SOVIET PHYSICS JETP VOLUME 25, NUMBER 1 JULY, 1967

SPIN-LATTICE RELAXATION IN CRYSTALS WITH DEFECTS AT LOW TEMPERATURES

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Submitted to JETP editor May 26, 1966

J. Exptl. Theoret. Phys. (U.S.S.R.) 52, 136-143 (January, 1967)

The probability $W_{\sigma\sigma'}$ of an adiabatic spin-lattice transition ($s > 1/2$) at low temperatures is calculated for the case of a simple cubic lattice containing an imperfect atom differing from the regular atoms in its mass and force constants. The kinetics of the relaxation process is investigated. The order of magnitude of $W_{\sigma\sigma'}$ and its dependence on the transition frequency (for small values of the latter), the temperature, and the concentration of defects agree with the experimental data.

THEORETICAL calculations of the spin-lattice relaxation time T_1 at low temperatures [1,2] yield, in the case $s > 1/2$ and for the harmonic lattice model, to an expression of the form

$$\frac{1}{2T_1} \sim \left(\frac{\omega_1^2}{\omega_D}\right)\left(\frac{T}{\Theta}\right)\left(\frac{\omega_t}{\omega_D}\right)^2, \tag{1}$$

where ω_1 is the spin-phonon interaction constant, ω_D and Θ are the Debye frequency and temperature, ω_t is the relaxation transition frequency ($\omega_t \ll \omega_D$), and T is the temperature. Equation (1), however, does not agree satisfactorily with experiment. In the first place, Eq. (1) gives an incorrect dependence of the time T_1 on the frequency ω_t: experimentally, in the region of small ω_t, the magnitude of T_1 is independent of the transition frequency [3] (or depends on it weakly according to a complex law). In the second place, the magnitudes of T_1 evaluated from Eq. (1) differ from the experimental values by several orders of magnitude.[4]

In previous papers [5,6] one of the present authors has shown that these deficiencies of Eq. (1) can be removed by taking into account the nonidealities of the lattice. In these papers estimates were made of the effect of isotopic impurities on the quantity $1/T_1$. In doing this it was found that the contribution to $1/T_1$ that is independent of ω_t is proportional to the concentration of isotopic defects for small values of ω_t.

Here we shall consider the quantity $W_{\sigma\sigma'} \sim 1/2T_1$—the probability per unit time of a relaxation transition between states σ and σ' of the spin operator $\hbar\mathcal{H}_s$ under the influence of the interaction $\hbar\mathcal{H}_{sp}$ between the spin and harmonic vibrations of the lattice, whose Hamiltonian $\hbar\mathcal{H}_p$ pertains to a lattice with one defect atom, which differs from the remaining atoms both in mass and force constants; for simplicity we shall consider a simple cubic lattice.

Let l be the number of an atom in the lattice ($l = (l_1, l_2, l_3)$; henceforth instead of l we shall write simply l) and let the defect atom be at the origin ($l = 0$). For the force constants and mass, following Kagan and Iosilevskiĭ,[7]

$$\Phi_{\alpha\beta}(l, l') = \Phi_{\alpha\beta}{}^0(l - l'), \quad l, l' \neq 0;$$

we use

$$\Phi_{\alpha\beta}(0, l) = (1-\gamma)\Phi_{\alpha\beta}{}^0(-l),$$

$$\Phi_{\alpha\beta}(l, 0) = (1-\gamma)\Phi_{\alpha\beta}{}^0(l);$$

$$m(l) = m, \quad l \neq 0, \qquad m(0) = m(1-\varepsilon) \tag{2}$$

(here and later the index 0 indicates that the corresponding quantity pertains to the regular lattice, which is obtained from the considered one when $\gamma = \epsilon = 0$). It should be noted that the lattice model (2) has the defect that it corresponds to an artificial binding of the atoms to their equilibrium positions. In addition, when $\gamma > 1$ and $\gamma < [1 - \langle\omega_0^2\rangle\langle\omega_0^{-2}\rangle]^{-1}$ (where $\langle\omega_0^n\rangle$ is the n-th moment of the distribution of the characteristic frequencies of the regular crystal), the potential energy of the crystal ceases to be in positive-definite form, so that the system becomes unstable. Because of this, the model has a limited range of applicability; in particular, we shall not in what follows consider values of γ close to the indicated limits.

The Hamiltonian of the system being considered is

$$\hbar\mathcal{H} = \hbar\mathcal{H}_p + \hbar\mathcal{H}_s + \hbar\mathcal{H}_{sp},$$

$$\mathcal{H}_p = \sum_{q,\nu} \omega_q [b_{q\nu}^+ b_{q\nu} + 1/2],$$

where ω_q are the characteristic frequencies of the crystal (q numbers the frequencies in increasing order), $b^+_{q\nu}$ and $b_{q\nu}$ are phonon creation and annihilation operators corresponding to the normal vibration q, ν (ν gives the degeneracy of the frequency). For the case $s > \frac{1}{2}$, and in accordance with[5,6,8] we write $\mathcal{H}_{sp}$ in the form

$$\mathcal{H}_{sp} = \sum_l A_{\alpha\beta\eta}(l) x_\alpha(l) s_\beta s_\eta, \qquad A_{\alpha\beta\eta}(l) \sim \omega_t/a, \tag{3}$$

where $A_{\alpha\beta\eta}(l)$ is the spin-phonon interaction constant, $x(l)$ is the displacement of the l-th atom from its equilibrium position, and a is the lattice constant (repeated Greek subscripts indicate summation).

The operator (3) pertains to the adiabatic mechanism of spin-lattice relaxation introduced by Van Vleck.[1] The coefficients $A_{\alpha\beta\eta}(1)$ rapidly diminish with increasing $|l - l_s|$, where l_s is the coordinate of the unpaired electron, so that in practice one needs to take into account in the sum over l only those terms for which $|l - l_s| < 2$. In addition, the coefficients in (3) satisfy the condition[5]

$$\sum_l A_{\alpha\beta\eta}(l) = 0, \tag{4}$$

which reflects the situation that the spin-lattice interaction depends only on the difference of the displacements of neighboring atoms.

Writing the general quantum-mechanical expression for the transition probability and averaging it over the equilibrium density matrix of the lattice at temperature T (this operation is signified by $\langle\,\rangle_T$), we find[2]

$$W_{\sigma\to\sigma'} = \langle\sigma|s_\beta s_\eta|\sigma'\rangle\langle\sigma'|s_{\beta'} s_{\eta'}|\sigma\rangle \sum_{l,l'} A_{\alpha\beta\eta}(l) A_{\alpha'\beta'\eta'}(l')$$
$$\times \int_{-\infty}^{\infty} \langle x_\alpha(l,t) x_{\alpha'}(l')\rangle_T \exp(i\omega_t t)\, dt,$$
$$x_\alpha(l,t) = \exp(i\mathcal{H}_p t) x_\alpha(l) \exp(-i\mathcal{H}_p t).$$

Expressing, as usual, the operators $x_\alpha(1)$ in terms of $b^+_{q\nu}$, $b_{q\nu}$, we obtain[8]

$$W_{\sigma\to\sigma'} = \frac{1}{2} \sum_{l,l',q,\nu} \langle\sigma|s_\beta s_\eta|\sigma'\rangle\langle\sigma'|s_{\beta'} s_{\eta'}|\sigma\rangle A_{\alpha\beta\eta}(l) A_{\alpha'\beta'\eta'}(l')$$
$$\times \omega_q^{-1} [m(l) m(l')]^{-1/2} \int_{-\infty}^{\infty} \exp(i\omega_t t) [B_{q\nu\alpha}(l) B^*_{q\nu\alpha'}(l')$$
$$\times \langle b_{q\nu}^+(t) b_{q\nu}\rangle_T + B^*_{q\nu\alpha}(l) B_{q\nu\alpha'}(l') \langle b_{q\nu} b_{q\nu}^+(t)\rangle_T]\, dt, \tag{5}$$

where the $B_{q\nu\alpha}(l)$ are the eigenvectors of the dynamic density matrix.

Generally speaking, the measured spin-lattice relaxation time is connected with the quantity $W_{\sigma\sigma'} = \frac{1}{2}(W_{\sigma\to\sigma'} + W_{\sigma'\to\sigma})$ by the relation $1/2T_1 \sim W_{\sigma\sigma'}$. We shall assume that $\hbar\omega_t \ll kT$ (however, the temperature is sufficiently low, $kT \ll \hbar\omega_{max}$, where ω_{max} is the maximum frequency of the quasi-continuous phonon spectrum, so that combination processes can be neglected). Then $W_{\sigma\to\sigma'}(\omega_t) = W_{\sigma'\to\sigma}(\omega_t)$. With this taken into account, we have from (5)

$$W_{\sigma\sigma'} = \pi kT \sum_{q,\nu} \omega_t^{-2} \delta(\omega_q - \omega_t)$$
$$\times \left| \sum_l A_{\alpha\beta\eta}(l) \langle\sigma|s_\beta s_\eta|\sigma'\rangle B^*_{q\nu\alpha}(l) [m(l)]^{-1/2} \right|^2. \tag{6}$$

Calculation of the sums in (6) requires knowledge of the proper frequencies and eigenvectors of the dynamic density matrix of the crystal. We remark that, because of the presence in (6) of the δ function and the condition $\omega_t \ll \omega_{max}$, always satisfied in EPR experiments, it is necessary for us to calculate ω_q and $B_{q\nu\alpha}(l)$ for those values of q which correspond to frequencies $\omega_q \ll \omega_{max}$.

Kagan and Iosilevskiĭ[7] have shown that the frequency spectrum of the defect crystal contains, besides the frequencies $\omega_0(\mathbf{k}, j)$ of the spectrum of the regular crystal ($\mathbf{k}$ is the wave vector, j the frequency branch), also triply degenerate "detached" frequencies, which alternate with the former on the frequency scale. The lattice vibrations at these frequencies, as can be shown, give a non-vanishing contribution to (6) as $\omega_t \to 0$. We denote by $\Delta\omega_q^2$ the difference between ω_{0q}^2 and the square of the frequency detached from it, and we let $\delta\omega_{0q}^2 = \omega_{0q+1}^2 - \omega_{0q}^2$. It can be shown that for an overwhelming number of frequencies the ratio $\Delta\omega_q^2/\delta\omega_{0q}^2$ for $\omega_{0q} \ll \omega_{max}$ is proportional to ω_{0q}/ω_{max}. Using this fact, as well as the results of Kagan and Iosilevskiĭ[7], it can be shown that when $\omega_q \ll \omega_{max}$ and l is not too large ($\omega_t R(l)/c_j \ll 1$, where $R(l)$ is the distance of the l-th lattice site from the defect and c_j is the speed of sound in branch j), the vectors $B_{q\nu\alpha}(l)$ for the detached frequencies have the form (the frequency from which ω_q was separated is denoted as $\omega_{0q'}$)

$$B_{q\nu\alpha}(l) = \left[\frac{\vartheta}{3NG(\omega_q^2)}\right]^{1/2} \Big\{ \delta_{\alpha\nu} \Big[1 - b(\omega_q^2) S(\omega_q^2)$$
$$+ \delta_{l0}\left(\frac{\sqrt{1-\varepsilon}}{1-\gamma} - 1\right)\Big] + \frac{\omega_q^2 b(\omega_q^2)}{N}$$
$$\times {\sum_{\mathbf{k},j}}' \frac{e_\alpha(\mathbf{k},j) e_\nu(\mathbf{k},j) \exp[i\mathbf{k}\mathbf{R}(l)]}{\omega_{0q'}^2 - \omega_0^2(\mathbf{k},j)} \Big\}, \quad \nu = 1, 2, 3, \tag{7}$$

where

$$G(\omega^2) = [1 - b(\omega^2)S(\omega^2)]^2 + \pi^2 b^2(\omega^2)\,\omega^4 g_0{}^2(\omega^2),$$

$$b(\omega^2) = \frac{1}{1-\gamma}\left[\frac{\varepsilon-\gamma}{1-\gamma} - \gamma\left(1 - \frac{\langle\omega_0{}^2\rangle}{\omega^2}\right)\right],$$

$$S(\omega^2) = \omega^2 \oint_0^{\omega^2_{max}} d\omega_0{}^2 \frac{g_0(\omega_0{}^2)}{\omega^2 - \omega_0{}^2},$$

$g_0(\omega^2)$ is the spectral density of the regular crystal, N is the number of atoms in the crystal, and $e(\mathbf{k}, j)$ is the polarization of the regular lattice vibration with frequency $\omega_0(\mathbf{k}, j)$. The prime on the summation symbol means that the frequency $\omega_{0q'}$ from which ω_q was separated is left out. In deriving (7) it was assumed that the magnitudes of $\omega_0^2(\mathbf{k}, j)$ are distributed equidistantly in small portions of the squared frequency scale and that the degeneracy of almost all of them is the same and equal to θ.

We transform the sum over **k**, j in (7) and shall calculate it up to terms of the order ω_q/ω_{max}:

$$\sum_{\mathbf{k},j}{}' \frac{e_\alpha(\mathbf{k}, j)\,e_\nu(\mathbf{k}, j)\,e^{i\mathbf{kR}(l)}}{\omega_{0q'}^2 - \omega_0{}^2(\mathbf{k}, j)} = \sum_{q''}{}' \frac{z_{q''}}{\omega_{0q'}^2 - \omega_{0q''}^2}$$

$$= \sum_{|q''-q'|\geqslant q_1} \frac{z_{q''}}{\omega_{0q'}{}^2 - \omega_{0q''}{}^2} + \sum_{|q''-q'|<q_1}{}' \frac{z_{q''}}{\omega_{0q'}{}^2 - \omega_{0q''}{}^2}, \tag{8}$$

where

$$z_q = \sum_{\mathbf{k},j} \frac{e_\alpha(\mathbf{k}, j)\,e_\nu(\mathbf{k}, j)\,e^{i\mathbf{kR}(l)}}{\omega_{0q'}^2 - \omega^2{}_0(\mathbf{k}, j)}, \qquad \omega_0(\mathbf{k}, j) = \omega_{0q}.$$

Using the assumption of equidistance on the frequency scale, we majorize the second sum in (8):

$$\sum_{|q''-q'|<q_1}{}' \frac{z_{q''}}{\omega_{0q'}{}^2 - \omega_{0q''}{}^2} \leqslant \frac{2\vartheta}{\delta\omega_{0q'}{}^2} \sum_{q''=1}^{q_1-1} \frac{1}{q''} \sim \frac{N}{\omega^2_{max}} \frac{\omega_q}{\omega_{max}} \ln q_1. \tag{9}$$

The first sum in (8) contains no singular points and can be replaced by an integral ($q_1 \gg 1$) in the usual way:

$$\sum_{q'',\,|q''-q'|\geqslant q_1} \frac{z_{q''}}{\omega_{0q'}^2 - \omega_{0q''}^2}$$

$$\to \sum_j \frac{V}{(2\pi)^3} \oint \frac{e_\alpha(\mathbf{k}, j)\,e_\nu(\mathbf{k}, j)\,e^{i\mathbf{kR}(l)}}{\omega_q{}^2 - \omega_0{}^2(\mathbf{k}, j)} d\mathbf{k}; \tag{10}$$

here V is the volume of the crystal and the integration over $d\mathbf{k}$ is carried out over the first Brillouin zone. The sign $\oint$ means that the integral is taken in the sense of the principal (equal-frequency) value; an evaluation of its magnitude yields $(N/\omega^2_{max})(a/R(l))$. It is seen from this that the second sum in (8) may be neglected for sufficiently small values of the parameter ω_q/ω_{max}; for this the following two conditions must apply jointly: $(\omega_q/\omega_{max}) \ln q_1 \ll 1$ and $q_1 \gg 1$. Actually, the conditions for the transformation of the sum over **k**, j in (8) are less stringent, since the majorization in (9) is too strong. Finally, we note that in the approximation we are using ω_q^2 should be omitted in the denominator in (10). After this, the integral can be extended over the entire range of values of **k**.

Thus, in (7) we can write

$$\sum_{\mathbf{k},j}{}' \frac{e_\alpha(\mathbf{k}, j)\,e_\nu(\mathbf{k}, j)\,e^{i\mathbf{kR}(l)}}{\omega_{0q'}^2 - \omega_0{}^2(\mathbf{k}, j)}$$

$$\approx -\frac{V}{(2\pi)^3} \sum_j \int \frac{e_\alpha(\mathbf{k}, j)\,e_\nu(\mathbf{k}, j)\,e^{i\mathbf{kR}(l)}}{\omega^2{}_0(\mathbf{k}, j)} d\mathbf{k}. \tag{11}$$

Using (11), we put (7) into the form

$$B_{q\nu\alpha}(l) = \left[\frac{\vartheta}{3NG(\omega_q{}^2)}\right]^{1/2} \Bigg\{\delta_{\alpha\nu}\Bigg[1 - b(\omega_q{}^2)S(\omega_q{}^2)$$

$$+ \delta_{l0}\left(\frac{\sqrt{1-\varepsilon}}{1-\gamma} - 1\right)\Bigg] - \frac{1}{(2\pi)^3}\frac{V}{N}\,\omega_q{}^2 b(\omega_q{}^2)$$

$$\times \sum_j \int \frac{e_\alpha(\mathbf{k}, j)\,e_\nu(\mathbf{k}, j)\,e^{i\mathbf{kR}(l)}}{\omega_0{}^2(\mathbf{k}, j)} d\mathbf{k}\Bigg\}. \tag{12}$$

We return to Eq. (6). Considering only the detached frequencies, we obtain

$$W_{\sigma\sigma'} = \pi kT \sum_\nu \left|\, \sum_l \frac{A_{\alpha\beta\eta}(l)}{[m(l)]^{1/2}} \langle\sigma|s_\beta s_\eta|\sigma'\rangle\, B_{\nu\alpha}{}^*(\omega_t|l)\right|^2$$

$$\times \sum_q \frac{\delta(\omega_{0q} - \omega_t)}{\omega_{0q}{}^2}. \tag{13}$$

Substituting (12) for $B^*_{\nu\alpha}(\omega_t|l)$ and keeping in mind that $\omega_t \ll \omega_{max}$, we find after simple transformations

$$W_{\sigma\sigma'} = (4\pi Nm)^{-1} V\,kT\,\langle c^{-3}\rangle\, F(\omega_t{}^2, \gamma)$$

$$\times \sum_{\nu=1}^{3} |\langle\sigma|s_\beta s_\eta|\sigma'\rangle(Y_{\nu\beta\eta} - A_{\nu\beta\eta}(0))|^2, \tag{14a}$$

$$\langle c^{-3}\rangle = \frac{1}{12\pi} \sum_j \int d\Omega_{\mathbf{k}} c_j{}^{-3}\left(\frac{\mathbf{k}}{|\mathbf{k}|}\right);$$

$$Y_{\nu\beta\eta} = \frac{V\langle\omega_0{}^2\rangle}{(2\pi)^3 N} \sum_j \int \omega_0{}^{-2}(\mathbf{k}, j)\,e_\alpha(\mathbf{k}, j)\,e_\nu(\mathbf{k}, j)$$

$$\times \sum_l A_{\alpha\beta\eta}(l)\,e^{i\mathbf{kR}(l)}\,d\mathbf{k},$$

$$F(\omega^2, \gamma) = \gamma^2[(1 - \gamma + \gamma\langle\omega_0{}^2\rangle\langle\omega_0{}^{-2}\rangle)^2$$

$$+ \pi^2\gamma^2\langle\omega_0{}^2\rangle^2 g_0{}^2(\omega^2)]^{-1}. \tag{14b}$$

As can be seen from these equations, the influence of the defect atom on the probability of a single-phonon transition is determined only by the change in the force constants and is independent of the mass of the defect.

It is not difficult to change the form of Eqs. (14) in such a manner that they can be applied also to the calculation of the probability of the "x-process," which consists of the simultaneous reorientation of the spins of an electron and of one of its nearest nuclei. The operator for the interaction of the spin of an unpaired electron with the spin I of a nucleus situated at the site l_I has, for the direct process, the form

$$\mathcal{H}_{sp} = A_{\alpha\beta\eta} s_\beta I_\eta (x_\alpha(l_s) - x_\alpha(l_I)).$$

It is obvious that for the calculation of $W_{\sigma I, \sigma' I'}$ in (14) it suffices to replace $\langle \sigma | s_\alpha s_\beta | \sigma' \rangle$ by $\langle \sigma I | s_\alpha I_\beta | \sigma' I' \rangle$ and set $A_{\alpha\beta\eta} = A_{\alpha\beta\eta}(l_s) = -A_{\alpha\beta\eta}(l_I)$, $A_{\alpha\beta\eta}(l) = 0$ for $l \neq l_s, l_I$.

There is a case when the magnitude of $W_{\sigma\sigma'}$ calculated by means of (14) is zero. That is, if the paramagnetic center relaxes by virtue of its coupling with pairs of neighboring atoms located on opposite sides of it, then in the case of Van Vleck relaxation (s-process) it can easily be shown that $A_{\alpha\beta\eta}(l_s) = 0$. If we set $l_s = 0$ in (14), then as a result of (4) we have $Y_{\alpha\beta\eta} = 0$ and $W_{\sigma\sigma'} = 0$. Thus, the fact that the paramagnetic center of a simple lattice is itself a defect does not affect the s-processes of spin-lattice relaxation.

If we consider the x-process and set $l_s = 0$, then the evaluation of the magnitude of $W_{\sigma\sigma'}$ can be carried out by the formula

$$W_{\sigma\sigma'} \approx (\omega_1^2 / \omega_{max})(T/\Theta) F(\omega_t^2, \gamma) |\langle\omega_0^2\rangle\langle\omega_0^{-2}\rangle - 1|^2, \quad (15)$$

where $\omega_1 \sim A_{\alpha\beta\eta}(0)/a$. This formula is obtained from (14) by means of the frequently applied Van Vleck model, according to which in complex lattices it is possible to set $R(l) \ll a$ for all atoms l with which the paramagnetic defect interacts.

We return now to the case $l_s \neq 0$ and $R(l_s) \gg a$ (but $\omega_t R(l_s)/c_j \ll 1$). Using the Debye model, it is easy to find from (14) in this case

$$W_{\sigma\sigma'} \sim \frac{\omega_1^2}{\omega_{max}} \frac{T}{\Theta} F(\omega_t^2, \gamma) \left(\frac{a}{R(l_s)}\right)^4. \quad (16)$$

In (16) a factor depending on the orientation of the paramagnetic center relative to the crystal axes and the defect has been omitted. For a sufficiently symmetric center this factor can be assumed to be unity. For the case when the paramagnetic center interacts only with one neighboring atom l_1, the factor omitted in (16) is

$$\left| \frac{[\mathbf{R}(l_s) - \mathbf{R}(l_1)][\mathbf{R}(l_s) + \mathbf{R}(l_1)]}{|\mathbf{R}(l_s) - \mathbf{R}(l_1)|\,|\mathbf{R}(l_s) + \mathbf{R}(l_1)|} \right|^2.$$

The quantity F in (16) is $\gamma^2 [\gamma - 1/(1 - \langle\omega_0^2\rangle\langle\omega_0^{-2}\rangle)]^{-2}$.

From a comparison of (16) with (1) it is seen that even for not very small transition frequencies the presence of defects must be taken into account in calculations of relaxation transition probabilities (thus, for $\omega_t \approx 2 \times 10^{10}$ Hz, which corresponds to a magnetic field $H_0 \sim 1000$ G, even for paramagnetic centers situated at a distance of 30a from the defect, Eq. (16) can give a value of $W_{\sigma\sigma'}$ that is no smaller than the contribution to this quantity from (1), determined for the regular lattice). From this it is seen that for values of ω_t that are not too large, a situation can be realized in which the spin-lattice relaxation is almost completely determined by the effect of defects. Let us consider the kinetics of this process.

In accordance with (16), we write for the probability of a relaxation transition under the influence of a defect located at a distance R from the paramagnetic center

$$W_{\sigma\sigma'}(R) = (a/R)^4 W_0. \quad (17)$$

It is obvious that Eq. (17) is invalid for small values of R; however, as we shall see, this region is insignificant for small concentrations of defects, and it is only such a case that we can indeed consider without taking into account interactions between the defects.

We shall assume that the defects are distributed throughout the crystal in random fashion. Then each paramagnetic center n has its own random distribution of neighboring defects l, leading to a relaxation law for the component M_z, for example, of the form

$$F_n(t) = \frac{M_{zn}(t) - M_{z0}}{M_{zn}(0) - M_{z0}} = \exp[-t \sum_l W(R_{nl})], \quad (18)$$

where M_{z0} is the equilibrium value of M_z; the sum is taken over all defects of the sample, $R_{nl} = |\mathbf{R}(l) - \mathbf{R}(n)|$; we assume that the effects of the defects are additive. On the average, one observes a relaxation law $F(t)$ which is the average of $F_n(t)$ over all n. Averaging (18) in the manner proposed by Burshteĭn and Kopyshev,[9] we find for the case of low concentrations of defects

$$F(t) = \exp\left\{4\pi \frac{N_d}{3N} \int_{R_0}^{\infty} R^3 e^{-tW(R)} \frac{\partial W(R)}{\partial R} dR\right\}, \quad (19)$$

where N_d is the number of defects in the sample, and R_0 is the minimum distance between a defect and the paramagnetic center; in our case $R_0 = a$. For $R < a$ the exponent under the integral is very small; hence R_0 can be set at zero, and it need not be taken into account that when $R < a$, Eq. (17) is known to be invalid. The integration of (19) gives

$$F(t) = \exp\left\{-\frac{N_d}{N}\Gamma\left(\frac{1}{4}\right)(W_0 t)^{3/4}\right\},\quad \Gamma\left(\frac{1}{4}\right) \cong 3{,}62. \quad (20)$$

As is seen from this expression, the relaxation law is not obtained in form $e^{-\alpha t}$, although it is close to it. It is interesting to note that graphically, Eq. (20) resembles the superposition of two exponentials, the relaxation times for which are essentially different; curves of this kind at low temperatures are frequently discussed in experimental papers,[10] and the second exponential is usually attributed to cross-relaxation processes. In all such cases it should be kept in mind that relaxation due to defects leads to a similar result.

We note, finally, that the dependence of the relaxation process on the defect concentration f follows from (20). We remarked above that the fact that the paramagnetic center is itself a defect atom does not affect the s-process. However, the fact that neighboring paramagnetic centers are themselves defects does affect the relaxation of a given center. Thus, as long as the concentration of paramagnetic centers exceeds the concentration of other defects, that is precisely what should be understood by N_d/N in (20). Experimentally, the presence of a dependence of T_1 on the concentration of paramagnetic centers at low temperatures is well known.[4]

Thus, the defect model we have treated has allowed us to obtain the correct order of magnitude for the relaxation transition probability $W_{\sigma\sigma'}$ at low temperatures and to explain the independence of $W_{\sigma\sigma'}$ on the transition frequency for the true (i.e., experimentally observed) temperature dependence, as well as to make possible an investigation of the concentration dependence of $W_{\sigma\sigma'}$. With the exception of the temperature dependence of T_1 in the low-temperature region, all the (experimentally observed) effects enumerated above cannot be understood on the basis of the regular lattice model and the spin-lattice interaction mechanisms known in the literature; they can, however, be explained by taking the non-idealities of the lattice into account.

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[1] J. Van Vleck, Phys. Rev. 57, 426 (1940).

[2] I. V. Aleksandrov, JETP 48, 869 (1965), Soviet Phys. JETP 21, 580 (1965).

[3] S. A. Al'tshuler and B. M. Kozyrev, Élektronnyĭ paramagnitnyĭ rezonans (Electron Paramagnetic Resonance), Fizmatgiz, 1961 (English Transl., Academic Press, N. Y., 1964).

[4] J. Van Vleck, Magnetic and Electric Resonance and Relaxation 1, Amsterdam, 1963.

[5] I. V. Aleksandrov, TÉKh 11, 67 (1966).

[6] I. V. Aleksandrov, Doctoral Dissertation, Institute of Chemical Physics, Academy of Sciences, USSR, 1965.

[7] Yu. Kagan and Ya. Iosilevskiĭ, JETP 42, 259 (1962), Soviet Phys. JETP 15, 182 (1962).

[8] R. Mattuck and M. Strandberg, Phys. Rev. 119, 1204 (1960).

[9] A. Burshteĭn and V. Kopyshev, TÉKh (in press).

[10] A. V. Kessenikh, A. A. Manenkov, and G. I. Pyatnitskiĭ, FTT 6, 632 (1964), Soviet Phys. Solid State 6, 495 (1964).

Translated by L. M. Matarrese
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