THE

PHYSICAL REVIEW

A journal of experimental and theoretical physics established by E. L. Nichols in 1893

SECOND SERIES, VOL. **154**, NO. 2 — 10 FEBRUARY 1967

Optical Phonons in Electron Spin Relaxation*†

CHAO-YUAN HUANG‡
Department of Electrical Engineering and Department of Physics,
Washington University, St. Louis, Missouri

(Received 21 July 1966; revised manuscript received 6 October 1966)

An approximate dispersion curve for the optical branch of the lattice vibration is used to estimate the spin-lattice relaxation time attributed to optical phonons. The relaxation rate is found to be $T_1^{-1}\propto \exp(-\hbar\omega_{0j}/kT)$, where ω_{0j} is an optical-phonon frequency at $\mathbf{k}=0$. It is also found that if the bandwidth of the optical mode is narrow, if the optical-phonon energy is low, and if the lattice vibration is even, then the spin-optical phonon relaxation process can dominate the conventional acoustical processes. The applications of the theory to some experimental results are also discussed.

I. INTRODUCTION

Many authors[1–7] have shown that the dominant electron spin-lattice interaction is through the modulation of the Stark field by the acoustic phonons. The contribution to the spin-lattice relaxation attributed to optical phonons has been neglected, because the Bose-Einstein factor

$$N(\omega)=[\exp(\hbar\omega/kT)-1]^{-1} \qquad (1)$$

is small at low temperatures. Here ω is the optical-phonon angular frequency. This fact, however, is not sufficient for us to ignore the importance of the spin-optical phonon interaction, since the density of states also plays an important role in the spin-phonon interaction. Usually, the phonon density of states of optical modes is much greater than that of the acoustical ones. In other words, the velocity of an optical phonon is much smaller than that of an acoustic phonon. This can easily be understood by noting that both an acoustic and an optical mode contain the same number of states and that the bandwidth of an optical mode is much narrower than an acoustic-phonon bandwidth. For instance, let us consider a one-dimensional case. Figure 1 shows a typical dispersion of a diatomic linear chain[8] with $m>m'$. The bandwidth of the optical mode is given by

$$\Delta\omega=(2\beta)^{1/2}[(1/m'+1/m)^{1/2}-(1/m')^{1/2}], \qquad (2)$$

where β is the force constant between two adjacent masses. Therefore, if the ratio of the two masses m'/m is very small, the bandwidth of the optical mode will

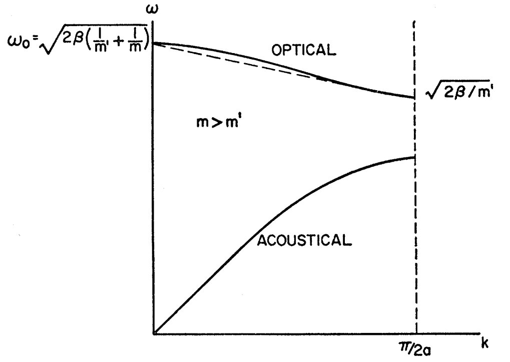

FIG. 1. Dispersion of optical and acoustical branches of a diatomic linear chain.

---

* A portion of this work was supported by the National Science Foundation under Grants Nos. NSF GP-3211 and NSF GP-5070, Washington University.

† Part of this work was done when the author was at Harvard University, Cambridge, Massachusetts, supported by U. S. Office of Naval Research Grant No. Nonr1866(16)7376-4.

‡ Present address: Department of Physics, Western Reserve University, Cleveland, Ohio.

[1] W. Heitler and E. Taylor, Proc. Roy. Soc. (London) **A155**, 629 (1936).

[2] M. Fierz, Physica **5**, 433 (1938).

[3] R. de L. Kronig, Physica **6**, 33 (1939).

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

[5] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

[6] P. L. Scott and C. D. Jeffries, Phys. Rev. **127**, 32 (1962).

[7] Chao-Yuan Huang, Phys. Rev. **139**, A241 (1965).

[8] See, for example, C. Kittel, *Introduction to Solid State Physics.* (John Wiley & Sons, Inc., New York, 1957), p. 111.

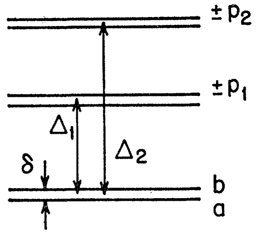

FIG. 2. A representative spin system of a Kramers salt.

be very narrow. It follows that the density of states of the optical mode is much greater than that of the acoustical mode, since the numbers of states for both modes are equal. Consequently, we can see that the contribution to the relaxation to be attributed to optical phonons might therefore be important. The theory based on this fact will be given in Sec. II, and it will be used in Sec. III to explain the experimental data obtained by the author and others.

II. THEORY

For simplicity, we shall restrict ourselves to the case in which only Kramers salts of the rare-earth ions will be considered. The extension to non-Kramers salts and to the transition-metal ions is straightforward. A representative spin system of a Kramers salt is as shown in Fig. 2, where δ is the Zeeman splitting, Δ_1, Δ_2, $\cdots$ are the crystalline-field splittings, $|a\rangle$ and $|b\rangle$ are the components of the ground Kramers doublet, and $|\pm p_1\rangle$, $|\pm p_2\rangle$, $\cdots$ are the excited Kramers doublets.

For the rare-earth ions, the spin-orbit interaction is normally included in the wave functions. Hence only the orbit-lattice interaction needs to be considered for the calculation of the spin-lattice relaxation time. Since the same technique used by Orbach[5] and the author[7,9] is to be used in this paper, we shall only point out the differences between the present theory and Orbach's theory.

The Van Vleck orbit-lattice interaction can be written as[4,7]

$$V_{01}=\sum_j v_j Q_j \tag{3}$$

where Q_j is the normal coordinate transforming like the jth irreducible representation of the molecular cluster,[10] and v_j is the associated electronic operator. As pointed out by Van Vleck, the displacements of the lth ion of the molecular cluster, (X_l,Y_l,Z_l), depend on the ith mode of thermal vibrations in the form

$$X_l=q_i\phi_{xi}\cos(\gamma_{li}-\delta_i)\,, \tag{4}$$

$$\gamma_{li}=k_i(\gamma_{xi}x_l^0+\lambda_{yi}y_l^0+\lambda_{zi}z_l^0)\,, \tag{5}$$

where q_i is the ith normal coordinate associated with the phonons, ϕ_{xi} is the direction cosine of the wave q_i, while k_i and λ_{xi} are, respectively, its wave vector and direction of polarization. The equilibrium coordinates of this ion are (x_l^0, y_l^0, z_l^0). Because only phonons with long wavelengths are involved in the *spin-acoustical phonon relaxation*, as given in Ref. 7, one normally assumes that $\gamma_{li}\ll 1$. This assumption is no longer correct for the calculation of the *spin-optical phonon relaxation time*. For optical modes, $\omega(k)$ varies slowly with respect to k, and the major contribution to relaxation comes from large values of k where the phonon densities of states are high. Then we can approximate the average value as[11]

$$\langle|\phi_{xi}\cos(\gamma_{li}-\delta_i)|^2\rangle_{\mathrm{av}} \simeq\langle\phi_{xi}^2\rangle_{\mathrm{av}}\langle\cos^2(\gamma_{li}-\delta_i)\rangle_{\mathrm{av}}=\tfrac{1}{6}\,, \tag{6}$$

in which $\langle\cdots\rangle_{\mathrm{av}}$ denotes the average. Furthermore, Born and Huang[12] have shown that the transverse motion of the optical vibrations of large wavelengths does not produce electric fields. This means that only longitudinal phonons of large wavelengths are important in the spin-optical phonon relaxation. However, as we pointed out earlier, the major contribution to the spin-optical phonon relaxation comes from large values of k, and hence the transverse optical waves are as important as the longitudinal ones.

For lack of the detailed knowledge of the optical-phonon dispersion an estimate of the relaxation time closer than to within one order of magnitude is not possible. In view of this fact, only very crude estimates can be made. Within the crude approximation, we shall assume that the results for the calculation for a diatomic linear chain still hold in a solid. For a narrow band, we may approximate the dispersion of an optical mode by a straight line as shown in Fig. 1, keeping the same bandwidth. The approximated dispersion is then expressed by

$$k=(\pi/2a(\Delta\omega))(\omega_0-\omega)\,, \tag{7}$$

where a is the interatomic distance, and ω_0 is the optical-phonon angular frequency at $k=0$. In consequence of this approximation, the summation over the phonon states of the jth optical mode can be replaced by an integration in the following way:

$$\sum_{i=1}^{N}=\frac{V}{2\pi^2}\int k^2dk=-\frac{\pi V}{2^4[a(\Delta\omega)]^3}\int_{\omega_{0j}-\Delta\omega}^{\omega_{0j}}(\omega_{0j}-\omega)^2d\omega\,, \tag{8}$$

where N is the total number of unit cells in the crystal, V is the volume of the crystal, and ω_{0j} is the optical-phonon angular frequency at $k=0$ which transforms like the jth irreducible representation of the lattice vibrations.

---

[9] Chao-Yuan Huang, doctoral thesis, Harvard University, 1964 (unpublished).

[10] See, for instance, C. Y. Huang and M. Inoue, J. Phys. Chem. Solids **25**, 889 (1964).

[11] This fact was pointed out to the author by Professor J. H. Van Vleck, to whom he is indebted.

[12] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, England, 1954), p. 87.

In practice, the optical-phonon energy is much greater than the Zeeman splitting δ. Consequently, optical phonons can only contribute to the two-phonon processes. In a two-phonon process, only phonons with energies $\hbar\omega_1$ and $\hbar\omega_1+\delta$ are involved. As a result, if $\hbar\Delta\omega<\delta$ and if $\hbar\omega_1$ falls within the range $\hbar\omega_0\geq\hbar\omega_1>\hbar(\omega_0-\Delta\omega)$, then within this particular optical-phonon branch it is not possible to find the second phonon of this particular two-phonon process having the energy $\hbar\omega_2=\hbar\omega_1+\delta$. Hence, if $\hbar\Delta\omega<\delta$, then the spin-optical phonon interaction cannot contribute to relaxation.

In the remainder of this section, we shall derive the expressions for T_1 within our crude approximation. Since the crystalline field splitting Δ_t plays an important role in the spin-lattice interaction, three cases, based on the crystalline field splitting relative to the optical-phonon energy, will be treated.

Case A. $\hbar\omega_{0j}\ll\Delta_t$

Let us first find the transition probabilities between $|a\rangle$ and $|b\rangle$ via the spin-lattice interaction. The transition probability per unit time to go from $|b\rangle$ to $|a\rangle$ can be written as

$$W_{b\to a}=\frac{2\pi}{\hbar}N_b\left\{\frac{\pi V}{2^4[a(\Delta\omega)]^3}\right\}^2 \times\int\int|\langle N(\omega)|\langle a|V_{\text{eff}}|b\rangle|N(\omega')\rangle|^2 \times\delta(\hbar\omega_1+\delta-\hbar\omega_2)(\omega_{0j}-\omega_1)^2(\omega_{0j}-\omega_2)^2d\omega_1d\omega_2\,, \quad (9)$$

in which N_b is the population of spins in $|b\rangle$, ω_1 and ω_2 are, respectively, the angular frequencies of the first and second optical phonons, $|N(\omega)\rangle$ and $|N(\omega')\rangle$ are the phonon wavefunctions, and V_{eff} is the effective orbit-lattice interaction for a two-phonon process introduced by Orbach.[5] For a Kramers salt, if $\Delta_t\gg\hbar\omega$, the "Van Vleck cancellation" results. Taking this fact into account, using Eq. (6), and making use of the facts that $\hbar\omega_0\gg\delta$, and $\omega_1\sim\omega_2$, we find

$$W_{b\to a}\cong\frac{\pi^3\hbar^2}{9\times2^7[a(\Delta\omega)]^6\rho^2}\sum_j\left|\sum_t\frac{\langle a|v_j|+p_t\rangle\langle+p_t|v_j|b\rangle}{\Delta_t^2}\right|^2 \times\int_{\omega_{0j}-\Delta\omega}^{\omega_{0j}}(\omega_{0j}-\omega_1)^2(\omega_{0j}-\omega_1-\delta/\hbar)^2 \times N_bN(\omega_1)[N(\omega_1+\delta/\hbar)+1]d\omega_1\,. \quad (10)$$

Here ρ is the density of the crystal, Δ_t is the energy spacing between the ground-state doublet and the excited state $|p_t\rangle$, and $N(\omega_1)$ is the Bose-Einstein factor evaluated at $\omega=\omega_1$. Similarly, the transition probability per unit time to go from $|a\rangle$ to $|b\rangle$ is

$$W_{a\to b}=\frac{\pi^3\hbar^2}{9\times2^7[a(\Delta\omega)]^6\rho^2}\sum_j\left|\sum_t\frac{\langle a|v_j|+p_t\rangle\langle+p_t|v_j|b\rangle}{\Delta_t^2}\right|^2 +\int_{\omega_{0j}-\Delta\omega}^{\omega_{0j}}(\omega_{0j}-\omega_1)^2(\omega_{0j}-\omega_1-\delta/\hbar)^2 \times N_aN(\omega_1+\delta/\hbar)[N(\omega_1)+1]d\omega_1\,. \quad (11)$$

The spin-lattice relaxation time is just a characteristic time for a spin temperature to relax to the temperature at thermal equilibrium, and hence is defined by the relation

$$\frac{d(N_b-N_a)}{dt}=-\frac{(N_b-N_a)-(N_b-N_a)_0}{T_1}\,, \quad (12)$$

where (N_b-N_a) is the population difference at the time t when the spin system is characterized by a spin temperature, and $(N_b-N_a)_0$ is the population difference at thermal equilibrium. If the bath temperature is sufficiently low such that only the ground-state doublet is populated, the rate equation can be written as

$$\frac{d(N_b-N_a)}{dt}=2(W_{b\to a}-W_{a\to b}) \simeq\frac{\pi^3\hbar^2}{9\times2^8[a(\Delta\omega)]^6\rho^2}\sum_j\left|\sum_t\frac{\langle a|v_j|+p_t\rangle\langle+p_t|v_j|b\rangle}{\Delta_t^2}\right|^2 \times[N_b\exp(\delta/kT)-N_a]\exp(-\delta/kT) \times\int_{\omega_{0j}-\Delta\omega}^{\omega_{0j}}(\omega_{0j}-\omega_1)^4\operatorname{csch}^2(\hbar\omega_1/2kT)d\omega_1\,. \quad (13)$$

By considering that $\omega_1\sim\omega_{0j}$ for a narrow band, and assuming that $\delta\ll kT\ll\hbar\omega_{0j}\ll\Delta_t$, the last expression becomes

$$\simeq\frac{\pi^3\hbar^2}{9\times5\times2^6a^6(\Delta\omega)\rho^2}\sum_j\left|\sum_t\frac{\langle a|v_j|+p_t\rangle\langle+p_t|v_j|b\rangle}{\Delta_t^2}\right|^2 \times(N_b-N_a)\exp(-\hbar\omega_{0j}/kT)\,. \quad (14)$$

Therefore, the spin-phonon relaxation time attributed to optical phonons is given by

$$\frac{1}{T_1}=\frac{\pi^3\hbar^2}{9\times5\times2^6a^6(\Delta\omega)\rho^2}\sum_j\left|\sum_t\frac{\langle a|v_j|+p_t\rangle\langle+p_t|v_j|b\rangle}{\Delta_t^2}\right|^2 \times\exp(-\hbar\omega_{0j}/kT)\,. \quad (15)$$

We see that the relaxation time of a Raman process involving optical phonons depends exponentially on the temperature, in marked contrast with a conventional acoustical Raman process via which the relaxation time is inversely proportional to the ninth power of the temperature.

The spin-lattice interaction operator given by Eq. (3) is invariant with respect to the symmetry transformations of a crystal. Therefore, according to group theory, both the electronic operator v_j and the normal coordinate Q_j must transform according to the same irreducible representation (the jth irreducible representation). As a result, if Q_j represents an odd vibration of the lattice, v_j is also an odd operator. For this reason, the excited state $|p_t\rangle$ must be within an excited configuration in order that the matrix element $\langle a|v_j|+p_t\rangle$ is nonvanishing. This means that Δ_t is greater than 10 000 cm^{-1}. In addition, in a diatomic linear chain the lattice vibrations of optical phonons are purely even at the Brillouin zone boundary at which the density of states is the highest. Hence, the effective spin-phonon interaction attributed to conventional Raman process will be much greater than that attributed to the processes involving optical phonons of *odd* vibrations. Consequently, only optical phonons of even vibrations are important in spin-lattice relaxation.

Case B. $\hbar\omega_{0j}\gg\Delta_t$

This case is very similar to the spin-lattice relaxation in a multilevel spin system, discussed by Orbach and Blume[13] and by others.[7,14] If we take into account that $\omega_1\sim\omega_{0j}$ and assume that $\delta\ll kT\ll\hbar\omega_{0j}$, then the spin-lattice relaxation rate is

$$\frac{1}{T_1}=\frac{\pi^3}{9\times5\times2^6a^6(\Delta\omega)\rho^2\hbar^2}\sum_j\left|\sum_t\langle a|v_j|+p_t\rangle\langle+p_t|v_j|b\rangle\right|^2\times\frac{\exp(-\hbar\omega_{0j}/kT)}{\omega_{0j}{}^4}. \quad (16)$$

The relaxation time of this process again depends exponentially on the temperature, and hence this process would be important at high temperatures. For a Kramers salt, we must also exclude all odd vibrations, because of the assumption that $\hbar\omega_{0j}\gg\Delta_t$, where $\hbar\omega_{0j}$ is in practice less than 1000 cm^{-1}.

Case C. $\hbar\omega_{0j}\sim\Delta_t$

This is essentially the case of a *two-phonon resonant process* involving optical phonons, but there is a difference between this process and an acoustical Orbach process. As we pointed out earlier, if $\hbar\Delta\omega<\delta$, and $\hbar\omega_{0j}\geq\hbar\omega_1\geq\hbar\omega_{0j}-\delta$, then optical phonons do not contribute to the spin-lattice relaxation. To date, most relaxation times are measured at microwave frequencies. It follows that in practice $\delta\ll\Delta\omega$. Based on the same argument presented earlier, if the crystalline field splitting falls in the region $\hbar\omega_{0j}\geq\Delta_t\geq\hbar\omega_{0j}-\delta$, then the two-optical phonon resonant process will not exist. In spite of this fact, the transition probability of the Raman process attributed to optical phonons with energies between $\hbar\omega_{0j}-\delta$ and $\hbar\omega_{0j}-\Delta\omega$ is still very great, since the energy denominators in the effective spin-lattice interaction $\hbar\omega-\Delta_t$ are small. For this special case, if the bandwidth $\Delta\omega$ is narrow, T_1 will also depend exponentially on the temperature. However, if the crystalline field splitting falls in the range $\hbar\omega_{0j}-\delta\geq\Delta_t\geq\hbar\omega_{0j}-\Delta\omega$, an optical phonon Orbach process can take place. Following the same technique used to calculate the relaxation time of an acoustical Orbach process, we find that the spin-lattice relaxation rate of an optical phonon Orbach process is given by

$$\frac{1}{T_1}=\frac{\pi^3\hbar^2}{9\times2^9[a(\Delta\omega)]^6\rho^2}\sum_j\sum_t(\pi/\hbar\Gamma_t)\operatorname{csch}^2(\hbar\omega_{0j}/2kT)\times|\langle a|v_j|+p_t\rangle\langle+p_t|v_j|b\rangle|^2\frac{(\omega_{0j}-\Delta_t/\hbar)^4}{\Delta_t{}^2}, \quad (17)$$

where

$$\Gamma_t=\frac{\pi^2\hbar}{3\times2^4[a(\Delta\omega)]^3\rho}\sum_j\sum_t\frac{(\omega_{0j}-\Delta_t/\hbar)^2}{\Delta_t}\frac{\exp(\hbar\omega_{0j}/kT)}{\exp(\hbar\omega_{0j}/kT)-1}\times(|\langle a|v_j|+p_t\rangle|^2+|\langle+p_t|v_j|b\rangle|^2). \quad (18)$$

Here we have used the approximation that $\exp(\hbar\omega_{0j}/kT)\simeq\exp(\Delta_t/kT)$. If there is only one excited state $|p_t\rangle$ whose energy falls within the range $\hbar\omega_{0j}-\delta\geq\Delta_t\geq\hbar\omega_{0j}-\Delta\omega$ for the jth optical branch, we have

$$\frac{1}{T_1}=\frac{\pi}{3\times2^3[a(\Delta\omega)]^3\rho}|\langle a|v_j|+p_t\rangle\langle+p_t|v_j|b\rangle|^2\times(|\langle a|v_j|+p_t\rangle|^2+|\langle+p_t|v_j|b\rangle|^2)^{-1}\times\frac{(\omega_{oj}-\Delta_t/\hbar)^2}{\Delta_t}\exp(-\hbar\omega_{0j}/kT). \quad (19)$$

Here we have assumed $\hbar\omega_{0j}\gg kT\gg\delta$. The factor $(\omega_{0j}-\Delta_t/\hbar)$ in the last equation demonstrates to us that the spin-lattice interaction becomes stronger if the phonons involved in the two-phonon process have high values of k. This consequence is compatible with the fact that the density of states is higher at the higher values of k. For this reason, the restriction that $\Delta\omega$ be narrow may not be serious.

As pointed out previously, when $\hbar\omega_{0j}\sim\Delta_t$, the energy denominators in V_{eff} will be small, and hence there is a strong Raman process attributed to optical phonons. Therefore, if $\hbar\omega_{0j}\sim\Delta_t$, then the relaxation time will be short compared to those given by Eqs. (15) and (16), even though Δ_t does not fall between $\hbar\omega_{0j}-\delta$ and $\hbar\omega_{0j}-\Delta\omega$.

Combining the results obtained above, we find that the relaxation time of a Kramers salt of the rare-earth ions depends exponentially on the temperature. The exponential temperature dependence comes about

---

[13] R. Orbach and M. Blume, Phys. Rev. Letters 8, 478 (1962).

[14] R. Bierig, M. Weber, and S. Warshaw, Phys. Rev. 134, A1504 (1964).

because $\omega_1 \sim \omega_{0j}$ and $\hbar\omega_{0j} \gg kT$. These two conditions are just characteristic of the host lattice and have nothing to do with the doped paramagnetic ions. In view of this, we will expect that the relaxation time of a non-Kramers salt of the rare-earth ions and a salt doped with the transition metal ions will have the same temperature dependence under the same conditions.

III. COMPARISON OF THEORY WITH EXPERIMENTAL RESULTS

It has been shown[7] that the relaxation rate of Nd^{3+} in yttrium aluminum garnet (YAlG) from 7 to 20°K is best fitted into an exponential form as

$$1/T_1 = 4.5\times 10^{10} \exp(-75\times 1.44/T) \text{ sec}^{-1}, \quad (20)$$

where T is in degrees Kelvin. From the optical spectra of Nd^{3+}: YAlG, Koningstein and Geusic[15] have demonstrated that the first excited electronic state is at 135 cm^{-1} above the ground Kramers doublet. As a result, Eq. (26) is certainly not the consequence of an acoustical Orbach process. Nonetheless, Sievers and Tinkham,[16] based on their data of far-infrared absorption, have reported that the vibration around 80 cm^{-1} is characteristic of all the garnets. In consequence of this fact, instead of being identified as due to an acoustical Orbach process, Eq. (20) can be considered to be attributed to an optical two-phonon process in which optical phonons of energies $\hbar\omega \sim \Delta$ are involved (Case C). Another possible example for the verification of the theory is the case of Nd^{3+} doped yttbium gallium garnets in which the relaxation rate is well described by[7]

$$1/T_1 = 17T + 9.0\times 10^{10} \exp(-85\times 1.44/T) \text{ sec}^{-1}. \quad (21)$$

If the same argument for the Nd^{3+} doped YAlG is taken, then the second term in Eq. (21) is also due to an optical two-phonon relaxation process.

Recently, Hartman *et al.*[17] found that the relaxation data of Cr^{3+} in MgO for temperatures from 80 to 150°K can be accurately fitted by

$$\begin{aligned}1/T_1 = 3\times 10^{6} &\exp(278\times 1.44/T) \\ &\times[\exp(278\times 1.44/T)-1]^{-2} \\ &+6.1\times 10^{7} \exp(-490\times 1.44/T) \text{ sec}^{-1}. \quad (22)\end{aligned}$$

Bennett *et al.*[18] also fit the experimental data of Fe^{3+} in the same host from 44 to 300°K to the equation

$$\begin{aligned}1/T_1 = 5\times 10^{7} &\exp(278\times 1.44/T) \\ &\times[\exp(278\times 1.44/T)-1]^{-2} \\ &+8\times 10^{8} \exp(-490\times 1.44/T). \quad (22')\end{aligned}$$

Since there is no electronic state at 490 cm^{-1} above the ground state, the second term cannot be due to an acoustical Orbach process. Notwithstanding, Imbusch *et al.*[19] have identified the 490 cm^{-1} peak in their fluorescent spectrum to correspond to an optical branch of the MgO phonon spectrum. Therefore, the last terms in Eqs. (22) and (22′) are attributed to the spin-two optical-phonon processes involving the 490 cm^{-1} optical phonons.

IV. CONCLUSION

Combining all the results for both spin-acoustical and optical-phonon relaxation processes, we find that the relaxation rate of a pair of time-conjugate states can be written as

$$\begin{aligned}1/T_1 = aT + bT^5 + cT^9 + d &\exp(-\Delta/kT) \\ &+ f\exp(-\hbar\omega_0/kT), \quad (25)\end{aligned}$$

where a, b, c, d, and f are constants. The first term in Eq. (23) represents a direct process which normally dominates at very low temperatures; the second term exists only when the ground state has more than two sublevels; the third term arises from a conventional Raman process; the fourth term is due to an acoustical Orbach process; and the fifth term describes a spin-optical phonon process. According to the theory presented in Sec. II and those experimental results discussed in Sec. III, an *optical two-phonon process* can dominate *acoustical two-phonon processes* at high temperatures, provided that the bandwidth of an optical branch of the lattice is narrow, the optical-phonon energy is not too high, and the lattice vibration is even. Since only the even optical phonons are involved in the spin-optical phonon relaxation process, the relaxation-time measurement could thus help identify optical modes of the lattice.

ACKNOWLEDGMENTS

The author wishes to thank Professor Orbach for his suggestions and encouragement during the early phases of this work, Professor J. H. Van Vleck for his comments, corrections, and discussions during the later phases, and Professor N. Bloemberger for helpful discussions. He would also like to thank Professor D. Bolef and Professor D. Huber for reading the manuscript.

---

[15] J. A. Koningstein and J. E. Geusic, Phys. Rev. **136**, A711 (1964).

[16] A. J. Sievers, III, and M. Tinkham, Phys. Rev., **129**, 1995 (1963).

[17] R. L. Hartmen, Alfred C. Daniel, J. S. Bennett, and J. G. Castle, Jr., Bull. Am. Phys. Soc. **11**, 313 (1966).

[18] J. S. Bennett, R. L. Hartman, and J. G. Castle, Bull. Am. Phys. Soc. **11**, 482 (1966).

[19] G. F. Imbush, W. M. Yen, A. L. Schawlow, D. E. McCumber, and M. D. Sturge, Phys. Rev. **133**, A1029 (1964).