

## CONTRIBUTION TO THE THEORY OF SPIN-LATTICE RELAXATION OF NUCLEAR SPINS IN IONIC CRYSTALS

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Relaxation of nuclear spins in ionic crystals at room temperature is examined theoretically with account of optical vibrations of the crystal lattice. Numerical calculations are made for NaCl type lattices. The agreement with experiment is satisfactory.

### 1. INTRODUCTION

IN the present theory of spin-lattice paramagnetic relaxation the thermal lattice vibrations are considered in the Debye approximation, i.e., only acoustic crystal vibrations are taken into account. However, the Debye method is meaningful only at low temperatures. At room temperatures there are sufficiently-excited optical vibrations at which the neighboring atoms move, on the average, in phase opposition and consequently their interaction varies more strongly than in acoustic vibrations. A disturbance causing transitions in the spin system will therefore be stronger, and this may noticeably affect the rate at which equilibrium is established between the spin system and the lattice. It is clear therefore that not only can the optical vibrations not be neglected, but in some cases the Debye model is not expected even to yield the correct order of magnitude of the spin-lattice relaxation time. This problem is best examined with the nuclear spin relaxation as an example.

Pound<sup>1</sup> has shown with a series of experiments that at room temperature quadrupole interactions can play a decisive role in the mechanism of nuclear spin-lattice relaxation. The first theory of nuclear spin-lattice relaxation in crystals was proposed by van Kranendonk.<sup>2</sup> He considered the interaction between a nucleus having a quadrupole moment and the field of point charges surrounding the ions. After calculating, in the Debye approximation, the variation of the gradient of the electric field under the influence of the thermal lattice vibrations, van Kranendonk found the probabilities of relaxation transitions in the spin system. The spin-lattice relaxation times  $T_1$ , determined with these probabilities, were found to be  $10^2$  to  $10^5$  times longer than the experimental val-

ues. Moriya and Yosida<sup>3</sup> have suggested that in real crystals the quadrupole interactions are much stronger than in the van Kranendonk model, owing to the partially-covalent character of the atomic bonds. The values of  $T_1$  which they calculated differ from the experimental ones by a factor of 3 to 10. Wikner and Das,<sup>4</sup> assuming the bond to be purely ionic, took into account the increase in the gradient of the electric field on the nucleus due to polarization of the electron shell in the field of the ions and of the nucleus. Comparison with experiment led to results analogous to those obtained by Yosida and Moriya.<sup>3</sup>

In the present paper we consider theoretically the spin-lattice relaxation of nuclear spins, due to quadrupole interactions, at sufficiently high temperatures. In Sec. 2 we obtain a more convenient form for the spin-lattice interaction operator than that given by van Kranendonk.<sup>2</sup> In Sec. 3 we calculate the probabilities of the relaxation transitions produced by optical and acoustic vibrations of a NaCl type crystal lattice. We consider the relations between the probabilities of the transitions and quantities that are measured experimentally in the study of the relaxation effects. The comparison with experiment and the discussion of the results are treated in Sec. 4.

### 2. THE SPIN-LATTICE INTERACTION OPERATOR

We consider a purely ionic bond. As in reference 2, we shall assume that the relaxing nuclei are in equivalent crystal fields and that we can neglect the influence of the magnetic dipole-dipole interactions on the quadrupole relaxation. Under these assumptions, we can consider the interaction between an individual nucleus and the electric field of the surrounding ions. Since this interaction is modulated by the thermal vibrations, tran-

sitions are induced between different spin states. We place the origin at the lattice site in which the nucleus under consideration is located, and direct the  $z$  axis along the external magnetic field  $H$ . That part of the Hamiltonian which describes the quadrupole interaction of the nucleus with the crystal field is written as the scalar product of two tensors, the nuclear quadrupole moment operator and the electric field gradient operator:<sup>1</sup>

$$\hat{H} = \sum_{\mu} (-1)^{\mu} \hat{Q}_{\mu} (\nabla E)_{-\mu}, \quad (1)$$

where

$$Q_0 = \frac{eQ}{2I(2I-1)} [3\hat{I}_z^2 - I(I+1)],$$

$$Q_{\pm 1} = \mp \sqrt{\frac{3}{2}} \frac{eQ}{2I(2I-1)} [(\hat{I}_x \pm i\hat{I}_y)\hat{I}_z + \hat{I}_z(\hat{I}_x \pm i\hat{I}_y)], \quad (2a)$$

$$Q_{\pm 2} = \sqrt{\frac{3}{2}} \frac{eQ}{2I(2I-1)} [(\hat{I}_x \pm i\hat{I}_y)^2],$$

$$(\nabla E)_0 = -\frac{1}{2} \frac{\partial E_z}{\partial z}, \quad (\nabla E)_{\pm 1} = \pm \frac{1}{\sqrt{6}} \left[ \frac{\partial E_x}{\partial z} \pm i \frac{\partial E_y}{\partial z} \right],$$

$$(\nabla E)_{\pm 2} = \frac{1}{\sqrt{6}} \left[ \frac{\partial E_x}{\partial x} - \frac{\partial E_y}{\partial y} \pm 2i \frac{\partial E_x}{\partial y} \right]. \quad (2b)$$

Here  $eQ$  is the quadrupole moment of the nucleus,  $I$  the nuclear spin, and  $\hat{I}$  its operator.

To obtain the spin-lattice interaction operator it is necessary to find the tensor components of the gradient of the electric field that results from the displacement of the ions by the thermal vibrations. If we introduce the coefficient  $\gamma_{\infty}$ , characterizing the degree of polarization of the electron shell of the ion under consideration, the gradient of the electric field on the nucleus can be represented as<sup>3</sup>

$$\nabla E = (1 - \gamma_{\infty}) \nabla E', \quad (3)$$

where  $\nabla E'$  is the gradient of the electric field produced by the surrounding ions. The potential of this field in the vicinity of the nucleus is

$$V = \sum_t e_t / R_t,$$

where  $e_t$  is the charge of the  $t$ -th ion and  $R_t$  is the distance from its center to the nucleus under consideration. We denote the displacement of the  $t$ -th atom due to the thermal vibrations by  $\mathbf{u}_t$ , and the displacement of this atom relative to the central atom by  $\mathbf{s}_t = \mathbf{u}_t - \mathbf{u}_0$ . Considering that the relative displacements  $\mathbf{s}_t$  are small compared with the interatomic distances, we expand  $V$  in a series of spherical functions

$$V = \sum_t \frac{e_t}{R_{0t}} \sum_{n=0}^{\infty} (-1)^n \frac{4\pi}{2n+1} \left( \frac{s_t}{R_{0t}} \right)^n \times \sum_{m=-n}^n Y_n^m(\theta_s^t, \varphi_s^t) Y_n^{-m}(\theta_R^t, \varphi_R^t). \quad (4)$$

Here  $R_{0t}$  is the equilibrium distance between the ions,  $\theta_s^t, \varphi_s^t$  and  $\theta_R^t, \varphi_R^t$  are respectively the angular coordinates of  $\mathbf{s}_t$  and the projections on the  $t$ -th ion. Since we are interested in room temperatures, at which two-phonon processes are known to play the decisive role, the spin-lattice interaction operator should be quadratic in  $\mathbf{s}_t$ . We need therefore consider only the term with  $n = 4$ , out of the entire sum of Eq. (4).

To find the components of the electric field gradient tensor, it is convenient to change to new coordinates

$$\xi_{\pm 1} = \mp (\mathbf{e}_x \pm i\mathbf{e}_y) / \sqrt{2}, \quad \xi_0 = \mathbf{e}_z, \quad (5)$$

where  $\mathbf{e}_q$  is a unit vector along the  $q$  axis of a Cartesian system. Using the well known expansions of the gradient in spherical functions [see, for example, reference 5, Eq. (2.57)], we obtain the following expression for the tensor components

$$\nabla_q \nabla_r V = 8\pi \sqrt{\frac{21}{5}} \sum_t \frac{e_t}{R_{0t}^5} s_t^2 \times \sum_m C(4, 1, 3; m, q) C(3, 1, 2; m+q, r) \times Y_2^{m+q+r}(\theta_s^t, \varphi_s^t) Y_4^{-m}(\theta_R^t, \varphi_R^t).$$

Here  $C$  are the Wigner coefficients. The unknown components  $(\nabla E'_{\mu})$  are

$$\begin{aligned} (\nabla E')_0 &= -4\pi \sqrt{\frac{21}{5}} \sum_t \frac{e_t s_t^2}{R_{0t}^5} \sum_m C(4, 1, 3; m, 0) \\ &\times C(3, 1, 2; m, 0) \\ &\times Y_2^m(\theta_s^t, \varphi_s^t) Y_4^{-m}(\theta_R^t, \varphi_R^t), \\ (\nabla E')_{\pm 1} &= \mp 8\pi \sqrt{\frac{7}{5}} \sum_t \frac{e_t s_t^2}{R_{0t}^5} \sum_m C(4, 1, 3; m, 0) \\ &\times C(3, 1, 2; m, \pm 1) Y_2^{m\pm 1}(\theta_s^t, \varphi_s^t) Y_4^{-m}(\theta_R^t, \varphi_R^t), \\ (\nabla E')_{\pm 2} &= -8\pi \sqrt{\frac{14}{5}} \sum_t \frac{e_t s_t^2}{R_{0t}^5} \sum_m C(4, 1, 3; m, \pm 1) \\ &\times C(3, 1, 2; m \pm 1, \pm 1) \\ &\times Y_2^{m\pm 2}(\theta_s^t, \varphi_s^t) Y_4^{-m}(\theta_R^t, \varphi_R^t). \end{aligned} \quad (6)$$

Using (1), (2a), and (6) we obtain an explicit expression for the spin-lattice interaction operator,

corresponding to spin transitions from the level  $m$  to the levels  $m-1$  and  $m-2$

$$\begin{aligned} \hat{W} = & \sqrt{10\pi} \frac{eQ(1-\gamma_\infty)}{I(2I-1)} \sum_t \frac{e_t}{R_{0t}^5} \{ (\hat{I}_{+1} \hat{I}_0 + \hat{I}_0 \hat{I}_{+1}) \\ & \times \left[ \sqrt{\frac{1}{8}} s_{-1} s_{-1} Y_4^1 - \sqrt{\frac{4}{5}} s_0 s_{-1} Y_4^0 + \frac{3}{4} s_0 s_0 Y_4^{-1} \right. \\ & \left. - \sqrt{2} s_0 s_{+1} Y_4^{-2} - \sqrt{\frac{7}{8}} s_{+1} s_{+1} Y_4^{-3} \right] \\ & + \hat{I}_{+1}^2 \sqrt{\frac{1}{10}} s_{-1} s_{-1} Y_4^0 - s_0 s_{-1} Y_4^{-1} \\ & \left. + \frac{3}{2} \sqrt{\frac{1}{2}} s_0 s_0 Y_4^{-2} - \sqrt{7} s_0 s_{+1} Y_4^{-3} + \sqrt{7} s_{+1} s_{+1} Y_4^{-4} \right\}. \end{aligned}$$

The notation of Eq. (5) is extended here to vectors and vector operators:  $B_{\pm 1} = \mp (B_x \pm iB_y)/\sqrt{2}$ ,  $B_0 = B_z$ . For the sake of brevity we omit the arguments of the functions  $Y_4^m(\theta_R^t, \varphi_R^t)$  and the summation index  $t$  in  $s_{t\mu}$ .

### 3. SPIN-LATTICE RELAXATION TIME

We continue our calculations as applied to crystals with a NaCl type lattice. The displacement of the  $p$ -th atom in the  $l$ -th elementary cell, in the case of free oscillations, can be written as a superposition of waves

$$u_p^l = A_p(\sigma) \exp(-i\omega t + i\sigma R_p^l/a), \quad (7)$$

where  $a\sigma$  is the wave vector,  $R_p^l$  is the radius vector of the equilibrium position of the  $p$ -th atom in the  $l$ -th elementary cell, and  $a$  is the shortest distance between lattice sites.

If the Cartesian axes are aligned with the principal cubic axes of the crystal,  $\sigma$  becomes

$$\sigma = \sigma_1(e_y + e_z - e_x) + \sigma_2(e_z + e_x - e_y) + \sigma_3(e_x + e_y - e_z),$$

and the solution (7) is unique if  $\sigma_1$ ,  $\sigma_2$ , and  $\sigma_3$  range from  $-\pi/2$  to  $+\pi/2$ . In this case the volume of the region of variation of  $\sigma$  is  $2\pi^3$ . We assume that this region is a sphere having this volume. Then the maximum value of  $\sigma$  is  $\sigma_0 = (3\pi^2/2)^{1/3}$ . Let us write down the number of natural oscillations contained within an energy interval  $dE$  inside a solid angle of the wave-vector space,  $d\Omega$ :

$$\rho dEd\Omega = (N/2\pi^3) \sigma^2 d\sigma d\Omega. \quad (8)$$

Here  $N$  is the number of elementary cells and  $\rho$  the density of the natural oscillations in the energy scale. For acoustic oscillations,  $dE$  has the simple form  $dE = \hbar d\omega = \hbar v d\sigma$ , where  $v$  is the velocity of sound. The density  $\rho$  is then found for acoustic oscillations directly:

$$\rho_{ac} = N\sigma^2/2\pi^3 \hbar v.$$

For optical oscillations, we do not know the analytic dependence of  $\omega$  on  $\sigma$ . We can write approximately  $\omega = -\Delta\omega \cdot \sigma/\sigma_0 + \omega_0$ , as can be verified by comparison with numerical computation of the natural-oscillation spectrum (cf., for example, reference 6). Here  $\omega_0$  is the frequency of the optical vibrations at  $\sigma = 0$ , and  $\Delta\omega$  is the interval of frequency variation. Inserting  $\omega$  in Eq. (8), we obtain  $\rho_{opt} = N\sigma_0\sigma^2/2\pi^3 \hbar \Delta\omega$ .

The probability of spin transition in combination scattering of phonons is determined by the usual formula

$$\begin{aligned} P(m, m+\mu) = & \sum_\alpha \frac{2\pi}{\hbar} \int \rho_\alpha(\sigma) \rho_\alpha(\sigma') \\ & \times |\langle m+\mu, n, n' | \hat{W} | m, n+1, n'-1 \rangle|^2 d\Omega d\Omega' dE. \end{aligned}$$

The summation indicates that all the modes of oscillations are taken into account. The energies of the emitted and absorbed phonons are connected by the relation  $\hbar\omega = \hbar\omega' + |\mu|g\beta H$  by virtue of the law of conservation of energy. Here  $|\mu|g\beta H$  is the energy corresponding to the transition between Zeeman sublevels,  $n$  the quantum number of the lattice oscillator, and  $m$  the magnetic quantum number.

To calculate the matrix elements that enter in Eq. (9), the displacements  $u_p^l$  must be expressed in terms of the normal coordinates  $q(\sigma)$

$$u_{px}^l = \sum_{\alpha\sigma} q^\alpha(\sigma) A_{px}^\alpha \exp(i\sigma R_p^l/a).$$

The matrix elements of the oscillator coordinate  $q(\sigma)$  are well known. Since our equations contain only the amplitudes of the relative displacements of the atoms, which depend little on  $\sigma$  (this follows from the work of Tolpygo<sup>6</sup>), we neglected this dependence. In calculating the probability of the transition due to optical oscillations, only the region directly surrounding the ions can be taken into account. The next nearest region is not of prime importance, since in that case the phase difference between the vibrations of the atoms of this region and those of the central atom is little and the change in the gradient of the electric field is small. In acoustic oscillations the contribution to the probability of transition from the next nearest region amounts to  $1/3$  of the contribution of the nearest neighbors. Taking this circumstance into account, and carrying out the corresponding integration over the wave-vector space, we obtain the following equation for the transition probability per unit time

$$P(m, m + \mu) = \pi^3 (1 - \gamma_\infty)^2 (e^2/a^5 m_0^2) |\langle m + \mu | \hat{Q}_\mu | m \rangle|^2 L_{|\mu|},$$

$$L_2 = \frac{(f^2 + 1)^2 + 2}{a^5 (f + 1)^2} \left[ \frac{1}{\Delta\omega_{\parallel} \omega_{\parallel}^2 \sinh^2(\hbar\omega_{\parallel}/2kT)} + \frac{2}{\Delta\omega_{\perp} \omega_{\perp}^2 \sinh^2(\hbar\omega_{\perp}/2kT)} \right] + \frac{k^2 T^2}{2\pi\hbar^2} \left( \frac{f}{f+1} \right)^2 \left[ \frac{1}{v_{\parallel}^5} + \frac{2}{v_{\perp}^5} \right],$$

$$\begin{aligned} & |\langle m + 1 | Q_1 | m \rangle|^2 \\ &= \frac{3}{2} [eQ/2I(2I-1)]^2 (2m+1)^2 (I-m)(I+m+1), \\ & |\langle m + 2 | Q_2 | m \rangle|^2 \\ &= \frac{3}{2} [eQ/2I(2I-1)]^2 (I-m-1)(I+m+2)(I-m) \\ & \times (I+m+1) \end{aligned} \quad (10)$$

$L_1$  differs from  $L_2$  only in the factor 11/20. Here  $m_0$  is the mass of the central ion,  $f$  the ratio of the mass of the central ion to that of the neighboring ion,  $\omega_{\parallel}$  and  $\omega_{\perp}$  are the frequencies of the longitudinal and transverse optical vibrations at  $\sigma = 0$ , and  $v_{\parallel}$  and  $v_{\perp}$  are the speeds of propagation of the longitudinal and transverse vibrations. It is assumed in the calculation that  $\hbar\Delta\omega\sigma/\sigma_0 \ll 2kT$ , and  $\hbar v\sigma/a \ll 2kT$ , which is true at room temperatures.

Knowing the probabilities of the relaxation transitions, we can determine the spin-lattice relaxation time. The relaxation of nuclear spins has been investigated heretofore mostly by the method of saturation of the nuclear magnetic resonance. One usually introduces here a time parameter  $T_1$  (ik), pertaining to the two levels at which resonance is observed

$$x = (1 + g^2 \beta^2 H_1^2 T_1(ik) / \hbar^2)^{-1},$$

where  $x$  is a saturation factor, equal to the ratio of the differences of the populations of the two levels in equilibrium state and in saturation,  $2H_1$  is the amplitude of the radio-frequency field, and  $T_2$  is the transverse relaxation time. In the case of a spin  $I = \frac{1}{2}$ ,  $T_1(-\frac{1}{2}, \frac{1}{2})$  has the usual meaning of longitudinal relaxation time. Using the expression given by Lloyd and Pake<sup>7</sup> for  $x$  in terms of the probabilities of the relaxation transitions, we obtain for  $T_1(-\frac{1}{2}, \frac{1}{2})$ , determined by saturation of the central peak of the nuclear-resonance spectrum, the same expressions as in reference 3:\*

$$\text{for } I = \frac{3}{2} \quad T_1 = 1/P(\frac{1}{2}, \frac{3}{2}) + 1/P(\frac{3}{2}, -\frac{1}{2}),$$

$$\text{for } I = \frac{5}{2} \quad T_1 = \left\{ \frac{1}{P(\frac{1}{2}, \frac{3}{2}) + [1/P(\frac{1}{2}, \frac{5}{2}) + 1/P(\frac{5}{2}, \frac{3}{2})]^{-1}} + \frac{1}{P(\frac{3}{2}, -\frac{1}{2})} \right\} \quad (11)$$

\*Reference 3 contains a misprint in the expression for  $T_1$  in the case of  $I = 5/2$ : it is necessary to replace  $P(3/2, 1/2)$  in the second term by  $P(3/2, -1/2)$ .

For simplicity we have omitted here the indices that designate the spin levels.

#### 4. COMPARISON WITH EXPERIMENT AND DISCUSSION OF THE RESULTS

The values of  $T_1$  (in seconds) calculated from Eqs. (10) and (11) are listed in the table together with the experimental values. Columns 3 and 4 contain for comparison the results of calculations made by others.<sup>3,4\*</sup>

Ion	Experiment	Reference 3	Reference 4	This Work
Br <sup>79</sup> in KBr	0.26	19.3	0.88	0.32
I <sup>127</sup> in KI	0.039	0.24	0.27	0.077
Br <sup>79</sup> in LiBr	0.028	0.20	0.086	0.031

We determined the velocity of sound from the elastic constants<sup>8</sup> and obtained the frequencies of the optical vibrations from the dispersion frequencies.<sup>9</sup> For LiBr we took  $\omega_{\perp} = 3.5 \times 10^{13} \text{ sec}^{-1}$ , since the literature gives data neither for the dispersion frequency of this crystal nor for the Debye temperature  $\Theta$  (in references 3 and 4,  $\Theta$  was assumed to be 180°). The values of  $\Delta\omega$  were estimated with the aid of the equations for the limiting frequencies of the optical vibrations of a diatomic chain, the quadrupole moments of the nuclei were taken from reference 11, while the values of  $\gamma_\infty$  were taken from reference 4. For the substances considered by us, the contribution of the optical vibrations to the probability of relaxation transition is of the same order of magnitude as the contribution of the acoustic vibrations, whereas in the case of Br<sup>79</sup> in LiBr this contribution is determined essentially by the optical lattice vibrations. Thus, the Debye model cannot be used to explain the relaxation effects of the spin system in crystals at room temperatures. Further refinement of the theory calls for, apparently, an exact determination of the amplitudes and of the spectral density of the natural oscillations of the lattice and for an accounting of the influence of the covalence effect on the relaxation. It is seen from the table that the influence of the covalence on the relaxation is insignificant. It is a maximum for KI and probably causes a certain deviation of our

\*In reference 3, the degree of covalence  $\lambda$  was determined from the experimental values of the chemical shift. The authors did not have experimental data for KBr and, putting  $\lambda = 0.013$ , they obtained  $T_1 = 0.77 \text{ sec}$ . However, it follows from the measurements of Bloembergen and Sorokin<sup>10</sup> that  $\lambda = 0.0026$ , corresponding to the value of  $T_1$  listed in the table. For I<sup>127</sup> in KI, the value of  $T_1$  is given in accordance with reference 10.

results from experiment in this case.

It is interesting to note that our equations give a higher value of  $T_1$  than experiment if the given substance has other spins, which relax more rapidly. For example, in the case of  $\text{Na}^{23}$  in  $\text{NaCl}$  the value of  $T_1$  is more than one order of magnitude greater than the experimental value.\* In this case, apparently, the most effective is another relaxation mechanism, in which the energy of the excited spin is transferred rapidly to the relaxing spins, owing to magnetic dipole-dipole interactions, and is transferred from them to the lattice vibrations. This relaxation process is analogous to that discussed in references 13–15. Preliminary estimates confirm this assumption.

In conclusion, the author expresses deep gratitude to S. A. Al'tshuler for suggesting the topic and for interest in the investigation.

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\*The experimental value  $T_1 = 7$  minutes, cited in reference 4 for  $\text{Na}^{23}$  in  $\text{NaCl}$ , is incorrect. The value of  $T_1$  is either 7.5 sec as measured by Proctor and Robinson<sup>12</sup> or 14.5 sec as measured by Bloembergen and Sorokin.<sup>10</sup> Consequently  $T_1$  (25 minutes) calculated in reference 4 is more than 100 times greater than the experimental value.

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