

Spin-Lattice Relaxation in Paramagnetic Substances with Allowance for Spin-Spin Interactions

L. K. AMINOV

Kazan' State University

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A formula is obtained connecting the spin-lattice relaxation time in paramagnetic substances with the correlation functions (or their spectral densities) of a spin system and a lattice that are isolated from one another. This formula serves as a convenient starting point for the discussion of various relaxation models in which the essential role is played by spin-spin interactions. As an example, we have considered a system of interacting paramagnetic ions with effective spin $S=1/2$, coupled to the lattice by the Kronig-Van Vleck mechanism. The dependence of the relaxation time on the magnitude and orientation of the external field is considered.

INTRODUCTION

SPIN-LATTICE relaxation in crystals is due principally to modulation by the lattice vibrations of the orbital motion of electrons of unfilled shells of paramagnetic ions (the Kronig-Van Vleck mechanism). The estimate of the relaxation time on the basis of this mechanism usually reduces to the calculation of the transition probabilities between a small number of lower levels of the paramagnetic ion.^[1] However, such an approach ceases to be satisfactory at low temperatures at which single phonon relaxation processes dominate. This is graphically demonstrated by the fact that the dependence on the value of the external magnetic field of the type $w \sim H^4$, predicted by the Van Vleck theory for the probability of direct transition between states of the Kramers doublet, is observed experimentally more frequently as an exception than as a rule. Moreover, at low temperatures, a dependence of the relaxation time on the concentration of paramagnetic ions and various anomalies of the temperature dependence are both observed. For the explanation of the observed peculiarities, the spin-lattice relaxation was proposed, to take into account the possibility of transfer of the energy of the spins to the lattice by means of a pair of ions coupled by strong exchange interaction,^[2] or through other rapidly relaxing centers.^[3] Here reference can be made to the assumption of Peskovatskii^[4] on the important role of the wings of the resonance line in the relaxation process. It is not excluded that the exchange of energy between the spin system and the lattice at low temperatures exists essentially because of other mechanisms of relaxation, for example, modulation by the lattice vibrations of exchange interactions between the spins.^[5] In the arbitrary case, it is seen to be necessary to take explicitly into account the interaction of paramagnetic centers with one another, which materially complicates the mathematical determination of the relaxation times. Therefore, the latter is usually estimated as a quantity that is the inverse in some fashion to the probability of relaxation transition of the individual paramagnetic ion, averaged over the spin system; in this connection, the problem naturally arises of a more rigorous basis of such a semiquantitative approach.

In the present work, we shall assume that the rate of establishing internal equilibrium in the spin system and in the lattice (which is identified with the thermostat) considerably exceeds the rate of spin-lattice relaxation. In this case, as is shown in Sec. 1, the relaxation time can be written down in the form of a convolution of certain spectral functions pertaining to the spin system and to the lattice. The resultant formula reduces the investigation of the spin-lattice relaxation to the calculation of the correlation functions for spin system and lattice that are isolated from one another. In Sec. 2, it is shown that the spectral function of the spin system is expressed in simple situations in terms of a function of the shape of the resonance line. In the concluding section 3, the problem of the field dependence of the spin-lattice relaxation time is discussed.

1. GENERAL FORMULA FOR THE SPIN-LATTICE RELAXATION TIME

If the spin-spin interaction in the paramagnetic material is much stronger than the spin-lattice interaction, then, after removal of the external perturbation, equilibrium is first established inside the spin system and is then preserved while equilibrium between the spins and the lattice is being established. In this case we can introduce the spin temperature T_S , and the equations for the populations of the levels of the spin system become the equations which determine the time change of the spin temperature. For not too low temperatures T_S and T (the lattice temperature), which exceeds, in the corresponding units, the splitting of the spin levels ω_{mn} , the equalization of the reciprocal temperatures takes place according to an exponential law, and the relaxation time is^[6,7]

$$\tau^{-1} = \left(\sum_{m,n} w_{mn} \omega_{mn}^2 \right) / 2 \sum_m \omega_m^2. \quad (1)$$

The indices m and n denote the stationary states of the spin system, w_{mn} is the transition probability between the states m and n , due to the spin-lattice interaction.

Equation (1), which was first proposed by Gorter,^[8] can be used very easily when the spin system consists of an individual paramagnetic ion. For a system consisting of a large number of mutually interacting para-

magnetic ions, it is impossible to find the stationary states and this formula becomes practically useless. We now alter it so as to connect the relaxation time with quantities which can at least in principle be investigated theoretically and experimentally.

We write down the transition probability between the states m and n in the form

$$w_{mn} = \frac{2\pi}{\hbar^2} \sum_{A,B} p_A |\langle mA | \mathcal{H}_i | nB \rangle|^2 \delta(\omega_{mn} + \omega_{AB}), \quad (2)$$

where \mathcal{H}_i is the Hamiltonian of spin-lattice interaction, $|A\rangle$ and $|B\rangle$ are the initial and final states of the lattice, and p_A is the probability of finding the lattice in the state $|A\rangle$. Further,

$$\begin{aligned} & \sum_{m,n} w_{mn} (E_n - E_m)^2 \\ &= -\frac{2\pi}{\hbar^2} \sum_{m,n,A,B} p_A \langle mA | [\mathcal{H}_S, \mathcal{H}_i] | nB \rangle \langle nB | [\mathcal{H}_S, \mathcal{H}_i] | mA \rangle \delta(\omega_{mn} + \omega_{AB}), \end{aligned} \quad (3)$$

where \mathcal{H}_S is the Hamiltonian of the spin system. We recall that in the writing out of Eq. (1), we used the high-temperature approximation $\hbar\Omega_{mn} \ll kT_S$ for an arbitrary pair of levels. In this approximation, the probability of finding the spin system in the state m has the form

$$p_m = \exp(-\beta E_m) / \sum_n \exp(-\beta E_n) \approx 1/Z,$$

where $\beta = \hbar(kT_S)^{-1}$, and Z is the number of states of the spin system. Keeping this in mind, we can introduce the factor Zp_m in Eq. (3) under the summation sign. But then, by definition (see, for example, ^[8]), the right side of (3) is nothing else than the spectral function J for the operator $[\mathcal{H}_S, \mathcal{H}_i]$:

$$\sum_{m,n} w_{mn} (E_m - E_n)^2 = -\frac{2\pi}{\hbar} ZJ([\mathcal{H}_S, \mathcal{H}_i], [\mathcal{H}_S, \mathcal{H}_i], 0), \quad (4)$$

and we arrive at the following expression for the relaxation time:

$$\tau^{-1} = -\frac{\pi}{\hbar} \frac{ZJ([\mathcal{H}_S, \mathcal{H}_i], [\mathcal{H}_S, \mathcal{H}_i], 0)}{\text{Sp } \mathcal{H}_S^2}. \quad (5)$$

The Hamiltonian of the spin-lattice interaction in the most general can be represented in the form

$$\mathcal{H}_i = \sum_{\alpha} V_{\alpha} Q_{\alpha}, \quad (6)$$

where V_{α} are the spin operators and Q_{α} the lattice operators. Making use of the delta function representation

$$\delta(\omega_{mn} + \omega_{AB}) = \int \delta(\omega_{mn} + \omega) \delta(\omega_{AB} - \omega) d\omega, \quad (7)$$

we rewrite Eq. (5) in its final form:

$$\tau^{-1} = \frac{\pi Z}{\text{Sp } \mathcal{H}_S^2} \sum_{\alpha,\beta} \int J_S([\mathcal{H}_S, V_{\alpha}], [\mathcal{H}_S, V_{\beta}], \omega) J_L(Q_{\alpha}, Q_{\beta}, -\omega) d\omega, \quad (8)$$

where the spectral functions J_S and J_L refer to the spin system and the lattice. The writing of the relaxation time in terms of the corresponding correlation functions can be shown to be sometimes more useful:

$$\tau^{-1} = \frac{Z}{2 \text{Sp } \mathcal{H}_S^2} \sum_{\alpha,\beta} \int \langle [\mathcal{H}_S, V_{\alpha}](t), [\mathcal{H}_S, V_{\beta}](0) \rangle_S \langle Q_{\alpha}(t), Q_{\beta}(0) \rangle_L dt. \quad (9)$$

The expression for the transition probability of the individual spin in terms of the correlation function of the lattice variables is widely used in the theory of paramagnetic relaxation in liquids (see, for example ^[8]), where these variables are random functions of time. In application to spin-lattice relaxation in solids, the method of lattice spectral functions has been developed by Aleksandrov.^[10] Equations (8) and (9) can be regarded as further generalizations of this method, as a result of which the spin variables in the expression for the spin-lattice relaxation times are also written down in the form of spectral densities of the individual correlation functions. In the following discussion, we shall concentrate our attention on this point, and we shall compute the spectral functions of the lattice variables with the help of very simple models.

2. DISCUSSION AND EXAMPLE OF USE OF THE GENERAL FORMULAS

In the derivation of Eqs. (8) and (9), we subdivided the paramagnetic material into a spin system and the lattice, but it is not necessary to mean by the lattice only the system of normal vibrations of the crystal. It can also be the system of conduction electrons and the system of rapidly relaxing centers—an arbitrary part of the thermostat, which is most tightly coupled with the spin system. Inasmuch as no special conditions are superimposed on the mechanism of spin-lattice relaxation, the resultant formulas can serve as the starting point for the consideration of quite varied relaxation models.

As an example, we consider a system of identical paramagnetic centers with effective spin $S = 1/2$ in a crystal possessing cubic symmetry. We assume that the relaxations take place basically as the result of the Kronig-Van Vleck mechanism, and we shall describe the vibrations of the lattice in the long wavelength approximation. Then the Hamiltonian of the spin-lattice interaction is written in the form

$$\begin{aligned} \mathcal{H}_i = & a(\mathbf{HS})(e_{xx} + e_{yy} + e_{zz}) + b[(\mathbf{HS} - 3H_z S_z)(e_{xx} + e_{yy} - 2e_{zz}) \\ & + 3(H_x S_x - H_y S_y)(e_{xx} - e_{yy})] + c[(H_x S_y + H_y S_x)e_{xy} \\ & + (H_x S_z + H_z S_x)e_{xz} + (H_y S_z + H_z S_y)e_{yz}], \end{aligned} \quad (10)$$

where a , b , and c are the constants of the spin-phonon interaction, \mathbf{H} is the external magnetic field, $e_{\alpha\beta}$ is the deformation tensor, and the coordinate axes are directed along the fourfold axes. In the long-wave approximation, the deformation at each point of the crystal is the same; therefore, the operator S in the Hamiltonian (10) represents the total spin of all the paramagnetic particles. Inasmuch as the total spin of the system is conserved in the absence of an external field, the Hamiltonian \mathcal{H}_i commutes with the field-independent part of the spin-Hamiltonian

$$\mathcal{H}_S = g\beta\mathbf{HS} + \mathcal{H}_S(0). \quad (11)$$

We also assume, for simplicity, that the magnetic field is directed along the z axis. Then, recognizing that $J_L(e_{yz}, e_{yz}, \omega) = J_L(e_{xz}, e_{xz}, \omega)$ by virtue of the cubic symmetry, we obtain the following expression for the relaxation time:

$$\tau^{-1} = \frac{2\pi(g\beta c)^2 H^4 Z}{\text{Sp } \mathcal{H}_S^2} \int J_{xx}(\omega) J_L(e_{yz}, e_{yz}, -\omega) d\omega, \quad (12)$$

where $J_{XX}(\omega) = J_S(S_X, S_X, \omega)$. As is seen, in the case considered, the spectral functions of the spin system in Eq. (8) reduce to the spectral density of the correlation function for the transverse component of the magnetization. This spectral density is connected with the imaginary part of the susceptibility,^[8] and through it with functions of the line shape $g(\omega)$ by the following relations:

$$2\pi\gamma^2 \text{th} \frac{\hbar\omega}{2kT_s} J_{xx}(\omega) = \chi''(\omega) = \frac{\pi N\gamma^2}{4} \text{th} \frac{\hbar\omega}{2kT_s} g(\omega), \quad (13)$$

where N is the number of paramagnetic ions.

We compute the lattice spectral function by means of the Debye model ($\omega_{qs} = |q|v_s$):

$$J_l(e_{vs}, e_{vs}, -\omega) = \frac{1}{4} \sum_{\mathbf{q}} \left(\frac{\hbar\omega_{\mathbf{q}s}}{2Mv_s^2} \right) (\lambda_v e_s + \lambda_t e_v)^2 \times [(1+n_{\mathbf{q}s})\delta(\omega_{\mathbf{q}s} - \omega) + n_{\mathbf{q}s}\delta(-\omega_{\mathbf{q}s} - \omega)] = \frac{1}{15} \frac{kT\omega^2}{\pi^2 d} \left(\frac{1}{v_l^2} + \frac{3}{2} \frac{1}{v_t^2} \right), \quad (14)$$

where \mathbf{q} is the wave vector, s the polarization, ω_{qs} the frequency of vibration of the lattice ($s = l$ for longitudinal and $s = t$ for transverse vibrations) λ the unit wave vector, v_s the sound velocity, \mathbf{e} the polarization vector, M the mass, d the density of the crystal, $n_{\mathbf{q}}$ the mean number of phonons of a given type. Further,

$$\text{Sp } \mathcal{H}_s^2 = (g\beta H)^2 \text{Sp } S_z^2 + \text{Sp } \mathcal{H}_{s0}^2(0) = \frac{NZ}{4} (g\beta)^2 (H^2 + H_{\text{loc}}^2), \quad (15)$$

where H_{loc}^2 is the mean square of the local field at the paramagnetic ions, due to the spin-spin interaction. If the local field, as is usually the case in paramagnets, is much weaker than the external field, then we have ultimately for a cubic crystal

$$\tau^{-1} = \frac{kT}{15\pi d\hbar} (cH)^2 \left(\frac{1}{v_l^2} + \frac{3}{2} \frac{1}{v_t^2} \right) \int g(\omega)\omega^2 d\omega. \quad (16)$$

If the external field is comparatively small, then we must expect that the Kronig-Van Vleck mechanism becomes ineffective and it is necessary to take into account the modulation of the spin-spin interactions with the vibrations of the lattice.

An expression similar to (16) was obtained for the relaxation rate by Peskovatskiĭ,^[4] with the spin system regarded as a set of two-level particles, the transition rates of which are distributed according to some definite law. Such a procedure, however, can serve only as a guideline, since it is practically impossible to take into account the fact that the mutual spin flips (which play an important role in energy transfer to the lattice) cause the initial distribution over the frequencies to change continuously. We see that the use of the general formula (8) eliminates the necessity of investigating in detail the behavior of the individual paramagnetic particles in the relaxation process.

3. FIELD DEPENDENCE OF THE SPIN-LATTICE RELAXATION TIMES

Equations (5), (8), and (9) are suitable for the investigation of the dependence of the spin-lattice relaxation on the magnitude and direction of the external magnetic field. When the relaxation is due to the Kronig-Van

Vleck mechanism, one can use the even simpler formula (16) for the discussion of the dependence on the magnitude of the field. If we consider a system of noninteracting spins $S = 1/2$, then $g(\omega) \sim \delta(\omega - \omega_0)$, $\hbar\omega_0 = g\beta H$ and the relaxation time, as has already been noted in the Introduction, is proportional to H^4 . Evidently, a dependence that is close to this will be obtained every time one has a sharp resonance line with rapidly decaying wings. If, say, the line then has a Lorentz shape with width σ and is cut off at the frequency $\Delta \gg \omega_0$, then, in addition to the component that is proportional to H^4 , the relaxation time will also contain a component $\sim H^2\sigma\Delta$. As follows from the experiments of Peskovatskiĭ^[11] the assumption that the wings of the resonance line are sufficiently long cannot be regarded as entirely without foundations. If this assumption is correct then, as is seen, the deviation from the law $\tau^{-1} \sim H^4$ can be explained within the framework of the Kronig-Van Vleck mechanism.

It is pertinent here to note that $g(\omega)$ in Eq. (16) is the line shape determined by the spin-spin interaction, and the fact that, because of the spin-lattice interaction, Lorentzian lines are also obtained for a system of isolated spins, with wings that extend up to frequencies of the order of the Debye frequency,^[12] gives nothing new for the field dependence of the spin-lattice relaxation time.^[13]

So far as the orientation dependence of τ^{-1} is concerned, it is very simply determined with the help of consideration of the invariance relative to transformation of the symmetry group of the crystal. In view of the fact that the numerator and denominator in the right side of Eqs. (5) and (8) are polynomials of low degree in H , the calculations reduce to the construction of the invariants of such polynomials. For definiteness, let us consider again the system of spins $S = 1/2$, assuming that the Zeeman energy materially exceeds the energy of the spin-spin interaction. Then

$$\text{Sp } \mathcal{H}_s^2 \sim g_{\alpha\beta} g_{\alpha\gamma} H_\beta H_\gamma = g_{\alpha\beta} g_{\alpha\gamma} n_\beta n_\gamma H^2 = g^2 H^2, \quad J_s([\mathcal{H}_s, \mathcal{H}_1], [\mathcal{H}_s, \mathcal{H}_1], 0) \sim H_\alpha H_\beta H_\gamma H_\delta, \quad (17)$$

where $g_{\alpha\beta}$ is the "g-tensor," and the relaxation time is rewritten in the form

$$\tau^{-1} = g^{-4} A_{\alpha\beta\gamma\delta} n_\alpha n_\beta n_\gamma n_\delta, \quad (18)$$

where $A_{\alpha\beta\gamma\delta}$ does not depend on the orientation of the magnetic field.

It is curious that the functional form of the orientation dependence turns out to be of the same accuracy as for a system of mutually isolated spins.^[14] The difference lies only in the magnitude of the constants, by which are multiplied the various invariants of the group symmetry, composed from the tensors $n_\alpha n_\beta n_\gamma n_\delta$.

In conclusion, we note that the proposed scheme can be used without practically any change for consideration of two-phonon processes in the first place, in spin-lattice interaction and in the second place, if the intermediate levels of the paramagnetic ions are separated from the fundamental intervals, significantly exceeding the limiting energy of the phonons.

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- ¹J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).
- ²J. H. Van Vleck, Quantum Electr., Columbia Univ. Press, New York, 1960, p. 392.
- ³V. A. Skrebnev, Phys. Status Solidi **36**, 81 (1969).
- ⁴S. A. Peskovatskiĭ, Phys. Status Solidi B **44**, 551 (1971).
- ⁵S. A. Al'tshuler, Zh. Eksp. Teor. Fiz. **43**, 2318 (1962) [Sov. Phys. JETP **16**, 1634 (1963)].
- ⁶C. J. Gorter, Paramagnetic Relaxations [Russian Translation, IIL, 1963].
- ⁷C. Slichter, Basic Theory of Magnetic Resonance [Russian Translation, Mir press, 1967].
- ⁸L. Bonch-Bruевич and S. V. Tyablikov, Metod funktsii Grina v statisticheskoi mekhanike (Green's Function Method in Statistical Mechanics) Fizmatgiz, 1951.
- ⁹A. Abragam, Nuclear Magnetism [Russian translation, IIL, 1963].
- ¹⁰I. V. Aleksandrov, Zh. Eksp. Teor. Fiz. **48**, 869 (1965) [Sov. Phys. JETP **21**, 580 (1965)].
- ¹¹S. A. Peskovatskiĭ, Phys. Status Solidi B **44**, 543 (1971).
- ¹²L. K. Aminov, Zh. Eksp. Teor. Fiz. **48**, 1398 (1965) [Sov. Phys. JETP **21**, 934 (1965)].
- ¹³L. K. Aminov, Materials of the All-Union Jubilee Conference on Paramagnetic Resonance, Part 2, Kazan' State University Press and Kazan' Physico-technical Institute, Academy of Sciences, USSR, Kazan', 1970, p. 15.
- ¹⁴L. K. Aminov, Fiz. Tverd. Tela **11**, 1707 (1969) [Sov. Phys. Solid State **11**, 1383 (1969)].

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