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Dependence of Nuclear Quadrupole Relaxation Times in Ionic Crystals on the Phonon Spectrum*

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Nuclear quadrupole relaxation times are calculated for the halogen and alkali nuclei in a number of alkali halides using lattice phonon density curves computed by Karo. The calculated values of T_1 at room temperature are generally lower than those obtained using the Debye model and in better agreement with experiment. The variation of T_1 with temperature has also been calculated over the range 20°K to room temperature for Na^{23} and I^{127} nuclei in NaI. Excellent agreement is obtained with the experimental data on the temperature variation of T_1 when use is made of the Karo distribution function. The Debye model gives a temperature variation comparable with experimental above 70°K but a relatively slower variation below 70°K.

I. INTRODUCTION

A NUMBER[1–10] of theoretical and experimental investigations have been made of the nuclear relaxation times T_1 in alkali halides. The basic theory for the explanation of the relaxation times in ionic crystals was first proposed by Van Kranendonk.[6] A number of authors[7–9] have subsequently considered possible extensions of the theory to take account of additional contributions to the fluctuating field gradients at the nuclei that arise out of the vibrations of the lattice. These latter authors, as well as Van Kranendonk, all employed a Debye spectrum for the lattice vibrations. The first investigation concerning the significant influence of the departure of the lattice spectrum from the Debye model on the relaxation time T_1 was made by Kochelaev.[10] Kochelaev used approximate distributions for the optical modes in conjunction with Van Kranendonk's mechanism for the origin of the field gradient to calculate T_1 in a few crystals. Subsequently, Weber[5] has made careful measurements of the temperature dependence of relaxation times in a number of crystals. He has compared his data with the theoretical dependence that one obtains with the Debye model and also when one uses some approximate distribution functions for the optical modes. Since detailed distribution functions for the lattice vibrations are currently available[11–13] in a number of alkali halides, it would be very helpful to calculate T_1 for some of the alkali halides using more realistic distribution functions than the Debye model. The motivations for such a calculation are twofold. First, one would like to see whether T_1 and its temperature dependence, as calculated with the more realistic distribution functions than the Debye spectrum, did in fact improve quantitative agreement with experiment or not. Secondly, it would be interesting to find out whether relaxation time data can be used as a sensitive test of the correctness of available vibrational distribution functions for the lattice.

In Sec. II, we consider the theory for calculating T_1 using a general lattice distribution function. These formulas reduce to the corresponding expressions given by Van Kranendonk,[6] and Wikner, Blumberg, and Hahn,[4] when one used the Debye model. In Sec. III, the calculated results for T_1 in a number of alkali halides at room temperature are presented, as well as the relaxation times for Na^{23} and I^{127} nuclei in NaI in the temperature range 20 to 298°K. The calculated results are compared with available experimental data and earlier theoretical results and the implications of this comparison are then discussed.

II. PROCEDURE FOR CALCULATION OF T_1

Four possible mechanisms have been proposed for the relaxation process. Van Kranendonk[6] has proposed that the vibrations of the lattice cause transient departures from cubic symmetry in the arrangement of the ionic charges around each nucleus. This departure in cubic symmetry causes fluctuating electric field gradients to appear at the nuclei which interact with the nuclear quadrupole moments to produce

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transitions within the spin levels of the nuclei. Wikner and Das[8] have considered the enhancement in the transient field gradients at the nuclei that are produced by the antishielding effects of the electrons on the ions. Wikner, Blumberg, and Hahn[4] have shown that the dipole moments induced in the ions during optical mode vibrations can have a profound effect on the fluctuating field gradients at the nuclei. Yosida and Moriya[7] have proposed that there is a certain amount of covalent binding in the alkali halides arising from the transfer of electrons from the negative ions to vacant electronic states of the positive ion. This electron transfer will be made to fluctuate by the vibrations of the lattice, leading to transient field gradients at the nuclei. Kondo and Yamashita,[9] on the other hand, have considered the overlap between the occupied electron orbitals of adjacent positive and negative ions which fluctuate in the course of the lattice vibrations, and this also leads to transient field gradients at the nuclei.

Analyses of nuclear quadrupole interaction data in free alkali halide molecules indicate[14] that there is very little electron-transfer covalency in these molecules. Since internuclear distances are larger in the solid state, as compared to the molecules, such electron-transfer covalency would be expected to be even less significant in the solid alkali halides. This observation argues against any important contribution from Yosida and Moriya's electron-transfer mechanism. The other three mechanisms are, however, comparable in importance depending on the crystal and nucleus in question. Since our aim in the present work is to investigate the sensitiveness of the relaxation process to the lattice spectrum, we have chosen to consider only Van Kranendonk's monopole, and Wikner, Blumberg, and Hahn's dipole mechanisms. The temperature dependence predicted for Kondo and Yamashita's overlap mechanism is identical with that expected for Van Kranendonk's monopole mechanism. We shall now briefly outline Van Kranendonk's, and Wikner, Blumberg, and Hahn's procedures and adapt them to a general frequency spectrum instead of the Debye model.

Following the procedure of Van Kranendonk,[6] one can write the perturbation Hamiltonian describing the interaction between the nuclear quadrupole moment and the time-dependent crystalline field produced by the lattice vibrations as

$$\mathcal{H}_2'=\sum_{\mu} Q_\mu \sum_{\lambda\lambda'} w_\mu(\lambda\lambda')q_\lambda q_{\lambda'},$$
$$w_\mu(\lambda\lambda')=\sum_{ij} \mathbf{A}_{\mu ij}:\mathbf{e}_\lambda\mathbf{e}_{\lambda'}B_iB_j. \qquad (1)$$

The various symbols in Eq. (1) have the same meaning as in Van Kranendonk's paper. The symbols Q_μ represent the components of the nuclear quadrupole moment tensor:

$$Q_0=P[3I_z^2-I(I+1)],$$
$$Q_1=Q_{-1}^*=(P/2)[I_z(I_x+iI_y)+(I_x+iI_y)I_z], \qquad (2)$$
$$Q_2=Q_{-2}^*=P(I_x+iI_y)^2,$$

with $P=eQ/I(2I-1)$, where Q is the conventionally defined nuclear quadrupole moment in barns (10^{-24} cm^2) and I is the nuclear spin. The components of the nuclear spin are represented by I_x, I_y, and I_z.

The normal coordinates q_λ describing the displacements of the nuclei, are given by

$$q_\lambda=\delta_{s1}(a_{\mathbf{k}p}+a_{-\mathbf{k}p})+i\delta_{s2}(a_{\mathbf{k}p}-a_{-\mathbf{k}p}). \qquad (3)$$

The normal modes are enumerated by the quantity $\lambda=(\mathbf{k},p,s)$ which describes the momentum $\hbar\mathbf{k}$, polarization p, and the additional index s for the lattice phonons. The tensor $\mathbf{A}_{\mu ij}$ describes the dependence of the field gradient tensor on the nuclear displacements. Thus, if the μth spherical harmonic component of the field tensor is denoted by W_μ, then

$$W_\mu=\sum_{ij} \mathbf{A}_{\mu ij}:\mathbf{r}_i\mathbf{r}_j, \qquad (4)$$

where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the displacements for the ith and jth nuclei from the equilibrium positions. Finally, the quantity B_i is given by

$$B_i(\mathbf{k},s)=\delta_{s,1}(\cos\mathbf{k}\cdot\mathbf{a}_i-1)+\delta_{s,2}\sin(\mathbf{k}\cdot\mathbf{a}_i), \qquad (5)$$

where $\mathbf{a}_i$ is the radius vector joining the ith nucleus to the central nucleus, the one in whose relaxation we are interested.

Using time-dependent perturbation theory for the perturbation Hamiltonian $\mathcal{H}_2'$ in (1), one can obtain the transition probability $P(m, m+\mu)$ between the levels m and $m+\mu$ of the nucleus due to a Raman-type scattering process in which a lattice phonon is scattered by the nucleus to provide the necessary energy difference between the initial and final nuclear states.

$$P(m, m+\mu)=(2\pi/\hbar)\int \sum_{p',p,s',s,k',k} |\mathcal{H}_{2if}'|^2$$
$$\times\rho(E_i)\rho(E_f)dE_idE_f, \qquad (6)$$

where

$$\mathcal{H}_{2if}=\langle m+\mu,\, p',\, s',\, \mathbf{k}'|\mathcal{H}_2'|m,\, p,\, s,\, \mathbf{k}\rangle.$$

The initial and final states

$$i(m,p,s,\mathbf{k}) \quad \text{and} \quad f(m+\mu,\, p',\, s',\, \mathbf{k}')$$

are delineated by the parameters describing the nuclear and phonon states before and after the transition. The lattice phonon densities in the neighborhood of the initial and final energies E_i and E_f of the phonon are given by $\rho(E_i)$ and $\rho(E_f)$, respectively. Since the energy of the nuclear system is much smaller than the energy

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[14] T. P. Das and M. Karplus, J. Chem. Phys. **30**, 848 (1959); J. Chem. Phys. (to be published).

of the phonons, $E_i \approx E_f$. Also the matrix elements[15] of q_λ are given by

$$\langle n_\lambda+1|q_\lambda|n_\lambda\rangle = \langle n_\lambda|q_\lambda|n_\lambda+1\rangle = (\hbar/M\omega)^{1/2}(n_\lambda+1)^{1/2}$$

and

$$\bar{n}_\lambda = 1/(e^x-1), \qquad x = \hbar w/KT, \tag{7}$$

where n_λ is the number of phonons in the state λ, and M is the molecular weight of the crystal (with K representing the Boltzmann constant and T the absolute temperature). Using Eqs. (6) and (7), one then gets the following expression for $P(m, m+\mu)$:

$$P(m, m+\mu) = (2\pi/M^2)|Q_{\mu m}|^2 \sum_n N_{\mu n} D_n (1-\gamma_\infty)^2, \tag{8}$$

where

$$D_n = \int_0^{\omega_m} \frac{\rho(\omega)}{\omega^2} \frac{e^x}{(e^x-1)^2} d\omega L_n(ka), \tag{9}$$

$$N_{\mu n} = \sum_{i,j,l,m} N_{\mu,i,j,l,m}, \tag{10}$$

where the summations over i, j, l, and m are to be taken over different sets of particles for different values of μ, namely

$$\begin{array}{lll} n=1 & i=\pm l, & j=\pm m \\ n=2 & i=\pm l, & j=\pm m \\ n=3 & i=\pm l, & j\neq\pm m \\ n=4 & i\neq\pm l, & j\neq\pm m. \end{array} \tag{11}$$

The factor $(1-\gamma_\infty)^2$ is introduced in Eq. (8) to take care of the antishielding effects[8] of the core electrons of the ion containing the nucleus under study. The functions $L_n(y)$ are given by

$$\begin{aligned} L_1(y) &= \{\tfrac{1}{2}-\tfrac{1}{2}f(2y)\}^2, \\ L_2(y) &= \{3/2-2f(y)+\tfrac{1}{2}f(2y)\}^2, \\ L_3(y) &= \{3/2-2f(y)+\tfrac{1}{2}f(2y)\}\{1-2f(y)+f(\sqrt{2}y)\}, \\ L_4(y) &= \{1-2f(y)+f(\sqrt{2}y)\}^2, \end{aligned} \tag{12}$$

with $f(y) = j_0(y)$.

If we use the Debye approximation,

$$\rho(\omega) = V\omega^2/2\pi^2 v^3, \tag{13}$$

where v is the velocity of the long wavelength sound waves and V is the volume of the crystal, we get Eq. (37) of Van Kranendonk's paper from our Eq. (9).

To obtain the contribution to the nuclear relaxation from the induced dipoles produced by the optical modes, we have to follow the procedure employed by Wikner, Blumberg, and Hahn.[4] However, their Eq. (19) is based on the Debye approximation, while we would like to employ an expression in terms of a general spectral function $\rho_{\text{opt}}(\omega)$. On revising the expression (18) of Wikner, Blumberg, and Hahn's paper to include a general frequency distribution spectrum for the optical modes, the modified equation for $P(m, m+\mu)$ due to the dipolar process becomes

$$P(m, m+\mu) = (2\pi/4M^2)|Q_{\mu m}|^2 N_\mu E(1-\gamma_\infty)^2, \tag{14}$$

where

$$E = \int_0^{\omega_m} G(\omega)d\omega = \int_0^{\omega_m} \frac{\rho_{\text{opt}}^2(\omega)}{\omega^2} \frac{e^x}{(e^x-1)^2} d\omega \tag{15}$$

and N_1 and N_2 for the rock-salt structure are given by

$$\begin{aligned} N_1 &= 5292(d\mu/d\epsilon)^2 a^{-10}, \\ N_2 &= 8140(d\mu/d\epsilon)^2 a^{-10}, \end{aligned} \tag{16}$$

where $d\mu/d\epsilon$ is the derivative of the dipole moment on an ion with respect to its relative displacement from its nearest-neighbor ion during the optical mode vibrations. Expressions for the derivatives $d\mu/d\epsilon$ for the positive and negative ions have been derived by Wikner, Blumberg, and Hahn[4] in terms of the polarizabilities of the ions.

$$\left(\frac{d\mu}{d\epsilon}\right)_\pm = Z\left[\frac{1}{1-(4\pi/3)\alpha_+ + \alpha_-)a^{-3}}\right]\frac{\alpha_\pm}{\alpha_+ + \alpha_-}, \tag{17}$$

Z being the effective charge on the nearest-neighbor ion. Thus, while considering the relaxation of the alkali nucleus, $(d\mu/d\epsilon)_-$ has to be used and $Z=+1$, while for the halogen nucleus, $(d\mu/d\epsilon)_+$ is pertinent and $Z=-1$. In Eq. (17), α_+ and α_- refer to the polarizabilities of the positive and negative ions and a is the nearest-neighbor distance.

In Eq. (15), ω_m is the upper limit for the optical frequency. From Karo's calculated curves ω_m is seen to equal the upper limit of the total distribution function used in Eq. (9). The lower limit for the integral in Eq. (9) is $\omega=0$ while the lower limit for Eq. (15) is the lower frequency cutoff $\omega_{\min}$ for the optical modes. However, taking $\rho_{\text{opt}}(\omega)$ equal to zero below $\omega_{\min}$, the lower limit in Eq. (15) can be put equal to zero.

In using Eq. (9) to calculate $P(m, m+\mu)$ for the monopole mechanism we need $L_n(ka)$, which requires a knowledge of k for various values of ω in Eq. (9). Such information can be obtained from theoretical or experimental dispersion curves.[11–13] However, k occurs only in the form $f(y) = (\sin ka)/ka$ which is rather insensitive to variations in k. We have therefore used the relation

$$\omega = vk \tag{18}$$

to relate k to ω, where the average velocity v is obtained from the Debye temperature by the relation

$$\Theta = \frac{\hbar v}{K}(3d/4\pi M N_A)^{1/3}, \tag{19}$$

K being the Boltzmann constant, d the density, M the molecular weight, and N_A the Avogadro number. Van

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[15] See for example, W. Heitler, *Quantum Theory of Radiation* (Oxford University Press, New York, 1954).

Kranendonk's Eq. (37), on the other hand, involves v^3 as a factor and therefore depends more sensitively on the assumptions in Eqs. (18) and (19). Equation (14) for $P(m, m+\mu)$ due to the dipolar mechanism produced by the optical modes does not require a knowledge of k and is therefore not affected by the approximation in (18).

Once the probabilities $P(m, m+\mu)$ are available, one can obtain the spin-lattice relaxation time T_1 using the relationship between T_1 and $P(m, m+\mu)$. In the work prior to Wikner, Blumberg, and Hahn,[4] an erroneous relationship was employed. For $I=\frac{3}{2}$, the relation used was

$$T_1=1/P_1+1/P_2, \qquad (20)$$

where

$$\begin{aligned} P_1&=P(\tfrac{1}{2},\tfrac{3}{2})=P(-\tfrac{1}{2},-\tfrac{3}{2}),\\ P_2&=P(-\tfrac{1}{2},\tfrac{3}{2})=P(\tfrac{1}{2},-\tfrac{3}{2}). \end{aligned} \qquad (21)$$

Wikner, Blumberg, and Hahn,[4] and Hebel and Slichter,[16] have shown that the use of Eq. (20) amounted to the neglect of the $\Delta m=\pm1$ processes that could occur due to the dipole-dipole interaction between the nuclei. They showed that the transition probability due to the dipole process P_0 was much stronger than P_1 and P_2. This meant that a common spin temperature could be assumed for all the Zeeman levels of the nucleus in an external magnetic field. Using the rate equations for the populations in the various Zeeman levels, the following expressions for T_1 are obtained:

$$I=\tfrac{3}{2},\quad 1/T_1=(\tfrac{2}{5})(P_1+4P_2) \qquad (22)$$

$$I=\tfrac{5}{2}\quad 1/T_1=(4/35)[(P_1+P_1')+4(P_2+P_2')]. \qquad (23)$$

In Eq. (23),

$$P_1'=P(\tfrac{3}{2},\tfrac{5}{2})=P(-\tfrac{3}{2},-\tfrac{5}{2})$$

and $$\qquad (24)$$

$$P_2'=P(\tfrac{1}{2},\tfrac{5}{2})=P(-\tfrac{1}{2},-\tfrac{5}{2}).$$

III. RESULTS AND DISCUSSIONS

The matrix elements $Q_{\mu m}$, that occur in Eqs. (8) and (14), are tabulated in Table I for $I=\frac{3}{2}$ and $I=\frac{5}{2}$. From Table I, it is clear that the matrix elements involved in P_1 and P_1' are related by a factor of $(5/2)^{1/2}$, while those in P_2 and P_2' are related by a factor of 3. In obtaining the theoretical values of T_1 for I^{127} it is therefore incorrect to take the matrix elements $Q_{\mu m}$ involved in the primed and unprimed transition probabilities as equal, as was done in Table II of Ref. 4.

TABLE I. Matrix elements[a] $Q_{\mu m}$ for $I=\frac{3}{2}$ and $\frac{5}{2}$.

$Q_{\mu m}$ / Spin	$m=\frac{3}{2}$	$m=\frac{1}{2}$		$m=-\frac{1}{2}$
	$\mu=1$	$\mu=1$	$\mu=2$	$\mu=2$
$I=\frac{3}{2}$		$\dfrac{(12)^{1/2}}{3}eQ$		$\dfrac{(12)^{1/2}}{3}eQ$
$I=\frac{5}{2}$	$\dfrac{4(5)^{1/2}}{10}eQ$	$\dfrac{4\sqrt{2}}{10}eQ$	$\dfrac{2(10)^{1/2}}{10}eQ$	$\dfrac{6\sqrt{2}}{10}eQ$

[a] The matrix elements other than those tabulated are related to these. Thus, for $I=\frac{3}{2}$, all the other possible $Q_{\mu m}$ are equal to $Q_{1,1/2}$. For $I=\frac{5}{2}$, $Q_{-1,-3/2}=Q_{1,3/2}$; $Q_{-1,-1/2}=Q_{-1,3/2}=Q_{1,-3/2}=Q_{1,1/2}$; $Q_{-2,1/2}=Q_{2,1/2}$; $Q_{-2,3/2}=Q_{-2,1/2}=Q_{2,-3/2}=Q_{2,-1/2}$.

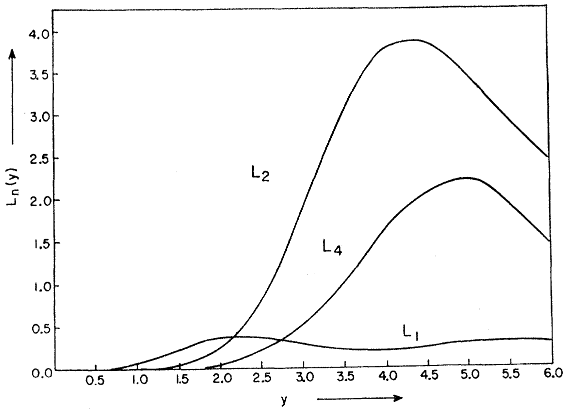

FIG. 1. Plots of $L_1(y)$, $L_2(y)$ and $L_4(y)$.

In Eq. (8) for $P(m, m+\mu)$ for the point charge process, the quantities $N_{\mu n}$ involved may be obtained from Table II of Van Kranendonk's paper. Substituting the values of $N_{\mu n}$ in Eq. (7), we find that one requires the following combination of integrals involving L_1, L_2 and L_4, namely,

$$D=D_1+D_2+0.665D_4=\int_0^{\omega_m}F(\omega)d\omega, \qquad (25)$$

where

$$F(\omega)=[\rho^2(\omega)/\omega^2][L_1(ka)+L_2(ka)+0.665L_4(ka)]\times[e^x/(e^x-1)^2].$$

Correspondingly, for the dipolar process, we have to compute the quantity E in Eq. (15). Unlike the Debye

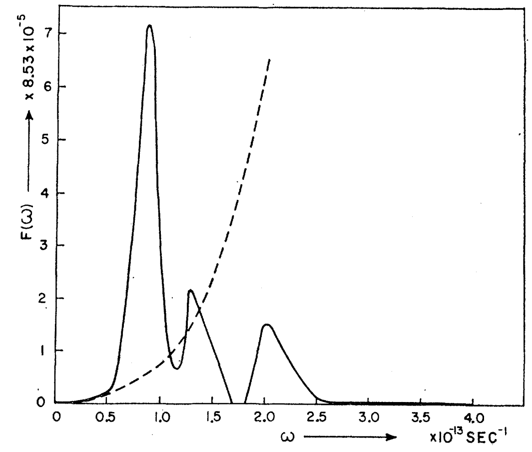

FIG. 2. Curves for $F(\omega)$ in NaI with Karo and Debye distribution functions at $T=298°$K. The solid curve is for the Karo function and the dashed curve for the Debye approximation.

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[16] L. C. Hebel and C. P. Slichter, Phys. Rev. **113**, 1504 (1959).

approximation, when a more realistic distribution is used, D and E cannot be obtained from the areas under the same curves in each case for all the alkali halides (with only the upper limit determined by the Debye temperature of the particular crystal in question). For the frequency distribution $\rho(\omega)$, we have used the calculated curves of Karo.[12] In our calculations, Karo's functions $\rho(\omega)$ have to be normalized according to the relation

$$\int_0^{\omega_m} \rho(\omega)d\omega = 2N, \qquad (26)$$

where N is the number of molecules in the unit cell of the crystal. The normalization integral is taken as $2N$ and not $6N$ because in Eq. (8) the summation over $p(=1, 2, 3)$ has already been performed and we have only to take account of the fact that there are two ions in each unit cell. In Fig. 1, the plots for $L_1(y)$, $L_2(y)$, and $L_4(y)$ are presented as functions of y. Since Karo's curves extend to much larger ω_m than in the Debye approximation, one has to plot the curves for $L_n(y)$ for larger values of the arguments y than is done in Van Kranendonk's paper.[6] In Fig. 2, $F(\omega)$ for NaI is plotted as a function of ω using Karo's $\rho(\omega)$. In the same figure we have also presented for comparison the function $F(\omega)$ that would be obtained using the Debye approximation. The temperature used in Fig. 2 is the room temperature $T=298°$K. The values of the Debye temperature for the various crystals that we have investigated were taken from Wikner, Blumberg, and Hahn.[4] These, together with the average velocities v obtained from Eq. (19), as well as the antishielding factors $(1-\gamma_\infty)$, are tabulated in Table II for the various alkali halides which we have considered. In Fig. 3 the curves for $G(\omega)$ against ω in NaI at $T=298°$K is compared with the curve obtained by Debye approximation. For all the alkali halides that we have considered, namely NaCl, NaBr, NaI, KCl, KBr, KI, RbCl, and RbBr, curves of the type in Figs. 2 and 3 were drawn at $T=298°$K. The areas under these curves were read off to be used in Eqs. (8), (15), and (25). Similar curves were also plotted at $T=200$, 100, 70, 40, and 20°K for NaI to calculate T_1 for Na^{23} and I^{127} nuclei as a function of temperature. The curves for $F(\omega)$ and $G(\omega)$ at $T=20°$K are presented in Figs. 4 and 5, respectively. When we compare Fig. 2 with Fig. 4 or Fig. 3 with Fig. 5, we find that at low temperatures the Bose factor $e^x/(e^x-1)^2$ reduces the relative contributions to the areas from the high-frequency regions of the $F(\omega)$ and $G(\omega)$ curves. For rigorous quantitative accuracy, the lattice distribution functions $\rho(\omega)$ for the particular temperature concerned should be employed. Unfortunately such curves are not available; we therefore made use of Karo's calculated curves at $T=298°$K. However, Karo has made a comparison between the calculated and experimental values of the

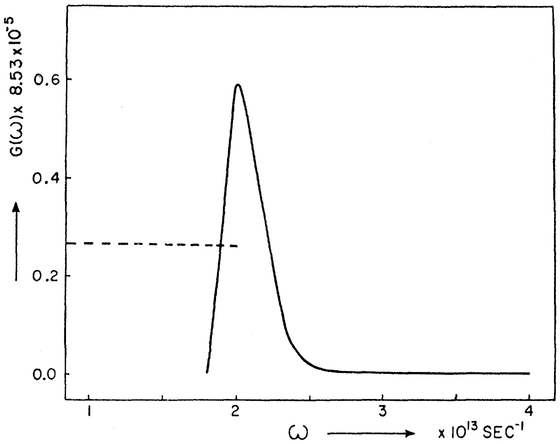

FIG. 3. Curves for $G(\omega)$ in NaI for both Karo and Debye distribution functions at $T=298°$K. The solid curve is for the Karo function and the dashed curve for the Debye Approximation.

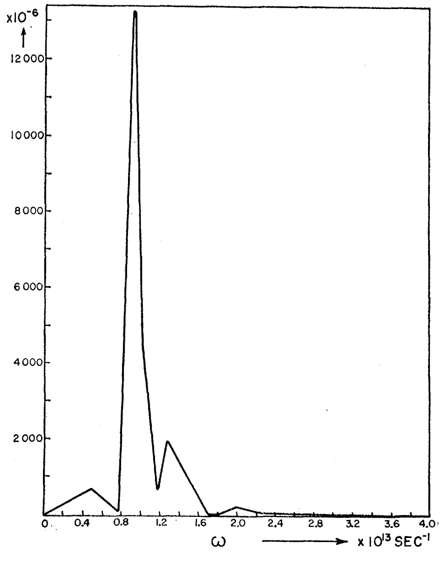

FIG. 4. Curve for $F(\omega)$ at $T=20°$K for NaI.

TABLE II. Values of Debye temperature Θ, average velocity v and antishielding factors used in the calculation of T_1.

Crystal	Debye temperature[a] Θ (°K)	v (m/sec)[b]	Antishielding factor for positive ion[c] $(1-\gamma_\infty)_+$	Antishielding factor for negative ion[c] $(1-\gamma_\infty)_-$
NaCl	281	3360	5.50	50.4
NaBr	200	2532	5.50	100.0
NaI	151	2076	5.50	180.0
KCl	227	3035	13.84	50.4
KBr	177	2481	13.84	100.0
KI	130	1949	13.84	180.0
RbCl	179	2518	50.30	50.4
RbBr	140	2050	50.30	100.0

[a] K. Lonsdale, Acta. Cryst. **1**, 144 (1958)

[b] Calculated from Θ using Eq. (18).

[c] E. G. Wikner and T. P. Das, Ref. 8. Although more recent values are available in some cases, the same values as the ones used by Wikner, Blumberg, and Hahn are used to facilitate comparison.

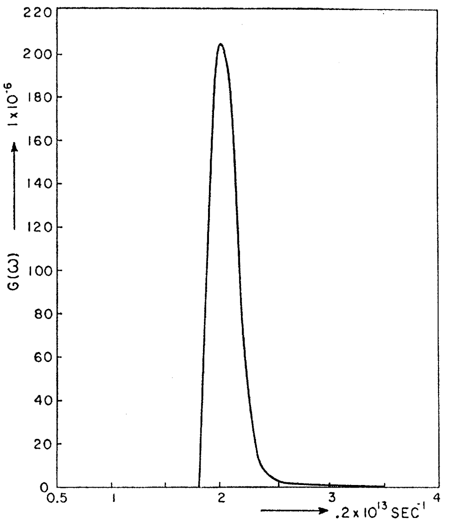

FIG. 5. Curve for $G(\omega)$ at $T=20°\mathrm{K}$ for NaI.

dispersion frequencies, Debye characteristic temperatures and moments of the distribution curves at 0 and 298°K. The agreement is quite good. It seems therefore that our use of a single $\rho(\omega)$ function for all temperatures should not be a significant source of error. Finally, to obtain the temperature dependence of T_1 according to the Debye model, we needed the corresponding values of D and E at various temperatures. The values of D can be obtained from Tables I and III of Van Kranendonk's paper, using the value of $\Theta=151°\mathrm{K}$ for the Debye temperature in NaI. To obtain the values of E with the Debye approximation, we had to calculate the integral $\int_0^{\Theta/T} x^2e^x/(e^x-1)^2dx$ for the various temperatures in which we were interested.

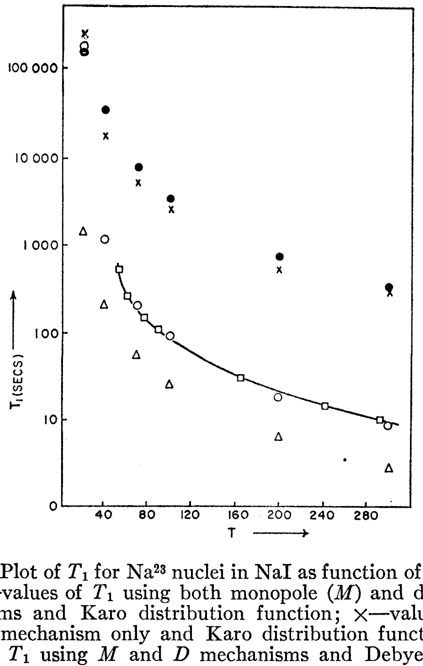

FIG. 6. Plot of T_1 for Na^{23} nuclei in NaI as function of temperature. ○—values of T_1 using both monopole (M) and dipole (D) mechanisms and Karo distribution function; ×—values of T_1 using M mechanism only and Karo distribution function; △—values of T_1 using M and D mechanisms and Debye approximation; ●—values of T_1 using M mechanism only and Debye approximation; □—experimental values of T_1.

In Table III we present our calculated results for room temperature (298°K) together with those of Wikner, Blumberg, and Hahn[4] and experimental results for comparison. In the first column, the alkali halide and nucleus of interest are listed. The second and third columns contain the calculated values of P_1 and P_2 (also P_1' and P_2' for $I=\frac{5}{2}$) for the monopole mechanism using the Karo distribution functions. The fourth and fifth columns give the values of P_1 and P_2 from the induced dipole mechanism calculated from Eq. (15) with the Karo distribution function for the optical modes. The values of the total P_1 and P_2, which are combinations of the contributions from the monopole and dipole mechanisms, are presented in the sixth and seventh columns. The calculated values of T_1 from the monopole and dipole mechanisms are presented in the eighth and ninth columns. Wikner, Blumberg, and Hahn's calculated values of T_1 using the Debye model are presented in the tenth and eleventh columns. Kochelaev's calculated values[10] for T_1 for two crystals and the experimental values of T_1 at room temperature are presented in the last two columns.

From Table III it appears that the calculated values for T_1 from the Karo distribution curves are consistently smaller than the values obtained by Wikner, Blumberg, and Hahn from the Debye model. This comparison with the theoretical values of Wikner, Blumberg, and Hahn is more meaningful for the monopole mechanism than for the combined effects of the monopole and dipole mechanisms. The reason for this is that the values of P_1 and P_2 for the dipole mechanism obtained by Wikner, Blumberg, and Hahn were overestimated since they used the total distribution function $\rho(\omega)$ in (15) instead of the distribution function for the optical modes only. This probably accounts for the fact that for Na^{23} nucleus in NaI, their calculated value for the total T_1 is smaller than our value, as opposed to the general trend in the other cases tabulated. In general Table III also indicates that the calculated values of T_1 with Karo distribution function are in better agreement with experiment than the values obtained by Wikner, Blumberg, and Hahn with the Debye spectrum. The calculated relaxation times are thus seen to be sensitive to the assumed frequency distribution function $\rho(\omega)$ and can therefore serve as an additional measure of the accuracy of calculated density functions $\rho(\omega)$. It would be interesting to recalculate T_1 with some of the other distribution functions $\rho(\omega)$ that are currently available[11,13] or become available in the future. However, one would not expect as remarkable a difference between values of T_1 obtained with different calculated functions $\rho(\omega)$ as is obtained with Karo and Debye functions. A comparison between the curves for $\rho(\omega)$ in NaI obtained by Karo[12] and by Cochran, Brockhouse, and Woods[13] shows general agree-

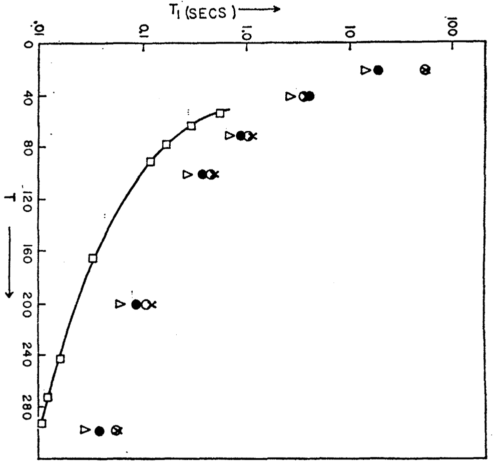

FIG. 7. Plot of T_1 for I^{127} nuclei in NaI as function of temperature. The notations for points have same meaning as in Fig. 6.

ment in gross features and only a slight difference in the relative peak heights for the optical- and acoustic-mode densities.

In Figs. 6 and 7, we have plotted the calculated values T_1 for Na^{23} and I^{127} in NaI as a function of temperature. Both the values of T_1 arising from the monopole mechanism alone, as well as the values obtained from the combined effects of the monopole and dipole mechanism have been plotted. For comparison, we have also plotted the values of T_1 obtained from the Debye model and the experimental values. It is apparent from these figures that the temperature dependence of T_1 calculated using the Karo model closely resembles experiment for both Na^{23} and I^{127} nuclei, although the absolute values for I^{127} are somewhat lower than experiment. This close agreement of the temperature dependence with experiment for both nuclei is remarkable; because, while the monopole mechanism is the leading contributor to relaxation for I^{127}, it is the dipole mechanism which is the leading contributor for Na^{23}. The dipole mechanism depends on the optical mode density $\rho_{\text{opt}}(\omega)$, while the monopole mechanism depends on the entire density function $\rho(\omega)$. In comparing the temperature dependences for both Na^{23} and I^{127} nuclei, we are therefore really subjecting the different parts of the density distribution function $\rho(\omega)$ to test. The good agreement between experiment and theory therefore indicates that both the low- and high-frequency regions of Karo's calculated $\rho(\omega)$ are substantially correct. At temperatures above 70°K, there is unfortunately no marked difference between the temperature dependence of T_1 calculated from Karo's distribution curve and the Debye model for both Na^{23} and I^{127} nuclei. But below 70°K the Debye model leads to a slower increase in T_1 with decreasing temperature than the Karo distribution function. The reason for this is clear from a comparison

TABLE III. Calculated values of transition probabilities and relaxation times from present work and comparison with earlier theoretical and experimental values of T_1.

Nucleus and Substance	Monopole mechanism[a]				Induced dipole mechanism				Total				Calculated[b]		WBH values		Kochelaev's values of T_1	Experimental[c] values of T_1
	P_1		P_2		P_1		P_2		P_1		P_2		$T_{1\,\text{monopole}}$	$T_{1\,\text{total}}$	$T_{1\,\text{monopole}}$	$T_{1\,\text{total}}$		
$Na^{23}Cl$	0.00603		0.00202		0.09180		0.14120		0.09783		0.14322		177	6.2215	420	30		12
$Na^{23}Br$	0.00459		0.00154		0.03382		0.05203		0.03841		0.05357		233	9.8935	340	10		6
$Na^{23}I$	0.00356		0.00119		0.03976		0.06116		0.04332		0.06235		300	8.5406	350	2.8		5, 10.5
$K^{39}Cl$	0.01215		0.00407		0.07926		0.12191		0.09141		0.12598		88	4.1994	202	28		6.2
$Rb^{87}Cl$	0.58960		0.19760		2.36795		3.64231		2.95755		3.83991		1.81	0.1365	4.51	0.845		0.250
$Rb^{87}Br$	0.70980		0.23790		6.52943		10.04337		7.23923		10.28127		1.50	0.0517	4.80	0.510		0.165
$NaCl^{35}$	0.30780		0.10310		0.04305		0.06622		0.35085		0.16932		3.47	2.4316	6.40	5.8		5.2
KCl^{35}	0.19450		0.06518		0.18991		0.29212		0.38441		0.35730		5.50	1.3785	12.50	7.0		8.5
$NaBr^{79}$	16.44		5.508		0.55999		0.86136		17		6.36936		0.065	0.0589	0.095	0.082		0.052
KBr^{79}	12.76		4.277		7.861		12.091		20.628		16.368		0.084	0.0290	0.244	0.133	0.320	0.072
$RbBr^{79}$	13.52		4.532		23.402		35.996		36.922		40.528		0.079	0.0126	0.252	0.098		0.065±0.04
	P_1	P_1'	P_2	P_2'	P_1	P_1'	P_2	P_2'	P_1	P_1'	P_2	P_2'						
NaI^{127}	44.62	17.87	7.48	13.46	0.3937	0.9484	1.3130	0.7294	45.0137	18.8184	8.793	14.1894	0.060	0.0560	0.138	0.104		0.012
KI^{127}	59.61	23.88	9.99	17.98	2.6131	6.5327	9.0435	5.0242	62.2231	30.4127	19.0335	23.0042	0.045	0.034	0.322	0.165	0.077	0.019

[a] All tabulated P are in units of sec^{-1}.

[b] All tabulated T_1 are in units of sec.

[c] Experimental values quoted are from the paper by WBH (Ref. 4) except the value $T_1 = 10.5$ sec for Na^{23} for NaI which is taken from Ref. 5, Fig. 3.

of the curves for $F(\omega)$ and $G(\omega)$ in Figs. 2 and 3 obtained from the Debye and Karo models. The Debye model involves a maximum frequency ω_m of about 2×10^{13} sec^{-1} as compared to 4×10^{13} sec^{-1} for the Karo distribution function. In addition, in contrast to the Debye distribution function, there is a break in the Karo distribution function at 1.8×10^{13} sec^{-1} between the acoustic and optic branches. These factors indicate that the Debye model emphasizes the lower frequency region and would therefore lead to a weaker temperature dependence at lower temperatures when there is a significant depletion in population of the high-frequency optic branches of the Karo distribution.

As regards the consistently higher absolute values of T_1 that we obtained at all temperatures from our calculations as compared to experiment for I^{127}, the following explanation could be offered. Since the calculated temperature variation of T_1 is in consistent agreement with experiment at all temperatures, we require an additional mechanism which will contribute to T_1 but have the same temperature dependence as our calculated result. Such a mechanism is the overlap mechanism considered by Kondo and Yamashita,[9] which would be expected to lead to exactly the same temperature dependence as D in Eq. (15). On the other hand, the temperature dependence of the induced dipole mechanism is different from that of the monopole or the Kondo-Yamashita overlap mechanism. The good agreement between experiment and theory for the absolute values of T_1 as well as its temperature dependence for Na^{23} in NaI indicates that the Kondo-Yamashita overlap mechanism is relatively less effective as compared to the dipole mechanism. This observation is in keeping with quadrupole coupling data in alkali halide molecules[14] which show that the quadrupole interaction for the positive ion nuclei can be interpreted quite well by the point multipole model while the negative ion nuclei seem to require a consideration of the overlap between the electronic wave functions for the ions. It would be interesting to study the temperature dependence of the T_1 for halogen nuclei in heavier alkali halides such as rubidium and cesium halides. The polarizabilities of Rb^+ and Cs^+ ions are substantial enough so that the induced dipole mechanism would be expected to be significant and one would expect that the observed temperature dependence cannot be explained by the monopole or Kondo and Yamashita's overlap mechanisms alone. Also a study of relaxation times and their temperature dependence as a function of pressure would be interesting. Since the overlaps of the ions depends exponentially on distance, the overlap mechanism would gain in effectiveness with increased pressure over the induced dipole mechanism and also the monopole mechanism. A marked change in the temperature dependence of T_1 would therefore be expected with pressure especially for the positive ion nuclei. In addition, with increasing pressure, Yosida and Moriya's covalent mechanism,[7] involving electron transfer from the negative ion to unoccupied states of the alkali ion, may become effective. This mechanism would, however, also have the same temperature dependence as D in (25), as is the case for the monopole and overlap mechanisms.

CONCLUSION

Our calculated results indicate that one can obtain a significant check of the correctness of calculated phonon distribution functions $\rho(\omega)$ using data on nuclear relaxation times and their temperature dependences for alkali halides, especially if careful measurements of temperature dependence of T_1 are made at low temperatures (70°K or lower). Using Karo's calculated distribution functions for a number of alkali halides, a fair overall agreement is found between experimental values of T_1 at room temperature and theoretical values obtained by using a combination of contributions from Van Kranendonk's monopole and Wikner, Blumberg, and Hahn's induced dipole mechanisms. The temperature dependence for T_1 obtained by our calculations for Na^{23} and I^{127} are also in very good agreement with experiment. It would be interesting to recalculate the values of T_1 and their temperature dependence when results of improved calculations, using the shell model, are available.[13] Also an additional test of theory would be made possible if the temperature dependence of T_1 under pressure were measured.[17]

ACKNOWLEDGMENT

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[17] Experiments to study T_1 and chemical shifts as function of pressure are being planned at Riverside by Professor R. R. Hewitt for a number of alkali halides.