g,2}{}^i)\}.\end{aligned}\tag{7}$$

Here $Y_L(\Gamma_\alpha{}^i)$ denotes the combination of spherical harmonics of angular momentum L forming a basis of the ith component of the irreducible representation Γ_α. The magnitudes of the constants A_i in Eq. (7) depend on the model of the charge distribution of the ligands. For Yb^{3+} ions in CaF_2, the lowest $J=\frac{7}{2}$ term splits up into Γ_{7g}, Γ_{8g}, and Γ_{6g} states with the Γ_{7g} doublet lying lowest.[6] The $J=\frac{5}{2}$ term is approximately 10300 cm^{-1} above the $J=\frac{7}{2}$ term. So if the $J=\frac{5}{2}$ term is neglected, terms in $V_{\text{O-L}}$ associated with the Γ_{1g} vibrational mode cannot cause admixing of excited levels with the ground Γ_{7g} doublet, and so can be left out of account for perturbation calculations here. Taking the interaction V to be Ze^2/r_{0i}, where r_{0i} is the distance between a point 0 near the magnetic ion and the ith ligand with effective charge Ze, we get the following expressions for the constants:

$$\begin{aligned}A_4&=-8(\pi/5)^{1/2}(Ze^2/R^4),\\A_5&=(80/9)(\pi/15)^{1/2}(Ze^2/R^6),\\A_6&=(56/3)(2\pi/91)^{1/2}(Ze^2/R^8),\\A_7&=(16/3)(\pi/5)^{1/2}(Ze^2/R^4),\\A_8&=-(200/9)(\pi/15)^{1/2}(Ze^2/R^6),\\A_9&=-(280/9)(2\pi/455)^{1/2}(Ze^2/R^8),\\A_{10}&=(20/3)(2\pi/5)^{1/2}(Ze^2/R^4),\\A_{11}&=0,\\A_{12}&=-(2/9)(455\pi)^{1/2}(Ze^2/R^8),\\A_{13}&=-(616/27)(2\pi/1001)^{1/2}(Ze^2/R^8),\end{aligned}$$

and

$$A_{14}=-(2/27)(1001\pi)^{1/2}(Ze^2/R^8). \tag{8}$$

In this derivation we have used the symmetry modes as given by Leushin[7] for the XY_8 complex. Perturbation calculations up to second order are done with $\mathcal{H}_{\text{Zeeman}}$ and $V_{\text{O-L}}$ between the Γ_{7g}, Γ_{8g}, and Γ_{6g} states[8] of the $J=\frac{7}{2}$ term, and we thus obtain the constants of the dynamical spin Hamiltonian

$$\begin{aligned}C_2&=\frac{192\sqrt{6}}{7\Delta_1}\frac{Ze^2}{R^4}\left(3\alpha_J\langle r^2\rangle+50\beta_J\frac{\langle r^4\rangle}{R^2}+735\gamma_J\frac{\langle r^6\rangle}{R^4}\right),\\C_3&=\frac{64\sqrt{6}}{7\Delta_1}\frac{Ze^2}{R^4}\left(16\alpha_J\langle r^2\rangle+125\beta_J\frac{\langle r^4\rangle}{R^2}+980\gamma_J\frac{\langle r^6\rangle}{R^4}\right),\\C_4&=\frac{320\sqrt{3}}{7\Delta_1}\frac{Ze^2}{R^4}\left(8\alpha_J\langle r^2\rangle+637\gamma_J\frac{\langle r^6\rangle}{R^4}\right).\end{aligned}\tag{9}$$

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[5] A. K. Raychaudhuri and D. K. Ray, Proc. Phys. Soc. (London) **90**, 839 (1967).

[6] W. Low, Phys. Rev. **118**, 1608 (1960).

[7] A. M. Leushin, Fiz. Tverd. Tela **5**, 605 (1963) [English transl.: Soviet Physics—Solid State **5**, 440 (1963)].

[8] Y. Ebina and N. Tsuya, Sci. Rept. Res. Inst. Tohoku Univ. Ser. (B) **12**, 165 (1960).

Here R is the distance between the ligand and the magnetic ions; α_J, β_J, γ_J are the usual coefficients of operator equivalents for the ground states of the Yb^{3+} ion; and Δ_1 is the separation of the excited Γ_{8g} level from the ground Γ_{7g} level. Numerical estimates of the above constants are made with the following values of the parameters involved: $\alpha_J=(2/63)$,[9] $\beta_J=-(2/1155)$,[9] $\gamma_J=4/(63\times143)$,[9] $\Delta_1=7.5\ \mathrm{cm}^{-1}$,[6] $R=4.47a_0$,[10] $\langle r^2\rangle=0.613a_0^2$,[11] $\langle r^4\rangle=0.960a_0^4$,[11] $\langle r^6\rangle=3.104a_0^6$,[11] and $Z=0.6$.[5] We then get

$$\begin{aligned}RC_2&=7.59\times10^2,\\ RC_3&=1.36\times10^3,\\ RC_4&=2.49\times10^3,\end{aligned}\tag{10}$$

for Yb^{3+} in CaF_2. To calculate the transition probability between the spin states we express the symmetry coordinates Q_i in terms of the phonon creation and annihilation operators as follows:

$$Q(\Gamma_g{}^i)=\sum_{\mathbf{k},p}a(\Gamma_g{}^i,\mathbf{k}p)q_{\mathbf{k}p},\tag{11}$$

where

$$q_{\mathbf{k}p}=(\hbar/2M\omega_{\mathbf{k}p})^{1/2}(b_{\mathbf{k}p}+b_{\mathbf{k}p}{}^\dagger),\tag{12}$$

M is the mass of the crystal, $\omega_{\mathbf{k}p}$ is the frequency corresponding to wave vector $\mathbf{k}$ and polarization p, and $b_{\mathbf{k}p}$, and $b_{\mathbf{k}p}{}^\dagger$ are the annihilation and creation operators for phonons. The expressions for $a(\Gamma_g{}^i,\mathbf{k}p)$ are given by Van Vleck[3] for the XY_6 complex, and by Huang[12] for XY_8 complex, in the long-wavelength approximation, which is justified for the single-phonon process. The total Hamiltonian of the spin system is

$$\mathcal{H}=\mathcal{H}_{\mathrm{static}}+\mathcal{H}_{\mathrm{dyn}},\tag{13}$$

where

$$\mathcal{H}_{\mathrm{static}}=g\beta\mathbf{H}\cdot\mathbf{S}\tag{14}$$

for the case of a Kramers doublet in cubic symmetry. Taking the direction of quantization along the Zeeman-field direction, we get the following expression for the transition probability between $|\frac{1}{2}\rangle$ and $|-\frac{1}{2}\rangle$ states from single-phonon processes:

$$\begin{aligned}W_{1/2\to-1/2}={}&(2\pi/\hbar)\,|\langle\tfrac{1}{2}\,|\,\mathcal{H}_{\mathrm{dyn}}(\mathrm{spin})\,|\,-\tfrac{1}{2}\rangle|^2\\ &\times\int\langle|\langle N_k\,|\,\mathcal{H}_{\mathrm{dyn}}(\mathrm{phonon})\,|\,N_k+1\rangle|^2\rangle_{\mathrm{Av}}\\ &\times[4\pi V/(2\pi)^3]k^2dk\,\delta(g\beta H-\hbar\omega_k),\end{aligned}\tag{15}$$

where V is the volume of the crystal and $\mathcal{H}_{\mathrm{dyn}}(\mathrm{spin})$ and $\mathcal{H}_{\mathrm{dyn}}(\mathrm{phonon})$ represent the spin and phonon parts of $\mathcal{H}_{\mathrm{dyn}}$, respectively. To calculate the matrix element $\langle\frac{1}{2}\,|\,\mathcal{H}_{\mathrm{dyn}}(\mathrm{spin})\,|\,-\frac{1}{2}\rangle$ the following transformation of the spin operators will be made:

$$(S_1H_1)_n(\Gamma_\alpha{}^i)=\sum_\mu D_n{}^{\Gamma_\alpha{}^i,\mu}(-\gamma,-\beta,-\alpha)(S_1H_1)_n{}^\mu,\tag{16}$$

where α, β, and γ are the Eulerian angles made by the crystal axes with the system of axes whose Z axis lies along the Zeeman-field direction, and $D_n{}^{\Gamma_\alpha{}^i,\mu}$ are the rotation group elements of rank n. For the spin part in Eq. (15) we thus get

$$\sum_i|\langle\tfrac{1}{2}\,|\,(S_1H_1)_2(\Gamma_{3g}{}^i)\,|\,-\tfrac{1}{2}\rangle|^2=\tfrac{1}{4}H^2[1-(l^4+m^4+n^4)]\tag{17}$$

and

$$\sum_i|\langle\tfrac{1}{2}\,|\,(S_1H_1)_2(\Gamma_{5g}{}^i)\,|\,-\tfrac{1}{2}\rangle|^2=\tfrac{1}{4}H^2[l^4+m^4+n^4].\tag{18}$$

For the phonon part we have to calculate the angular average of $[a(\Gamma_{\alpha g}{}^i,kp)]^2$. In the Debye model for the phonons and the long-wavelength approximation, $\langle a(a(\Gamma_{\alpha g}{}^i,kp))^2\rangle_{\mathrm{Av}}$ is the same for $\alpha=3$, and 5 irreducible representations and their components. Also,

$$\langle a(\Gamma_{\alpha g}{}^i,kp)a(\Gamma_{\alpha' g}{}^{i'},kp)\rangle_{\mathrm{Av}}=0$$

for $\alpha\neq\alpha'$ and $i\neq i'$. This ensures that each symmetry mode contributes independently to the relaxation rate and there is no correlation between the different modes.

The final expression for the relaxation time for Co^{2+} in MgO is given by

$$\begin{aligned}1/T_1={}&\frac{R^2g^3\beta^5H^5}{120\pi\rho\hbar^4}\left(\frac{2}{v_l{}^5}+\frac{3}{v_t{}^5}\right)\coth\frac{g\beta H}{2kT}\\ &\times[C_1{}^2+C_2{}^2\{1-(l^4+m^4+n^4)\}+C_3{}^2(l^4+m^4+n^4)],\end{aligned}\tag{19}$$

where ρ is the density of the crystal, and v_l and v_t are the velocities of the longitudinal and transverse phonons, respectively. From the numerical values of C_1, C_2, and C_3 as given in Eqs. (5) and (6), we can neglect $C_1{}^2$ and $C_3{}^2$ in comparison with $C_2{}^2$ and write the following simplified expression of the relaxation time for Co^{2+} ions in MgO:

$$\begin{aligned}1/T_1={}&\frac{R^2g^3\beta^5H^5}{120\pi\rho\hbar^4}\left(\frac{2}{v_l{}^5}+\frac{3}{v_t{}^5}\right)\\ &\times\coth\frac{g\beta H}{2kT}C_2{}^2\{1-(l^4+m^4+n^4)\}.\end{aligned}\tag{20}$$

Considering the experimental and theoretical values of C_2, we get

$$(1/T_1)_{\mathrm{expt}}=7.7\{1-(l^4+m^4+n^4)\}\ \mathrm{sec}^{-1}$$

and

$$(1/T_1)_{\mathrm{theor.}}=7\times10^2\{1-(l^4+m^4+n^4)\}\ \mathrm{sec}^{-1},\tag{21}$$

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[9] M. T. Hutchings, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1964), Vol. 16, p. 252.

[10] R. W. G. Wyckoff, *Crystal Structures*, (Interscience Publishers, Inc., New York, 1963), Vol. I. p., 241.

[11] A. J. Freeman and R. E. Watson, Phys. Rev. **127**, 2058 (1962).

[12] C. Y. Huang, Phys. Rev. **139**, A241 (1965).

where we have used $g=4.278$,[13] $g\beta H=1\ \text{cm}^{-1}$,[13] $\rho=3.58\ \text{gm/cm}^3$,[14] $v_l=9.2\times10^5$ cm/sec,[15] $v_t=6.7\times10^5$ cm/sec,[15] and $T=4.2$°K. For Yb^{3+} in CaF_2, there is no contribution to the relaxation rate from the $\Gamma_{5g,2}$ mode, in the long-wavelength approximation, because

$$\langle (a(\Gamma_{5g,2}{}^i;\ kp))^2\rangle_{\text{Av}}=0,$$

and we get

$$1/T_1=\frac{R^2g^3\beta^5H^5}{90\pi\rho\hbar^4}\left(\frac{2}{v_l{}^5}+\frac{3}{v_t{}^5}\right)\coth\frac{g\beta H}{2kT}$$
$$\times[C_2{}^2+(C_3{}^2-C_2{}^2)(l^4+m^4+n^4)].\quad(22)$$

Substituting the values of C_2 and C_3 from Eq. (10), we have

$$(1/T_1)_{\text{theor.}}=[6.8+14.9(l^4+m^4+n^4)]\times10^2\ \text{sec}^{-1},\quad(23)$$

where we have used $g=3.426$,[6] $g\beta H=\frac{1}{3}\text{cm}^{-1}$,[6] $\rho=3.21\ \text{gm/cm}^3$,[12] $v_t=3.34\times10^5$ cm/sec,[12] $v_l=7.36\times10^5$ cm/sec,[12] and $T=4.2$°K.

3. DISCUSSION

For Co^{2+} in MgO, the anisotropy of the relaxation rate will follow the function $1-(l^4+m^4+n^4)$. So in this case, the relaxation rate will be a maximum when the Zeeman field is along one of the body diagonals of the octahedron, and a minimum when the Zeeman field is along any one of the crystal axes. Thus, from Eq. (21), we find that for the Zeeman field along the [111] direction, T_1 is 0.19 or 2.14×10^{-3} sec, according as we assume the experimental or the theoretical value of C_2. For the Zeeman field along the [100] direction, T_1 reaches its maximum value, which in this approximation is infinitely large. The terms proportional to $C_1{}^2$ and $C_3{}^2$ which were neglected in deriving Eq. (20) will determine the true maximum value of T_1. Though the above conclusions are derived under the approximation of the Debye model for low-frequency phonons, it is expected[16] that these results will remain unaltered if a more realistic model[17] of the phonon distribution is considered. The anisotropy as well as the magnitude of T_1 for Co^{2+} in MgO will therefore be mainly determined by the dynamical-Hamiltonian constants. It will be interesting to measure T_1 at low temperature with different orientations of the Zeeman field about the crystal axes and verify the large range of variation in T_1 as predicted above. Moreover, the minimum value of the experimentally measured T_1 in this sample will justify the correctness of the perturbation expression for the transition probability. The results will, however, be substantially changed if minute traces of any fast-relaxing ion such as Cr^{2+} are present in the crystal.

For Yb^{3+} in CaF_2, the Eq. (23) shows that the relaxation time is a maximum when the Zeeman-field direction is along a body diagonal, and a minimum when it is along a crystal axis. The maximum and minimum values of T_1 are, respectively, 0.4×10^{-3} and 0.2×10^{-3} sec. These values are obtained from a point-charge model of ligand ions, and are expected to be increased by covalency effects, though the covalency factor will not be as important as for the iron-group ions.

In general, for Kramers doublets in cubic crystals, the anisotropy of the spin-lattice relaxation time will depend on the relative contributions to it from Γ_{3g} and Γ_{5g} symmetry modes. If one of the modes dominates the other, then the relaxation time is expected to be fairly anisotropic; if the modes contribute equally, then the relaxation time will be isotropic. Also, the derivations in this paper have been carried out under the condition that the phonons are in thermal equilibrium, and it will be interesting to study the deviations when phonon equilibrium is not assumed.

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[13] W. Low, Phys. Rev. **109**, 256 (1958).

[14] *Handbook of Chemistry and Physics*, edited by C. D. Hodgman (The Chemical Rubber Publishing Co., Cleveland, Ohio, 1961), p. 603.

[15] N. S. Shiren, in *Proceedings of the Colloque Ampere (Atomes et Molecules par des Etudes Radioelectriques), 1962* (North-Holland Publishing Company, Amsterdam, 1963), p. 114.

[16] D. K. Ray, T. Ray, and S. K. Gupta, J. Appl. Phys. Suppl. (to be published).

[17] G. Peckham, Proc. Phys. Soc. (London) **90**, 657 (1967).