RELAXATION ABSORPTION OF SOUND IN A PARAMAGNETIC SUBSTANCE

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The acoustical absorption in paramagnetic crystals due to spin-lattice interactions is considered theoretically. The estimates obtained for the acoustical absorption coefficient show that the effect may be quite easily observed experimentally.

1. The possibility of affecting the spin system of a paramagnet by excitation with acoustical vibrations was first pointed out by Al'tshuler.[1] He developed the theory of the resonance absorption of sound by the spin system, which is the analogue of paramagnetic resonance.

Along with resonance methods of studying the dynamic properties of a spin system, considerable use is made of the susceptibility dispersion and the energy dissipation in the paramagnet on applying an alternating magnetic field parallel to the constant one; these effects are caused by relaxation processes in the spin system. It can be expected that the acoustical analogue of these phenomena exists. In the present paper we discuss the acoustical absorption in paramagnetic crystals due to relaxations between the spin system and the thermal lattice vibrations. The calculation is made semiphenomenologically, using a method developed by Mandel'shtam and Leontovich[2] and by Shaposhnikov,[3] which allows the behavior of a system subject to time-dependent excitation to be considered in a thermodynamic way.

2. We assume that the paramagnet can be subdivided into two subsystems which interact weakly with one another; the spin system belongs to one of the subsystems and the remaining degrees of freedom (of the lattice) belong to the other. The thermodynamic state of the lattice will be taken to be independent of the state of the spin system. In other words, we will consider paramagnets for which the spin-lattice relaxation time τ is much longer than the spin-spin relaxation time τ_s; in addition, the temperature of the paramagnet must not be too low (otherwise the second assumption will not be satisfied).

The state of the spin system in complete thermodynamic equilibrium is completely characterized by a temperature T, equal to the lattice temperature T_1, and by the value of the external magnetic field H. We choose the components of the deformation tensor for the external parameters characterizing the state of the spin system when sound is propagated in the paramagnet.

We consider a small volume of the crystal, of which the linear dimensions, L, are such that L ≪ λ, where λ is the wavelength of the sound; this volume should, however, contain a sufficiently large number of atoms for a macroscopic description to be possible. We assume henceforth that when sound is propagated in the paramagnet both subsystems of the volume under consideration pass through a series of equilibrium states. It is then necessary that the frequency of the sound, ω, be much smaller than $1/\tau_s$.

If the sound propagates along one of the coordinate axes, for example z, and the oscillations are longitudinal (which corresponds to the usual experimental conditions), the number of components of the deformation tensor reduces to one

$$u_{zz} = u = u_0 \cos(qz) e^{i\omega t} = u' e^{i\omega t}, \tag{1}$$

where q is the wave number. The work performed on the spin system of the volume considered when the parameter u is changed is

$$\delta A = \sigma du, \quad \sigma = \sigma(u, \mathbf{H}, T) = -\partial\Psi/\partial u. \tag{2}$$

Here Ψ is the free energy of the spin system in the presence of the external magnetic field H, and σ is the generalized force corresponding to the coordinate u.

If the amplitude of the sound wave is small, the departure of the system from the state of complete thermodynamic equilibrium can be taken as infinitesimal. Therefore, the departure of the parameters σ, T, and T_1 from their equilibrium values σ_0 and T_0 will be small, which we utilize below by writing all equations in a linear approximation in terms of the quantities u, $\xi = \sigma - \sigma_0$, $\theta = T - T_0$, and $\theta_1 = T_1 - T_0$.

The dissipative properties of the spin system can be conveniently described by introducing (in analogy with the magnetic susceptibility) the "acoustical susceptibility of the spin system" by the following equation:

$$\xi / u = \zeta = \zeta' - i\zeta'', \qquad (3)$$

where ζ' and ζ'' are real. It is easily seen that the attenuation of a sound wave in the paramagnet, caused by the dissipative properties of the spin system, is determined by the imaginary part of the acoustical susceptibility. The energy absorbed in unit time is

$$\overline{E} = \overline{\Lambda U} = \tfrac{1}{2}\,\omega\zeta''\,(u')^2, \qquad (4)$$

where Λ and U are the real parts of the variables σ and u; the point signifies differentiation, and the bar averaging over time.

Thus, our problem reduces to finding ζ''. A series expansion of σ in terms of θ and u close to equilibrium gives

$$\xi = (\Psi_{uT})_0\,\theta + (\Psi_{uu})_0 u, \qquad \Psi_{xy} \equiv \partial^2\Psi / \partial x \partial y. \qquad (5)$$

To determine θ we apply the equation of thermal balance to the spin system. The quantity of heat δQ which the spin system exchanges with its surroundings consists of two parts:

1) The heat given up by the lattice in time dt:

$$\delta Q' = -\varkappa_1 (T - T_1)\, dt = -\varkappa_1 (\theta - \theta_1)\, dt.$$

Here $\varkappa_1$ is the thermal conductivity between the spin system and the lattice.

2) The heat flowing out to the remaining parts of the spin system:

$$\delta Q'' = -dt \int \mathrm{div}\,(-\varkappa_2\,\mathrm{grad}\,T)\, dV,$$

where $\varkappa_2$ is the thermal conductivity for the spin system. The linear dimensions of the volume V are much less than the acoustical wavelength, and, consequently, grad T does not change within its limits, so that we may write $\delta Q'' = \varkappa_2 V \nabla^2 \theta$.

Considering what has been said in Sec. 1, the lattice vibrations can be considered adiabatic at each point; thus the difference of the lattice temperature from its equilibrium value will be [4]

$$\theta_1 = -T\alpha_V\,\rho \left(v_l^2 - \tfrac{4}{3}\,v_t^2\right) u c_1^{-1} = -Bu. \qquad (6)$$

Here α_V is the thermal expansion coefficient, ρ is the density of the crystal, v_l and v_t are the velocities of sound polarized longitudinally and transversely, and c_1 is the lattice thermal capacity under constant pressure. From the equation of thermal balance we find

$$\theta = [T\,(\Psi_{Tu})_0\,i\omega - B\varkappa_1] / [i\omega c_H + \varkappa_1 + \varkappa_2 V], \qquad (7)$$

where c_H is the thermal capacity of the spin system under constant magnetic field.

Using (3), (5), and (7), we obtain the imaginary part of the acoustical susceptibility for unit volume of the paramagnet:

$$\zeta'' = -\left[\frac{T\,(\Psi_{Tu})_0\,(1 + \varkappa_2\tau\omega^2 / v_l^2 C_H) + BC_H}{(1 + \varkappa_2\tau\omega^2 / v_l^2 C_H)^2 + \omega^2\tau^2}\right]\frac{(\psi_{Tu})_0\,\omega\tau}{C_H}, \qquad (8)$$

where $\tau = C_H / \varkappa_1$ is the spin lattice relaxation time, C_H is the thermal capacity of the spin system for unit volume, and $\psi = \Psi/V$.

3. In order to express ζ'' in terms of known quantities, it remains to find $(\Psi_{Tu})_0$ explicitly. By definition

$$\Psi = -kT \ln\left[\mathrm{Sp}\exp\left(-\frac{\hat{\mathcal{H}}}{kT}\right)\right]. \qquad (9)$$

Because the parameter u is small, the Hamiltonian of the spin system, $\hat{\mathcal{H}}$, can be expanded in power series of u:

$$\hat{\mathcal{H}} = \hat{\mathcal{H}}_0 + \hat{F}u + \ldots, \qquad (10)$$

where $\hat{\mathcal{H}}_0$ is the spin-system Hamiltonian in the absence of sound.

We assume that the spectrum of the spin system consists of two groups of levels, separated in energy by an interval $\Delta E \gg kT$ while the lower group of levels lies within the limits $\Delta E' \ll kT$. This assumption is true for the majority of paramagnets in a wide temperature range (down to liquid-helium temperature). In this case the effect of the upper levels on the behavior of the system in the acoustical field is insignificant, and, expanding (9) in powers of $1/kT$, we obtain the following formula for $(\Psi_{Tu})_0$ on taking into account the first nonzero term of the expansion:

$$(\Psi_{Tu})_0 = \frac{1}{kT^2\eta}\left[\mathrm{Sp}\,\hat{\mathcal{H}}_0\hat{F} - \frac{1}{\eta}\,\mathrm{Sp}\,\hat{\mathcal{H}}_0\,\mathrm{Sp}\,\hat{F}\right], \qquad (11)$$

where η is the number of states of the spin system.

Substituting (11) and (8) in (4), and averaging throughout the volume of the crystal, the general formula can be written down for the acoustical absorption coefficient, defined as the ratio of the energy absorbed in unit volume to twice the flux of acoustical energy. We will write down the formula for the absorption coefficient, taking into account the following facts. Bloembergen[5] has evaluated the thermal conductivity: $\varkappa_2 = C_H a^2/50\tau_s$, where a is the shortest distance between spins. This estimate shows that, at temperatures above liquid helium, for reasonable acoustical frequencies and for the majority of paramagnets, we have

$$\varkappa_2\tau\omega^2 / v_l^2 C_H = 4\pi^2 a^2\tau / 50\,\lambda^2\tau_s \ll 1. \qquad (12)$$

It is seen from formulae (6) and (8) that the part of ζ'' caused by the change of lattice temperature under the effect of acoustical vibrations leads to a multiplier C_H/C_l, the value of which is insignificant at not too low a temperature. Thus we obtain the following formula for the acoustical absorption coefficient in unit volume of the paramagnet:

$$\alpha = \frac{1}{\rho v_l^3 k^2 T^3 C_H \eta^2} \left[\mathrm{Sp}\, \hat{\mathcal{H}}_0 \hat{F} - \frac{1}{\eta} \mathrm{Sp}\, \hat{\mathcal{H}}_0 \, \mathrm{Sp}\, \hat{F} \right]^2 \frac{\omega^2 \tau}{1 + \omega^2 \tau^2}. \quad (13)$$

4. We now make numerical estimates of the acoustical absorption coefficient for typical paramagnets.

1) We consider first paramagnetic salts with ions whose spin, S, is greater than $\frac{1}{2}$; e.g. Cr^{3+} and Ni^{2+} ions ($S = \frac{3}{2}$ and $S = 1$, respectively) surrounded octahedrally by diamagnetic particles X. In the absence of sound the Hamiltonian of the spin system has the form

$$\hat{\mathcal{H}}_0 = \sum_j \left[g\beta (H_x \hat{S}_{jx} + H_y \hat{S}_{jy} + H_z \hat{S}_{jz}) \right.$$
$$\left. + \frac{1}{6} D (\hat{S}_{jx} + \hat{S}_{jy} + \hat{S}_{jz})^2 \right] + \hat{\mathcal{H}}_{ss}. \quad (14)$$

Here H is the strength of the external magnetic field, $\hat{S}_x$, $\hat{S}_y$, $\hat{S}_z$ are the operators projecting the spin onto the coordinate axes directed at the X particles, D is the constant describing the splitting of the spin levels in the crystalline electric field of trigonal symmetry, $\hat{\mathcal{H}}_{ss}$ is the spin-spin interaction Hamiltonian, β is the Bohr magneton. We neglect g-factor anisotropies.

Using the results obtained by van Vleck,[6] we write down the operator $\hat{F}$ for the case when the electric charge of the X particles is zero (water molecules):

$$\hat{F} = \sum_j \{ \varepsilon_1 R3^{-1/2} [(\gamma_1^2 + \gamma_2^2 - 2\gamma_3^2)(2\hat{S}_{jz}^2 - \hat{S}_{jx}^2 - \hat{S}_{jy}^2)$$
$$+ 3(\gamma_1^2 - \gamma_2^2)(\hat{S}_{jy}^2 - \hat{S}_{jx}^2)] + \varepsilon_2 R [\gamma_1\gamma_2(\hat{S}_{jx}\hat{S}_{jy} + \hat{S}_{jy}\hat{S}_{jx})$$
$$+ \gamma_1\gamma_3(\hat{S}_{jx}\hat{S}_{jz} + \hat{S}_{jz}\hat{S}_{jx}) + \gamma_2\gamma_3(\hat{S}_{jy}\hat{S}_{jz} + \hat{S}_{jz}\hat{S}_{jy})] \};$$

$$\varepsilon_1 = 54\sqrt{3} \frac{l^2}{\Delta^2}\left(\frac{e\mu}{R^3}\right)\frac{\overline{r^4}}{R^4},$$

$$\varepsilon_2 = \frac{12324}{175} \frac{l^2}{\Delta^2}\left(\frac{e\mu}{R^3}\right)\left(\frac{\overline{r^2}}{R^2} - \frac{55}{36}\frac{\overline{r^4}}{R^4}\right), \quad (15)$$

where γ_1, γ_2, γ_3 are the direction cosines of the acoustical propagation direction, l is the spin-orbit coupling constant, r is the radius of the d electron, Δ is the total splitting of the orbital levels of the paramagnetic ion in the crystalline cubic field, μ is the electric dipole moment of particle X, and R is the distance to it.

Substituting (15) and (14) in (13) gives

$$\alpha = (AN^2 / T^3 C_H)\, \omega^2 \tau / (1 + \omega^2 \tau^2);$$

$$A = 2 \cdot 10^{-3} (\varepsilon_2^2 D^2 R^2 / \rho v_l^3 k^2) [4S^2 (S + 1)^2$$

$$- 3S(S + 1)]^2 (\gamma_1\gamma_2 + \gamma_1\gamma_3 + \gamma_2\gamma_3)^2, \quad (16)$$

where N is the number of paramagnetic ions in unit volume. It is clear from this formula that a strong variation of the acoustical absorption coefficient on the propagation direction of the sound in the crystal should be observed. In particular, α has a maximum if the sound propagates along the trigonal symmetry axis of the crystalline field, and becomes zero if it is directed along the cubic axis. For example, if in potassium chromium alum the sound is directed along the principal cubic axis of the crystal, then $\alpha = 0$. (Strictly speaking $\alpha \neq 0$, since van Vleck,[6] neglected in the calculation of F a small contribution proportional to H, which will give acoustical absorption four orders of magnitude smaller than that being considered.) If the sound is directed along the trigonal symmetry axis of the crystalline field of one of the ions in the elementary cell (the elementary cell of alums contains four non-equivalent ions, whose trigonal axes are directed in space along the diagonals of a cube), then the absorption coefficient is $\alpha \approx 10^{-6}$ cm^{-1} when the following values for the constants are assumed: $l = 88$ cm^{-1}, $\Delta = 50,000$ cm^{-1}, $v_l = 2.3 \times 10^5$ cm sec^{-1}, $\overline{r^2} = 1.23 \times 10^{-16}$ cm^2, $\overline{r^4} = 2.46 \times 10^{-32}$ cm^4, $R = 2 \times 10^{-8}$ cm, $\mu = 2 \times 10^{-18}$ cgs esu units, $\omega = 3 \times 10^7$ cps, $T = 300°$ K, $H = 0$, $\tau = 0.5 \times 10^{-8}$ sec.

2) For the case of paramagnetic ions with spin $S = \frac{1}{2}$, the spin-lattice interaction energy in crystals is proportional to the magnetic field, as a consequence of Kramer's theorem. We take magnetic dipole-dipole interactions into account by considering the magnetic field close to the paramagnetic ion to consist of the external magnetic field plus a local field created by all the remaining magnetic particles.

As a concrete example we consider a salt of divalent copper, in which the Cu^{2+} ion is in octahedral surroundings. As a rule, one of the fourfold axes (we choose it as the z axis) is different-the octahedron is compressed or extended along this axis. Using the spin-lattice interaction operator of Bashkirov [7] we obtain, after calculations analogous to those made in Item 1, the following expression for the acoustical absorption coefficient:

$$\alpha = (A'N^2 / T^3 C_H)\, \omega^2 \tau / (1 + \omega^2 \tau^2);$$

$$A' = (\varepsilon^2 \beta^4 / \rho v_l^3 k^2)\, [(\varphi_1^2 - \varphi_2^2)^2\, H^4$$

$$+ \tfrac{4}{3}(\varphi_1^2 + \varphi_2^2) H^2 K^2 + \tfrac{4}{9} K^4]\, (\gamma_1^2 - \gamma_2^2)^2,$$

$$\varepsilon = \tfrac{64}{7}(e\mu l \overline{r^2} / \Delta \delta R^4). \qquad (17)$$

Here the local magnetic field values have been averaged assuming that they are distributed for the various ions according to a Gaussian law with an effective field constant of K. The quantities δ and Δ are the splittings of the orbital levels in the tetragonal and cubic internal crystalline fields, respectively, and φ_1, φ_2, φ_3 are the direction cosines of the external magnetic field.

It should be noted that the angular variation of the absorption coefficient in formula (17) may be inaccurate, since, when calculating the spin lattice interaction, Bashkirov[7] only took into account the quadratic terms of the expansion in the electronic coordinates of the d electron energy in the electric field of the crystal; there is reason to suppose that the following term in the expansion (of fourth degree in the coordinates) may be important (cf.[6]).

If the sound and field are directed so that for one of the ions in the elementary cell of a $CuSO_4 \cdot 5H_2O$ crystal we have $(\gamma_1^2 - \gamma_2^2) = 1$ and $(\varphi_1^2 - \varphi_2^2) = 1$, and we use the following values for the constants, $\delta = 1400$ cm^{-1}, $\Delta = 12300$ cm^{-1}, $l = 695$ cm^{-1},[7] $H = 10^4$ oe, $K \ll H$ (the remaining values of the constants are the same as for the alums), the acoustical absorption coefficient is $\alpha \approx 10^{-5}$ cm^{-1}.

The estimates made for the acoustical absorption coefficient show that the effect considered can be experimentally observed. The strong variation of the acoustical absorption coefficient on the value of the external magnetic field simplifies the separation of the paramagnetic absorption of sound from other mechanisms. The mechanism we have considered will, apparently, always play an unimportant role in the general absorption of acoustical energy in the crystal. We note that the variation $\alpha = \alpha(H)$ is markedly different for ions with spin $S = \frac{1}{2}$ and $S > \frac{1}{2}$. When $S > \frac{1}{2}$ the paramagnetic absorption of sound in most cases apparently disappears as H increases; if $S = \frac{1}{2}$ the acoustical absorption coefficient increases according to the law $\alpha \propto H^2$ as $H \rightarrow \infty$.

Apart from its intrinsic interest, the experimental study of the effect we have considered will give important information on the spin-lattice interaction in paramagnetic crystals, which, as is well known, has been studied so far quite inadequately.

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