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Temperature Dependence of Spin-Lattice Relaxation in Alkali Halides

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The nuclear spin-lattice relaxation time T_1 has been measured in NaF, KBr, KI, NaI, and LiBr at temperatures ranging from 20–800°K to determine the sensitivity of T_1 to changes in the lattice vibrational spectrum and the relative importance of acoustic and optic phonons for quadrupolar relaxation. The theoretical temperature dependence for T_1 derived by Van Kranendonk for two-phonon Raman processes using a Debye spectrum does not fit the data for all crystals. The discrepancies are attributed to the importance of optic phonons for quadrupolar relaxation in crystals having large mass ratios. Different temperature dependences are expected for relaxation arising from acoustic and optic phonons. A simple temperature dependence for T_1 obtained by approximating the frequency distribution of the acoustic vibrations by a Debye spectrum and the optic vibrations by an Einstein spectrum is discussed and applied to the data for KI and NaI.

INTRODUCTION

THE rate of nuclear and electron spin-lattice relaxation in solids arising from interactions with lattice vibrations depends upon the temperature and lattice vibrational spectrum. In this paper the temperature dependence of the spin-lattice relaxation time T_1 in alkali halides is investigated to determine the sensitivity of T_1 to the exact form and nature of the lattice vibrational spectrum and the relative importance of acoustic and optic vibrations for relaxation.[1]

Whereas the low-frequency end of the phonon spectrum in crystals may be approximated by a simple Debye spectrum, the more dense high-frequency portion differs from crystal to crystal and usually exhibits maxima associated with individual acoustic and optic vibrational branches. These high-frequency phonons are active at high temperatures in multiple phonon spin-lattice relaxation processes. The transition probabilities for these processes are calculated by summing over combinations of phonon frequencies which conserve the energy of the spin transition. The resulting temperature dependence of T_1 is governed by the assumptions and treatment made of the spin-lattice interactions and lattice dynamics. Since the relaxation processes involve an integrated effect of the total vibrational spectrum, their rate and temperature dependence may be expected to be relatively insensitive to the detailed properties of the lattice vibrations of a given crystal.[2] Nevertheless, a careful study of the temperature dependence of two-phonon Raman relaxation should provide some information about gross features of the phonon spectrum.

Alkali halide crystals are an attractive choice for such a study because (1) the relaxation of nuclei[3] with spin $I>1/2$ is predominantly quadrupolar and has been investigated both theoretically and experimentally,[4] (2) the vibrational frequency distributions have been calculated[5] and related experimental data are available, and (3) by selecting compounds having different mass ratios of the positive and negative ions, the over-all form of the vibrational spectrum and the relative location of the acoustic and optic branches can be varied. As we shall be interested in quadrupolar relaxation arising from two-phonon processes, one must be careful

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[1] A brief report of this work was presented at the International Conference on Magnetic and Electric Resonance and Relaxation, Eindhoven, Netherlands, July, 1962.

[2] A somewhat analogous situation occurs in the theory of specific heats where it is well known that specific heat curves are quite independent of changes in the lattice vibrational spectrum.

[3] Raman relaxation can also be investigated in electron paramagnetic resonance, however, in cases where the paramagnetic ion is introduced as an impurity into a diamagnetic host lattice, the lattice vibrations may be modified due to localized vibrational modes. [P.G. Klemens, Phys. Rev. **125**, 1795 (1962).]

[4] E. G. Wikner, W. E. Blumberg, and E. L. Hahn, Phys. Rev. **118**, 631 (1960), and references therein.

[5] A. M. Karo, J. Chem. Phys. **31**, 1489 (1959) and **33**, 7 (1960).

to distinguish these from competing relaxation mechanisms of magnetic or quadrupolar origin due to effects such as the presence of paramagnetic impurities and diffusional motion. The identification of competing processes can usually be established by their different temperature dependences.

Van Kranendonk[6] (VK) has calculated a detailed temperature dependence for Raman quadrupolar relaxation probabilities in a point charge NaCl-type lattice. An isotropic monotonic lattice having a simple Debye lattice frequency spectrum was assumed in the derivation. This treatment has received considerable attention in experimental and theoretical investigations of quadrupolar relaxation and has been successfully used to interpret measurements of the temperature dependence of T_1 for many crystals, even including crystals having different lattice structures. In spite of the averaging effects of Raman processes, Van Kranendonk's temperature dependence is not expected to be universally applicable to lattice induced quadrupolar relaxation in all solids. Whether the use of a simple Debye lattice approximation is sufficient to yield a T_1 temperature dependence adequate for all alkali halides will depend upon the sensitivity of T_1 to the exact form of the quadrupolar spin-lattice coupling and the lattice vibrational spectrum. Some of the past success is probably due to the fact that many measurements and comparisons were made at temperatures $T \gtrsim 0.5\Theta$, where Θ is the Debye temperature for the crystal. In this region the temperature dependence of a two-phonon Raman process approaches a T^2 law independent of the form of the spin-lattice coupling or the vibrational spectrum.

By the nature of Van Kranendonk's assumptions, no explicit treatment is made of the optic vibrational modes in the diatomic NaCl lattice. The effects of optic phonons for quadrupolar relaxation have been considered by Kochelaev[7] and Blumberg[4,8] who predict that in several alkali halides the optic vibrations are the dominant source of relaxation at room temperature. Using their results one generally obtains better agreement between theoretical and experimental T_1 values than with the VK theory alone. Since the optic branches usually occur as a high, narrow range of frequencies in the vibrational spectrum, they will depopulate more rapidly with decreasing temperature than the lower frequency acoustic branches. Thus, the temperature dependence of T_1 should be different for those cases in which the relaxation is due principally to optic or acoustic vibrations, particularly at low temperatures. This, in principle, should provide a means of establishing the relative importance of acoustic and optic phonons for relaxation in addition to magnitude arguments.

In the experiments and discussion to follow, an attempt has been made to investigate nuclear relaxation systematically over a wide temperature range for a single crystal symmetry, but in samples having different vibrational spectra. Alkali halides with mass ratios ranging from approximately one for sodium fluoride to eleven for lithium bromide have been studied. Due to present ambiguities in determining the operative spin-lattice coupling mechanisms for quadrupolar relaxation in many alkali halides,[4] we shall concern ourselves almost exclusively with the temperature dependence rather than the absolute magnitude of the relaxation time.

EXPERIMENTAL

Measurements of the spin-lattice relaxation time T_1 were made using pulsed nuclear magnetic induction techniques. The spectrometer was of conventional design and consisted of a pulsed oscillator and narrow-band receiver operating in the frequency range 10–12 Mc/sec. A 90°–90° pulse sequence was used to determine T_1. To insure complete saturation of the spin system at time $t=0$, a series of closely spaced approximately 90° pulses were applied. The recovery of the spin system toward equilibrium was measured by varying the time interval between the two pulse series and observing the relative free-precession signal amplitudes following the first pulse of each series. The relaxation exhibited a simple exponential time dependence with a characteristic time defined as T_1. Data were recorded by photographing the oscilloscopic display of the detected free-precession decay signals. Since the signal amplitudes varied greatly over the temperature range investigated and from sample to sample, the linearity of the over-all receiver response was carefully checked. The experimental points represent an average of several measurements at each temperature; the estimated error of the data is in the range 5–10%.

A wide range of sample temperatures was obtained using several different methods. The sample fit snugly inside a solenoidal rf transmit-receiver coil which was enclosed in a copper shielding can and connected by rigid stainless steel coaxial lines to the pulsed oscillator and receiver. This unit was placed inside a single glass Dewar in the 2-in. gap of a 12-in. Varian electromagnet. An adjustable flow of helium gas from a container of liquid helium was used to cool the sample in the temperature range 10–50°K. Fixed temperatures of 77, 90, and 243°K were obtained by filling the Dewar with liquid nitrogen, oxygen, and Freon 12 (CCl_2F_2), respectively. By pumping on the nitrogen and Freon 12 at different rates, the temperature could be varied within the ranges 53–77°K and 165–243°K. Measurements in NaI were made in a metal Dewar in which a continuous range of temperatures from 77–300°K was controlled by a variable heater inserted in the thermal conducting path between the sample and a reservoir of liquid coolant. For temperatures between room temperature

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[6] J. Van Kranendonk, Physica **20**, 781 (1954).

[7] B. I. Kochelaev, Zh. Eksperim. i. Teor. Fiz. **37**, 242 (1959) [translation: Soviet Phys.—JETP **10**, 171 (1960)].

[8] W. E. Blumberg, Ph.D. thesis, University of California, 1959 (unpublished).

$\Delta\omega_t$ and $\Delta\omega_l$ are the frequency widths of the optic branches, and v_t and v_l are the propagation velocities of acoustic vibrations. The multiplicative constant K contains the strength of the quadrupole coupling and crystal lattice constant a. Equation (3) was derived for the high-temperature region where $\hbar vq, \hbar\Delta\omega q/q_{\max} \ll 2kT$. Another relaxation contribution considered by Blumberg[4,8] is the modification of the ionic model arising from the induced electric dipole moment associated with optic vibrational modes. The induced dipoles produce strong time-dependent electric field gradients which couple to the quadrupole moment of nuclei at neighboring lattice sites. The interaction is expected to be more pronounced in cases where the resonant nuclei are surrounded by ions having large atomic polarizabilities.

The over-all temperature dependence of T_1 due to optic vibrations should be different from that due to acoustic vibrations. Both Raman mechanisms are expected to yield a T^{-2} limit at high temperatures; however, since the optic branches usually occur at a higher range of frequencies in the vibrational spectrum than the acoustic, they will depopulate more rapidly with decreasing temperature, thereby resulting in a greater rate of change in T_1. No detailed temperature dependence for optic mode relaxation has been developed. Kochelaev derived his results for the high-temperature limit only. Blumberg used a Debye spectrum to facilitate a comparison with the VK theory while acknowledging that it was probably an unrealistic approximation.

An approximate temperature dependence of optic mode relaxation can be derived by treating the optic vibrations as a set of Einstein lattice oscillators of a single average frequency characterized by Θ_E. Unlike the simple diatomic chain, the optic branches in ionic crystals exhibit a large frequency spread. To assess the effect of this frequency spread on the temperature dependence, the T_1 vs T curve found using a delta-function frequency distribution at $\nu_E = k\Theta_E/h$ was compared with those derived using a sine squared distribution of variable width centered at ν_E. The differences were found to be $\lesssim 10\%$ for $T > 0.2\Theta_E$ even when the total spread in the latter was $0.5\nu_E$. A delta-function frequency distribution, of course, cannot be strictly correct since we must have some frequency spread to allow for conservation of the spin transition energy $h\nu_0$. Since $\nu_{\text{phonon}} \gg \nu_0$, the additional width required will have a negligible effect upon the temperature dependence. The T_1 temperature dependence $\sinh^2(\Theta_E/2T)$ obtained by using an Einstein spectrum is compared with the VK result in Fig. 8. The two curves have been normalized in the high-temperature limit $T_1 \propto T^{-2}$ for $T > \Theta$. Significant differences appear at lower temperatures. Whereas Van Kranendonk obtained the familiar limit for Raman relaxation $T_1 \propto T^{-7}$ for $T < 0.02\Theta$, the optic mode relaxation based on an Einstein model reaches a limit $T_1 \propto \exp(\Theta_E/T)$.

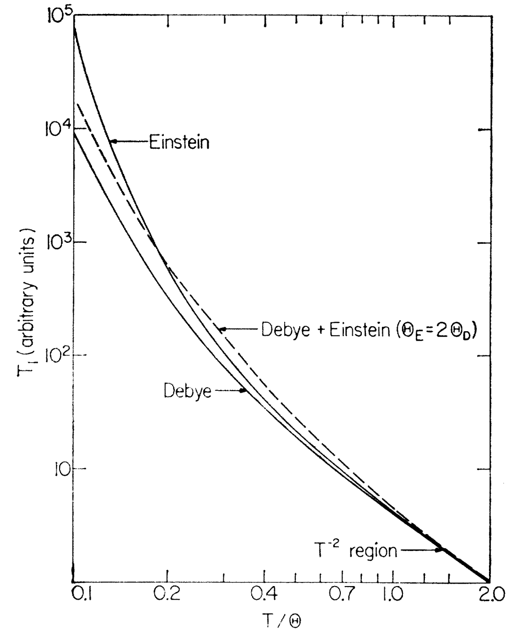

FIG. 8. Temperature dependences of T_1 using a Debye vibrational spectrum (Van Kranendonk theory), a single frequency Einstein spectrum, and a hypothetical spectrum combining a Debye spectrum and an Einstein spectrum with $\Theta_E = 2\Theta_D$, each contributing equally to the relaxation at high temperatures.

In general, a spin may be relaxed by a combination of mechanisms involving both acoustic and optic vibrations. To obtain an over-all temperature dependence for T_1, assume that the acoustic branches of the vibrational spectrum may be approximated by Debye spectra with appropriate cutoff frequencies $k\Theta_D/h$ and the optic branches by Einstein spectra located at $k\Theta_E/h$ and furthermore that the VK theory provides an adequate description of the quadrupolar relaxation caused by acoustic phonons. Then for a hypothetical crystal in which the acoustic and optic vibrations make equal contributions to the relaxation at high temperatures and $\Theta_E = 2\Theta_D$ the two temperature dependences above combine to yield the resultant dashed curve shown in Fig. 8. The initial deviation of T_1 from a T^{-2} law with decreasing temperature corresponds mainly to the rapid depopulation of the optic modes; eventually, however, the probability for optic mode relaxation becomes so small that relaxation proceeds principally via acoustic mode relaxation with a temperature dependence paralleling that derived for a Debye spectrum. The width and location of the transition region will, in general, depend upon the relative magnitudes of the optic and acoustic mode relaxation at high temperatures and their respective Θ's.

DISCUSSION

Van Kranendonk's temperature dependence derived from Eq. (2) has been applied to the present T_1 data. A comparison was made using the Debye Θ obtained

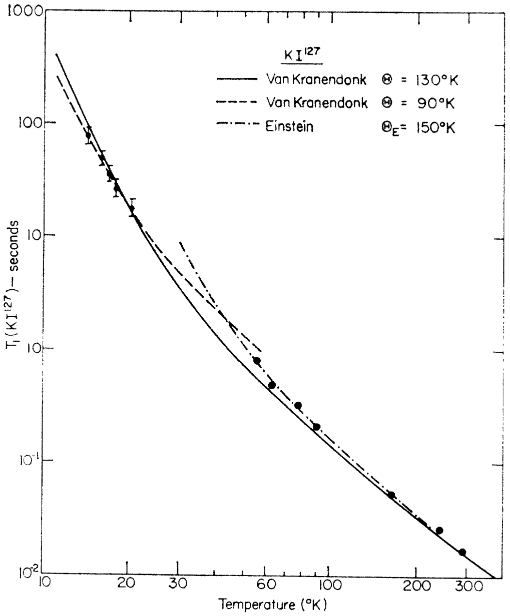

FIG. 2. Comparison of the temperature dependence of T_1(KI^{127}) with three different theoretical curves. The 14–20°K points are from Briscoe and Squire (reference 15).

in the sample used in fractional concentrations $\sim 10^{-5}$. Using the known impurity relaxation rate of Na^{23} in NaF and the impurity concentrations, lattice parameters, and T_2's of Na^{23} in NaF and NaI, an estimated T_1 due to paramagnetic impurities in the order of $\sim(10^3\text{–}10^4)$ sec is predicted for the NaI sample used. Since the measured $T_1(Na^{23}I)$ at 38°K was 1200 sec, the true quadrupolar T_1 may be longer than the results shown in Fig. 3 for $T < 50$°K. Relaxation in NaI due to other mechanisms such as diffusion motional relaxation are reported[12] only at temperatures >550°K.

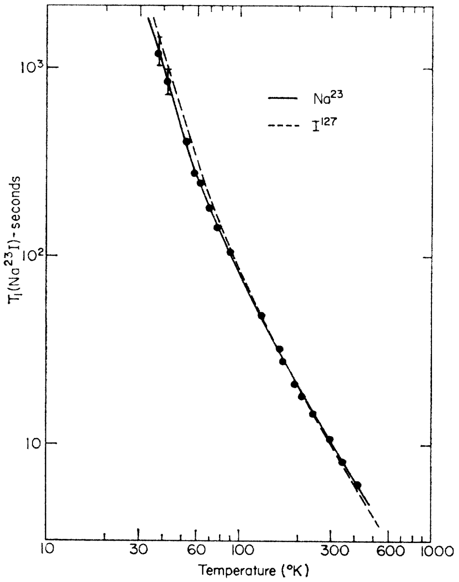

FIG. 3. Comparison of the temperature dependence of T_1 for Na^{23} and I^{127} in NaI. The data for I^{127} in Fig. 4 have been normalized to the Na^{23} results at $T = 195$°K.

An investigation was made of the angular dependence of T_1 for both Na^{23} and I^{127} at room temperature. All variations were less than 10%, the experimental error. Solomon echoes[16] of the type observed in KI were seen for I^{127}. This result together with the observed change in resonance intensity with rotation angle of the crystal about a [110] direction indicates the presence of quadrupole interactions due to dislocations[17] in the NaI sample used. These quadrupole effects were found to be a minimum for the magnetic field applied parallel to a [100] direction. The measurements in Figs. 3 and 4 were made at this orientation.

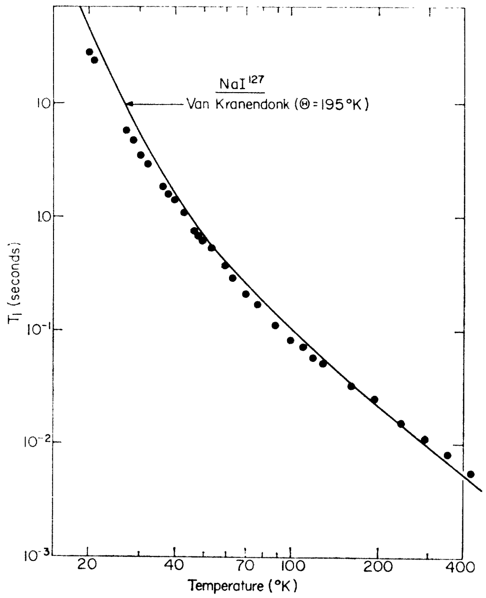

FIG. 4. Temperature dependence of T_1(NaI^{127}). Van Kranendonk's theoretical curve is normalized to the data at $T = \theta$.

Lithium Bromide

The temperature dependence of the relaxation times of Li^7 and Br^{81} in LiBr are recorded in Figs. 5 and 6. From measurements of the ratios of T_1 for the two bromine isotopes, the bromine relaxation mechanism was found to be predominantly quadrupolar at all temperatures investigated. The rapid decrease of T_1 from a T^{-2} dependence at high temperatures and the observed minimum at $T \sim 350$°K is attributed to a quadrupolar relaxation mechanism involving diffusion of charged vacancies.[18] It was not possible to verify that

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[16] I. Solomon, Phys. Rev. **110**, 61 (1958).

[17] J. F. Hon and P. J. Bray, J. Appl. Phys. **30**, 1425 (1959); H. O. Hooper and P. J. Bray, Bull. Am. Phys. Soc. **6**, 245 (1961).

[18] F. Reif, Phys. Rev. **100**, 1597 (1955).

the relaxation is again governed by lattice processes with a T^{-2} dependence at high temperatures due to an increasing poor signal-to-noise ratio.

The temperature dependence of $T_1(\mathrm{Li}^7\mathrm{Br})$ in two different samples did not provide any useful information about quadrupolar relaxation arising from lattice vibrations. Because of the small quadrupole moment and antishielding factor of Li^7, the quadrupolar relaxation at low temperatures is very long and was masked by relaxation via paramagnetic impurities (iron transition group elements were present in concentrations $\sim 10^{-4}$–10^{-5}). The long T_1's (approximately 1 h at 77°K) also made it difficult to determine accurately the temperature-independent impurity relaxation time. At temperatures above room temperature, the principal relaxation mechanism is caused by time-dependent interactions arising from diffusional motion of the lithium ions rather than thermal lattice vibrations. A more complete description of the spin-lattice relaxation properties in LiBr will be reported elsewhere.[19]

THEORY

Before analyzing the experimental results, we review the treatment of Raman spin-lattice relaxation in solids to see explicitly how the spectral density of phonon states and the temperature enter and what assumptions and approximations are commonly made in calculating the transition probabilities and their temperature dependences. We limit ourselves to two-phonon processes since no evidence of higher order processes such as Khutsishvili's four-phonon term[20] has appeared. In a Raman relaxation process a spin transition of frequency ν_0 from a magnetic state m_i to state m_f is accompanied by the creation of one phonon and the annihilation of another to conserve energy. The transition probability of this process is calculated by summing over the total phonon frequency spectrum $\rho(\nu)$ and is given by

$$W(m_i,m_j)$$

$$=\frac{1}{\hbar^2}\int\int\sum_{s,t}\{|\langle m_f, n_s+1, n_t-1|\mathcal{H}_{\mathrm{SL}}|m_i, n_s, n_t\rangle|^2$$

$$\times\rho(\nu_s)\rho(\nu_t)\delta(\nu_s-\nu_0-\nu_t)\}d\nu_s d\nu_t, \quad (1)$$

where $\mathcal{H}_{\mathrm{SL}}$ is the effective Hamiltonian coupling the spins to the thermal lattice vibrations, and n_s and n_t are the initial phonon quantum numbers in mode-branch s and t. The curly bracket denotes an appropriate averaging over all directions of phonon propagation and polarization vectors.

The temperature T enters into the integrand of Eq. (1) via the equilibrium phonon occupation numbers $\langle n_s\rangle_{\mathrm{av}}$ and $\langle n_t+1\rangle_{\mathrm{av}}$ arising from the square of the matrix elements of the phonon operators in $\mathcal{H}_{\mathrm{SL}}$.

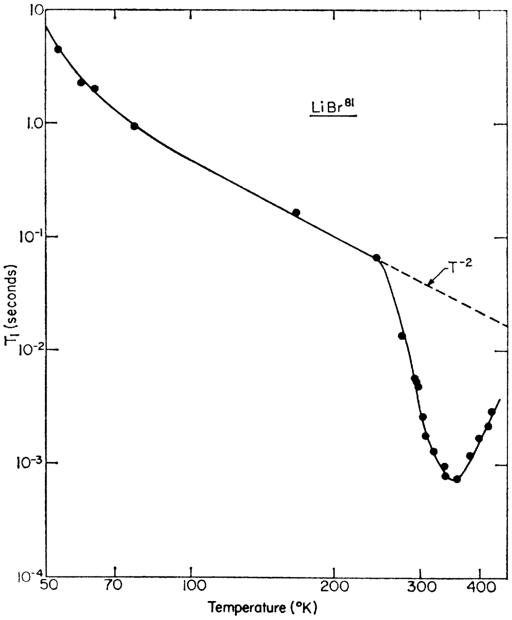

FIG. 5. Temperature dependence of $T_1(\mathrm{LiBr}^{81})$. The deviation of T_1 from a T^{-2} curve and the minimum at $T\sim 350$°K is due to a relaxation mechanism involving diffusional motion.

Applying Bose-Einstein statistics to the phonon field, $\langle n_s\rangle_{\mathrm{av}}$ is given by $[\exp(h\nu_s/kT)-1]^{-1}$. In the limit $kT\gg h\nu(\max)$, $\langle n_s\rangle_{\mathrm{av}}$ and $\langle n_t+1\rangle_{\mathrm{av}}$ are proportional to T and the resulting T^2 can be taken outside the integral. Thus, the familiar high-temperature limit $W\propto T^2$ for two-phonon processes is independent of the explicit

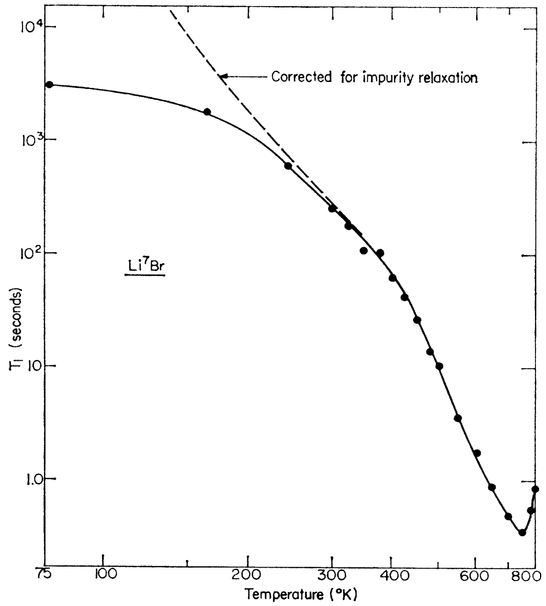

FIG. 6. Temperature dependence of $T_1(\mathrm{Li}^7\mathrm{Br})$. The relaxation at low temperatures is limited by the presence of paramagnetic impurities and at high temperatures by a mechanism involving diffusional motion.

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[19] R. R. Allen and M. J. Weber (to be published).

[20] G. R. Khutsishvili, Zh. Eksperim. i. Teor. Fiz. **31**, 424 (1956) [translation: Soviet Phys.—JETP **4**, 382 (1957)].

form of $\mathcal{H}_{SL}$ and $\rho(\nu)$ in Eq. (1). In general, however, this is not the case. To obtain a relationship between the relaxation transition probabilities and the temperature, the integral in Eq. (1) must be evaluated for each value of the parameter T. This requires information about the nature of the lattice vibrations and the form of the spin-lattice interaction and, depending upon the extent of this knowledge, a more or less laborious calculation for each crystal and relaxation mechanism of interest. In practice, numerous simplifying assumptions are made in the treatment of the lattice dynamics; the justification being, in addition to one of practicality, that since Raman relaxation involves an integrated effect of all lattice vibrations it is not sensitive to their detailed properties.

In spin-lattice relaxation theory the lattice is usually treated in a Debye approximation. At low temperatures where one-phonon direct relaxation processes are dominant, the probability for relaxation is proportional to the spectral density of phonon states at the resonance frequency. Since the wavelengths involved are long compared to the lattice spacing, the crystal should, to a good approximation, be describable by a Debye model of an elastic continuum with a phonon frequency distribution proportional to ν^2. This simple Debye spectrum, however, does not provide an adequate description of the high-frequency portion of the phonon spectrum. For a crystal containing n atoms per primitive unit cell, there are $3n$ branches in the vibrational spectrum; three acoustic branches for which $\nu \rightarrow 0$ as the wave vector $\mathbf{q} \rightarrow 0$ and $3n-3$ optic branches for which ν remains finite as $\mathbf{q} \rightarrow 0$. In certain special directions the normal vibrations are strictly longitudinal or transverse because of symmetry; in general, however, the polarization is neither but is determined by the details of the interatomic forces. The vibrational spectrum for a typical alkali halide NaI, where $n=2$, is shown in Fig. 7 together with the Debye approximation. The dissimilarities are great throughout the high-frequency region which is important for Raman relaxation.

Van Kranendonk[6] has treated spin-lattice relaxation arising from interactions between the nuclear quadrupole moment and the fluctuating electric field gradient due to the thermal lattice vibrations of the six nearest-neighbor point charges of a NaCl-type crystal. An explicit temperature dependence for T_1 is derived by treating the lattice dynamics in a Debye approximation; that is, an elastically isotropic monatomic lattice is assumed with a phonon frequency distribution $\rho(\nu) \propto \nu^2$. The transition probabilities for Raman relaxation and their temperature dependences are found by evaluating integrals of the form

$$T^3 \int_0^{\Theta/T} \frac{\rho^2(x) e^x}{x^2(e^x-1)^2} L_n(cTx/\Theta) dx, \tag{2}$$

where $x = h\nu/kT$, $c = (6\pi^2)^{1/3}$, and $n = 1, 2, 3, 4$. The crystal is characterized by a temperature parameter Θ corresponding to the maximum phonon frequency. In a Raman process, the principal contribution to the transition probability comes from the more dense high-frequency portion of the vibrational spectrum where $\nu_s \approx \nu_t \gg \nu_0$ in Eq. (1). The functions L_n arise from averages of the spin-lattice coupling over the normal vibrational modes under the assumptions that the phonon frequency and velocity are independent of the direction of propagation and polarization. The temperature dependences derived from the four L_n's are different. The final temperature dependence of T_1 is obtained from a combination of transition probabilities appropriate to the allowed relaxation modes of the spin system and the technique of measuring T_1.

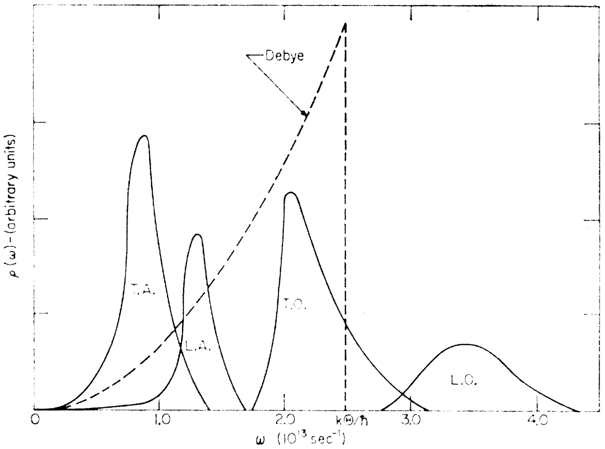


FIG. 7. Lattice vibrational frequency distribution for NaI as calculated by Karo (reference 5). T. A., L. A., T. O., and L. O. denote the transverse and longitudinal acoustic and optic branches. The dashed curve is the normalized Debye spectrum for NaI, where Θ is the Debye temperature.

Although the total number of vibrational modes is counted correctly in the VK theory, no explicit treatment is made of the optic vibrations. This has been done, however, by Kochelaev[7] who has treated quadrupolar relaxation due to both optic and acoustic vibrations in ionic crystals with an NaCl-type lattice. His probabilities for $\Delta m = \pm 1$ and ± 2 transitions are of the form

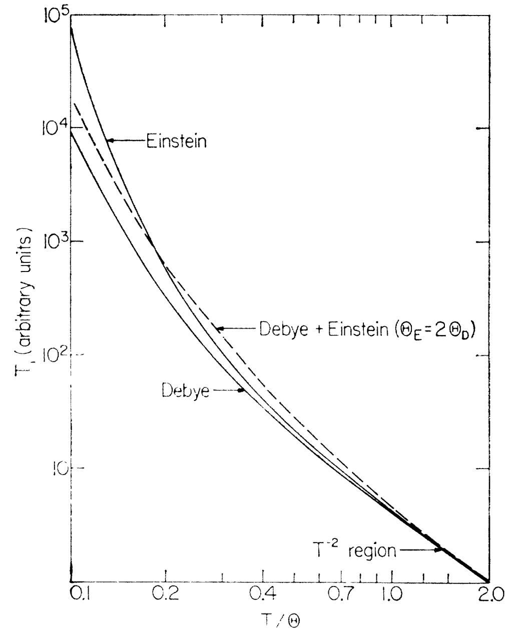
$$\frac{K}{(M_1+M_2)^2} \left\{ \left[\left(\frac{M_1}{M_2}\right)^2 + 2 + 3\left(\frac{M_2}{M_1}\right)^2 \right] \times \left[\frac{1}{\omega_l^2 \Delta\omega_l \sinh^2(\hbar\omega_l/2kT)} + \frac{2}{\omega_t^2 \Delta\omega_t \sinh^2(\hbar\omega_t/2kT)} \right] + \frac{k^2T^2a^5}{2\pi\hbar^2} \left(\frac{1}{v_l^5} + \frac{2}{v_t^5} \right) \right\}, \tag{3}$$

where M_1 is the mass of the central ion and M_2 that of its nearest neighbor, ω_t and ω_l are the frequencies of transverse and longitudinal optic vibrations at $q=0$,

$\Delta\omega_t$ and $\Delta\omega_l$ are the frequency widths of the optic branches, and v_t and v_l are the propagation velocities of acoustic vibrations. The multiplicative constant K contains the strength of the quadrupole coupling and crystal lattice constant a. Equation (3) was derived for the high-temperature region where $\hbar vq, \hbar\Delta\omega q/q_{\max} \ll 2kT$. Another relaxation contribution considered by Blumberg[4,8] is the modification of the ionic model arising from the induced electric dipole moment associated with optic vibrational modes. The induced dipoles produce strong time-dependent electric field gradients which couple to the quadrupole moment of nuclei at neighboring lattice sites. The interaction is expected to be more pronounced in cases where the resonant nuclei are surrounded by ions having large atomic polarizabilities.

The over-all temperature dependence of T_1 due to optic vibrations should be different from that due to acoustic vibrations. Both Raman mechanisms are expected to yield a T^{-2} limit at high temperatures; however, since the optic branches usually occur at a higher range of frequencies in the vibrational spectrum than the acoustic, they will depopulate more rapidly with decreasing temperature, thereby resulting in a greater rate of change in T_1. No detailed temperature dependence for optic mode relaxation has been developed. Kochelaev derived his results for the high-temperature limit only. Blumberg used a Debye spectrum to facilitate a comparison with the VK theory while acknowledging that it was probably an unrealistic approximation.

An approximate temperature dependence of optic mode relaxation can be derived by treating the optic vibrations as a set of Einstein lattice oscillators of a single average frequency characterized by Θ_E. Unlike the simple diatomic chain, the optic branches in ionic crystals exhibit a large frequency spread. To assess the effect of this frequency spread on the temperature dependence, the T_1 vs T curve found using a delta-function frequency distribution at $\nu_E = k\Theta_E/h$ was compared with those derived using a sine squared distribution of variable width centered at ν_E. The differences were found to be $\lesssim 10\%$ for $T > 0.2\Theta_E$ even when the total spread in the latter was $0.5\nu_E$. A delta-function frequency distribution, of course, cannot be strictly correct since we must have some frequency spread to allow for conservation of the spin transition energy $h\nu_0$. Since $\nu_{\text{phonon}} \gg \nu_0$, the additional width required will have a negligible effect upon the temperature dependence. The T_1 temperature dependence $\sinh^2(\Theta_E/2T)$ obtained by using an Einstein spectrum is compared with the VK result in Fig. 8. The two curves have been normalized in the high-temperature limit $T_1 \propto T^{-2}$ for $T > \Theta$. Significant differences appear at lower temperatures. Whereas Van Kranendonk obtained the familiar limit for Raman relaxation $T_1 \propto T^{-7}$ for $T < 0.02\Theta$, the optic mode relaxation based on an Einstein model reaches a limit $T_1 \propto \exp(\Theta_E/T)$.



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In general, a spin may be relaxed by a combination of mechanisms involving both acoustic and optic vibrations. To obtain an over-all temperature dependence for T_1, assume that the acoustic branches of the vibrational spectrum may be approximated by Debye spectra with appropriate cutoff frequencies $k\Theta_D/h$ and the optic branches by Einstein spectra located at $k\Theta_E/h$ and furthermore that the VK theory provides an adequate description of the quadrupolar relaxation caused by acoustic phonons. Then for a hypothetical crystal in which the acoustic and optic vibrations make equal contributions to the relaxation at high temperatures and $\Theta_E = 2\Theta_D$ the two temperature dependences above combine to yield the resultant dashed curve shown in Fig. 8. The initial deviation of T_1 from a T^{-2} law with decreasing temperature corresponds mainly to the rapid depopulation of the optic modes; eventually, however, the probability for optic mode relaxation becomes so small that relaxation proceeds principally via acoustic mode relaxation with a temperature dependence paralleling that derived for a Debye spectrum. The width and location of the transition region will, in general, depend upon the relative magnitudes of the optic and acoustic mode relaxation at high temperatures and their respective Θ's.

DISCUSSION

Van Kranendonk's temperature dependence derived from Eq. (2) has been applied to the present T_1 data. A comparison was made using the Debye Θ obtained from specific heat studies and normalizing the experimental data to the theoretical curve at $T=\Theta$. Within experimental error, satisfactory agreement between theory and experiment is obtained for NaF and KBr, as shown in Fig. 1. The data for KI, NaI, and LiBr, however, cannot be fitted to a single VK curve over the temperature range investigated using the Debye Θ.

There are several possible sources of the above discrepancies with the VK theory such as the parameter Θ used, inadequate treatment of the optic vibrations, and the neglect of the thermal expansion of the lattice or the change in phonon velocity and vibrational spectrum with temperature. The temperature parameter Θ used in spin-lattice relaxation theory to characterize the crystal has usually been compared to or chosen to be the Debye temperature Θ_D determined from specific heat or elastic constants measurements. In the sense that Θ corresponds to a maximum phonon frequency $k\Theta/h$, it has the same significance in specific heat and spin-lattice relaxation theory. In general, however, the Θ derived from fitting T_1 vs T curves to Raman relaxation theory need not equal Θ_D or Θ values obtained from measurements of different physical properties. For example, in place of Eq. (2), specific heats in the Debye theory are evaluated from integral expressions of the form

$$T^3\int_0^{\Theta_D/T}\frac{\rho(x)x^2e^x}{(e^x-1)^2}dx. \tag{4}$$

Whereas, this is a one-parameter theory, our present knowledge and treatment of the spin-lattice coupling and calculation of the magnitude of T_1 are far from adequate to evaluate Θ correspondingly. It is well known[21] that a major difficulty of the Debye theory of specific heats is that one Θ_D is usually not sufficient for all temperatures. This originates from the treatment of the crystal as an elastic continuum rather than as a discrete lattice as in the Born-von Karman theory. To preserve the VK theory, relaxation times could be fitted to the VK curve using different Θ's at each temperature with suitable normalization. Using the T_1 results for NaI and KI, the required behavior of Θ with temperature does not correspond to Θ_D vs T curves for the alkali halides obtained from specific-heat studies.[22] An attempt to satisfy a theoretical curve by adjusting $\Theta(T)$ might be convenient for recording data but is not instructive in itself.

Although an explicit treatment of optic vibrations has been omitted in the VK theory, reasonable agreement between the theoretical temperature dependence and experiment is nevertheless obtained in many cases including NaF and KBr in the present investigation. Of the alkali halides studied here, NaF is more in the spirit of Van Kranendonk's treatment since (1) it most nearly represents an isotropic monatomic lattice and (2) its acoustic and optic branches combine to form an over-all vibrational spectrum approximating a Debye spectrum. These comments apply to a lesser extent to KBr. The lack of any noticeable discrepancies in the KBr fit may be because the measurements were not carried to sufficiently low temperatures, i.e., $T\ll\Theta_D$. The remaining crystals, KI, NaI, and LiBr, have larger mass ratios. As one examines the vibrational spectra[5] of a series of alkali halides with increasing mass ratios, a gradual separation and narrowing of the acoustic and optic branches is observed with distinct gaps appearing for very large mass ratios. If these high-frequency optic branches are important for relaxation, the resulting different temperature dependence for T_1 may account for the present disagreements with a simple VK curve. Using Eq. (3), the acoustic and optic vibrations are predicted to contribute about equally to the relaxation transition probabilities for KI^{127} at room temperature, while for NaI and LiBr the dominant relaxation mechanism for all nuclei is predicted to arise from optic vibrations.

To approximate the temperature dependence of T_1 when both acoustic and optic vibrations contribute to the relaxation, a combination of the simplified curves discussed previously has been applied; that is, the acoustic mode relaxation is described by Van Kranendonk's temperature dependence based upon a Debye spectrum and the optic mode relaxation by a temperature dependence derived from a delta-function Einstein spectrum.[23] The data for $T_1(KI^{127})$ together with measurements in the region 14–20°K taken from the work of Briscoe and Squire[15,24] are shown in Fig. 2. Briscoe and Squire combined their data at low temperatures with a measurement at room temperature and fitted them to a VK curve using $\Theta=130°K$, the Debye temperature for KI at 0°K. Our data from 300–55°K show a gradual departure from this curve with decreasing temperature. This region can, however, be fitted to the temperature dependence for optic mode relaxation using $\Theta_E\approx150°K$. A measure of the frequencies of the transverse optic modes is provided by the infrared dispersion frequency; for KI it corresponds to 141°K which is within the experimental accuracy of the above result. If, as predicted, the rates of relaxation of I^{127} in KI due to acoustic and optic phonons are approximately equal at high temperatures, then in the range 14–20°K the relaxation should be governed principally by acoustic vibrations since the optic modes will be frozen out. A better fit to Briscoe and Squire's low-temperature

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[21] M. Blackman, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. VII, Part 1.

[22] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. Roy. Soc. (London) **A242**, 478 (1957); W. T. Berg and J. A. Morrison, *ibid.* **A242**, 467 (1957).

[23] We shall not attempt to differentiate between the "transverse" and "longitudinal" acoustic and optic branches.

[24] Combining the two data appears justified even though there may be some uncertainty due to the use of different crystals, resonance frequencies, sample orientation, and method of measuring T_1.

data in Fig. 2 is obtained by using a VK curve with $\Theta = 90°$K rather than 130°K. A Debye cutoff frequency of 90°K corresponds closely to the maximum acoustic vibration frequency for KI. This suggests that Van Kranendonk's treatment yields a good approximation to the temperature dependence of acoustic mode relaxation at low temperatures.

More complete temperature-dependence measurements were made for NaI since the relaxation of both nuclei can be readily studied and information about the lattice dynamics is available from neutron diffraction experiments.[25] The data for I^{127}, Fig. 4, show departures from a VK curve over the entire temperature range investigated, where again the Θ used is the high-temperature specific heat Θ_D. When a smooth curve is drawn through the experimental points, a slight hump and a definite change in the temperature dependence of T_1 is observed in the vicinity of $T \approx 50°$K. Such a gradual transition is expected as the optic modes depopulate and the acoustic vibrations become relatively more important for the relaxation (see Fig. 8). The data for $T > 50°$K can be fitted to optic mode relaxation with $\Theta_E \approx 160°$K; the infrared dispersion frequency for NaI is 164°K which agrees with the neutron diffraction results. Above 150°K, however, the agreement fails due to the departure of T_1 from a T^{-2} law. At high temperatures, $T > \Theta_D$, $T_1(\mathrm{Na}^{23}\mathrm{I}) \propto T^{-1.82}$ and $T_1(\mathrm{NaI}^{127}) \propto T^{-1.87}$. Clark[12] has reported $T_1 \propto T^{-n}$, where $n < 2$, for several alkali halides; our results for NaI agree with his.

The deviation of T_1 from the expected T^{-2} law at high temperatures may be due to the neglect of other temperature dependent variables in the calculation of the relaxation times. Thus far the temperature has appeared only in the equilibrium number of phonons per mode. No account has been made of the thermal expansion of the lattice or the change in phonon velocity and vibrational spectrum with temperature. These effects, though small, may not be totally negligible. For example, thermal expansion of the lattice can affect the strength of the quadrupole coupling which is sensitive to the interionic spacing both in the case of a point charge model[6] or where covalency[26] and charge overlap[27] are important. Thus, the lattice expansion with increasing temperature could reduce the quadrupole coupling, thereby generating a temperature dependence of T_1 less than T^{-2}. A calculation of the exact temperature dependence would require knowledge of the form of the quadrupolar interaction.

The temperature dependence of $T_1(\mathrm{Na}^{23}\mathrm{I})$ is shown in Fig. 3 and compared with that of I^{127}. The curves are essentially equal within experimental error over their common temperature range. The induced dipole relaxation mechanism proposed by Blumberg[4,8] predicts that for NaI the Na^{23} should be very strongly relaxed by optic vibrations due to the large polarizability of iodine whereas the optic and acoustic mode contributions to the I^{127} relaxation are approximately equal at room temperature. Hence, the Na^{23} relaxation should continue to exhibit a more rapid change with temperature to lower temperatures than for I^{127} due to depopulation of the optic modes. This could not be verified in our experiments because of difficulties in extending the measurements reliably to sufficiently low temperatures and because of the possible presence of paramagnetic impurity relaxation. The results do indicate, however, that optic vibrations are important for the relaxation of both Na^{23} and I^{127} for $T > 50°$K.

Lithium bromide had the largest mass ratio of the crystals studied, its acoustic and optic branches are well separated, and the relaxation of both Li^7 and $\mathrm{Br}^{79,81}$ should, according to Kochelaev,[7] be due to optic vibrational modes. Unfortunately, as explained earlier and is evident from Fig. 6, the Li^7 relaxation from lattice vibrations was always masked by competing relaxation processes in the samples used. The T_1 region corrected for paramagnetic impurity relaxation exhibits a very rapid change with temperature but was not considered reliable enough to warrant comparison with theoretical curves. The Br^{81} relaxation in Fig. 5 appears to reach a T^{-2} dependence before the relaxation due to diffusing charged defects becomes prominent. Since the optic branches in LiBr have frequencies corresponding to temperatures greater than 300°K, the T^{-2} limit for optic mode relaxation should not appear until higher temperatures. The temperature dependence arising from depopulation of the optic modes may be partially canceled by other temperature dependences as in the case of NaI; however, it was not possible to verify this by accurately determining the high-temperature limit of T_1. Attempts to fit the Br^{81} data below 100°K yield Θ's which are too low for the optic branches and too high for the acoustic branches assuming they are located approximately as calculated by Karo.[5] The results from our samples of LiBr are, therefore, inconclusive.

The presence of different temperature dependences for Raman relaxation involving acoustic or optic phonons may be observable in other crystals where (1) optic phonons are equally or more important than acoustic phonons for relaxation at high temperatures, (2) the acoustic and optic branches are well separated in frequency, and (3) measurements are made over a sufficiently large temperature range. Mieher,[14] in an extension of the VK theory to investigate quadrupolar relaxation in crystals having the zincblende lattice structure, has made detailed measurements of the temperature dependence of the In^{115} relaxation in InP from 77–300°K. A best fit of the data to a VK curve was obtained using a Θ of 400°K. An examination of Mieher's data plotted in his[14] Fig. 2 reveals a very

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[25] A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

[26] K. Yosida and T. Moriya, J. Phys. Soc. Japan **11**, 33 (1956).

[27] J. Kondo and J. Yamashita, J. Phys. Chem. Solids **10**, 245 (1959).

gentle hump in the T_1 vs T points and a departure from the VK curve below 100°K similar to that found for I^{127} in NaI. Relaxation via paramagnetic impurities could produce such behavior but was considered by Mieher to be negligible in the sample used. In InP the transverse and longitudinal acoustic and optic branches are located in temperature units at 91, 182, 455, and 490°K, respectively[28]; hence, the optic modes are considerably less populated at 100°K than the acoustic modes. Although no treatment has been made to determine the relative importance of optic and acoustic phonons for relaxation in the zincblende lattice, the temperature dependence of T_1 suggests that the optic mode contribution to the In^{115} relaxation in InP becomes relatively small below 100°K.

Germanium also has the zincblende structure and being a lattice with two atoms per unit cell has three acoustic and three optic branches in its lattice vibrational spectrum. This spectrum has been investigated both experimentally[29] and theoretically.[30] The transverse acoustic branches which extend in frequency up to about 150°K and the longitudinal optic branch centered about 400°K are well separated in the spectrum but the longitudinal acoustic and transverse optic branches overlap at ≈ 340°K. The high-temperature specific heat Θ_D is 360°K and temperature dependent. Wyluda[31] has reported T_1 measurements of the Ge^{73} resonance in an n-type germanium sample at temperatures of 20, 77, 90, 195, and 295°K. The data, as Wyluda found, fit a VK curve very well using the above Θ_D, except for the datum at 20°K which is about one order of magnitude too short. This may be due to paramagnetic relaxation or the effect of the depopulation of the higher frequency branches in the phonon spectrum. The data from 77–295°K, however, do not fit the simple optic mode relaxation temperature dependence using $\Theta_E \approx 350$–400°K. It should be noted that whereas Mieher's treatment of quadrupolar relaxation in the zincblende lattice is based upon an ionic model of the quadrupole coupling, germanium is covalently bonded which may change the temperature dependence.

CONCLUSIONS

The results have shown that Van Kranendonk's relaxation temperature dependence derived from a Debye spectrum is not directly applicable to all alkali halide crystals, particularly those having large mass ratios and in which optic vibrations make an important contribution to the relaxation. The differences in the temperature dependences are small, however, and indicate that since Raman relaxation processes involve an integrated effect of the lattice vibrations, their rate and temperature dependence are relatively insensitive to the detailed properties of the lattice dynamics. In view of this and the accuracy with which T_1 can be measured, any attempt to obtain a useful lattice vibrational spectrum from a mathematical inversion of a theoretical expression for T_1 and the temperature dependence of the relaxation does not appear warranted. The discrepancies between a VK curve and experiment have been attributed to and support the importance of optic vibrations for nuclear quadrupolar relaxation in diatomic crystals having large mass ratios. The temperature dependence of Raman relaxation is also, however, a function of the form of the spin-lattice coupling and, hence, any change in the relative importance of different lattice induced quadrupolar relaxation mechanisms with temperature would alter the temperature dependence of T_1. Detailed theoretical treatments of the temperature dependence of T_1 for various spin-lattice interactions including details of the lattice dynamics are lacking. Such calculations, together with careful T_1 measurements at temperatures $T<\Theta$, would be required to obtain more than qualitative information about the form and nature of the spin-lattice interactions and lattice vibrational spectra.

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[29] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958); B. N. Brockhouse, Phys. Rev. Letters **2**, 256 (1959).

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[31] B. J. Wyluda, J. Phys. Chem. Solids **23**, 63 (1962).