ON THE THEORY OF THE SHAPE OF PARAMAGNETIC RESONANCE LINES

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The dependence of the spin-lattice relaxation time on the frequency of an alternating external field is investigated in paramagnetic crystals, using the diagram technique developed for an arbitrary approximation to an external perturbation. The dependence leads to a high-frequency "cut-off" of the absorption line. The line shape near the resonant frequency is affected only if the main contribution to relaxation is due to single-phonon processes. Some effects not accounted for by the linear theory are also considered.

THE phenomenological Bloch equations[1] are widely used to describe the variation of the magnetization of a paramagnetic substance with time in an alternating external field. In these equations, relaxation effects are taken into account by means of two constant time parameters, T_1 and T_2. The stationary solutions in the case of an oscillating field perpendicular to the dc field indicate the presence of a resonant absorption of energy from the alternating field. The intensity of the absorption as a function of the frequency of the external field is a Lorentz function, and the width of the corresponding curve is determined by the parameters T_1 and T_2. It is clear, however, that the alternating external field should have some effect on the relaxation processes in the system, and one would expect the parameters T_1 and T_2 to be, generally speaking, functions of the frequency and amplitude of this field. In a recent paper[2] Argyres and Kelley paid particular attention to this fact and its result, namely, that the shape of the absorption line will be non-Lorentzian. It would be interesting to find out just how great the theoretically predicted deviations from the Lorentzian shape would be in the case of any real model.

Absorption lines that are nearly Lorentzian in shape are observed when the dipole-dipole interactions in the paramagnetic substance can be neglected either because of a low concentration of paramagnetic centers or because these interactions are averaged out in motion. Hence an appropriate model for study is a collection of identical independent spins that are interacting with a surrounding thermal reservoir. We shall treat the crystal lattice as this reservoir.

For the calculations we shall use a diagram method, which we formulate following Konstantinov and Perel',[3] but for an arbitrary order in the external perturbation rather than being limited to the linear approximation. Besides the possibility of a relatively easy extension beyond the linear theory, this technique, compared to the usual Green function method, has the further advantage that by means of it relaxation processes of arbitrary order are easily taken into account. The first section of this paper outlines the method. In the second section we carry out a calculation of the susceptibility of the system in the oscillating external field, and in the third section we discuss the results obtained.

1. DIAGRAM TECHNIQUE FOR CALCULATING THE EFFECTS OF AN ARBITRARY ORDER IN THE EXTERNAL PERTURBATION

Let $\mathcal{H} = \mathcal{H}_0 + V$ be the Hamiltonian of the system in the absence of the alternating field, and $\mathcal{H}'(t) = -AH(t)$ be the Hamiltonian of the interaction of the system with the field, described by a tensor $H(t)$ and being turned on adiabatically at time $t = -\infty$. Solving the equation for the density matrix of the system

$$i\frac{\partial\rho}{\partial t} = [\mathcal{H} + \mathcal{H}'(t), \rho]$$

by successive approximations, we find the corrections to the unperturbed density matrix (cf. [4]):

$$\rho_0 = \exp(-\beta\mathcal{H}) / \mathrm{Sp}\exp(-\beta\mathcal{H}), \quad \beta = (kT)^{-1},$$

$$\Delta_k\rho = \left(\frac{1}{i}\right)^k \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \ldots \int_{-\infty}^{t_{k-1}} dt_k \exp(-i\mathcal{H}t)[\mathcal{H}_{t_1}'[\mathcal{H}_{t_2}' \ldots [\mathcal{H}_{t_k}', \rho_0]\ldots]] \exp(i\mathcal{H}t). \tag{1}$$

Here

$$\mathcal{H}_t' = \exp(i\mathcal{H}t)\mathcal{H}'(t)\exp(-i\mathcal{H}t).$$

Now the correction of k-th order in the external perturbation for an arbitrary physical quantity B pertaining to the system can be written in the form

$$\Delta_k B = \mathrm{Sp}\,\Delta_k\rho\cdot B.$$

Writing out the commutators in the trace and using the identity

$$\exp\{-i\mathcal{H}(z_1-z_2)\} = \exp\{-i\mathcal{H}_0 z_1\}\left[T_L \exp\left(\frac{1}{i}\int_{z_2}^{z_1} V_z dz\right)\right]\exp\{i\mathcal{H}_0 z_2\}, \quad (2)$$

we obtain

$$\Delta_k B = \sum_C (-1)^s \left(\frac{1}{i}\right)^k \times (\mathrm{Sp}\exp(-\beta\mathcal{H}))^{-1}\int_{-\infty}^{t}\ldots\int_{-\infty}^{t_{k-1}} \mathrm{Sp}\Big\{\exp(-\beta\mathcal{H}_0) \times T_C\Big[\exp\Big(\frac{1}{i}\int_C V_z dz\Big)\mathcal{H}_1'\ldots\mathcal{H}_k' B_0\Big]\Big\} dt_1\ldots dt_k + \mathrm{c.c.} \quad (3)$$

In (2) the integral is taken over a contour L drawn in arbitrary fashion in the complex "time" plane from z_2 to z_1. The operators following the symbol T_C should be ordered on the contour C, i.e., they are arranged from left to right on this contour in order of the increase in their "times." The contours C that correspond to the different terms in (3) are conveniently drawn such that they consist of a vertical part $t_i + i\beta \to t_i$ ($t_i = t, t_1, \ldots, t_{k-1}$), appearing at the beginning of the contour, and upper and lower horizontal parts.

The upper horizontal part divides into two—the left $t_i \to t_k$, which is the continuation of the contour, and the right, which appears at the end of the contour and ends at the "terminal" t_i. The vertical and left upper horizontal parts of the contour do not contain terminals (the moments of time at which the system exchanges energy with the external field); the right part contains the terminal t_i as well as an arbitrary selection of terminals $t_1, \ldots, t_{i-1}$; the remaining terminals lie in the lower horizontal part. All possible contours C for the case k = 3 are shown in Fig. 1.

In Eq. (3), s equals the number of terminals in the upper horizontal portion of the contour, and all operators are written in the interaction representation with unperturbed Hamiltonian $\mathcal{H}_0$:

$$V_z = \exp(i\mathcal{H}_0 z)V\exp(-i\mathcal{H}_0 z),$$
$$\mathcal{H}_k' = \exp(i\mathcal{H}_0 t_k)\mathcal{H}'(t_k)\exp(-i\mathcal{H}_0 t_k).$$

Expanding now the T-exponent in Eq. (3), we represent $\Delta_k B$ in the form of a series:

$$\Delta_k B(t) = \sum_C \sum_n \int_{-\infty}^{\infty}\ldots\int_{-\infty}^{\infty} H(\omega_1)\ldots H(\omega_k) G_C^n(\omega_1,\ldots,\omega_k)\, d\omega_1 \ldots d\omega_k + \mathrm{c.c.}$$

$$G_C^n(\omega_1,\ldots,\omega_k) = (-1)^{s+k}\left(\frac{1}{i}\right)^{n+k}(\mathrm{Sp}\exp(-\beta\mathcal{H}))^{-1}\int_{-\infty}^{\infty} e^{s_1 t_1}dt_1 \ldots \int_{-\infty}^{\infty} e^{s_k t_k}dt_k \int_C dz_1 \ldots \int_C^{z_{n-1}} dz_n\, \mathrm{Sp}\{\exp(-\beta\mathcal{H}_0) \times T_C[V_{z_1}\ldots V_{z_n} A_1 \ldots A_k B_0]\}. \quad (4)$$

Here $s_i = i\omega_i + \sigma$, where σ is a positive, infinitely small quantity.

We shall in what follows consider a system of identical paramagnetic ions interacting with the vibrations of the crystalline lattice (the phonon field) in which they are imbedded. Let us apply an alternating magnetic field $\mathbf{H}(t)$ to the system and inquire after the behavior of the magnetization $\mathbf{M}$. We have then

$$A = B = \mathbf{M} = \gamma\sum_i \mathbf{S}^i, \quad \mathcal{H}_0 = \sum_i \mathcal{H}_i + \mathcal{H}_l, \quad V = \sum_i V^i,$$

where γ is the gyromagnetic ratio, and the index i numbers the individual ions (spins), $\mathcal{H}_l$ is the Hamiltonian of the lattice (equal to the sum of the energies of the individual normal vibrations), and V^i is the Hamiltonian of the interaction of the i-th spin with the lattice, which we write in the form

$$V^i = i\sum_{\mathbf{q},\nu} F_{\mathbf{q}\nu}(S^i)\left(b_{\mathbf{q}\nu}\exp(i\mathbf{q}\mathbf{r}_i) - b_{\mathbf{q}\nu}^+\exp(-i\mathbf{q}\mathbf{r}_i)\right). \quad (5)$$

The operator $F_{\mathbf{q}\nu}(S^i)$ acts only on states of the i-th spin, $b_{\mathbf{q}\nu}^+$ and $b_{\mathbf{q}\nu}$ are the creation and annihilation operators of a phonon with wave vector $\mathbf{q}$ and polarization ν, and $\mathbf{r}_i$ is the radius-vector of the i-th spin. Writing down the Hamiltonian for the perturbation in this form means that only a single-frequency mechanism of spin-lattice interaction (the Kronig-Van Vleck mechanism[5]) is being considered. But then, this assumption is not a very strong limitation on the theory and is necessary only to make the model concrete.

The trace in Eq. (4), after substitution into it of $\mathcal{H}_0$ and V decomposes into a product of spin and lattice parts. It is convenient to display the dependence of this trace on time in explicit form by

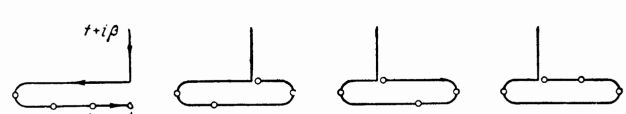

FIG. 1.

using a representation in which $\mathcal{H}_0$ is diagonal, and to represent the integrals over $z_1, \ldots, z_n$ as sums of integrals with a different arrangement of the times z on the contour of integration C relative to the terminals and relative to each other, which permits the successive integration over the times z_l and t_i to be carried out (cf. [3]). (We shall call the points representing the times z on the contour "vertices.") Further, the lattice part of the trace is expanded by Wick's theorem,[6] as a result of which it is resolved into a sum of all possible product pairs of the type

$$\mathrm{Sp}\,\{\rho_{00}\, T\,[(b_{\mathbf{q}\nu}^{+})_{z_1}\,(b_{\mathbf{q}\nu})_{z_2}]\},$$

each of which can be correlated with a line directed from the point z_1 of the appropriate contour to the point z_2. We shall call the phonon line "regular" if z_1 precedes z_2 on the contour; otherwise we call the line "irregular."[3] The spin part of the trace decomposes into a product of the traces from the operators that pertain to the individual spins. We stipulate that lines joining the appropriate points correspond to the spin states in one or another "time" interval on the contour. The lines pertaining to the same spin form a cycle, and all lines of the cycle, with the exception of one—that joining the "latest" point of the cycle with the "earliest" one—are regular. By ρ_{00} above we mean the quantity

$$\exp(-\beta\mathcal{H}_0)\,/\,\mathrm{Sp}\exp(-\beta\mathcal{H}_0).$$

We shall construct further horizontal and vertical sections between every two neighboring points plotted on the contour.

As a result we obtain that G_C^n is written as a sum of all possible terms, to each of which corresponds a graph—the contour C with its k terminals and n vertices, the spin and phonon lines, the vertical and horizontal sections. To the elements of the graph correspond factors of the analytical expressions according to the following rules:

1. To each vertex corresponds a factor $[F_{\mathbf{q}\nu}(S^i)]_{mn}$, where the subscripts $\mathbf{q}$ and ν pertain to a phonon arriving at the vertex, and the subscripts m and n to the spin states entering and leaving the vertex. To each terminal corresponds a factor of the form γS^i_{mn}. In addition, to each vertex in the lower horizontal portion there corresponds the factor $-i$, in the upper the factor i, and in the vertical part the factor -1; to each terminal in the lower horizontal portion (apart from t) corresponds the factor i, in the lower the factor $-i$. The factor corresponding to the terminal t is $\exp[(s_1 + \ldots + s_k)t]$.

2. To each vertical section corresponds the factor $(\sum^{l} s_i + i\omega_{ab})^{-1}$, where ω_{ab} is the difference in the energies of the lines entering the area to the right of the section and leaving it, and l is the number of terminals to the left of the section. To each horizontal section corresponds the factor $(p + \omega_{ab})^{-1}$, where ω_{ab} is the difference in the energies of lines entering the area below the section and leaving it.

3. To each regular phonon line corresponds the factor $(1 + n_{\mathbf{q}\nu})\exp(i\mathbf{q}\cdot\mathbf{r}_{ij})$, to an irregular line, $n_{\mathbf{q}\nu}\exp(i\mathbf{q}\cdot\mathbf{r}_{ij})$. Here $n_{\mathbf{q}\nu} = \mathrm{Sp}(\rho_{00} b^{+}_{\mathbf{q}\nu} b_{\mathbf{q}\nu})$; i (j) is the number of the spin with which a phonon interacts and is annihilated (created); $\mathbf{r}_{ij} = \mathbf{r}_i - \mathbf{r}_j$. In addition, to each irregular spin line corresponds the Boltzmann factor

$$n_m = \exp(-\beta E_m)\,/\,\mathrm{Sp}\exp(-\beta\mathcal{H}_i),$$

where m is the quantum number of the state described by this line.

The summation is carried out over the repeated indices, and to obtain G_C^n it is necessary to carry out an inverse Laplace transformation from the variable p to β.

Although in formulating this technique the relative magnitudes of $|\mathcal{H}_0|$, $|V|$, $|\mathcal{H}'|$ do not play a role, the method acquires real value for $|V|$, $|\mathcal{H}'| \ll |\mathcal{H}_0|$. Henceforth we shall assume that these conditions are fulfilled.

2. CALCULATION OF THE SHAPE OF THE ABSORPTION LINE OF A PARAMAGNETIC SUBSTANCE

Now let the alternating magnetic field be periodic and directed along the x axis:

$$H(t) = iH\cos\omega t, \quad H(\omega') = \tfrac{1}{2}H[\delta(\omega' - \omega) + \delta(\omega' + \omega)].$$

Representing the correction to the magnetization M_x in the form

$$\Delta M_x(t) = \chi'(\omega)H\cos\omega t + \chi''(\omega)H\sin\omega t + \ldots,$$

we find that only graphs with an even number of terminals contribute to $\chi''(\omega)$.

It is convenient to modify the correspondence rule so that it is possible to write down directly an expression for χ''. For this, it is sufficient to place the factor $\frac{1}{2}(H/2)^{k-1}(\pm i)$ in correspondence with the terminal t instead of the factor $\exp[(s_1 + \ldots + s_k)t]$, and to agree to choose only those graphs for which $\Sigma s_l = \pm i\omega + \sigma$, whereby the sign in front of $i\omega$ in the last expression also determines the sign of the added factor. In particular, in the linear approximation and without taking the internal interactions in the system into account, we have

$$\chi_1''(\omega) = \sum_{m,n} I_{mn}\delta(\omega - \omega_{mn}),$$

$$I_{mn} = \pi N\gamma^2 |(S_x)_{mn}|^2 (n_n - n_m), \qquad (6)$$

where N is the number of spins.

We return to the calculation of $\chi''(\omega)$ in the presence of the spin-lattice interaction. Here we shall not consider interactions of the spins via the phonon field, which will permit us to do the problem of a single particle and take into account diagrams with only one spin cycle.

Diagrams with a different number of vertices in the vertical part correspond to terms of the power series in $|V|/kT$ and $|V|/|\mathcal{H}_0|$ of the perturbation theory. Without any essential loss of generality of the considered problem, we can set $|V| \ll kT$, and, considering further that $|V| \ll |\mathcal{H}_0|$, we limit ourselves to investigating diagrams without vertices in their vertical parts. Actually, this is equivalent to the approximation $\rho_0 \approx \rho_{00}$.

When the frequency of the external field approaches one of the intervals between the spin levels ω_{nm}, the quantity $(s + i\omega_{mn})^{-1}$ increases without limit. Hence it is necessary for us to sum up the diagrams with an arbitrary number of identical "resonant" denominators of the type $(s + i\omega_{mn})^{-1}$, which are obtained when only two spin lines pass through the vertical section.

As a preliminary step, we carry out a partial summation of diagrams differing from each other only in the number of "irreducible" parts between two neighboring terminals. A part of the graph that is bounded by two resonant sections and does not contain within itself any other such sections and terminals, is called irreducible.[3] We shall represent the sum of all possible irreducible parts in the graph as a square; then the aforementioned partial summation is pictured graphically as in Fig. 2. As a result, we obtain that the calculation of the spin-lattice interaction leads simply to a replacement of the denominator $(s + i\omega_{mn})^{-1}$ by

$$(s + i\omega_{mn} + \Gamma_{nm})^{-1} \equiv s_{nm}^{-1},$$

where $\Gamma_{nm}(s)$ is an analytical expression corresponding to the sum of the irreducible parts.

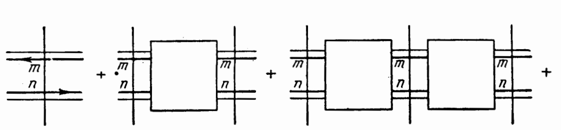

FIG. 2.

We now assume that the spin levels are not equidistant, and the spectrum consists of well-resolved lines. In other words, the conditions $|\omega_0 - \omega_0'| \gg |V|$, where ω_0 and ω_0' are the different frequencies of the spin system, should be fulfilled. Then it turns out to be possible to neglect diagrams that contain simultaneously the factors $(s - \omega_0)^{-1}$ and $(s - \omega_0')^{-1}$. Actually, for example, the contribution of a diagram with a factor $[(s - \omega_0)(s - \omega_0')]^{-1}$ compared to the contribution of a diagram to which corresponds a factor $(s - \omega_0)^{-2}$, is of order $(\omega - \omega_0)/(\omega - \omega_0')$; in the limits of the line width at frequency ω_0 this is less than $|V|/(\omega_0 - \omega_0')$. In a similar fashion it is possible to show that it is sufficient to consider only diagrams in which the phonon lines join vertices only between pairs of neighboring terminals. As a result, it turns out to be possible to make use of "skeleton" diagrams, in which only terminals and spin lines are plotted; to each vertical section of such a diagram will correspond a factor of the type s_{nm}^{-1}.

Let us consider diagrams of the third order. The analytical expression for χ'' corresponding to them is the following:

$$\chi_3''(\omega) = \sum_{m,n}\left(\frac{I_{mn}}{\pi}\operatorname{Re}\frac{1}{s_{mn}}\right)\left(-\frac{|\gamma H(S_x)_{mn}|^2}{\Gamma_{mn}'}\right)\operatorname{Re}\frac{1}{s_{mn}}$$
$$+\sum_{m,n,k}\left\{\left(\frac{\gamma H}{2}\right)^2\operatorname{Re}\frac{1}{(2s)_{mk}}\left(\frac{1}{s_{mn}}-\frac{1}{s_{nk}}\right)\right.$$
$$\times\left[-\frac{I_{mn}}{\pi}|(S_x)_{kn}|^2\frac{1}{s_{mn}}+\frac{I_{nk}}{\pi}|(S_x)_{mn}|^2\frac{1}{s_{nk}}\right]$$
$$+\frac{(\gamma H)^2}{2\Gamma_{nn}}\operatorname{Re}\frac{1}{s_{mn}}\operatorname{Re}\frac{1}{s_{nk}}\left[\frac{I_{mn}}{\pi}|(S_x)_{kn}|^2\right.$$
$$\left.\left.+\frac{I_{nk}}{\pi}|(S_x)_{mn}|^2\right]\right\},$$

$$\Gamma_{mn}' = 2\Gamma_{mm}\Gamma_{nn}/(\Gamma_{mm}+\Gamma_{nn}). \qquad (7)$$

In obtaining Eq. (7), we took into account the equality $\Gamma_{mn}(s) = \Gamma_{mn}^*(s^*)$, which is easily obtained by a comparison of the corresponding diagrams.

In the region of resonant frequencies, the greatest contribution to χ_3'' is given, obviously, by the first sum. The same situation also occurs for the higher order corrections, and, taking only such contributions into account, we obtain as a result the summation

$$\chi''(\omega)$$
$$= \sum_{m,n}\frac{I_{mn}}{\pi}\frac{T_{nm}(\omega)}{1+(\omega-\omega_{mn}')^2T_{nm}^2(\omega)+\gamma^2H^2T_{nm}(\omega)T_{nm}'};$$

$$T_{nm}(\omega) = 1/\mathrm{Re}\,\Gamma_{nm}(\omega), \quad T_{nm}' = |(S_x)_{mn}|^2/\Gamma_{mn}',$$
$$\omega_{mn}' = \omega_{mn} - \mathrm{Im}\,\Gamma_{nm}(\omega) \quad (8)$$

(T' is independent of frequency). A similar expression is obtained also when the spin has equidistant levels; hence we shall not give this case any special consideration.

3. DISCUSSION OF RESULTS

First we shall make the following observation concerning the terms that were discarded in obtaining $\chi''(\omega)$. The first two members of the triple sum in (7) show that in third order with respect to the alternating field there arise additional resonance lines at frequencies that are half-sums of the fundamental frequencies (see, for example, [5]). In the vicinity of resonance this contribution to χ'' has the form

$$\delta_1\chi''(\omega) = \sum_{m,n,k} \frac{2\Gamma_{km}}{(2\omega-\omega_{mk})^2+\Gamma_{mk}^2}\frac{(\gamma H)^2}{\pi(\omega_{mn}-\omega_{nk})^2}$$
$$\times [I_{mn}|(S_x)_{nk}|^2 + I_{nk}|(S_x)_{mn}|^2]. \quad (9)$$

The following terms in the triple sum in (7) can turn out to be important at low temperatures. Consider a three-level system (non-equidistant, Fig. 3). In the linear approximation the absorption at frequency ω_{mn} at low temperatures can be very small on account of the low population of levels m and n. In the third approximation this absorption will be determined by the population of the lower level. The ratio of the intensities of absorption in the third and first orders is found to be equal to

$$\frac{J_3}{J_1} = \frac{|\gamma H(S_x)_{nk}|^2}{(\omega_{mn}-\omega_{nk})^2}\frac{\Gamma_{nk}}{2\Gamma_{nn}}\frac{n_k-n_n}{n_n-n_m}. \quad (10)$$

It follows from this that in some cases the resonance effect for the upper levels, which vanishes as the temperature is lowered, can be evoked anew by increasing the radio-frequency field. For example, when $\omega_{mn} \approx 1\ \mathrm{cm}^{-1}$, $T \approx 0.1°$ K, $|\omega_{mn} - \omega_{nk}| \approx 10$ Oe, $H \approx 0.1$ Oe, the ratio $J_3/J_1 \approx 3$. It is seen that rather exceptional conditions are required to observe the effect.

We note further that Eq. (8) corresponds to the solution of the unmodified Bloch equations (see [1]), namely, χ'' goes to zero if the spin levels are not split in the absence of the alternating field. This is because we used the approximation $\rho_0 \approx \rho_{00}$, which is valid only for $|V| \ll |\mathcal{H}_0|$. Basically, Eq. (8) differs from the solution to the Bloch equations in that the quantity T_{nm} turns out to be independent of frequency. Graphs with differing numbers of vertices determining $\Gamma_{nm}(\omega)$ correspond to relaxation processes with participation of one, two, or more phonons.

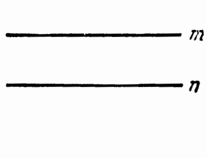

FIG. 3.

At sufficiently low temperatures, single-phonon processes constitute the main contribution. The corresponding expression for $\Gamma_{mn}(s)$ can be obtained from the diagram equation shown in Fig. 4.

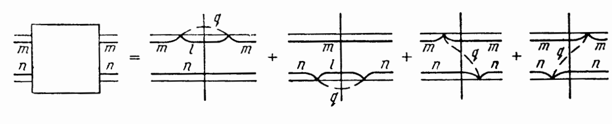

FIG. 4.

Replacing the summation over the wave vectors of the phonons by an integration, we obtain for the real part the expression

$$\mathrm{Re}\,\Gamma_{mn}(\omega) = \pi\sum_\nu\Big\{\sum_l\Big[\langle(1+n_q)|F_{ml}|^2\rho\rangle|_{\omega_q=-\omega-\omega_{nl}}$$
$$+\langle n_q|F_{ml}|^2\rho\rangle|_{\omega_q=\omega+\omega_{nl}} + \langle(1+n_q)|F_{nl}|^2\rho\rangle|_{\omega_q=\omega+\omega_{lm}}$$
$$+\langle n_q|F_{nl}|^2\rho\rangle|_{\omega_q=-\omega-\omega_{lm}}\Big]$$
$$-\langle F_{mm}F_{nn}(1+2n_q)\rho\rangle|_{\omega_q=\pm(\omega+\omega_{nm})}\Big\}. \quad (11)$$

Here ρ is the distribution function for the lattice vibrations, and the brackets $\langle\ldots\rangle$ indicate integration over the directions of the phonons of a given frequency.

At resonance ($\omega \approx \omega_{mn}$), Eq. (11) is the sum of relaxation transition probabilities from levels m and n to all the others. Thus, the usual quantum mechanical interpretation of the parameters $\Gamma_{mn}(T_{mn})$ is valid only in the vicinity of the resonance frequency. At high frequencies ($\omega > \omega_{lim}$) the distribution function ρ is equal to zero, and $\Gamma_{mn} \to 0$. Thereby, from the high-frequency side the line appears to be cut-off in a natural way.

Let us consider in somewhat more detail the frequency dependence of Γ_{mn} for a two-level system, assuming for simplicity that the Debye model of lattice vibrations is valid. We single out in Eq. (11) in an explicit way the dependence on ω_q, by considering that

$$\rho_{q\nu} \sim \omega_q^2 \ (\omega_q < \omega_{\mathrm{lim}}), \quad n_q = (e^{\beta\omega_q}-1)^{-1}, \quad F_{q\nu} \sim \omega_q^{1/2}$$

(see, for example, [7]):

$$\operatorname{Re} \Gamma_{mn}(\omega) = (A_{mn} + B_{mn} e^{\beta\omega}) \frac{\omega^3 \theta(\omega_{1\mathrm{im}} - \omega)}{e^{\beta\omega} - 1}. \quad (12)$$

Here θ is a unitary discontinuous function. Once again we emphasize that in the phenomenological theory the parameter Γ_{mn} is regarded as a constant, and its quantum mechanical calculation by perturbation theory is carried out according to Eq. (11) or (12), with the assumption that $\omega = \omega_{mn}$.

We now point out some other consequences of the dependence of the relaxation term Γ on frequency. The function $\chi''(\omega)$ turns out to be different from Lorentzian in all frequency regions and is asymmetric. The half-width of the resonance line is:

$$\Delta\omega_{mn} \approx (\Delta\omega_{mn})_0 \left[1 - \frac{3}{2} \frac{(\Delta\omega_{mn})_0^2}{\omega_{mn}^2} \right],$$

where $(\Delta\omega_{mn})_0 = \operatorname{Re} \Gamma_{mn}(\omega_{mn})$ is the half-width of a Lorentzian line. From this it is clear that the strongest departure from the Lorentzian shape should be observed in the case of wide lines.

For spin-lattice relaxation processes of higher order, the frequency dependence of Γ_{mn} is found to be more weakly expressed and will be important only at very high frequencies, so that at high temperatures, when single-phonon processes play an insignificant role, the observed part of the line will be practically purely Lorentzian. For relaxation processes with the participation of any number of phonons, however, the limitation of the spectrum of lattice vibrations will lead to a cutoff of the line at sufficiently high frequencies. Of course, the sudden drop of the function $\chi''(\omega)$ at these or other frequencies is associated with the Debye model of lattice vibrations. Actually, by the term "cut-off" one should understand a transition to a region of frequencies where the function begins to diminish very much faster. The shift in the resonance lines caused by the spin-lattice interaction also depends very weakly on frequency.

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