THEORY OF QUADRUPOLAR NUCLEAR SPIN-LATTICE RELAXATION

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Synopsis

General theoretical expressions are derived for the nuclear spin-lattice relaxation in crystalline solids arising from the interaction of the nuclear electric quadrupole moment with the crystalline electric field. The importance of shielding, antishielding and co-valent effects for the quadrupolar spin-lattice coupling is discussed, and the complete temperature dependence of the transition probability P for a nuclear spin making a transition as a result of the thermal Raman processes is determined on the basis of some simplifying assumptions about the nature of the lattice vibrations. At low temperatures the P are developed in ascending powers of the temperature T, the first term being proportional to T^7. It is found that this power series is rapidly convergent only for T smaller than about 0.02Θ, where Θ is the Debije temperature. At high temperatures, the P are developed in descending powers of T, and it is found that an expression of the form $T^2(a - b/T^2)$ gives a good representation of the temperature dependence of P down to about $T = \frac{1}{2}\Theta$. General expressions are derived for the dependence of the probabilities P on the direction of the external magnetic field relative to the crystal axes. Finally, a simple, one-parameter model is discussed, in which the crystalline field at a nucleus is assumed to arise from a number of equal point charges placed on the nearest neighboring lattice sites. The magnitude q of these charges is a measure for the quadrupolar spin-lattice coupling, and is the adjustable parameter of the model. Detailed calculations are made with this model for crystals of the NaCl-type. The calculated relaxation times $1/P$ are of the same order of magnitude as the experimental ones for values of q of the order of $10^2 - 10^3 e$, where e is the electronic charge. The significance of this result is discussed. Finally, the dependence on the direction of the external field is calculated, and the probability for a transition $\Delta m = \pm 1$ for the (111) direction is found to be about 50% larger than for the (100) direction, while the probability for a transition $\Delta m = \pm 2$ for the (111) direction is about 10% smaller than for the (100) direction.

§ 1. *Introduction.* P o u n d [1] [2] [3]) has shown that the presence of a nuclear electric quadrupole moment can have important consequences for the nuclear magnetic resonance absorption. In particular, P o u n d has shown that the nuclear spin-lattice relaxation resulting from the coupling of the nuclear electric quadrupole moment to the electric field set up by the charges outside the nucleus can often be the dominant relaxation mechanism. No detailed theory of this relaxation phenomenon has been

given, however, and it is the purpose of the present paper to develop a general theory of this quadrupolar spin-lattice relaxation in crystalline solids. The existing theories of the nuclear spin-lattice relaxation are concerned with the "magnetic" relaxation due to the dipolar interaction of the magnetic moments of the nuclei, and with the "impurity" relaxation due to the presence of electronically paramagnetic impurities. The theory of B l o e m b e r g e n, P u r c e l l and P o u n d [4] [5] of the magnetic relaxation in liquids is based on the assumption that each pair of nuclei contributes independently to the relaxation, and that the relative motion of a pair of nuclei is a randomly fluctuating function of the time. This theory appears to work well for liquids, but it can hardly be applied to solids. However, the theory of W a l l e r [6] for the magnetic spin-lattice relaxation in solids for the electronic case can be adapted easily to the nuclear case, but it is found that the relaxation times calculated in this way are much larger than the observed ones. It has been shown by R o l l i n and H a t t o n [7] [8] and by B l o e m b e r g e n [9] that for nuclei with a spin $I = \frac{1}{2}$, which have no quadrupole moment, the observed spin-lattice relaxation times can be satisfactorily accounted for by assuming that they are due to the presence of electronically paramagnetic impurities. For nuclei with a spin $I > \frac{1}{2}$, however, P o u n d has obtained conclusive evidence [1] that in pure crystals at not too low temperatures the quadru-polar relaxation may be more important than the impurity relaxation. The quadrupolar relaxation, just as the magnetic relaxation, is strongly dependent on the temperature and becomes rapidly ineffective at lower temperatures. The impurity relaxation, on the other hand, is much less temperature dependent, so that at low temperatures the impurity relax-ation is usually more important than the quadrupolar relaxation. Therefore it is necessary to develop a theory of the quadrupolar relaxation, which is valid not only at low temperatures but also at high temperatures. Ac-cordingly, we cannot assume that the wave-length of the lattice waves involved in the relaxation process is large compared to the lattice constant, and this complicates the theory considerably. Fortunately, the theory can still be carried through without having to introduce too drastic simpli-fications, and the complete temperature dependence of the fundamental transition probabilities can then be obtained.

In the present paper a general theory of the quadrupolar relaxation is developed on the basis of the following assumptions: (i) The dependence of the crystalline field at a nucleus on the displacements of the nuclei composing the solid from their equilibrium positions is restricted to this nucleus and its nearest neighbors. (ii) The frequencies of the normal lattice vibrations are assumed to be independent of the direction of the wave number vector k and of the polarization. However, the resulting frequency spectrum need not be of the Debije form. In § 2 we will derive the general

expressions for the interaction energy arising from the nuclear quadrupole moment. In § 3 the normal lattice vibrations are discussed, and in § 4 the general expressions for the transition probabilities are derived. In § 5 the temperature dependence of the relaxation is determined by means of numerical integration for the case that the frequency spectrum of the crystal is approximated by a Debije spectrum, and in § 6 the dependence of the relaxation on the direction of the external magnetic field relative to the crystal axes is discussed. In § 7, a simple, one-parameter model is discussed, and the theory is compared with the available experimental data. Finally, the dependence of the relaxation on the direction of the external field is calculated explicitly for crystals of the NaCl-type.

§ 2. *Derivation of the general expression for the interaction energy.* For the sake of simplicity we shall assume that the nuclei involved in the spin-lattice relaxation are located at equivalent lattice sites, so that they are subjected to similar crystalline fields. We shall further neglect the influence on the quadrupolar relaxation of the coupling between the nuclear spins, which results from the interaction between the magnetic moments of the nuclei and from possible other effects. The relaxation can then be expressed in terms of the transition probabilities indicating the rate at which the thermal fluctuations in the crystalline field induce transitions between the various spin states of a particular nucleus. In the Born-Oppenheimer approximation, the Hamiltonian that describes the orientation of the spin of this nucleus, and its coupling to the lattice vibrations and the external field, is given by the average of the total energy of the crystal, including the electronic energy, over the ground electronic state, which state depends parametrically on the coordinates of the centres of gravity and on the orientations of the spins of all the nuclei. Since we neglect the coupling between the spins, we may omit the terms that depend on the spins of the other nuclei, and the resulting Hamiltonian can then be written in the form:

$$H = H_L + H_Z + H'. \tag{1}$$

H_L is the energy of the lattice vibrations of the crystal, and H_Z is the Zeeman energy of the magnetic moment of the central nucleus in the external magnetic field $\boldsymbol{H}$:

$$H_Z = -\gamma\hbar\,\boldsymbol{H}.\boldsymbol{I}, \tag{2}$$

$\boldsymbol{I}$ is the nuclear spin operator expressed in units $\hbar$, and γ is the nuclear gyromagnetic ratio. Finally H' is that part of the total energy that is due to the presence of the nuclear electric quadrupole moment. H' is a function of $\boldsymbol{I}$ and of the coordinates of the centres of gravity of all the nuclei. It is necessary to define H' in this rather elaborate way, because in general H' is not equal to the energy $H'^{(0)}$ of the nuclear quadrupole moment in

the crystalline field that would result if the nuclear quadrupole moment would be zero. The difference between H' and $H'^{(0)}$ is due to the polarization of the charge cloud surrounding the nucleus by the nuclear quadrupole moment, which polarization has recently been discussed by S t e r n-h e i m e r [10] [11] and by S t e r n h e i m e r and F o l e y [12] [13]. By definition $H'^{(0)}$ is given by the expression

$$H'^{(0)} = \int \varrho(\mathbf{r}) \, V^{(0)}(\mathbf{r}) \mathrm{d}\mathbf{r}, \qquad (3)$$

in which $\varrho(\mathbf{r})$ is the charge density of the nucleus, and in which $V^{(0)}(\mathbf{r})$ is the potential of the crystalline field in the neighborhood of the central nucleus in the absence of a nuclear quadrupole moment. H' differs from $H'^{(0)}$, because the crystalline field interacts not only with the nuclear quadrupole moment, but also with the quadrupole and higher moments induced by the quadrupole moment in the charge cloud surrounding the nucleus. The induced quadrupole moment can be much larger than the nuclear quadrupole moment, and is such as to reinforce the nuclear quadrupole moment. This is called the antishielding, or polarization, effect. F o l e y, S t e r n h e i m e r and T y c k o [13] find that in ions (Cl⁻, Cu⁺, Rb⁺, Cs⁺) the induced quadrupole moment is a factor 10 to 100 larger than the nuclear quadrupole moment. In ionic crystals the resulting quadrupolar spin-lattice coupling H' can therefore be expected to be a factor 10–100 larger than the coupling $H'^{(0)}$ obtained without taking account of the polarization effect. We shall assume that the magnitude of the induced quadrupole moment is independent of the orientation of the nuclear quadrupole moment with respect to the crystal axes, and that the induced higher moments are negligible. The polarization effect can then be taken into account by means of a multiplication factor α, and we have:

$$H' = \alpha H'^{(0)} = \alpha \int \varrho(\mathbf{r}) \, V^{(0)}(\mathbf{r}) \mathrm{d}\mathbf{r}. \qquad (4)$$

We remark in passing that if H' is not equal to a constant times $H'^{(0)}$, the selection rule $\Delta m = 0, \pm 1, \pm 2$ for the transitions induced by the quadrupolar coupling breaks down. But this is probably a small effect in most crystals. We further remark that there is another multiplication factor that plays a role in the theory of the quadrupolar spin-lattice coupling. This factor comes up when we try to calculate $V^{(0)}(\mathbf{r})$, the potential of the crystalline field prevailing in the absence of the nuclear quadrupole moment. In an ionic crystal, for instance, the crystalline field at a nucleus cannot be obtained by simply calculating the direct field arising from the ionic charges. In the first place, this direct field from the surrounding ions polarizes the central ion, and this leads to an additional field at the nucleus oppositely directed to the direct field. This is the shielding effect. In the second place, a co-valent effect comes up, which is usually much more important than the shielding effect: if the lattice is deformed by the lattice

vibrations, some p-, or d-, like orbitals are mixed in to the originally s-like wave functions of the ions, and the electrons in these non-spherically symmetric orbitals give rise to an electric field gradient at the nucleus, which can interact with the nuclear quadrupole moment. The resulting quadrupolar spin-lattice coupling can be much larger than that arising from the direct field alone, while the dependence of the interaction energy on the displacements of the nuclei from their equilibrium positions will in general be much stronger than for the direct interaction. To indicate orders of magnitude, one may again use a multiplication factor, β, but the true potential is in general not equal to a constant times the potential of the direct field.

We shall now pursue the analysis on the basis of the expression (4) for the interaction energy. We develop the quantity $aV^{(0)}(r)$ in powers of the distance, r, from the centre of gravity of the central nucleus. The term independent of r gives rise to a force on the nucleus, which has already been included in H_L. Since the nucleus has only a quadrupole moment, we need further retain only the terms that are quadratic in $r = x, y, z$. These may be written in the form

$$aV^{(0)}(r) = \Sigma_{\mu=-2}^{+2} W_\mu Y_\mu(r), \tag{5}$$

in which

$$Y_0 = 3z^2 - r^2; \quad Y_{\pm 1} = z(x \pm iy); \quad Y_{\pm 2} = (x \pm iy)^2. \tag{6}$$

The expression (4) for the interaction energy then becomes:

$$H' = \Sigma_\mu W_\mu \int \varrho(r) Y_\mu(r) \, dr = \Sigma_\mu W_\mu Q_\mu. \tag{7}$$

The Q_μ are the components of the nuclear quadrupole moment, the equivalent-operators of which, in the subspace $I = \text{constant}$, are given by [1]:

$$\left. \begin{array}{l} Q_0 = B \, [3I_z^2 - I(I+1)], \\ Q_1 = Q_{-1}^* = B[I_z(I_x + iI_y) + (I_x + iI_y)I_z]/2, \\ Q_2 = Q_{-2}^* = B[I_x + iI_y]^2, \end{array} \right\} \tag{8}$$

in which

$$B = eQ/I(2I - 1), \quad eQ = \langle II|Q_0|II\rangle. \tag{9}$$

e being the elementary charge, and $|II\rangle$ the $m = I$ state of the nucleus. Thus the only non-vanishing matrix elements of Q_μ are $\langle m + \mu|Q_\mu| m\rangle$.

The coefficients W_μ appearing in (5) are functions of the displacements $r_i = s_i - s_0$ of the nuclei relative to the displacement s_0 of the central nucleus, and we can therefore develop W_μ in powers of the r_i:

$$W_\mu = A_\mu + \Sigma_i \boldsymbol{A}_{\mu i} \cdot \boldsymbol{r}_i + \Sigma_{ij} \mathsf{A}_{\mu ij} : \boldsymbol{r}_i \boldsymbol{r}_j + \ldots, \tag{10}$$

The summations over $i, j, \ldots$ must be extended independently over all the

nuclei except the central nucleus; the tensors $A_{\mu i j}$ are chosen in such a way that $A_{\mu i j}(a, b) = A_{\mu j i}(b, a)$, where a and b are equal to x, y or z; and the double dot indicates the complete inner product, *i.e.*

$$ \mathbf{t} : \mathbf{s} = \Sigma \ (a, b) \ t(a, b) \ s(a, b). $$

When we substitute (10) in the expression (7) for the interaction energy H', we get the corresponding development of H' in powers of the r_i,

$$ H' = H_0' + H_1' + H_2' + \ldots, \tag{11} $$

where $H_0' = \Sigma_\mu \ Q_\mu A_\mu$, etc. The constant term H_0' gives rise to the static quadrupolar interaction which pertubs the originally equally spaced Zeeman levels of the nucleus in the external magnetic field. This leads to a splitting of the magnetic resonance line, and in the absence of an external magnetic field, to the occurrence of the pure quadrupole spectrum. We shall assume for the sake of simplicity that H_0' is small compared to the Zeeman energy, so that the states of the nuclear spin can be characterized by the magnetic quantum number m. However, the theory can easily be generalized, in particular to the pure quadrupole case.

The higher-order terms H_1', H_2', ... give rise to the relaxation processes. It turns out that for all practical purposes only the first-order effect of the quadratic term H_2' need be considered. The linear term H_1' gives in first order rise to the so-called direct processes in which the nuclear spin makes a downward (upward) transition and one of the lattice oscillators is excited (de-excited). The probability of this process is proportional to the number of lattice oscillators the frequency of which is equal to the resonance frequency, and since this frequency is in the radiofrequency region, the contribution of the direct processes is completely negligible. In second order, the linear term H_1' gives rise to the so-called Raman processes in which the nuclear transition is accompanied by the excitation of one and the de-excitation of another lattice oscillator. This second order process due to H_1' involves the interaction twice, and the contribution of these second-order Raman processes proves to be completely negligible. The first-order effect of the quadratic term H_2' gives also rise to Raman processes, and these prove to be the relevant relaxation processes. The higher-order effects of H_2' are also negligible, and the first-order effects of the terms H_3', H_4', ..., in which more than two phonons are involved, become of importance only at very high temperatures $(T \gg \Theta)$, in which we are not interested. Thus only the first-order Raman processes due to H_2' remain, and these will be discussed in § 4.

§ 3. *The expressions for the relative displacements in terms of the normal vibrational coordinates.* In order to make a theoretical treatment of the relaxation process feasible, it is necessary to use a simplified model for the

lattice vibrations of the crystal. Fortunately, a 'summation over all the lattice oscillators is involved in the calculation of the relaxation due to the Raman processes, and one may expect that the result will be independent of the detailed properties of the lattice vibrations. It will be interesting to see whether such a model works as well here as it does for instance in the case of the specific heat. We shall assume that as far as the lattice vibrations are concerned, all the nuclei in the crystal are equivalent, so that the unit cell may be chosen in such a way that it contains only one nucleus. The displacement s_i of nucleus i from its equilibrium position R_i can then be written in the form

$$s_i = \Sigma_{kp} \, a_{kp} \, e_{kp} \exp (i k . R_i), \tag{12}$$

The sum over k runs over the N lattice points k in the first zone of the reciprocal lattice, and the sum over p over the three directions of polarization e_{kp}. We shall assume that for each value of k the three unit vectors e_{kp} are mutually orthogonal,

$$e_{kp} . e_{kp'} = \delta_{pp'}, \tag{13}$$

and that the frequency ω_k of the lattice vibrations is independent of p and of the direction of k. The expression for the relative displacement $r_i = s_i -$ $- s_0$ can be written in the form

$$r_i = \Sigma'_\lambda \, q_\lambda \, B_i \, e_\lambda. \tag{14}$$

The prime indicates that in the summation over k only one of the points $\pm \, k$ has to be taken; $\lambda = (k, \, p, \, s)$ and $s = 1,2$. The real normal coordinates q_λ and the quantities B_i are defined as follows:

$$q_\lambda = \delta(s, \, 1) \, (a_{kp} + a_{-kp}) + i\delta(s, \, 2) \, (a_{kp} - a_{-kp}), \tag{15}$$

$$B_i = B_i \, (k, \, s) = \delta(s, \, 1) \, (\cos k . a_i - 1) + \delta(s, \, 2) \sin k . a_i, \tag{16}$$

where $a_i = R_i - R_0$.
The non-vanishing matrix elements of q_λ are given by

$$\langle n_\lambda + 1 | q_\lambda | n_\lambda \rangle = \langle n_\lambda | q_\lambda | n_\lambda + 1 \rangle = (\hbar/M\omega_k)^{1/2} \, (n_\lambda + 1)^{1/2}, \tag{17}$$

where n_λ is the number of quanta with which the oscillator is excited, and M is the mass of the crystal. When the lattice oscillators are in thermal equilibrium at the temperature T, the average value of n_λ is given by

$$\bar{n}_\lambda = (e^x - 1)^{-1}, \qquad x = \hbar\omega_k/\varkappa T, \tag{18}$$

in which $\varkappa$ is Boltzmann's constant.

§ 4. *Derivation of the general expressions for the transition probabilities.* The quantity of interest in connection with the relaxation is the probability $P(m, m + \mu)$ that the nuclear spin makes a transition from the state m

to the state $m + \mu$ as a result of the Raman processes discussed in § 2, the lattice oscillators being supposed to be in thermal equilibrium at a definite temperature T. This quantity P is given by the following expression:

$$P(m, m + \mu) = \frac{V^2}{8\pi^3\hbar^2 v^2} \int_0^{\omega_m} k^4 f(\omega_k)^2 \sum \{|H_2'(\lambda, \lambda')|^2\} \, d\,\omega_k. \qquad (19)$$

$H_2'(\lambda, \lambda')$ is the matrix element of H_2' corresponding to the process in which the nuclear spin makes the transition $m \to m + \mu$, a lattice oscillator $\lambda = \boldsymbol{k}ps$ is excited, and a lattice oscillator $\lambda' = \boldsymbol{k}'p's'$ is de-excited. The frequency difference $\omega_k - \omega_{k'}$ lies in the radio-frequency region, and is therefore very small compared to the frequency ω_k of practically all of the lattice oscillators, so that we may put $\omega_k = \omega_{k'}$. The Σ sign in Eq. (19) represents a summation over all values of p, p', s and s', and the curly brackets indicate an averaging over all directions of $\boldsymbol{k}$ and $\boldsymbol{k}'$. The fact that this average occurs in Eq. (19) is due to our assumption that ω_k is independent of the direction of $\boldsymbol{k}$, and that the first Brillouin zone may be replaced by a sphere. Finally, the function $f(\omega)$ is defined in such a way that the number of oscillators $\lambda = \boldsymbol{k}ps$ with ω in $d\omega$ is given by

$$\varrho(\omega)d\omega = (V/2\pi^2 v) f(\omega)k^2 \, d\omega, \qquad (20)$$

where V is the volume of the crystal, and v the velocity of propagation of the long wavelength sound waves, which is assumed to be independent of p.

To evaluate the matrix elements $H_2'(\lambda, \lambda')$, we must express H_2' in terms of the normal coordinates q_λ of the lattice vibrations. According to Eqs. (7), (10), (11) and (14), the expression for H_2' in terms of the q_λ is

$$H_2' = \Sigma_\mu \, Q_\mu \, \Sigma_{\lambda\lambda'} \, w_\mu \, (\lambda, \lambda') \, q_\lambda \, q_{\lambda'}, \qquad (21)$$

$$w_\mu(\lambda, \lambda') = \Sigma_{ij} \, (B_i B_j') \, \mathsf{A}_{\mu ij} : \, \boldsymbol{e}_\lambda \, \boldsymbol{e}_{\lambda'}, \qquad (22)$$

In virtue of the relation $A_{\mu ij}(a, b) = A_{\mu ji}(b, a)$, we have $w_\mu(\lambda, \lambda') = w_\mu(\lambda', \lambda)$, so that the matrix elements $H_2'(\lambda, \lambda')$ of H_2' are given by

$$H_2'(\lambda, \lambda') = (2\hbar \, Q_{\mu m}/M\omega_k) \, [(n_\lambda + 1)n_{\lambda'}]^{1/2} \, w_\mu(\lambda, \lambda'), \qquad (23)$$

$$Q_{\mu m} = \langle m + \mu \mid Q_\mu \mid m \rangle. \qquad (24)$$

When we substitute (23) in Eq. (19), we get the desired expression for P:

$$P(m, m + \mu) = \frac{|Q_{\mu m}|^2}{2\pi^3 \, d^2 v^2} \int_0^{\omega_m} \frac{k^4 f(\omega)^2}{\omega^2} \frac{e^x}{(e^x - 1)^2} M_\mu \, (ka) \, d\,\omega. \qquad (25)$$

Here $x = \hbar\omega/\varkappa T$, $d = M/V$ is the mass density of the crystal, and the functions $M_\mu \, (ka)$ are given by

$$M_\mu(ka) = \Sigma_{ss'} \, \Sigma_{ijlm} \, N_{\mu ijlm} \, L_{sil; \, s'jm} \, (ka), \qquad (26)$$

$$L_{sil; \, s'jm} \, (ka) = \{B_i(\boldsymbol{k}, s) \, B_l(\boldsymbol{k}, s)\} \{B_j \, (\boldsymbol{k}', s') \, B_m \, (\boldsymbol{k}', s')\}, \qquad (27)$$

$$N_{\mu ijlm} = \mathsf{A}_{\mu ij} : \mathsf{A}_{\mu lm}, \qquad (28)$$

where the $B_i(\boldsymbol{k}, s)$ are given by Eq. (16). In the derivation of Eq. (25), use has been made of the relation

$$\Sigma_{pp'} (A^*_{\mu ij} : \boldsymbol{e}_\lambda \boldsymbol{e}_{\lambda'}) (A_{\mu lm} : \boldsymbol{e}_\lambda \boldsymbol{e}_{\lambda'}) = A^*_{\mu ij} : A_{\mu lm}, \tag{29}$$

which is a consequence of (13), while the fact that the expression (29) appears in the expression for P is due to our assumption that ω_k is independent of the polarization p. If the central lattice site is a centre of inversion symmetry, transitions between a sine- and a cosine-like wave are forbidden, and one may then take $s = s'$ in Eq. (26). This selection rule follows from the fact that for such a crystal we have $A_{\mu ij} = A_{\mu -i-j}$, where $-i$ denotes the lattice site that is obtained from the lattice site i by an inversion with respect to the central lattice site, while for $s \neq s'$ we have $B_i B'_j = -B_{-i} B'_{-j}$. The term ij in Eq. (22) then cancels the term $-i-j$, so that we have $w_\mu(\lambda, \lambda') = 0$ for $s \neq s'$.

For the sake of definiteness, we shall now restrict ourselves to simple cubic crystals and to crystals of the NaCl-type. Then there are six nearest neighbors the equilibrium positions of which form a regular octohedron. Among the 2.6^4 functions $L_{sil, sjm}$, $s = 1,2$ and $i, j, l, m = \pm 1, \pm 2, \pm 3$, where $+i$ and $-i$ designate opposite corners of the octohedron, there then occur only 4 different functions, viz:

$$s = 1: L_{1il, \, 1jm} = (\pm) \{S_1^2\}^2 = (\pm) L_1, \text{ for } i = \pm l, j = \pm m; \tag{30}$$

$$s = 2: L_{2il, \, 2jm} = \begin{cases} \{C_1^2\}^2 = L_2 & \text{for} \quad i = \pm l, \, j = \pm m; \\[2mm] \{C_1^2\} \{C_1 C_2\} = L_3 \text{ for } \begin{cases} i = \pm l, \, j \neq \pm m; \\ i \neq \pm l, \, j = \pm m; \end{cases} \\[2mm] \{C_1 C_2\}^2 = L_4 & \text{for} \quad i \neq \pm l, \, j \neq \pm m; \end{cases} \tag{31}$$

$$C_i = \cos \boldsymbol{k}.\boldsymbol{a}_i - 1; \qquad S_i = \sin \boldsymbol{k}.\boldsymbol{a}_i; \qquad (i = 1, 2) \tag{32}$$

in which $\boldsymbol{a}_1$ and $\boldsymbol{a}_2$ are two mutually orthogonal vectors of length a, where a is the distance between nearest neighbors. In Eq. (30) the $+$ sign holds when the number of minus signs in the row of indices $iljm$ is even, the $-$ sign when this number is odd. The averaging over all directions of $\boldsymbol{k}$ occurring in the expressions (30) and (31) for the functions $L_1, \ldots, L_4$ can be carried out by means of elementary integrations, and the result is:

$$\{S_1^2\} = \tfrac{1}{2} - \tfrac{1}{2}f(2y); \qquad \{C_1^2\} = \tfrac{3}{2} - 2f(y) + \tfrac{1}{2}f(2y); \left.\right\} \tag{33}$$
$$\{C_1 C_2\} = 1 - 2f(y) + f(\sqrt{2}y); \quad f(y) = \sin y/y; \; y = ka. \left.\right\}$$

With the help of these expressions, the functions $L_n(y)$ can be easily evaluated, and the resulting functions $L_n(y)$ are shown graphically in fig. 1. According to Eq. (26), the functions $M_\mu(ka)$ appearing in the expression (25) for P can now be expressed in terms of these functions $L_n(y)$:

$$M_\mu(y) = \Sigma_{n=1}^4 N_{\mu n} L_n(y). \tag{34}$$

The coefficients $N_{\mu n}$ are given by

$$N_{\mu 1} = \Sigma\ (\pm)\ N_{\mu ijlm};\ N_{\mu n} = \Sigma\ N_{\mu ijlm};\ (n = 2, 3, 4), \tag{35}$$

where the Σ 's indicate summations over i, j, l and m, which are restricted by the conditions indicated in Eqs. (30) and (31), and where the $(\pm)$ sign has the same significance as in Eq. (30). This concludes the formal evaluation of the expression (25) for the transition probabilities $P(m, m + \mu)$. In the
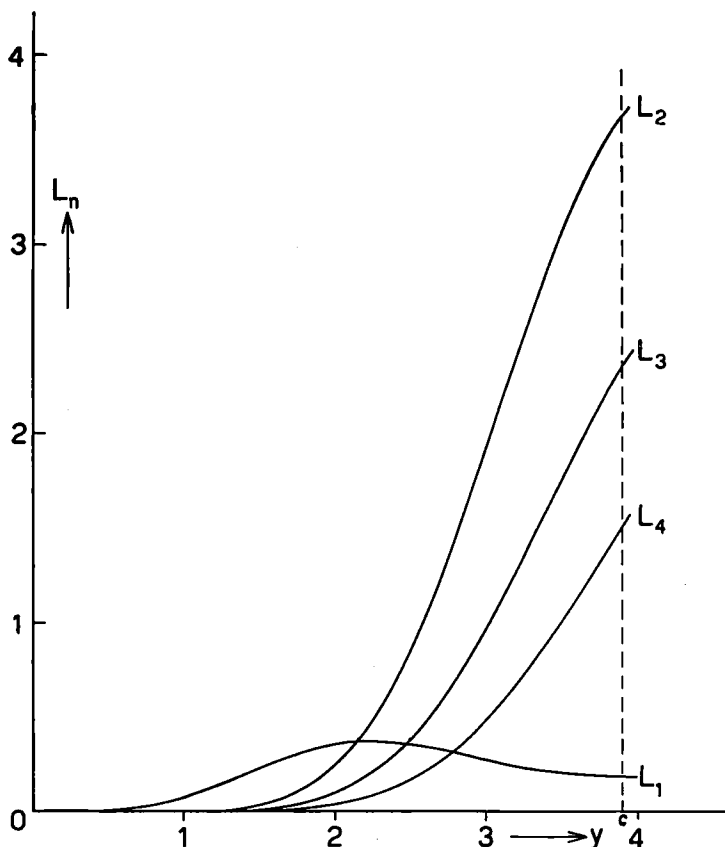

Fig. 1. The functions $L_n(y)$ in the range $0 < y < c$, where $c = (6\pi^2)^{1/3}$ and $y = ka$.

next section we shall obtain the temperature dependence of the $P(m, m + \mu)$ for the case that the frequency spectrum of the crystal is approximated by the Debije spectrum.

§ 5. *The temperature dependence of the transition probabilities for the Debije case.* From the definition (20) of $f(\omega)$ we see that the Debije case is characterized by $f(\omega) = 1$. Substituting this in Eq. (25), and introducing the

Debije temperature Θ and the reduced temperature T^*,

$$\hbar\omega_m = \hbar v k_m = \varkappa\Theta; \quad T^* = T/\Theta, \tag{36}$$

we get the following expression for the transition probabilities:

$$P(m, m + \mu) = C_{\mu m} T^{*2} \Sigma_{n=1}^{4} N_{\mu n} D_n (T^*), \tag{37}$$

$$D_n(T^*) = T^* \int_0^{1/T^*} \frac{x^2 e^x}{(e^x - 1)^2} L_n (cT^*x) \, \mathrm{d}x, \tag{38}$$

$$C_{\mu m} = (3|Q_{\mu m}|^2/\pi \, d^2 v^3 a^3); \quad c = k_m a = (6\pi^2)^{1/3}. \tag{39}$$

The functions $D_n(T^*)$ defined in Eq. (38) can be easily evaluated numerically, and this has been done for a number of temperatures. The results are given in table I, and the functions $D_n(T^*)$ are shown graphically in

TABLE I

Numerical values of the integrals $D_n(T^*)$				
T^*	$D_1(T^*)$	$D_2(T^*)$	$D_3(T^*)$	$D_4(T^*)$
0.0	0	0	0	0
0.1	0.0369	0.0159	0.0120	0.0058
0.2	0.0975	0.268	0.139	0.0737
0.3	0.138	0.507	0.269	0.146
0.4	0.162	0.650	0.348	0.190
0.5	0.171	0.734	0.397	0.216
0.6	0.178	0.791	0.425	0.233
0.7	0.184	0.822	0.443	0.244
0.8	0.188	0.843	0.456	0.251
0.9	0.190	0.858	0.465	0.257
1.0	0.192	0.871	0.472	0.260
∞	0.200	0.924	0.502	0.276

fig. 2 together with the low- and high-temperature approximations which we will now discuss. At low temperatures ($T^* \ll 1$), we can get approximate expressions for the functions $D_n(T^*)$ by replacing the upper limit $1/T^*$ of the integrals (38) by infinity, which is equivalent to replacing the maximum frequency ω_m of the lattice oscillators by infinity. The integrals (38) can then be expressed analytically as functions of the temperature with the help of the Langevin function and its derivative. However, these expressions are rather unwieldy and not very useful for our purposes, and we shall therefore not write them down here. It is found that this approximation is good for $T^* < 0.1$, and it is interesting to remark that this implies that the contribution of the lattice oscillators the frequency of which is near the maximum frequency ω_m is negligible only below $T^* = 0.1$. The functions $D_n'(T^*)$ obtained from the $D_n(T^*)$ by replacing $1/T^*$ by infinity can be developed in ascending powers of T^*. The first terms of these ex-

pansions are found to be

$$D'_1 = (1.88 \times 10^4)T^{*5}; \qquad D'_2 = (4.84 \times 10^8)T^{*9};$$
$$D'_3 = (1.61 \times 10^8)T^{*9}; \qquad D'_4 = (5.38 \times 10^7)T^{*9}. \qquad \Big\} \qquad (40)$$

The convergence of these power series is very bad: it is found that the difference between the first terms (40) and the correct values (38) is smaller than about 10% for $T^* < 0.02$. This bad convergence is due to the fact
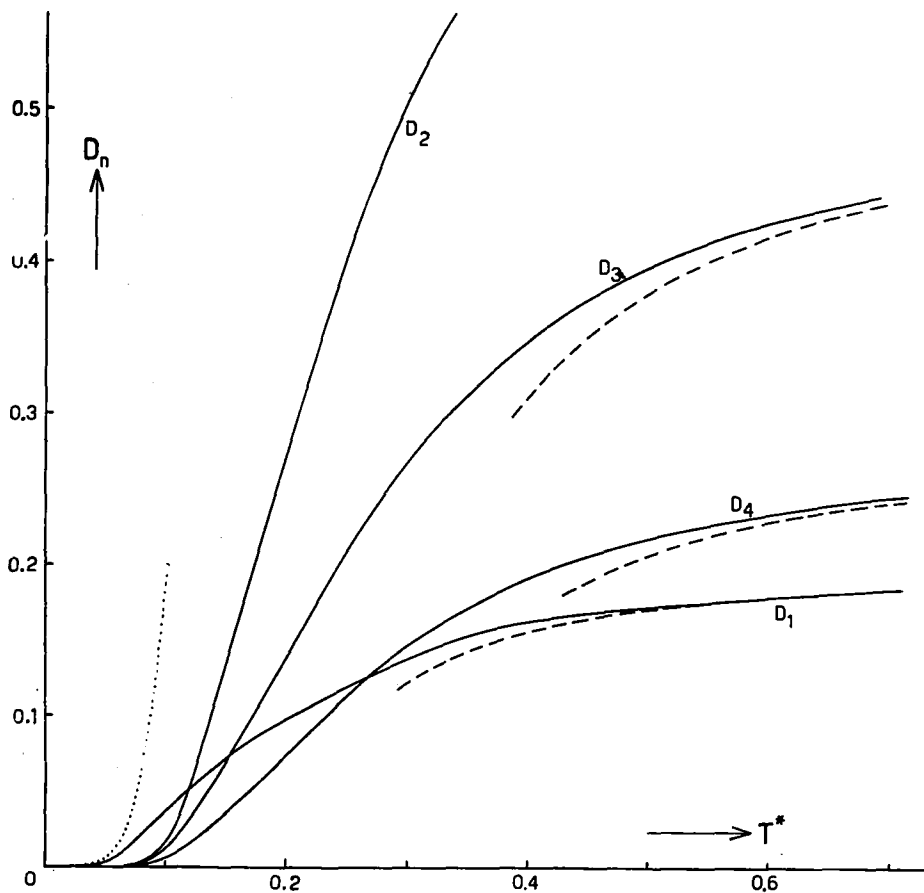

Fig. 2. The functions $D_n(T^*)$. The high-temperature approximations $a_n - b_n/T^{*2}$ of D_1, D_3 and D_4 are shown by the broken curves, and the first term $c_1 T^{*5}$ of the low-temperature expansion of D_1 is shown by the dotted curve.

that the expansions of the functions $D'_n(T^*)$ in powers of T^* are in reality power series in $\pi c T^*$. The expansion of $D'_1(T^*)$, for instance, can be written in the form

$$D'_1 = \frac{16\pi^2}{25} T^* \left[\tfrac{1}{7} (\pi c\ T^*)^4 - \tfrac{8}{25} (\pi c\ T^*)^6 + \dots \right], \qquad (41)$$

where $c = k_m a$, a being the lattice constant and k_m the maximum wave number occurring in the Debije model, so that $\check{c} = (6\pi^2)^{1/3}$ and $\pi c T^* \approx$ $\approx 12.25 T^*$. From these values it follows that at $T^* = 0.05$ the second term in (41) is already equal to the first term.

From the fact that the expansion of D_1' starts with a T^{*5}-term, while D_2', D_3' and D_4' start with T^{*9}-terms, it follows that for sufficiently small values of T^* the transition probabilities P are proportional to T^{*7}. This is the well-known T^7-law for the transition probabilities arising from the Raman processes. Our calculations show that at least in the case of the quadrupolar relaxation this law holds good only at very low temperatures $(T^* < 0.02)$.

At high temperatures, the functions $D_n(T^*)$ can be developed in descending powers of T^*. These expansions can be written in the form

$$D_n(T^*) = L_{n0} - \tfrac{1}{12} L_{n2} \cdot (cT^*)^{-2} + \ldots, \tag{42}$$

in which the moments L_{np} of the functions L_n are defined by

$$L_{np} = (1/c) \int_0^c x^p L_n(x) \, dx. \tag{43}$$

The first two moments $p = 0,2$ have been evaluated numerically, and the resulting expansions of the functions $D_n(T^*)$ are:

$$\left.\begin{aligned}
D_1(T^*) &= 0.200 - 0.00705/T^{*2} + \ldots, \\
D_2(T^*) &= 0.924 - 0.0547/T^{*2} + \ldots, \\
D_3(T^*) &= 0.502 - 0.0306/T^{*2} + \ldots, \\
D_4(T^*) &= 0.276 - 0.0174/T^{*2} + \ldots.
\end{aligned}\right\} \tag{44}$$

In fig. 2 the curves corresponding to the first two terms of the expansions of D_1, D_3 and D_4 are shown by the broken lines, and it is seen that they constitute a good approximation down to about $T^* = 0.5$. In the important temperature region $T^* > 0.5$, the temperature dependence of the transition probabilities P is therefore to a good approximation given by an expression of the form $T^2(a - b/T^2)$.

§ 6. *The dependence of the transition probabilities on the direction of the external magnetic field.* We shall obtain the dependence of the transition probabilities on the direction of the external field H for the case that the static quadrupolar interaction is small compared to the Zeeman energy, so that the component of the nuclear spin in the direction of H is a good quantum number. Let $P'(m', m' + \mu')$ be the probability for a transition $m' \rightarrow m' + \mu'$ for the case that the magnetic field points in the z'-direction, where m' is the component of the spin in the z'-direction. The expression for $P'(m', m' + \mu')$ can be obtained from the expression (25) for the probability $P(m, m + \mu)$ corresponding to the magnetic field in the z-direction

by replacing $Q_{\mu m}$ by $Q'_{\mu'm'}$ and $A_{\mu ij}$ by $A'_{\mu'ij}$. For $m' = m$ and $\mu' = \mu$, however, we have $Q'_{\mu'm'} = Q_{\mu m}$, so that $P'(m, m + \mu)$ can be obtained from $P(m, m + \mu)$ by replacing the tensors $A_{\mu ij}$ by the transformed tensors $A'_{\mu ij}$. To find the $A'_{\mu ij}$, we must go back to the Eqs. (7) and (10). In Eq. (7) the interaction H' is developed in terms of the components Q_μ of the nuclear quadrupole moment in the xyz-system. We must now develop this same H' in terms of the components $Q'_{\mu'}$ of the quadrupole moment in the $x'y'z'$-system, where z' is the new direction of the external field, and where we choose the x'-axis to lie in the xy-plane in such a way that the angle between the x- and the x'-axis is $\varphi - \tfrac{1}{2}\pi$; ϑ and φ are the polar angles of the z'-axis with respect to the z-axis as polar axis and the xz-plane as azimuth plane. Then we get

$$H' = \Sigma_\mu \, W_\mu \, Q_\mu = \Sigma_{\mu'} \, W'_{\mu'} \, Q'_{\mu'}. \qquad (45)$$

The components Q_μ transform according to the 5-dimensional representation of the rotation group, so that we have

$$Q_\mu = \Sigma_{\mu'} \, U_{\mu'\mu} \, (\vartheta, \varphi) \, Q'_{\mu'}, \qquad (46)$$

where the $U_{\mu'\mu}$ are the representation coefficients as functions of the polar angles ϑ, φ. The new coefficients $W'_{\mu'}$ are therefore given by

$$W'_{\mu'} \, (\boldsymbol{r}_i) = \Sigma_\mu \, U_{\mu'\mu} \, (\vartheta, \varphi) \, W_\mu \, (\boldsymbol{r}_i). \qquad (47)$$

This relation must hold for any values of the displacements $\boldsymbol{r}_i$, and when we substitute the expansion (10) of W_μ, and the corresponding expansion of $W'_{\mu'}$, viz.

$$W'_{\mu'} \, (\boldsymbol{r}_i) = A'_{\mu'} + \Sigma_i \, \boldsymbol{A}'_{\mu'i} \cdot \boldsymbol{r}_i + \Sigma_{ij} \, A'_{\mu'ij} : \boldsymbol{r}_i \, \boldsymbol{r}_j + \dots, \qquad (48)$$

we get the desired relation:

$$A'_{\mu'ij} = \Sigma_\mu \, U_{\mu'\mu} \, (\vartheta, \varphi) \, A_{\mu ij}. \qquad (49)$$

This concludes the formal evaluation of the dependence of the transition probabilities P on the direction of the external field. The $P'(m, m + \mu)$ can be obtained from the $P(m, m + \mu)$ by replacing the $A_{\mu ij}$ appearing in the expression (25) for $P(m, m + \mu)$ by the functions (49) of the angles ϑ, φ specifying the direction of the external field relative to the xyz-axes. In particular, we may take the xyz-axes to lie along the symmetry axes of the crystal, and P' is then the transition probability as a function of the direction of the external field with respect to the crystal axes. In this particular xyz-frame, the tensors $A_{\mu ij}$ have definite symmetry properties which are a consequence of the crystal symmetry, and this leads to definite properties of the dependence of the transition probabilities on the direction of the external field. However, we shall not discuss these properties in this general case.

The coefficients $U_{\mu'\mu}$ are defined by Eq. (46), or equivalently by the equation

$$Y_\mu (x, y, z) = \Sigma_{\mu'} U_{\mu'\mu} (\vartheta, \varphi) Y_{\mu'} (x', y', z'), \qquad (50)$$

and are given by:

$$
\left.
\begin{aligned}
& U_{22} = - \tfrac{1}{4}(1 + 2c + c^2)a^2, & & U_{12} = - is(1 + c)a^2, \\
& U_{21} = \tfrac{1}{2}s(1 + c)a, & & U_{11} = \tfrac{1}{2}i(1 - c - 2c^2)a, \\
& U_{20} = - \tfrac{3}{4}(1 - c^2), & & U_{10} = 3isc, \\[6pt]
& U_{02} = \tfrac{1}{2}s^2 a^2, & & c = \cos \vartheta, \\
& U_{01} = \tfrac{1}{2}sca, & & s = \sin \vartheta, \\
& U_{00} = \tfrac{1}{2}(3c^2 - 1), & & a = \exp i\varphi,
\end{aligned}
\right\} \qquad (51)
$$

$$U_{-\mu\nu} (\vartheta, \varphi) = U_{\mu\nu} (\pi - \vartheta, \varphi + \pi); \qquad U_{-\mu-\nu} (\vartheta, \varphi) = U_{\mu\nu} (\vartheta, \varphi)^*. \quad (52)$$

The matrix $U_{\mu'\mu}$ is not unitary, because the functions (6) are not normalized. The $U_{\mu'\mu}$ therefore differ from the usual unitary representation matrices $D_{\mu'\mu}$ by a similarity transformation.

§ 7. *Calculation of the crystalline field and of the transition probabilities in the point-charge model.* We shall now describe the application of the general theory to the calculation of the quadrupolar relaxation in ionic crystals of the NaCl-type on the basis of the one-parameter point-charge model. As we have explained in § 2, the calculation of the spin-lattice coupling arising from the nuclear quadrupole moment is a complicated matter, because of the shielding, antishielding and co-valent effects. No detailed calculations of the contribution of these effects to the spin-lattice coupling in ionic crystals have been made up till now, and the tensors $A_{\mu ij}$ that describe the nature and the strength of the spin-lattice coupling, *cf*. Eqs. (7) and (10), are therefore unknown. The theory thus contains a large number of "adjustable" parameters, and to make a useful comparison with the experimental data possible, it is necessary to reduce this number of adjustable parameters. In the so-called point-charge model all the tensor components $A_{\mu ij}(a, b)$ are expressed in terms of a single parameter by assuming that the spin-lattice coupling is due to the interaction of the nuclear quadrupole moment with the electric field arising from six equal point-charges placed on the six neighboring lattice sites. All other charges are supposed to be removed from the crystal, so that we consider a bare nucleus in the field of six point charges. The magnitude q of these charges is the only adjustable parameter of the model. When we write $q = \gamma e$, where e is the ionic charge, the dimensionless quantity γ is a measure for the strength of the spin-lattice coupling, which can be determined by comparing the experimental values of the relaxation time with the values

calculated with the point-charge model. As we shall show, the values of γ thus obtained are much larger than unity, of the order $10^2 - 10^3$. This shows the importance for the spin-lattice coupling of the effects discussed in § 2. The quantity γ is the product of the multiplication factors α and β introduced in § 2, and it is therefore not surprising that we find such large values of γ.

We shall first consider the case that the external magnetic field is directed along one of the cubical symmetry axes of the crystal, which we shall take as the z-axis, while the two other cubical axes will be taken as the x- and y-axes. Let $V_i(\mathbf{r})$ be the potential of the field arising from the charge q on the nucleus i when the displacement $\mathbf{r}_i = \mathbf{s}_i - \mathbf{s}_0$ of nucleus i relative to the displacement $\mathbf{s}_0$ of the central nucleus is zero ($i = 1, 2, 3$ indicates the nearest neighbors on the positive x-, y- and z-axes; $i = -1, -2, -3$ those on the negative x-, y- and z-axes). When the displacements $\mathbf{r}_i$ are not zero, the total potential $V(\mathbf{r})$ at the distance $\mathbf{r}$ from the central nucleus is given by:

$$V(\mathbf{r}) = \Sigma_i\, V_i(\mathbf{r} - \mathbf{r}_i). \tag{53}$$

We are interested only in the terms that are biquadratic in $\mathbf{r}_i$ and $\mathbf{r} = x$, $y, z, cf.$ Eqs. (5) and (10), and for $i = 3$, for example, we may therefore take

$$V_3(\mathbf{r}) = 2A(35z^4 - 30z^2r^2 + 3r^4),\quad A = q/16a^5, \tag{54}$$

where a is the equilibrium distance between nearest neighbors. When (54) is substituted in Eq. (53), the biquadratic terms can be expressed in terms of the $Y_\mu(\mathbf{r})$ defined in Eq. (7). The contribution to $V(\mathbf{r})$ of the other terms in Eq. (53) can be evaluated in the same way, and when we compare the resulting expression with the definition (10) of the $A_{\mu ij}$, we get the following result:

$$A_{\mu ij} = 0 \text{ for } i \neq j;\quad A_{-\mu ii} = A_{\mu ii}^*;\quad A_{\mu-i-i} = A_{\mu ii}; \tag{55}$$

$$A_{0ii} = A\begin{bmatrix} a_i & 0 & 0 \\ 0 & b_i & 0 \\ 0 & 0 & c_i \end{bmatrix};\quad A_{1ii} = A\begin{bmatrix} 0 & 0 & e_i' \\ 0 & 0 & f_i' \\ e_i' & f_i' & 0 \end{bmatrix};\quad A_{2ii} = A\begin{bmatrix} a_i'' & d_i'' & 0 \\ d_i'' & b_i'' & 0 \\ 0 & 0 & c_i'' \end{bmatrix} \tag{56}$$

where the components $a_i, \ldots, d_i''$ are given in table II. When we substitute these values in the expressions (28) and (35) for the coefficients $N_{\mu n}$, the

TABLE II

Values of the components of the tensors $A_{\mu ii}$								
i	a_i	b_i	c_i	e_i'	f_i'	a_i''	b_i''	c_i''	d_i''
1	-24	6	18	-48	$-12i$	36	-21	-15	$24i$
2	6	-24	18	12	$48i$	21	-36	15	$24i$
3	-24	-24	48	-48	$48i$	6	-6	0	$-6i$

expression (37) for the transition probability P becomes:

$$P(m, m + \mu) = \gamma^2 |Q_{\mu m}|^2 C . T^{*2} E_\mu(T^*), \left.\begin{array}{c} \\ \end{array}\right\}$$
$$C = (27e^2/32\pi d^2 v^3 a^{13}), \tag{57}$$

in which the functions $E_\mu(T^*)$ are given by

$$\begin{array}{rl} E_0\ (T^*) = & 296(D_1 + D_2) + 292D_4, \\ E_{\pm 1}(T^*) = & 1056(D_1 + D_2) + 512D_4, \\ E_{\pm 2}(T^*) = & 354(D_1 + D_2) + 283D_4, \end{array} \left.\begin{array}{c} \\ \\ \\ \end{array}\right\} \tag{58}$$

and the functions $D_n(T^*)$ are given in Eq. (38) and Table I. For $T^* > 0.1$ the quantities $E_\mu(T^*)$ are approximately proportional to each other, to within about 1%, so that for all practical purposes we may assume that the function $E^*(T^*) = E_\mu(T^*)/E_\mu(\infty)$ is independent of μ. Introducing this approximation in Eq. (57), we finally get the following expression for P:

$$P(m, m + \mu) = \gamma^2 |Q_{\mu m}| C E_\mu(\infty) . T^{*2} E^*(T^*). \tag{59}$$

The values of the dimensionless quantities $E_\mu(\infty)$ are given by

$$E_0(\infty) = 413; \quad E_{\pm 1}(\infty) = 1330; \quad E_{\pm 2}(\infty) = 476, \tag{60}$$

and the function $E^*(T^*)$ is given in Table III, and is shown graphically in fig. 3 together with the low- and high-temperature expansions

$$\begin{array}{ll} T^* \lesssim 0.02: & E^* = (1.4 \times 10^4)T^{*2}; \\ T^* \gtrsim 0.5: & E^* = 1 - 0.0056/T^{*2}; \end{array} \left.\begin{array}{c} \\ \\ \end{array}\right\} \tag{61}$$

which expansions can be obtained from the corresponding expansions of the functions $D_n(T^*)$ discussed in § 5.

TABLE III

Values of the function $E^*(T^*)$									
T^*	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
E^*	0.044	0.318	0.569	0.719	0.804	0.860	0.895	0.918	0.934	0.947

This concludes the evaluation of the transition probabilities for the case that the external field is directed along one of the cubical axes of the crystal. From Eq. (59) we see that $P(m, m + \mu)$ is expressed in terms of: (a) the dimensionless multiplication factor γ which is a measure for the strength of the spin-lattice coupling; (b) the matrix element $Q_{\mu m}$ of the nuclear quadrupole moment; (c) the quantity C, given in Eq. (57), which depends on the mass density d of the crystal, the velocity of sound v, and the distance a between nearest neighbors; (d) the dimensionless quantities $E_\mu(\infty)$ which depend on the crystal structure, and which are given for a cubical structure in Eq. (60); (e) a function $T^{*2}E^*(T^*)$ of the reduced temperature $T^* = T/\Theta$, which is given in Table III and Eq. (61). These transition

probabilities $P(m, m + \mu)$ are the basic quantities describing the spin-lattice relaxation. Since $I > \frac{1}{2}$, there is no unique relaxation time, but we shall define a relaxation time τ by means of the equation $\tau = 1/\overline{P}$ where $\overline{P}$ is the average value of P, averaged over all values of m and μ. At high temperatures $(T^* > 1)$ we can then write $\tau = \tau_0/\gamma^2 T^{*2}$, where τ_0 is a quantity that is characteristic for the nucleus and the crystal under consideration. As an example we give the values of τ_0 for some typical nuclei in alkali halide crystals, calculated with the help of Eq. (59):

$$\begin{cases} \text{Br}^{81} \text{ in KBr:} & \tau_0 = 1.5 \times 10^4 \text{ sec,} \\ \text{I}^{127} \text{ in KI:} & \tau_0 = 4 \times 10^4 \text{ sec,} \\ \text{Li}^7 \text{ in LiI:} & \tau_0 = 1 \times 10^6 \text{ sec,} \\ \text{Li}^7 \text{ in LiF:} & \tau_0 = 3 \times 10^3 \text{ sec.} \end{cases} \qquad \tau = \tau_0/\gamma^2 T^{*2}. \quad (62)$$
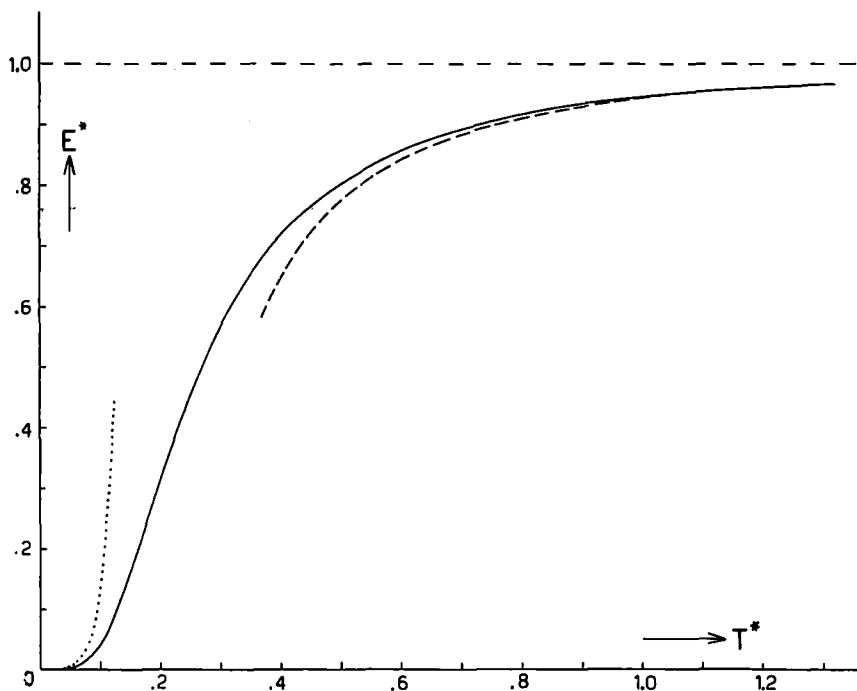

Fig. 3. The function $E^*(T^*)$. The dotted curve is $(1.4 \times 10^4)T^{*5}$ and the broken curve is $1 - 0.0056/T^{*2}$; cf. Eq. (61).

From these values we see that, in the absence $(\gamma = 1)$ of the co-valent and polarization effects discussed in § 2, the quadrupolar relaxation times are very long, of the order of magnitude of some hours. Unfortunately, quantitative experimental data on quadrupolar relaxation times are still very scarce. In the case of I^{127} in KI, however, it is known [1] that at room temperature $\tau < 0.02$ sec, and this leads to $\gamma > 10^3$. In connection with this large value of γ, it should be remarked that the transition probability (59)

is proportional to a^{-13}, where a is the lattice constant. A factor a^{-3} is due to the fact that for a given total volume of the crystal the number of lattice oscillators, and hence the transition probability, is proportional to a^{-3}. The remaining factor a^{-10} expresses the strong dependence on a of the strength of the spin-lattice coupling arising from the direct field of the ionic charges in our point-charge model. It is this strong dependence on a which, for instance, is responsible for the large difference in the value of τ_0 for LiF and LiI, cf. Eq. (62). If the spin-lattice coupling in LiF and LiI is due to the co-valent effect (cf. § 2), it can be expected to be of roughly the same order of magnitude in the two crystals, and with comparable relaxation times in LiF and LiI, the factor γ for LiI would then turn out to be much larger than for LiF, because of the fact that the value of a for LiI is 50% larger than for LiF. The large value $\gamma > 10^3$ obtained for KI, for which a is large (3.5Å, while for LiI it is 3.0Å and for LiF only 2.0Å), is thus an indication that the spin-lattice coupling in KI is due to the co-valent effect.

Finally we shall calculate the dependence of the transition probabilities on the direction of the external magnetic field relative to the crystal axes. From Eqs. (37), (49), (55) and (56), we get:

$$P'(m, m + \mu) = \gamma^2 |Q_{\mu m}|^2 \, C \cdot T^{*2} E'_\mu(T^*). \tag{63}$$

where the new functions E'_μ are given by (cf. Eqs. (64) and (65)),

$$\left.\begin{aligned}
E'_0 &= (296 - 360a^2) \, (D_1 + D_2) + (292 - 620a^2)D_4; \\
E'_{\pm 1} &= (1056 + 1440a^2) \, (D_1 + D_2) + (512 + 2480a^2)D_4; \\
E'_{\pm 2} &= (354 - 90a^2) \, (D_1 + D_2) + (283 - 155a^2)D_4;
\end{aligned}\right\} \tag{64}$$

in which $a^2 = a_1^2 a_2^2 + a_1^2 a_3^2 + a_2^2 a_3^2$ and a_1, a_2, a_3 are the direction cosines of the magnetic field with respect to the crystal axes. At high temperatures $(T^* > 1)$ we get from (63) and (64) that $P'(m, m \pm 1)$ is about 50% larger in the (111) than in the (100) direction, while $P'(m, m \pm 2)$ is about 10% smaller in the (111) than in the (100) direction. The fact that the angular dependence of $P'(m, m + \mu)$ depends only on a^2 is due to the fact that we have assumed that the polarization effect can be taken into account with the help of a constant multiplication factor, cf. Eq. (5). If the polarization effect is not isotropic, the angular dependence is more complicated.

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