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SPIN-LATTICE PARAMAGNETIC RELAXATION AND THE SHAPE OF EPR LINES IN A MAGNETICALLY DILUTE SOLID

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A method in which spin-lattice interaction is described in terms of the spectral density of a heat reservoir is applied to paramagnetic relaxation processes in a solid. General formulas are obtained for calculating the spin-lattice relaxation time T_1 for the direct and Raman processes. The formulas relate T_1 to the coefficients of the spin-phonon Hamiltonian and parameters of the solid. As an example, spin-lattice relaxation of radicals in a solid is considered.

The shape of EPR lines in a solid due to spin-lattice interaction is considered. It is shown that in the harmonic approximation the effect of narrowing of the EPR lines as a result of the vibrational motion of the nuclei does not occur. The absorption line is Gaussian in its wings, and the phenomenological Bloch equations are not applicable (the transverse relaxation time T_2 has no meaning). If anharmonicity (or the finite mean free path of the phonon) is taken into account, the line is of the Lorentz type.

In the theory of paramagnetic relaxation in liquids and gases, the motion of the particles of a thermal wave in contact with a paramagnetic system is described by some random process. The probability characteristics of this process determine the shape of the absorption signal in magnetic resonance $g(\omega)$ and the rate of attainment of equilibrium between the bath and the paramagnetic system (the spin-lattice relaxation time T_1). In this paper we show that this approach to relaxation phenomena can be extended to the case of solids, when the relaxation takes place by the Kronig-Van Vleck mechanism.[1,2] Using the same (and sometimes more general) assumptions as in [2], we shall obtain a general formula for T_1 involving the coefficients of the spin-phonon Hamiltonian and certain parameters of the solid, and we shall determine the form of $g(\omega)$ in the solid (if there are no interactions affecting the line width other than spin-lattice relaxation). Neither of these results can be obtained if the usual method of calculating the Kronig-Van Vleck mechanism is followed.[2]

1. STATISTICAL DYNAMICS OF THE LATTICE

We shall consider the solid as a collection of harmonic oscillators with coordinates q_k (k is the wave vector, q_k the corresponding normal coordinate). If the normal velocities are symbolized by v_k, then, according to the Gibbs distribution for the oscillators, q_k and v_k are distributed according to the normal law

$$W(q_\mathbf{k}, v_\mathbf{k}) = (2\pi\omega_\mathbf{k}\sigma_\mathbf{k}^2)^{-1} \exp(-q_\mathbf{k}^2 / 2\sigma_\mathbf{k}^2 - v_\mathbf{k}^2 / 2\omega_\mathbf{k}^2\sigma_\mathbf{k}^2), \quad (1)$$

where ω_k is the frequency of the normal vibration k, and σ_k^2 is, from [3],

$$\sigma_\mathbf{k}^2 = \frac{\hbar}{2M\omega_\mathbf{k}} \operatorname{cth}\left(\frac{\hbar\omega_\mathbf{k}}{2kT}\right), \quad (2)^*$$

where M is the mass of the crystal and T is the temperature.

We symbolize the coordinate of the nucleus of the n-th atom in the direction α by $x_{n\alpha}$ and consider $x_{n\alpha}$ as a random function of time. Clearly, because of the linearity of the transformation from q_k to $x_{n\alpha}$ the distribution law for $x_{n\alpha}$ is also normal.[4] More detailed calculations show that if we let p represent the aggregate of indexes n and α, and the instant of time is t, then the multi-dimensional vector with components x_p is a random vector with a normal distribution law, and its correlation function in the case of an isotropic solid is

$$\lambda_{pp'}^{(x)}(t) = \langle x_{n\alpha}(t) x_{m\beta}(0) \rangle = \delta_{\alpha\beta} \sum_\mathbf{k} \sigma_\mathbf{k}^2 \cos \mathbf{k}\mathbf{R}_{nm} \cos \omega_\mathbf{k} t, \quad (3)$$

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*cth = coth.

where R_{nm} is the distance between the nuclei n and m.

If it is necessary to consider the anharmonicity of the lattice vibrations, then we must write instead of Eq. (3)

$$\lambda_{pp'}^{(x)\mathrm{anh}}(t)=\delta_{\alpha\beta}\sum_{\mathbf{k}}\sigma_{\mathbf{k}}{}^{2}\cos\mathbf{k}\mathbf{R}_{nm}\cos\omega_{\mathbf{k}}t\exp(-\Gamma_{\mathbf{k}}|t|), \quad (4)$$

where the quantity $\Gamma_{\mathbf{k}}$ represents the damping of a harmonic vibration due to anharmonicity and has the significance of the inverse time of the free path of a phonon with wave vector **k**.

Since a more detailed presentation of our results will be published later, we shall omit most of the intermediate steps in the derivation of Eqs. (3), (4), and the rest, and present only the most important equations.

As calculation shows, the quantum mechanical correlation function,[5] equal to

$$\lambda_{n\alpha,m_{\beta}}^{(x)}(t)=\langle\{x_{n\alpha}(t)x_{m\beta}\}\rangle, \qquad \{AB\}={}^{1}/_{2}(AB+BA),$$

$$A(t)=\exp(i\mathscr{H}t)A\exp(-i\mathscr{H}t), \quad (5)$$

where $\mathcal{H}$ is the phonon Hamiltonian in frequency units, coincides with Eqs. (3) and (4). By using the Debye model for the solid, the summation over **k** in these expressions can be replaced by an integration over ω_{k}, which gives

$$\lambda_{n\alpha,m\beta}^{(x)}(t)=\delta_{\alpha\beta}\hbar\omega_{D}{}^{2}\int_{0}^{1}\operatorname{cth}\frac{z\Theta}{2T}\frac{\sin r_{nm}z}{r_{nm}}\cos z\omega_{D}t\frac{dz}{4\pi^{2}\rho u^{3}}, \quad (6)$$

where $r_{nm}=\omega_{D}R_{nm}/u$; ω_{D}, Θ are respectively the Debye frequency and temperature, ρ is the density of the sample, and u is the velocity of sound.

Anharmonicity is approximately taken into account (as follows from Eqs. (3) and (4)) by the correlation function

$$\lambda_{n\alpha,m\beta}^{(x)\mathrm{anh}}(t)=\exp(-\Gamma|t|)\lambda_{n\alpha,m\beta}^{(x)}(t), \quad (7)$$

where Γ^{-1} is the effective mean time of the free path of the phonon, which depends on temperature.

A formula similar to Eq. (6) can also be obtained for the correlation functions of the velocities of the nuclei $v_{n\alpha}$ of atoms n and m:

$$\lambda_{n\alpha,m\beta}^{(v)}(t)=\langle\{v_{n\alpha}(t)v_{m\beta}\}\rangle=-\frac{d^{2}}{dt^{2}}\lambda_{n\alpha,m\beta}^{(x)}(t). \quad (8)$$

The function $\lambda_{n\alpha,m\beta}^{(v)\mathrm{anh}}(t)$, which approximately accounts for the anharmonicity, is obtained by multiplying Eq. (8) by $\exp(-\Gamma|t|)$.

Finally, we give the result of the quantum mechanical calculation of the correlation functions:

$$\lambda_{n\mu m\nu,p\xi l\eta}^{(x)}(t)=\langle\{x_{n\mu}(t)x_{m\nu}(t)x_{p\xi}x_{l\eta}\}\rangle,$$

$$\lambda_{n\mu m\nu,p\xi l\eta}^{(v)}(t)=\langle\{v_{n\mu}(t)v_{m\nu}(t)v_{p\xi}v_{l\eta}\}\rangle,$$

$$\lambda_{n\mu m\nu,p\xi l\eta}^{(vx)}(t)=\langle\{v_{n\mu}(t)x_{m\nu}(t)v_{p\xi}x_{l\eta}\}\rangle,$$

which we shall need for calculations of the quantity T_1:

$$\lambda_{n\mu m\nu,p\xi l\eta}^{(x)}(t)=\lambda_{n\mu,p\xi}^{(x)}(0)\lambda_{m\nu,l\eta}^{(x)}(0)+\lambda_{n\mu,p\xi}^{(x)}(t)\lambda_{m\nu,l\eta}^{(x)}(t)$$
$$+\lambda_{n\mu,l\eta}^{(x)}(t)\lambda_{m\nu,p\xi}^{(x)}(t)-\delta_{\mu\xi}\delta_{\nu\eta}\theta_{np}^{(x)}(t)\theta_{ml}^{(x)}(t)$$
$$-\delta_{\mu\nu}\delta_{\eta\xi}\theta_{nl}^{(x)}(t)\theta_{mp}^{(x)}(t),$$

$$\theta_{nm}^{(x)}(t)=\hbar\omega_{D}\int_{0}^{1}\frac{\sin r_{nm}z}{r_{nm}}\sin\omega_{D}tz\frac{dz}{4\pi^{2}\rho u^{3}}, \quad (9)$$

and similarly for $\lambda_{n\mu m\nu,p\xi l\eta}^{(v)}(t)$, if instead of $\lambda_{n\mu,p\xi}^{(x)}$ we substitute $\lambda_{n\mu,p\xi}^{(v)}(t)$, and instead of $\theta_{nm}^{(x)}(t)$

$$\theta_{nm}^{(v)}(t)=-\frac{d^{2}}{dt^{2}}\theta_{nm}^{(x)}(t).$$

For the "mixed" correlation function we obtain

$$\lambda_{n\mu m\nu,p\xi l\eta}^{(xv)}(t)=-\frac{d^{2}}{dt^{2}}\lambda_{n\mu m\nu,p\xi l\eta}^{(x)}(t). \quad (10)$$

2. PROBABILITY OF RELAXATION TRANSITIONS

It will be assumed that the state of the paramagnetic particle (ion or radical) in the absence of a magnetic field is degenerate only with respect to the spin variables and non-degenerate with respect to the orbital quantum numbers of the electrons, and that the spacing between the orbital levels is considerably greater than the vibrational quanta of the nuclei and the Zeeman energy of the electronic spins (in the case of a paramagnetic ion, this means that the Stark splitting in the crystalline field is greater than the Debye frequency, although it can be significantly less than the spacing between the ground electronic terms). Then averaging of the Hamiltonian over the orbital motion of the electrons with regard for the necessary approximation of perturbation theory of spin-orbit interaction gives an operator that depends on the coordinates and momenta (velocities) of the nuclei and the spin coordinates, which we will call the spin-phonon Hamiltonian. Expanding the spin-phonon Hamiltonian in a series, we obtain for the operator of the interaction of the spin system with the phonon reservoir (in units of frequency):

$$\mathscr{H}'=A_{\alpha\mu}{}^{n}x_{n\mu}S_{\alpha}+A_{\alpha\mu\nu}^{nm}x_{n\mu}x_{m\nu}S_{\alpha}+\ldots+B_{\alpha\beta\mu}^{n}x_{n\mu}S_{\alpha}S_{\beta}$$
$$+B_{\alpha\beta\mu\nu}^{nm}x_{n\mu}x_{m\nu}S_{\alpha}S_{\beta}+\ldots+C_{\alpha\mu}{}^{n}v_{n\mu}S_{\alpha}+C_{\alpha\mu\nu}^{nm}v_{n\mu}v_{m\nu}S_{\alpha}$$
$$+\ldots+D_{\alpha\beta\mu}^{n}v_{n\mu}S_{\alpha}S_{\beta}+D_{\alpha\beta\mu\nu}^{nm}v_{n\mu}v_{m\nu}S_{\alpha}S_{\beta}$$
$$+\ldots+E_{\alpha\mu\nu}^{nm}x_{n\mu}v_{m\nu}S_{\alpha}+F_{\alpha\beta\mu\nu}^{nm}x_{n\mu}v_{m\nu}S_{\alpha}S_{\beta}+\ldots \quad (11)$$

In what follows we shall limit ourselves to a consideration of terms containing the first degree of the spin S_α (for $S = 1/2$ all the remaining terms vanish; for $S > 1/2$ higher degrees of S play an important role, if because of symmetry considerations the coefficients of the lower terms vanish; the treatment of these terms is completely analogous to the analysis of the first terms of the series with the exception of the complication of the tensor symbols) and the first or second degree of the coordinates or velocities of the nuclei. We remark that the terms containing $x_{n\mu}$ and $x_{n\mu}x_{m\nu}$ respectively cause adiabatic direct and two-quantum transitions (these terms exist in the adiabatic approximation to the motion of the electrons and nuclei). Terms containing $v_{n\mu}$ and $v_{n\mu}v_{m\nu}$ are responsible for purely non-adiabatic transitions.[1] Cross terms of the form $x_{n\mu}v_{m\nu}$ bring about "mixed" transitions. The coefficients in (11) are to be determined by the usual procedure for finding the spin Hamiltonian.[6]

We note that since the interaction of the spin with the nuclear vibrations depends only on the relative coordinates of the nuclei, the coefficients in (1) can be chosen so that

$$\sum_n A^n_{\alpha\mu} = \sum_n A^{nm}_{\alpha\mu\nu} = \sum_m A^{nm}_{\alpha\mu\nu} = \sum_{nm\mu\nu} A^{nm}_{\alpha\mu\nu}\langle x_{n\mu}x_{m\nu}\rangle = 0 \quad (12)$$

and similarly for the coefficients C, D, E, and F, if the interaction depends only on the relative velocities of the nuclei.

Now it is not difficult to obtain the following equation for the probability of a relaxation transition under the influence of the first term in (11) between the states σ and σ' of the spin subsystem:

$$\frac{1}{T_1} \sim W_{\sigma\sigma'} = A^n_{\alpha\mu}A^m_{\beta\nu}(S_\alpha)_{\sigma\sigma'}(S_\beta)_{\sigma\sigma'}\int_{-\infty}^{\infty}\lambda^{(x)}_{n\mu,\,m\nu}(t)\,e^{i\omega_0 t}\,dt, \quad (13)$$

$\omega_0 = \omega_{\sigma\sigma'}$ is the frequency corresponding to the transition $\sigma \rightarrow \sigma'$. Equation (13) is the general quantum mechanical formula of perturbation theory[5]. At the same time Eq. (13) can be written also on the basis of a representation in which $x_{n\alpha}(t)$ is a random process, the correlation function of which is determined by Eq. (6).

Substituting (6) into (13) and noting that $R_{nm}\omega_0/u \ll 1$ (R_{nm} is the equilibrium distance between the nuclei with which the unpaired electron interacts; it is assumed that the electron is localized near a small number of nuclei), for $\hbar\omega_0/kT \ll 1$ we find for the direct adiabatic processes in the harmonic approximation:

$$W_{\sigma\sigma'} = \omega_0{}^2 kTA_{\alpha\mu}{}^n A_{\beta\mu}{}^m R_{nm}{}^2(S_\alpha)_{\sigma\sigma'}(S_\beta)_{\sigma'\sigma}\,/\,(12\pi\rho u^5). \quad (14)$$

For the nonadiabatic transitions (the interaction depends only on the relative velocities), we obtain an analogous expression (replacing $A^n_{\alpha\mu}$ by $C^n_{\alpha\mu}$ and ω_0^2 by ω_0^4).

From Eqs. (13) and (6) it is easy to see that the quantity

$$\delta_{\mu\nu}j^{(x)}_{nm}(\omega) = \int_{-\infty}^{\infty}\lambda^{(x)}_{n\mu,\,m\nu}(t)\exp(i\omega t)\,dt,$$

which represents the matrix of the spectral density of the random vector x_p, in the harmonic approximation, tends toward zero as $\omega \rightarrow 0$. Accounting for anharmonicity according to Eq. (7), $j_{nm}(0) \sim \Gamma$ and does not go to zero. Hence for the direct transitions at a frequency $\omega_0 \ll \omega_D$ the anharmonicity should play a significant role. Direct calculation gives

$$W^{\text{anh}}_{\sigma\sigma'} = \hbar\omega_D{}^2\Gamma A^n_{\alpha\mu}A^m_{\beta\mu}(S_\alpha)_{\sigma\sigma'}(S_\beta)_{\sigma'\sigma}R^2_{nm}/\pi^2\rho u^5, \quad (15)$$

which differs from (14) by a factor of the order

$$(\omega_D/\omega_0)^2\hbar\Gamma/kT \sim (\omega_D/\omega_0)^2\hbar u/l_0kT, \quad (16)$$

where l_0 is the mean free path of the phonon. At helium temperatures l_0 does not exceed 0.1 cm; hence the factor (16) is of the order 10 when $\omega_0 \sim 10^{10}$ cps and $\omega_D \sim 10^{13}$ cps. From Eq. (15) it is also seen that T_1 can depend on the dimensions of the sample, if these limit the free path of the phonon.

For non-adiabatic transitions the anharmonicity increases the probability of the transition $(\omega_D/\omega_0)^4\hbar\Gamma/kT$ times; it is obvious that at low temperatures only the effect of non-adiabaticity need be taken into account.

In calculations of the probabilities of two-phonon transitions the spectral density of the process $x_{n\alpha}x_{m\beta}$, the matrix of which corresponds to the correlation matrix (9), does not go to zero when $\omega \rightarrow 0$. Hence the anharmonicity in this case can be neglected. Direct calculation gives for the adiabatic transitions

$$W_{\sigma\sigma'} = \omega_D{}^7\hbar^2 J_6 A^{nm}_{\alpha\mu\nu}A^{pl}_{\beta\mu\nu}R^2_{np}R^2_{ml}(S_\alpha)_{\sigma\sigma'}(S_\beta)_{\sigma'\sigma}/144\pi^3\rho^2u^{10},$$

$$J_n = \int_0^1 x^n\exp(x\Theta/T)\,(1-\exp(x\Theta/T))^{-2}\,dx. \quad (17)$$

In the derivation of (17) we took it into account that $(\omega_0/\omega_D) \ll 1$, and, as in (2), we assumed $R_{nm}\omega_D/u \ll 1$; actually $R_{nm}\omega_D/u \lesssim 1$; however, it can be shown that this circumstance only slightly alters the value of T_1 calculated according to (17).

For purely nonadiabatic and "mixed" transitions, we obtain respectively

$$W_{\sigma\sigma'}^{\text{nonad}} = \omega_D{}^{11}\hbar^2 J_{10} C_{\alpha\mu\nu}^{nm} C_{\beta\mu\nu}^{pl} R_{np}^2 R_{ml}^2 (S_\alpha)_{\sigma\sigma'} (S_\beta)_{\sigma'\sigma} / 144\pi^3\rho^2 u^{10},$$

$$W_{\sigma\sigma'}^{\text{mix}} = \omega_D{}^{9}\hbar^2 J_8 E_{\alpha\mu\nu}^{nm} E_{\beta\mu\nu}^{pl} R_{np}^2 R_{ml}^2 (S_\alpha)_{\sigma\sigma'} (S_\beta)_{\sigma'\sigma} / 144\pi^3\rho^2 u^{10}. \tag{18}$$

Equations (14), (17), and (18) contain as special cases the results of Van Vleck[2]; for specific calculations of T_1 it suffices to know the coefficients of the spin Hamiltonian determined for each special case; the interaction of the spin with the lattice vibrations is then already completely taken into account.

We remark further that the above analysis of the role of anharmonicity gives us an understanding of why the Van Vleck theory agrees poorly with experiment at helium temperatures,[7] and (at least semi-quantitatively) removes the existing discrepancies (a complete quantitative analysis requires the calculation of the functional dependence $\Gamma(\mathbf{k})$ in Eq. (4) and the following formulas for the correlation functions that account for the anharmonicity).

Examples of the application of Eqs. (14), (15), (17), and (18) to the calculation of T_1 of radicals in a solid are given below; specific calculations of the coefficients of the spin Hamiltonian are presented in papers by the author and Kessenikh.[8]

3. SHAPE OF THE EPR LINE IN A MAGNETICALLY-DILUTE SAMPLE

In this section we go through an analysis of the shape of the EPR line, starting from the assumption that the motions of the atoms in the lattice can be described classically. It can be shown that the quantum mechanical calculation (at least for the harmonic model of the structure of the solid) leads to the same results. This is because the shape of the line is determined principally by the linear terms of (11), and the classical and quantum descriptions for the correlation functions of these terms lead to the very same result. For simplicity, we shall henceforth assume that $S = 1/2$.

We consider first the case when the spin Hamiltonian contains only adiabatic terms:

$$\mathscr{H} = \omega_0 S_z + A_{\alpha\mu}{}^n x_{n\mu} S_\alpha, \tag{19}$$

where $x_{n\mu}$ is a random function of time. The quantity ω_1, determined by the relation

$$\omega_1{}^2 = \langle (A_{z\beta}{}^n x_{n\beta})^2 \rangle, \tag{20}$$

represents the mean square of the interaction of the spin with the nuclear vibrations. For a radical with a highly anisotropic g factor, $\omega_1 \sim \Delta g \omega_0 \Delta R/R$ (ΔR is the mean square displacement of the nuclei, R is the equilibrium internuclear separation). for a paramagnetic ion, $\omega_1 \sim \hbar\lambda^2 \Delta R \delta / \Delta E^2 R$ (λ is the spin-orbit interaction constant, δ, ΔE are the splittings of the levels in a crystalline field of low and high symmetry, respectively). Now, the secular part of (19) can be written in the form

$$\mathscr{H}_{\text{sec}} = \omega_0 S_z + \omega_1 y S_z, \tag{21}$$

where

$$y = A_{z\beta}{}^n x_{n\beta} / \omega_1 \tag{22}$$

is a random function with a normal distribution (because of the linearity of the transformation (22)).

Following the arguments of Abragam[9] (Chap. X), it is easy to show that precisely the secular part of the Hamiltonian (19), i.e., the operator (21), determines the shape of the absorption line, if the nucleus is immobile. In liquids, as is known,[10] random molecular motion causes the contribution of the secular terms to the line width to be lessened when the characteristic frequency of the molecular motion, equal to the reciprocal of the correlation time τ_c, becomes comparable to the magnitude of ω_1. When $\omega_1\tau_c \ll 1$, we encounter the case of strong narrowing: the contributions of the secular and non-secular terms are of the same order of magnitude, and the absorption line has a Lorentz shape. However, a correlation time for a random process τ_c can be introduced only when $\int_0^\infty t\,|\lambda(t)|\,dt$ ($\lambda(t)$ is the correlation function) converges. But if the solid is considered as a collection of harmonic oscillators, then, in accordance with Eqs. (3) and (22), $\int_0^\infty t\,|\langle y(t)y\rangle|\,dt \to \infty$; thus the arguments of Kubo and Tomita[10] leading to a narrowing and a Lorentzian line shape are inapplicable.

We therefore conclude that if the analysis of the line width $\Delta\omega$ caused by the secular Hamiltonian (21) leads to values $\Delta\omega \gg T_1^{-1}$ ($1/T_1$ represents in order of magnitude the contribution of the non-secular terms for any kind of motion of the particles[10]), then it is reasonable to consider the secular Hamiltonian (21) instead of the complete Hamiltonian (19).

So, we shall consider the operator (21). Then for $S = 1/2$ calculation of the line shape amounts to solving a modulation problem, i.e., to calculating the expression[9]:

$$G(t_1 - t_2) = \langle \exp(i\omega_1 \int_{t_1}^{t_2} y(t)\,dt) \rangle. \tag{23}$$

The distribution function $W(y_1 \dots y_p \dots)$,

$y_p = y(t_p)$ is not difficult to write down in integral form, since y is a linear combination of the normal coordinates and velocities q_k and v_k, the distribution function of which (1) is known.[4] Exact calculation of $g(\omega)$ by the formula

$$g(\omega) = \int_{-\infty}^{\infty} G(\tau) \exp(i(\omega + \omega_0)\tau)\, d\tau \tag{24}$$

with a value of G corresponding to (23) would lead to a collection of a huge number of δ-functions at frequencies ω_r, which are combinations of the frequency ω_0 and the frequencies of the normal vibrations ω_k (the motion of the nuclei is periodic in the absence of anharmonicity):

$$g(\omega) = \sum_r a_r \delta(\omega - \omega_r).$$

In order to obtain a smooth function $g(\omega)$, it is necessary to average $G(\tau)$ over an interval of time δt small compared to τ but large compared to ω_k^{-1}. If we carry out this averaging (symbolized by a bar) of the distribution function $W(y_1 \ldots y_p \ldots)$, it can be shown that

$$(\partial / \partial t_p)\overline{W} = 0. \tag{25}$$

We now introduce the auxiliary quantity[11]

$$A(y_1, t_1, t_2) = \overline{\langle \exp(i\omega_1 \int_{t_1}^{t_2} y(t)\, dt) \rangle_{y_1}}, \tag{26}$$

where $\langle \overline{\ldots} \rangle_{y_1}$ means that the averaging is carried out by means of the distribution function $\overline{W}$ for a fixed value of y_1. Then, differentiating (26) with respect to t_1 we have, on the basis of (25):

$$\partial A / \partial t_1 + i\omega_1 y A = 0, \tag{27}$$

and $A(y_1, t_1, t_1) = 1$.

The solution of Eq. (27) is

$$A = \exp[-i\omega_1 y_1 (t_1 - t_2)].$$

Since

$$\overline{G}(t_1 - t_2) = \int_{-\infty}^{\infty} \overline{W}(y_1) A(y_1, t_1, t_2)\, dy_1,$$

and y has a normal distribution with a single dispersion (according to Eqs. (20) and (22)), then

$$\overline{G}(\tau) = \exp(-\omega_1^2 \tau^2),$$

$$\bar{g}(\omega) = (2\pi\omega_1)^{-1} \exp[-(\omega_0 - \omega)^2 / 2\omega_1^2]. \tag{28}$$

We now note that the terms containing squares of the nuclear coordinates in the expansion (11), which we did not take into account in deriving (28), can be neglected in determining the line shape in the harmonic approximation. In this case the role of $\omega_1 y$ is played by the quantity $\omega_2 Z = A_{\mu\nu}^{nm} x_{n\mu} x_{m\nu}$. It can be shown that the dispersion of this quantity is proportional to the factor $(\langle v^2 \rangle / u^2)^2$, whereas $\omega_1^2 \sim \langle v^2 \rangle / u^2$, where $\langle v^2 \rangle$ is the mean square velocity of the nuclei; since up to the melting point $\langle v^2 \rangle / u^2 \ll 1$, then this means that the quadratic terms give a smaller contribution to the line width (in the harmonic approximation) than the linear ones.

It can be shown that this averaging operation on the distribution function leads to the correct form of $g(\omega)$ for very high frequencies ω. For small ω, values of $G(\tau)$ for large τ are important in Eq. (24), which can be correctly found only with regard for anharmonicity or other "non-idealities" of the lattice that lead to a finite lifetime of an individual normal vibration.

Calculation of the anharmonicity by means of Eqs. (3) or (7) removes the reason for the inapplicability of the general theory of narrowing,[10] and instead of τ_c in the formulas of[10] it is necessary to substitute the quantity $1/\Gamma$, and not $1/\omega_D$, as would appear at first sight.

Therefore, the following cases are possible in a solid.

1. For small anharmonicity $(\omega_1/\Gamma \gg 1)$ the line is Gaussian in the wings; the phenomenological equations are inapplicable; the ratio between ω_1 and the spin-lattice relaxation time on the basis of the formulas in Sec. 2 has the form (for $T/\Theta < 1$)

$$T_1^{-1} \sim \frac{\omega_1^2}{\omega_D} \left[\frac{T}{\Theta} \left(\frac{\omega_0}{\omega_D} \right)^n + \frac{4\Gamma}{\omega_D} + \frac{1}{3} J_{4+n} \right], \tag{29}$$

where $n = 2$ for the adiabatic and $n = 4$ for the non-adiabatic ("mixed") mechanism of relaxation.

2. Weak narrowing $(\omega_1^2/\Gamma \gg T_1^{-1}, \omega_1/\Gamma < 1)$; the line is Lorentzian; The Bloch equations are applicable; the ratio between T_1 and T_2 has the form (see Eq. (15)):

$$T_2^{-1} = (2T_1)^{-1} + W_{\sigma\sigma}^{\mathrm{anh}} \tag{30}$$

3. Strong narrowing $(\omega_1/\Gamma \ll 1, \omega_1^2/\Gamma \ll T_1^{-1})$; in the Bloch equations $T_1 = T_2$. The first two terms in square brackets in Eq. (29) play the dominant role at helium temperatures (direct relaxation process); near the Debye temperature the last term is dominant (Raman processes). We emphasize further that the quantity Γ, which is connected with the mean free path of the phonon l_0 by the relation $\Gamma \sim u/l_0$, essentially depends on temperature; indeed, at low temperatures it can happen that l_0 is determined by the linear dimensions of the sample.

4. SPIN-LATTICE RELAXATION OF RADICALS IN A SOLID PHASE

A comparison of the formulas obtained above for the probabilities of relaxation transitions with the work of Van Vleck[2] shows that all the results of[2] can be obtained from Eqs. (14), (17), and (18). It then turns out that the adiabatic processes are the most important ones for Cr^{3+}, whereas the spin-lattice relaxation of Ti^{3+} is due to non-adiabatic (at helium temperatures) and mixed (at higher temperatures) spin-phonon interactions. At low temperatures agreement with the experimental data is attained if one takes into account the anharmonicity parameter Γ, as was indicated in Sec. 2.

As a further example of the application of the apparatus presented above, we give certain results pertaining to spin-lattice relaxation of radicals in a solid sample.

As is known, in liquids the spin-lattice relaxation is associated with the rotation of the radical as a whole.[12] The spectrum of rotational motions in a solid, generally speaking, is essentially different from the Debye spectrum. However, in an isotropic body, for which there exists only one acoustic branch of vibrations and the radical can be considered as an impurity that does not disturb the elastic properties of the body, small angular rotations of the radical can be related to the elastic vibrations of a medium described by the Debye model. In this connection one should realize that Eqs. (31)—(34) below may not be suitable, for example, in cases when the intermolecular interaction in a molecular crystal depends on the mutual orientation of the molecules.

Let the anisotropy of the g factor Δg be the cause of the relaxation, as in liquids[12]; with the aid of the formulas of Sec. 2, we find for T_1 in the harmonic approximation at low temperatures (direct processes)

$$\frac{1}{2T_{1d}}=\left(\frac{\Delta g}{g}\right)^2\frac{\omega_0^4kT}{24\pi\rho u^5}\left(1-3\sin^2\vartheta\cos^2\vartheta+\cos^4\vartheta\right), \quad (31)$$

where ϑ is the angle between the magnetic field and the principal axis of the axially-symmetric g tensor.

Taking anharmonicity into account, we have

$$\frac{1}{2T_{1d}^{\mathrm{anh}}}=\left(\frac{\Delta g}{g}\right)^2\frac{\omega_0^2\omega_D\hbar}{24\pi\rho u^4l_0}\left(1-3\sin^2\vartheta\cos^2\vartheta+\cos^4\vartheta\right). \quad (32)$$

At higher temperatures (Raman processes)

$$\frac{1}{2T_{1R}}=\left(\frac{\Delta g}{g}\right)^2\frac{\hbar^2\omega_0^2\omega_D^7}{36\pi^3\rho^2u^{10}}J_6\left(1+3\sin^2\vartheta\cos^2\vartheta\right). \quad (33)$$

If anisotropy of hyperfine structure is the cause of relaxation,[13] then a dependence on the number of the hyperfine component appears in the expressions for T_1 (i.e., a dependence on the nuclear spin projection M_I):

$$\begin{aligned}1/2T_{1d} &= \Delta A^2kT\omega_0^2I(I+1)\left[a+bM_I^2\right]/2\pi^2\rho u^5,\\ 1/2T_{1d}^{\mathrm{anh}} &= \Delta A^2\hbar\omega_D^2I(I+1)\left[a+bM_I^2\right]/2\pi^2\rho u^4l_0,\\ 1/2T_{1R} &= \Delta A^2\omega_D^7\hbar^2J_6I(I+1)\left[a'+b'M_I^2\right]/36\pi^3\rho^2u^{10}; \quad (34)\end{aligned}$$

the coefficients a, a′, and b, b′ are of the order of unity and depend on the equilibrium orientation of the radical relative to the external magnetic field; the quantity ΔA is expressed in frequency units.

In the simultaneous calculation of the anisotropy ΔA and Δg, there appear terms in Eq. (34) proportional to $\Delta A\Delta g$ and linear in M_I.

Using the ideas in Sec. 3 one can consider for a solid the problem of modulation of the intramolecular vibrations of the radical by the lattice vibrations, which leads to spin-lattice relaxation as a consequence of the modulation of the isotropic part of the hyperfine interaction (in liquids this mechanism has been considered by Valiev[14]).

The result of a calculation in the harmonic approximation[8] shows that in a solid the indicated mechanism is not effective, because it turns out that $1/T_1$ is proportional to the small quantity $\exp\left[-\Omega^2/2\Delta\Omega^2\right]$, where Ω is the frequency of the intramolecular vibrations, and $\Delta\Omega$ is the line width of Raman scattering or infrared absorption due to interaction with the remaining molecules of the sample in which the given radical is an impurity.

As calculation has shown, the non-adiabatic mechanism of relaxation associated with progressive vibrations of a many-electron radical is also weakly effective (the term of the form $p_\alpha v_\alpha$ in the electronic Hamiltonian, where p_α is the momentum of the electron). Numerical estimates show that processes associated with the hyperfine interaction can play a dominant role in the paramagnetic relaxation of radicals.

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