QUANTUM THEORY OF RESONANCE AND RELAXATION ABSORPTION OF ULTRASOUND IN PARAMAGNETIC CRYSTALS

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The double-time Green's function technique is used to develop a theory of resonance and relaxation spin-phonon absorption of ultrasound in paramagnetic crystals. A chain of equations is obtained for the Green's functions of the spin operator components for $S = 1/2$ and $S = 1$. This chain is found to be closed if only one-quantum phonon absorption and emission processes are considered. The absorption coefficient is found as a function of the frequency and the applied magnetic field. A relation is established between the absorption coefficient and the paramagnetic spin-lattice relaxation times.

THE resonance absorption of sound by paramagnetic spin systems is established as the most effective method for studying the spin-phonon interaction (see, for example,[1,2]). Comparatively recently, Kutuzov[3] discovered the relaxation paramagnetic absorption of ultrasound, which depends on the value and direction (relative to the axes of the crystal) of the constant external magnetic field.

Theoretical consideration of the resonance effect and its quantitative estimate were first published by Al'tshuler as early as 1952.[4] Further theoretical researches were principally devoted to detailed calculation of the probabilities of spin-phonon transitions for specific paramagnetic crystals. However, the formula obtained by Al'tshuler[4] for the coefficient of resonance sound absorption contains, in addition to the transition probabilities, also the function $g(\omega)$ of the absorption line shape, which was not computed; certain assumptions made relative to its shape made it possible, for example, to compute the moments of the absorption curves.[5] It is especially important to know the function $g(\omega)$ in detail to find the frequency dependence of the relaxation sound absorption.

The goal of the present research is the quantum statistical calculation[1)] of the sound absorption coefficient as a function of the frequency for arbitrary direction and polarization of the sound wave relative to the crystallographic axes and applied external magnetic field.

In analogy with the tensor of paramagnetic susceptibility, we introduce the fourth rank tensor $\chi_{iklm}(\omega)$ of paraacoustic susceptibility, the imaginary part of which determines the sound absorption coefficient as a function of frequency in an anisotropic crystal. Both the resonance and the relaxation interactions of the sound wave with the paramagnetic centers are described by certain combinations (determined by the experimental conditions) of the components of this tensor.

The experimental determination of the components of χ_{iklm} essentially reduces to the measurement of the constants of spin-phonon interaction.

1)A semi-phenomenological calculation of the relaxation sound absorption for the one-dimensional case has been performed by Kochelaev.[6]

1. GENERAL RELATIONS

In the approximation of the deformation potential, it is convenient to connect the general expression for the operator of interaction of the electron spin S with phonons with the spin Hamiltonian in the following way:

$$\mathscr{H}_{\text{c}\Phi} = \beta H_i \delta g_{ik} S_k + S_i \delta D_{ik} S_k \quad (i,\ k = x,\ y,\ z), \tag{1}$$

where δg_{ik} and δD_{ik} are the variations of the tensors g and D of the spin Hamiltonian with the elastic vibrations of the lattice, which depend linearly on the deformation tensor e_{ik}:

$$\delta g_{ik} = F_{iklm} e_{lm}; \quad \delta D_{ik} = G_{iklm} e_{lm}. \tag{2}$$

The tensors F and G can be found from experiments on the sound absorption[7] or by the method of uniaxial static deformation.[8] The problem of the number of independent components of the tensors F and G permitted by the symmetries of the crystal was considered in detail in[9,10]. It was shown in[9] that one can always neglect the tensor δg (for spin $S > 1/2$) in comparison with δD. Obviously, $\delta D = 0$ for $S = 1/2$. In what follows, the cases $S = 1/2$ and $S > 1/2$ will be considered separately.

By means of (1) and (2), it is easy to write down the operator $\hat{h}(t)$ of interaction of the electron spins with the sound field. For this case, it is necessary to substitute in (2) the values of the deformation created by the standing ultrasonic wave

$$u_i = 2A_i \cos \mathbf{qr} \cos \omega t \quad (i = x,\ y,\ z) \tag{3}$$

at the point of location of the spin. (A_i are the components of the polarization vector and $\mathbf{q}$ is the wave vector.)

Thus, for $S = 1/2$,

$$\hat{h}(t) = F_{iklm} H_i S_k{}^j e_{lm}^{(0)}(\mathbf{r}_j) \cos \omega t = \sigma_{lm}^{(F)} e_{lm}^{(0)} \cos \omega t, \tag{4}$$

for $S > 1/2$,

$$\hat{h}(t) = G_{iklm} S_i{}^j S_k{}^j e_{lm}^{(0)}(\mathbf{r}_j) \cos \omega t = \sigma_{lm}^{(G)} e_{lm}^{(0)} \cos \omega t, \tag{5}$$

where

$$e_{lk}^{(0)}(\mathbf{r}_j) = -|\mathbf{A}|\,|\mathbf{k}|\,(a_l \tilde{q}_k + a_k \tilde{q}_l),$$

$a_l = A_l / |\mathbf{A}|$, $\tilde{q}_k = q_k / |\mathbf{q}|$ are the direction cosines of the polarization and of the wave vector of the sound wave. The tensors $\sigma_{lm}^{(F)}$ and $\sigma_{lm}^{(G)}$ can be called the the magnetoacoustic stresses. Finally, we introduce the tensor χ_{iklm}—the paraacoustic susceptibility, which connects the magnetoacoustic stress with the static deformation:

$$\overset{(0)}{\sigma}_{iklm}(\mathbf{r}_j) = \overset{(0)}{\chi}_{iklm}\, e_{lm}(\mathbf{r}_j). \qquad (6)$$

In an alternating acoustic field (3), this tensor becomes the complex function $\chi(\omega) = \chi'(\omega) - i\chi''(\omega)$ and its imaginary part determines the energy of absorption as a function of the frequency:

$$\langle \dot{E} \rangle = \omega \chi''_{iklm}(\omega)\, \overline{e_{ik}^{(0)}(\mathbf{r})\, e_{lm}^{(0)}(\mathbf{r})}. \qquad (7)$$

By $\langle \dot{E} \rangle$ is meant the mean energy absorbed in a unit volume of a paramagnet whose transverse dimensions are much greater than the wavelength of the ultrasound (this condition is always satisfied). The superior bar indicates the averaged value of the products of the components of the deformation tensor produced by the standing wave in a unit volume:

$$\overline{e_{ik}^{(0)}(\mathbf{r})\, e_{lm}^{(0)}(\mathbf{r})} = A^2 k^2 \{a_i q_k\}\{a_l q_m\}\, \overline{\sin^2 \mathbf{kr}}. \qquad (8)$$

$\{a_i b_k\} = a_i b_k + b_i a_k$ is the symmetrized product.

The average elastic energy passing through a unit area in one second is equal to $I = \frac{1}{2}\rho v^3 = \rho A^2 \omega^2 v\, \overline{\cos^2 \mathbf{k}\cdot\mathbf{r}}$ (v is the speed of the sound wave). From (7) and (8) we get for the absorption coefficient

$$K(\omega) = \frac{\langle \dot{E} \rangle}{I} = \frac{\omega}{\rho v^3}\{a_i q_k\}\{a_l q_m\}\, \chi''_{iklm}(\omega). \qquad (9)$$

Using the linear quantum statistical theory of irreversible processes,[11] it is easy to obtain an expression for $\chi_{iklm}(\omega)$ in terms of the double-time retarded Green's function.[12] For this purpose, it is sufficient to find the solution of the equation for the matrix density $\rho(t)$ of a paramagnetic system with the Hamiltonian $\mathscr{H} + \hat{h}(t)$, which is linear in the external field of deformations $e_{ik}(t)$. We have

$$\chi_{iklm}(\omega) = 2\pi \mathscr{T}_{iklm}(\omega), \qquad (10)$$

where $\mathscr{T}_{iklm}(\omega)$ is the Fourier component of the retarded Green's function:

$$\mathscr{T}_{iklm}(t, t') = -i\hbar^{-1}\theta(t-t')Q^{-1}\,\mathrm{Sp}\,\{\exp(-H/kT)\cdot \times[\sigma_{ik}(t)\sigma_{lm}(t') - \sigma_{lm}(t')\sigma_{ik}(t)]\} \equiv \langle\langle \sigma_{ik}(t) \,|\, \sigma_{lm}(t') \rangle\rangle. \qquad (11)$$

Here Q is the statistical sum for the canonical Gibbs ensemble,

$$\theta(\tau) = \begin{cases} 1 & \tau > 0 \\ 0 & \tau < 0 \end{cases}$$

$$\sigma_{ik}(t) = \exp(i\hbar^{-1}\mathscr{H}t)\,\sigma_{ik}\exp(-i\hbar^{-1}\mathscr{H}t)$$

are the Heisenberg representation of the operator σ_{ik} with the Hamiltonian $\mathscr{H}$ which does not depend explicitly on the time.

The imaginary part of the retarded Green's function can be found with the help of the limiting relation[12]:

$$\mathrm{Im}\,\mathscr{T}(\omega) = \tfrac{1}{2}\lim_{\varepsilon\to 0}\{\mathscr{T}(\omega + i\varepsilon) - \mathscr{T}(\omega - i\varepsilon)\}. \qquad (12)$$

In the next section, we obtain the equation of motion for the Green's function (11) and find its solution for the specific form of the total Hamiltonian $\mathscr{H}$ of the paramagnetic system. As a model, we select an ideal crystal with small concentrations of paramagnetic centers. In such a dilute paramagnetic, we can neglect the magnetic dipole-dipole interactions, and assume that each spin interacts with the crystalline lattice as with a thermostat.

2. EQUATIONS OF MOTION FOR THE GREEN'S FUNCTION

1. $S = \frac{1}{2}$. The total Hamiltonian for a single-particle spin-phonon interaction has the form

$$\hbar^{-1}\mathscr{H} = \omega_0 \sum_j S_0^j + \sum_{q,\nu}\omega_{q\nu}(b_{q\nu}^+ b_{q\nu} + \tfrac{1}{2}) + \sum_{q,\nu,\alpha,j}\varepsilon_{q\nu}^{\alpha} S_{-\alpha}^j [b_{q\nu}\exp(i\mathbf{q}\mathbf{r}_j) - b_{q\nu}^+\exp(-i\mathbf{q}\mathbf{r}_j)]. \qquad (13)$$

The first term is the Zeeman energy of the spins in an external magnetic field H_0 ($\hbar\omega_0 = g\beta H_0$); the second term is the energy of the lattice; $b_{q\nu}^+$ and $b_{q\nu}$ are the creation and annihilation operators for phonons of frequency $\omega_{q\nu}$ with the wave vector $\mathbf{q}$ and polarization ν; the last term is the energy of spin-phonon interaction, where S_α^j is a component of the spin localized at the point $\mathbf{r}_j$ ($\alpha = 0, \pm 1$),

$$\varepsilon_{q\nu}^{\alpha} = \tfrac{1}{2} i\hbar^{-1} F_{i\alpha lm} H_i [\hbar\omega_{q\nu} / 2Mv_\nu^2]^{1/2}\{a_l q_m\}, \qquad (14)$$

M is the mass of the crystal, u_ν is the speed of acoustic phonons of polarization ν.

The function (11) which we need reduces to the Green's function of the components of the spin operators

$$\mathscr{T}_{iklm}(t, t') = \sum_{j,j'} F_{p\alpha lk} F_{q\beta lm} H_p H_q \langle\langle S_\alpha^j(t) \,|\, S_\beta^{j'}(t') \rangle\rangle. \qquad (15)$$

For convenience in subsequent calculations, we have introduced

$$F_{p0ik} = F_{pzik}, \qquad F_{p\pm ik} = \tfrac{1}{2}(F_{pxik} \pm iF_{pyik}).$$

The equations of motion for the operators S_α^j have the form

$$\frac{idS_\alpha^j}{dt} = -\alpha\omega_0 S_0^j + \sum_{q,\nu,\gamma}(-1)^{\alpha-\gamma}\varepsilon_{q\nu}^{\gamma}(\alpha+\gamma) S_{\alpha-\gamma}^j [b_{q\nu}\exp(i\mathbf{q}\mathbf{r}_j) - b_{q\nu}^+\exp(-i\mathbf{q}\mathbf{r}_j)]. \qquad (16)$$

In the derivation of (16), we have used the commutation relation

$$S_\alpha^j S_\beta^{j'} - S_\beta^{j'} S_\alpha^j = \delta^{jj'}(-1)^{\alpha+\beta}(\alpha-\beta) S_{\alpha+\beta}^j \quad (\alpha, \beta = 0, \pm 1). \quad (17)$$

We also introduce the Green's function

$$\langle\langle S_\alpha^j(t) \,|\, S_\beta^{j'}(t') \rangle\rangle_+ \equiv \langle\langle \alpha^j \,|\, \beta^{j'} \rangle\rangle \qquad (18)$$

of the anticommutator of the spin operators. The Fourier component (18) is connected with the Fourier components of the Green's function in (15) by the relation[13]

$$\langle\langle S_\alpha^j(t) \,|\, S_\beta^{j'}(t') \rangle\rangle = \mathrm{th}(\hbar\omega / 2kT)\langle\langle \alpha^j \,|\, \beta^{j'} \rangle\rangle. \qquad (19)$$

Using (16), we find the equation of motion for the Green's function (18):

$$i\frac{d}{dt}\langle\langle \alpha^j \beta^{j'} \rangle\rangle = \frac{1}{2}\delta_{\alpha,-\beta}\delta^{jj'}(1+\alpha^2)\delta(t-t') - \alpha\omega_0\langle\langle \alpha^j | \beta^{j'} \rangle\rangle + \sum_{q,\nu,\gamma}(-1)^{\alpha-\gamma}(\alpha+\gamma)\varepsilon_{q\nu}^{\gamma}\{\langle\langle {}^{j}_{\alpha-\gamma};\, {}^{-}_{q\nu} | \beta^{j'} \rangle\rangle \exp(i\mathbf{q}\mathbf{r}_j) - \langle\langle {}^{j}_{\alpha-\gamma};\, {}^{+}_{q\nu} | \beta^{j'} \rangle\rangle \exp(-i\mathbf{q}\mathbf{r}_j)\}. \qquad (20)$$

In (20) there appear the "mixed" Green's functions of the products of spin and phonon operators:

$$\langle\langle \overset{j}{\alpha-\gamma} b^{\pm}_{q\nu} | S_{\beta}^{j'} \rangle\rangle \equiv \langle\langle \overset{j}{\alpha-\gamma}; \overset{\pm}{q\nu} | \beta^{j'} \rangle\rangle. \qquad (21)$$

We first write out the equations of motion for the product of the operators:

$$i\frac{d}{dt}(S^{j}_{\alpha-\gamma} b^{\pm}_{q\nu}) = [(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0 \mp \omega_{q\nu}] S^{j}_{\alpha-\gamma} b^{\pm}_{q\nu}$$
$$+ \sum_{q',\nu',\gamma'} (-1)^{\alpha-\gamma-\gamma'}(\alpha-\gamma+\gamma')\varepsilon^{\gamma'}_{q'\nu'} S^{j}_{\alpha-\gamma-\gamma'}[b_{q'\nu'} b_{q\nu}\exp(i\mathbf{q}'\mathbf{r}_j)$$
$$- b^{+}_{q'\nu'} b^{\pm}_{q\nu}\exp(-i\mathbf{q}'\mathbf{r}_j)] \mp \sum_{\alpha', j'} \varepsilon_{q\nu}{}^{\alpha'} S^{j'}_{-\alpha'} S^{j}_{\alpha-\gamma}\exp(\pm i\mathbf{q}\mathbf{r}_{j'}). \qquad (22)$$

The last term in (22) corresponds to the two-particle interaction of spins by means of the field of the phonons. This interaction was considered in detail in[14-16], where it was shown that it falls off with the distance as $|\mathbf{r}_i - \mathbf{r}_j|^3$. Inasmuch as we consider a dilute paramagnet, the last term in (22) will be discarded in the equations of motion for the Green's functions (21):

$$i\frac{d}{dt}\langle\langle \overset{j}{\alpha-\gamma}; \overset{\pm}{q\nu} | \overset{j'}{\beta} \rangle\rangle = [(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0 \mp \omega_{q\nu}]\langle\langle \overset{j}{\alpha-\gamma}; q\nu | \overset{j'}{\beta} \rangle\rangle$$
$$+ \sum_{q',\nu',\gamma'} (-1)^{\alpha-\gamma-\gamma'}(\alpha-\gamma+\gamma')\varepsilon^{\gamma'}_{q'\nu'}\{\langle\langle \overset{j}{\alpha-\gamma-\gamma'}; q'\nu'; \overset{\pm}{q\nu} | \overset{j'}{\beta} \rangle\rangle \exp(i\mathbf{q}'\mathbf{r}_j)$$
$$- \langle\langle \overset{j}{\alpha-\gamma-\gamma'}; \overset{+}{q'\nu'}; \overset{\pm}{q\nu} | \overset{j'}{\beta} \rangle\rangle \exp(-i\mathbf{q}'\mathbf{r}_j)\}. \qquad (23)$$

In Eqs. (23), the inhomogeneous term with δ functions has also been omitted. This term is linear in the operators $b^{\pm}$ and averaging gives a result that is different from zero only in higher order in the spin-phonon interaction. If we limit ourselves to the approximation that is quadratic in the spin-phonon interaction, it is possible to disconnect the chain of equations (20) and (23), assuming

$$\langle\langle \overset{j}{\alpha-\gamma-\gamma'}; \overset{-}{q'\nu'}; \overset{\pm}{q\nu} | \overset{j'}{\beta} \rangle\rangle \sim \delta_{qq'}\delta_{\nu\nu'}(n_{q\nu}+1)\langle\langle \overset{j}{\alpha-\gamma-\gamma'} | \overset{j'}{\beta} \rangle\rangle,$$
$$\langle\langle \overset{j}{\alpha-\gamma-\gamma'}; \overset{+}{q'\nu'}; \overset{\pm}{q\nu} | \overset{j'}{\beta} \rangle\rangle \sim \delta_{qq'}\delta_{\nu\nu'} n_{q\nu}\langle\langle \overset{j}{\alpha-\gamma-\gamma'} | \overset{j'}{\beta} \rangle\rangle, \qquad (24)$$

where

$$n_{q\nu} = [\exp(\hbar\omega_{q\nu}/2kT) - 1]^{-1}.$$

Using (24) with $\gamma' = -\gamma$ in (23), we get a closed system of three equations which we write down for the Fourier components of the Green's functions entering into it:

$$(\omega+\omega_0)\langle\langle \alpha^{j} | \beta^{j'} \rangle\rangle_\omega - \sum_{q,\nu,\gamma} (-1)^{\alpha-\gamma}(\alpha+\gamma)\varepsilon^{\gamma}_{q\nu}\{\langle\langle \overset{j}{\alpha-\gamma}; \overset{-}{q\nu} | \beta^{j'} \rangle\rangle_\omega \exp(i\mathbf{q}\mathbf{r}_j)$$
$$+ \langle\langle \overset{j}{\alpha-\gamma}; \overset{\mp}{q\nu} | \overset{j'}{\beta} \rangle\rangle_\omega \exp(-i\mathbf{q}\mathbf{r}_j)\} = \delta^{jj'}\delta_{\alpha,-\beta}(1+\alpha^2), \qquad (25)$$

$$\langle\langle \overset{j}{\alpha-\gamma}; \overset{\pm}{q\nu} | \overset{j'}{\beta} \rangle\rangle_\omega = \pm\frac{(-1)^{\alpha}(\alpha-2\gamma)\varepsilon^{-\gamma}_{q\nu}\exp(\pm i\mathbf{q}\mathbf{r}_j)}{\omega-(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0 \pm \omega_{q\nu}}(n_{q\nu} + 1/2 \pm 1/2)\langle\langle \overset{i}{\alpha} | \overset{j'}{\beta} \rangle\rangle_\omega.$$

Then

$$\langle\langle \alpha^{j} | \beta^{j'} \rangle\rangle_\omega = \frac{1}{4\pi}\frac{\delta^{jj'}\delta_{\alpha,-\beta}(1+\alpha^2)}{\omega+\alpha\omega_0 - M_\alpha(\omega)}, \qquad (26)$$

where

$$M_\alpha(\omega) = \sum_{q,\nu,\gamma}(-1)^{\gamma}(\alpha+\gamma)(\alpha-2\gamma)|\varepsilon_{q\nu}{}^{\gamma}|^2$$
$$\times\left\{\frac{n_{q\nu}+1}{\omega-(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0+\omega_{q\nu}} + \frac{n_{q\nu}}{\omega-(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0-\omega_{q\nu}}\right\} \qquad (27)$$

In Eqs. (26) and (27), ω is the complex frequency. By means of the limiting relation (12) we find

$$\mathrm{Im}\langle\langle \alpha^{j} | \beta^{j'} \rangle\rangle_\omega = \frac{\delta^{jj'}\delta_{\alpha,-\beta}}{2\pi}\frac{(1+\alpha^2)\gamma_\alpha(\omega)}{[\omega+\alpha\omega_0-M_\alpha(\omega)]^2+\gamma_\alpha{}^2(\omega)}. \qquad (28)$$

Here $M_\alpha(\omega \pm i\epsilon) = M_\alpha(\omega) \mp i\gamma_\alpha(\omega)$ (ω is real),

$$M_\alpha(\omega) = \mathrm{P}\sum_{q,\nu,\gamma}(-1)^{\gamma}(\alpha+\gamma)(\alpha-2\gamma)|\varepsilon_{q\nu}{}^{\gamma}|^2$$
$$\times\left\{\frac{n_{q\nu}+1}{\omega-(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0+\omega_{q\nu}} + \frac{n_{q\nu}}{\omega-(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0-\omega_{q\nu}}\right\},$$
$$\gamma_\alpha(\omega) = \pi\sum_{q,\nu,\gamma}(-1)^{\gamma}(\alpha+\gamma)(\alpha-2\gamma)|\varepsilon_{q\nu}{}^{\gamma}|^2$$
$$\times\{(n_{q\nu}+1)\delta[\omega-(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0+\omega_{q\nu}]$$
$$+ n_{q\nu}\delta[\omega-(-1)^{\alpha-\gamma}(\alpha-\gamma)\omega_0-\omega_{q\nu}]\}, \qquad (29)$$

P in front of the sum means that the corresponding integral is taken in the sense of its principal value.

Finally, we get from (15), (10), (9) for the coefficient of sound absorption,

$$K(\omega) = \frac{N\omega}{\rho v^3}\mathrm{th}(\hbar\omega/2kT)\bar{F}_{p\alpha ik}F_{q\alpha lm}\{a_i q_k\}\cdot\{a_l q_m\}H_p H_q g_\alpha(\omega), \qquad (30)$$

where the shape function is

$$g_\alpha(\omega) = \frac{(1+\alpha^2)\gamma_\alpha(\omega)}{[\omega+\alpha\omega_0-M_\alpha(\omega)]^2+\gamma_\alpha{}^2(\omega)}$$

It is seen from (30) that for $\alpha = \pm 1$, a resonance curve[2] of the Lorentz type should be observed; here the shift of the resonance frequency M_α and the width γ_α are themselves functions of the frequency. For $\alpha = 0$, the frequency dependence $K(\omega)$ has a relaxational character. Thus, both the resonance and the non-resonance absorption of sound are described by completely definite combinations of the components of the tensor F_{iklm} which are determined by the wave vector and the polarization of the sound wave, the direction of the applied magnetic field and the symmetry of the crystal.

2. For an example, we consider a crystal of cubic symmetry (classes T_d, O and O_h). The Hamiltonian (1) for $S = 1/2$ has the form[9]

$$\mathcal{H}_{\mathrm{sph}} = 3F_{11}(S_x H_x e_{xx} + S_y H_y e_{yy} + S_z H_z e_{zz})$$
$$+ F_{44}[\{H_y S_z\}e_{yz} + \{H_x S_z\}e_{xz} + \{H_x S_y\}e_{xy}]. \qquad (31)$$

It is seen from (30) and (31) that if the magnetic field is directed along the z axis, then nonresonance absorption should be observed for a longitudinal wave propagating along the z axis. From (30), we get for the absorption coefficient

$$K(\omega) = 36F_{11}{}^2\frac{NH_0{}^2}{\rho v^3}\mathrm{th}(\hbar\omega/2kT)\frac{\omega\tau_0}{\omega^2\tau_0{}^2(1-\Delta)+1}, \qquad (32)$$

where τ_0 and Δ, in accord with (29), generally depend on the frequency:

$$\tau_0{}^{-1} = \gamma_0(\omega) = 2\sum_{q,\nu,\alpha}|\varepsilon_{q\nu}{}^{+}|^2$$
$$\times\{(n_{q\nu}+1)\delta(\omega-\alpha\omega_0+\omega_{q\nu}) + n_{q\nu}\delta(\omega-\alpha\omega_0-\omega_{q\nu})\},$$
$$\Delta = \frac{\mathrm{P}}{\omega^2}\sum_{q,\nu,\alpha}|\varepsilon_{q\nu}{}^{+}|^2\left\{\frac{n_{q\nu}+1}{\omega-\alpha\omega_0+\omega_{q\nu}} + \frac{n_{q\nu}}{\omega-\alpha\omega_0-\omega_{q\nu}}\right\}. \qquad (33)$$

The value of the relaxational shift Δ can always be

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2) Resonances at $\alpha = \pm 1$ express the fact that the effect is symmetric relative to the inversion of the magnetic field (replacement of ω_0 by $-\omega_0$).

neglected. The δ function in (33) expresses the laws of conservation of the energy for processes, thanks to which the relaxation spin-phonon absorption takes place in the assumed approximation: namely, owing to the nonsecular part of the operator $\mathcal{H}_{\text{sph}}$, spin-phonon transitions take place with absorption of a magnon of frequency ω_0, as a consequence of the reorientation of the spin, and a phonon of frequency ω from an external generator, and with appearance of a phonon of frequency $\omega_q = \omega_0 + \omega$ in the lattice. Less probable (in the region of growth of the spectral density of phonons as a function of the frequency) is the process in which two phonons are absorbed with frequencies ω and ω_q, and a magnon is emitted with frequency ω_0 ($\omega_q = \omega_0 - \omega$).

In relaxation experiments, one usually measures the sound absorption coefficient as a function of the amplitude of the applied magnetic field.[3] In the approximation of the Debye model, from (33), $\tau_0^{-1}\,\alpha H_0^2(\omega+\omega_0)^2$ and in the region $\omega \ll \omega_0$, the dependence of the relaxation time on the frequency is not important, i.e., $\tau_0^{-1} \sim H_0^4$.

The formula (32) does not coincide with the result of the semi-phenomenological calculation of Kochelaev,[6] according to which τ = const, while $K \sim N^2 H_0^2$. The dependence of the absorption coefficient on the square of the concentration of paramagnetic centers is entirely incomprehensible from the viewpoint of the physical model considered in [6].

For a transverse wave propagating along the z axis and polarized in the direction of the y axis, resonance absorption is observed. The absorption coefficient from (30) is equal to

$$K(\omega) = 2F_{44}{}^2 \frac{NH_0{}^2}{\rho v^3} \sum_\alpha \frac{\omega\, \mathrm{th}(\hbar\omega/2kT)\gamma_\alpha(\omega)}{[\omega + \alpha\omega_0 - M_\alpha(\omega)]^2 + \gamma_\alpha{}^2(\omega)}. \tag{34}$$

Here $\gamma_\alpha(\omega)$ and $M_\alpha(\omega)$, defined in (29), are respectively the width of the observed line and the shift in the resonance frequency.

3. S = 1. We limit ourselves to a consideration of systems with tetragonal and trigonal symmetry of the internal crystalline field on a paramagnetic center. Then the total Hamiltonian can be represented in the form

$$\hbar^{-1}\mathcal{H} = \sum_j \Big\{\omega_0 S_0{}^j + \omega_D Q_0{}^j + \sum_{q,\nu} \varepsilon_{q\nu}{}^{-\alpha} Q_\alpha{}^j [b_{q\nu}\exp(i\mathbf{q}\mathbf{r}_j) - b_{q\nu}{}^+\exp(-i\mathbf{q}\mathbf{r}_j)]\Big\} + \sum_{q,\nu}\omega_{q\nu}(b_{q\nu}{}^+ b_{q\nu} + {}^1\!/_2), \quad (\alpha = 0, \pm1, \pm2). \tag{35}$$

Here $\omega_D = D\hbar^{-1}$ (D is the constant of fine splitting in the spin Hamiltonian); $Q_0 = S_0 - (1/3)S(S+1)$, $Q_{\pm1} = \{S_0 S_\pm\}$, $Q_{\pm2} = S_\pm S_\pm$,

$$\varepsilon_{q\nu}{}^\alpha = {}^1\!/_2 i\hbar^{-1}[\hbar\omega_{q\nu}/2Mv_\nu{}^2]^{1/2}\tilde{G}_{\alpha lm}\{a_l q_m\},$$

where

$$\tilde{G}_{\pm1lm} = {}^1\!/_2(G_{x0lm} \pm iG_{y0lm}), \quad \tilde{G}_{\pm2lm} = {}^1\!/_2(G_{xxlm} - G_{yylm} \pm iG_{xylm}), \quad \tilde{G}_{0lm} = G_{zzlm}.$$

According to (5) and (11), it is necessary to calculate the Green's function of the quadrupole components of the spin operators

$$\mathcal{T}_{iklm}(t, t') = \sum_{j,j'} \tilde{G}_{\alpha ik}\tilde{G}_{\beta lm}\langle\langle Q_\alpha{}^j(t) \,|\, Q_\beta{}^{j'}(t')\rangle\rangle. \tag{36}$$

Similarly to (18), we shall write the equations of motion for the anticommutator of the quadrupole operators $\langle\langle Q_\alpha^j(t) \,|\, Q_\beta^{j'}(t')\rangle\rangle_+ \equiv \langle\langle \alpha^j \,|\, \beta^{j'}\rangle\rangle^{(S)}$. The superscript (s) in lieu of (q) will be used for the functions $\langle\langle S_\alpha^j(t) \,|\, Q_\beta^{j'}(t')\rangle\rangle_+ = \langle\langle \alpha^j \,|\, \beta^j\rangle\rangle^{(S)}$ which appear in the chain of equations. The operators $Q_\alpha(t)$ and $S_\alpha(t)$ satisfy the following equations of motion:

$$i\frac{d}{dt}Q_\alpha{}^j = -\alpha\omega_0 Q_\alpha{}^j - \alpha\omega_D S_\alpha{}^j + \sum_{q,\nu,\gamma}\varepsilon_{q\nu}^{-\gamma}(-1)^{\alpha+\gamma}(\alpha-\gamma)S^j_{\alpha+\gamma}\cdot[b_{q\nu}\exp(i\mathbf{q}\mathbf{r}_j) - b_{q\nu}{}^+\exp(-i\mathbf{q}\mathbf{r}_j)],$$

$$i\frac{d}{dt}S_\alpha{}^j = -\alpha\omega_0 S_\alpha{}^j - \alpha\omega_D Q_\alpha{}^j + \sum_{q,\nu,\gamma}\varepsilon_{q\nu}^{-\gamma}C_\alpha{}^\gamma Q^j_{\alpha+\gamma}[b_{q\nu}\exp(i\mathbf{q}\mathbf{r}_j) - b^+_{q\nu}\exp(-i\mathbf{q}\mathbf{r}_j)]. \tag{37}$$

In the derivation of (37) we used in addition to (17) the commutation relations

$$[Q_\alpha{}^j, Q_{\alpha'}{}^{j'}]_- = \delta^{jj'}(-1)^{\alpha+\alpha'}(\alpha-\alpha')S_{\alpha+\alpha'} \quad (\alpha, \alpha' = 0, \pm1, \pm2; \quad |\alpha+\alpha'| = 1), \tag{38}$$

$$[S_\alpha{}^j, Q_{\alpha'}{}^{j'}]_- = \delta^{jj'}C_\alpha{}^{\alpha'}Q^j_{\alpha+\alpha'} \quad (\alpha = 0, \pm1; \ \alpha' = 0, \pm1, \pm2; \ |\alpha+\alpha'| = 2),$$

where the coefficients $C_\alpha^{\alpha'} = -C_{-\alpha}^{-\alpha'}$ are taken from the following table:

α′	α: 1	0	−1
2	0	2	−2
1	−2	1	−6
0	−1	0	1

(39)

From (37), we get the equations of motion for the corresponding Green's functions:

$$i\frac{d}{dt}\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(q)} = \delta^{jj'}\delta_{\alpha,-\beta}\langle\{Q_\alpha, Q_{-\beta}\}\rangle - \alpha\omega_0\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(q)} - \alpha\omega_D\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(s)} + \sum_{q,\nu,\alpha'}(-1)^{\alpha+\alpha'}(\alpha-\alpha')\varepsilon_{q\nu}^{-\alpha'}[\langle\langle^{j}_{\alpha+\alpha';\,q\nu}{}^{-}|\beta^{j'}\rangle\rangle^{(s)}\exp(i\mathbf{q}\mathbf{r}_j) - \langle\langle^{j}_{\alpha+\alpha';\,q\nu}{}^{+}|\beta^{j'}\rangle\rangle^{(s)}\exp(-i\mathbf{q}\mathbf{r}_j)], \tag{40}$$

$$i\frac{d}{dt}\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(s)} = \delta^{jj'}\delta_{\alpha,-\beta}\langle\{S_\alpha, Q_{-\alpha}\}\rangle - \alpha\omega_0\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(s)} - \alpha\omega_D\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(q)} + \sum_{q,\nu,\alpha'}C_\alpha^{\alpha'}\varepsilon_{q\nu}^{-\alpha'}[\langle\langle^{j}_{\alpha+\alpha';\,q\nu}{}^{-}|\beta^{j'}\rangle\rangle^{(q)}\exp(i\mathbf{q}\mathbf{r}_j) - \langle\langle^{j}_{\alpha+\alpha';\,q\nu}{}^{+}|\beta^{j'}\rangle\rangle^{(q)}\exp(-i\mathbf{q}\mathbf{r}_j)].$$

If we write out the equations of motion for the mixed Green's functions $\langle\langle^{j}_{\alpha+\alpha';q\nu}{}^{\pm}|{}^{j'}_{\beta}\rangle\rangle^{(q,s)}$ and make approximations of the type (24), we obtain a closed set of six equations which, after simple transformations, reduce to two equations for the Fourier components:

$$[\omega + \alpha\omega_0 + P_\alpha(\omega)]\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(q)}_\omega + (\alpha\omega_D - R_\alpha(\omega))\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(s)}_\omega = \frac{1}{2\pi}\delta^{jj'}\delta_{\alpha,-\beta}\langle\{Q_\alpha, Q_{-\alpha}\}\rangle,$$

$$[\omega + \alpha\omega_0 + M_\alpha(\omega)]\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(s)}_\omega + (\alpha\omega_D - N_\alpha(\omega))\langle\langle\alpha^j|\beta^{j'}\rangle\rangle^{(q)}_\omega = \frac{1}{2\pi}\delta^{jj'}\delta_{\alpha,-\beta}\langle\{S_\alpha, Q_{-\alpha}\}\rangle, \tag{41}$$

where
$$M_\alpha(\omega) = \sum_{q,\nu,\gamma}(-1)^\alpha(\alpha+2\gamma)C_\alpha{}^\gamma|\varepsilon_{q\nu}{}^\gamma|^2 f_{\alpha\gamma}{}^{q\nu}(\omega),$$

$$N_\alpha(\omega) = \sum_{q,\nu,\gamma}C_\alpha{}^\gamma C_{\alpha+\gamma}^{-\gamma}|\varepsilon_{q\nu}{}^\gamma|^2\varphi_{\alpha\gamma}{}^{q\nu}(\omega),$$

$$P_\alpha(\omega) = \sum_{q,\nu,\gamma}(-1)^{\alpha+\gamma}(\alpha-\gamma)C_{\alpha+\gamma}^{-\gamma}|\varepsilon_{q\nu}{}^\gamma|^2 f_{\alpha\gamma}{}^{q\nu}(\omega),$$

$$R_\alpha(\omega) = \sum_{q,\nu,\gamma}(-1)^\gamma(\alpha-\gamma)(\alpha+2\gamma)|\varepsilon_{q\nu}{}^\gamma|^2\varphi_{\alpha\gamma}{}^{q\nu}(\omega);$$

$$f_{\alpha\gamma}{}^{qv}(\omega)=\frac{[\omega+(\alpha+\gamma)\omega_0+\omega_{qv}](n_{qv}+1)}{[\omega+(\alpha+\gamma)\omega_0+\omega_{qv}]^2-(\alpha+\gamma)^2\omega_D^2}+\frac{[\omega+(\alpha+\gamma)\omega_0-\omega_{qv}]n_{qv}}{[\omega+(\alpha+\gamma)\omega_0-\omega_{qv}]^2-(\alpha+\gamma)\omega_D^2}$$

$$\varphi_{\alpha\gamma}{}^{qv}(\omega)=\frac{(\alpha+\gamma)\omega_D(n_{qv}+1)}{[\omega+(\alpha+\gamma)\omega_0+\omega_{qv}]^2-(\alpha+\gamma)^2\omega_D^2}+\frac{(\alpha+\gamma)\omega_D n_{qv}}{[\omega+(\alpha+\gamma)\omega_0-\omega_{qv}]^2-(\alpha+\gamma)\omega_D^2}. \quad (42)$$

It is expedient in what follows to seek a solution of (41) separately for the values $|\alpha| = 2$ and $|\alpha| = 0, 1$, inasmuch as the Green's functions with index (s) are identically equal to zero if $|\alpha| = 2$.

Moreover, for $|\alpha| = 2$ (transitions with $\Delta m = \pm 2$), the right side of the second equation in (41) vanishes, whence we immediately find

$$\langle\langle\alpha^j|\beta^{j'}\rangle\rangle_\omega^{(q)}=\frac{\delta^{jj'}\delta_{\alpha,-\beta}}{2\pi}\frac{\langle\{Q_\alpha,Q_{-\alpha}\}\rangle}{\omega+\alpha\omega_0+P_\alpha(\omega)}. \quad (43)$$

Finding the imaginary part of (43) is completely analogous to (28) and we write down the final result for the coefficient of resonance absorption due to resonance transitions with $\Delta m = \pm 2$:

$$K(\omega)=\frac{N\omega}{\rho v^3}\operatorname{th}(\hbar\omega/2kT)\sum_\alpha G_{\alpha ik}G_{-\alpha lm}\{a_iq_k\}\{a_lq_m\}g_\alpha(\omega), \quad (44)$$

where

$$g_{\pm2}(\omega)=\frac{4\langle S_0^2\rangle\gamma_{\pm2}(\omega)}{[\omega\pm2\omega_0-M_{\pm2}(\omega)]^2+\gamma_{\pm2}^2}$$

Resonance transitions with $\Delta m = \pm 1$ correspond to solutions (41) with $|\alpha| = 1$. Carrying out summation over γ in (42) with the use of (39), we find that in this case

$$P_\alpha=M_\alpha(\omega)=\sum_{q,v}|\varepsilon_{qv}{}^0|^2 f_{\alpha 0}{}^{qv}(\omega),\quad N_\alpha=R_\alpha(\omega)=\sum_{q,v}|\varepsilon_{qv}{}^0|^2\varphi_{\alpha0}{}^{qv}(\omega). \quad (45)$$

The solution of (41) and finding the imaginary part with the help of the limiting relation (12) lead to the absorption coefficient (44) with $\alpha = \pm 1$, and the shape function

$$g_\alpha(\omega)=\frac{3\langle Q_0\rangle\gamma_\alpha^{(+)}(\omega)}{[\omega+\alpha\omega_0-\omega_D+M_\alpha^{(+)}]^2+[\gamma_\alpha^{(+)}]^2}+\frac{[{}^4/_3S(S+1)+\langle Q_0\rangle]\gamma_\alpha^{(-)}}{[\omega+\alpha\omega_0+\omega_D+M_\alpha^{(-)}]^2+[\gamma_\alpha^{(-)}]^2} \quad (46)$$

corresponds to two resonance lines at frequencies $\omega = \omega_0 \pm \omega_D$. Here $M_\alpha^{(\pm)} = \mathrm{Re}[M_\alpha(\omega) \pm N_\alpha(\omega)]$, $\gamma_\alpha^{(\pm)} = \mathrm{Im}[M_\alpha(\omega) \pm N_\alpha(\omega)]$.

And, finally, for $\alpha = 0$, the system (41) reduces to the equations

$$[\omega+P_0(\omega)]\langle\langle 0^j|\beta^{j'}\rangle\rangle_\omega^{(q)}-R_0(\omega)\langle\langle 0^j|\beta^{j'}\rangle\rangle_\omega^{(s)}=\frac{\delta^{jj'}\delta_{0\beta}}{2\pi}B,$$
$$-3R_0(\omega)\langle\langle 0^j|\beta^{j'}\rangle\rangle_\omega^{(q)}+[\omega+M_0(\omega)]\langle\langle 0^j|\beta^{j'}\rangle\rangle_\omega^{(s)}=\frac{\delta^{jj'}\delta_{0\beta}}{2\pi}C, \quad (47)$$

where

$$B={}^4/_9(2S+1)-{}^2/_3\langle Q_0\rangle,\quad C={}^2/_3\langle S_0\rangle.$$

The solution of (47) reduces to the shape function $g_0(\omega)$ in (44) corresponding to relaxation absorption of sound:

$$g_0(\omega)=\frac{B\tau_1(1+\tau_1/\tau_2)}{\omega^2\tau_1^2(1-\Delta_0)+1}. \quad (48)$$

The relaxation times τ_1 and τ_2 and the value of the non-resonance shift in (48) are determined from the expressions

$$\tau_1^{-1}=4\sum_\alpha(\gamma_\alpha^{(+)}+\gamma_\alpha^{(-)})\quad(\alpha=\pm1,\pm2),$$

$$\tau_2^{-1}=\sum_{\alpha=\pm1}\{4(\gamma_{2\alpha}^{(+)}+\gamma_{2\alpha}^{(-)})+(1+C/B)\gamma_\alpha^{(+)}+(1-C/B)\gamma_\alpha^{(-)}\},$$

$$\Delta_0=\frac{8P}{\omega^2}\sum_{q,v,\alpha}|\varepsilon_{qv}{}^\alpha|^2f_{0\alpha}{}^{qv}(\omega)\quad(\alpha=\pm1,\pm2), \quad (49)$$

where

$$\gamma_\alpha^{(\pm)}(\omega)=\pi\sum_{q,v}|\varepsilon_{qv}{}^\alpha|^2\{(n_{qv}+1)\delta(\omega+\alpha\omega_0\pm\omega_D+\omega_{qv})+n_{qv}\delta(\omega+\alpha\omega_0\pm\omega_D-\omega_{qv})\}.$$

In (49) the reciprocal values of the relaxation times are expressed in terms of linear combination of the probabilities of all possible spin-phonon transitions between the spin levels S = 1. The frequency dependence of the absorption coefficient for S = 1 is shown to be the same as for $S = \frac{1}{2}$ ($\tau_1/\tau_2 \sim 1$), while the observed relaxation time $\tau_1^{-1} = 4\sum_{i>k}\tau_{ik}^{-1}$ (τ_{ik}^{-1} is the probability of transition per unit time between the levels i and k). However, the dependence of τ_1 on the external magnetic field will be essentially different from the case of half-integer spin. If $\omega \ll \omega_0 \ll \omega_D$ (initial splittings in a zero field greater than the Zeeman splitting), then τ_1 generally does not depend on the field. In strong fields, when $\omega \ll \omega_0 \gg \omega_D$, $\tau_1^{-1} \sim H_0^2$.

4. The paramagnetic ion is found in a crystal of trigonal symmetry (C_{3v}, D_3, D_{3d}). Then the Hamiltonian (1) for S = 1 can be represented in the form

$$\mathcal{H}_{\rm sph}=Q_0\{G_{33}e_{zz}-(G_{11}+G_{12})(e_{xx}+e_{yy})\}+{}^1/_2\sum_{\alpha=\pm1}Q_\alpha\{G_{41}[e_{xy}-i\alpha(e_{xx}-e_{yy})]+G_{44}(e_{xz}-i\alpha e_{yz})\}+\frac{1}{4}\sum_{\alpha=\pm1}Q_{2\alpha}(G_{11}-G_{12})[2(e_{xx}-e_{yy})-i\alpha e_{xy}]. \quad (50)$$

For a longitudinal wave along an axis of third order, the relaxational absorption ($\alpha = 0$) should be observed and, in accord with (44),

$$K(\omega)=4G_{33}{}^2\frac{N\omega}{\rho v^3}\operatorname{th}(\hbar\omega/2kT)g_0(\omega). \quad (51)$$

If the wave vector of the longitudinal wave is directed perpendicular to the C_3 axis, then resonance maxima should be observed against the background of the relaxation curve; in accord with (44) and (46), these resonances should be proportional to $G_{41}^2 g_{\pm1}(\omega)$ and $(G_{11} - G_{12})^2 g_{\pm2}(\omega)$.

The coefficient G_{44} is connected with the resonance absorption of transverse waves propagating along C_3. Here, the resonance transitions with $\Delta m = \pm 1$ are excited in the spin system, and the absorption coefficient $\alpha G_{44}^2 g_{\pm1}(\omega)$. Resonance transitions with $\Delta m = \pm 2$, can be excited by a transverse wave with wave vector parallel to the y axis besides the longitudinal waves in the xy plane.

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