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Resonance Absorption of Ultrasound in Paramagnetic Salts

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A theory is given of resonance absorption of ultrasound in various paramagnetic salts under the assumption that spin-lattice interaction is caused by the modulation of the internal electric field of the crystal by the elastic vibrations of the lattice. The coefficient of sound absorption has been computed for salts of elements of the iron group (titanium-cesium and chromium alums), for salts of rare earth elements (cerium nitrate, praseodymium ethyl sulfate), and in salts whose magnetic ions are in the S state (iron alum). In certain cases the coefficient σ is so considerable that the effect of paramagnetic absorption of sound ought to be easily observable.

1. INTRODUCTION

In the present work there is considered the resonance absorption of ultrasound in paramagnetic salts which occurs as the result of transitions between the energy levels of a spin system placed in a constant magnetic field. Such absorption takes place if the resonance condition

$$h\nu = g\beta H, \tag{1}$$

is satisfied, where ν is the ultrasonic frequency, g the spectroscopic splitting factor, β the magneton, and H the intensity of the applied magnetic field.

The phenomenon under consideration is analogous to the effect of paramagnetic resonance, discovered by Zavoiskii[1]. This latter phenomenon, as is well known, consists of the resonance absorption of the energy of a radio frequency electromagnetic field by the spin system, as a result of magnetic dipole transitions between sublevels, brought about by a constant magnetic field applied perpendicularly to a variable magnetic field. Equation (1) must be satisfied in this case also, but ν now represents the frequency of the variable magnetic field. The possibility of resonance absorption of the energy of sound vibrations by paramagnetic salts was also discussed by Zavoiskii.

The nature of the mechanism which brings about the transfer of the energy of sound vibrations to the paramagnetic particles is evidently the same as that in paramagnetic relaxation. In paramagnetic relaxation thermodynamic equilibrium is established by the transfer of energy of the magnetic atoms to the thermal vibrations of the lattice. This energy exchange between the spin system and the vibrations of the lattice is brought about by processes of second order, i. e., by the multiple scattering of phonons, at least down to liquid helium temperatures. Single phonon processes play a dominant role only at very low temperatures.

The resonance absorption of ultrasound can be considered as the reverse phenomenon of paramagnetic lattice relaxation, for it consists of the absorption by the lattice of the energy of vibration of a set of magnetic atoms. The forces which act on the magnetic atoms will change periodically, under the action of ultrasound, and transitions from one magnetic energy sublevel to another will occur. The high population of the lower sublevels causes the number of transitions connected with the absorption of energy to exceed the number of reverse processes. Equilibrium will be established as a result of transfer of the excess energy of the paramagnetic particles to the thermal vibrations of the lattice.

It must be kept in mind that the paramagnetic sound absorption results from first order processes which involve the complete absorption of phonons whose frequency satisfies the resonant condition (1). Therefore, calculation of the paramagnetic sound absorption coefficient is analogous to the computation of the relaxation time τ of the paramagnetic lattice at liquid helium temperatures. We can, therefore, immediately estimate the magnitude of this effect in solids.

The probability A of the absorption of a phonon per second under the action of the thermal vibration of the lattice is approximately $1/2\,\tau$. Furthermore, this probability is proportional to the number of vibrations per unit frequency interval, $\rho\nu$, at frequency ν, and to the mean value of the quantum number n_ν at the temperature T_0 of the crystal, since

$$A = A_0\,\rho_\nu n_\nu, \tag{2}$$

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[1] E. K. Zavoiskii, Sow. Phys. **10**, 197 (1946)

$$\rho_\nu = 4\pi\nu^2 V / v^3, \quad n_\nu = kT_0 / h\nu.$$

Here V is the volume of the crystal and v is the velocity of sound. We shall consider the sound to be virtually monochromatic. If the mean width of sound frequency band is $\Delta\nu$, the intensity of the sound wave, i. e. the energy developed per second per square centimeter, will be equal to $I = I_\nu \Delta\nu$, where $I_\nu = v\rho_a n_a h\nu / V$. Here ρ_a and n_a have the same meanings as ρ_ν and n_ν in (2) but refer to the sound vibrations. The energy of these vibrations absorbed per unit volume of paramagnetic material per second at a temperature T is equal to

$$E = NA_0\rho_a n_a \frac{(h\nu)^2}{kT}\frac{\Delta\nu}{\nu_{1/2}}, \tag{3}$$

where N is the number of magnetic atoms per unit volume.

We have assumed that the interval $\Delta\nu$ is much less than the half width of the paramagnetic resonance absorption line, $\nu_{1/2}$. The factor $\frac{h\nu}{kT}$ defines the excess of absorption events over events of phonon emission. We obtain the sound absorption coefficient σ from (2) and (3):

$$\sigma = \frac{E}{I} = \frac{h^2}{8\pi k^2}\frac{Nv^2}{\tau T_0\, T\nu_{1/2}}. \tag{4}$$

All measurements of the relaxation time T, carried out for the compounds

$$CrK(SO_4)_2 \cdot 12H_2O, \quad Gd_2(SO_4)_3 \cdot 8H_2O,$$
$$FeNH_4(SO_4)_2 \cdot 12H_2O, \quad CuK_2(SO_4)_2 \cdot 6H_2O,$$

at the temperatures of liquid helium[2] give values for τ close to 10^{-2} sec, increasing slightly with increase in the applied magnetic field. Hence we obtain a value of about 0.1 cm^{-1} for the coefficient σ at room temperature. Of course it must be recalled that frequencies higher than 10^9/sec play a decisive role in the spin-lattice interactions that define the quantity τ, because of internal magnetic fields. Therefore an estimate of the absorption coefficient σ can be made for sound frequenices of the order 10^9/sec., with the aid of (4); for lower frequencies, one must take into account the fact that σ is ordinarily proportional to the square of the frequency ν.

Thus, the effect we seek is of measurable size. We have therefore carried out calculations of the absorption coefficient σ for various substances. In most paramagnetic salts the internal electric field of the crystal plays a fundamental role in spin-lattice interactions. In these substances the sound vibrations of the lattice alter the electric field of the crystal and periodically react on the orbital motion of the electrons of the magnetic atom. Consequently a change results in the spin direction of the atom relative to the external magnetic field. We have considered only sound absorption resulting from the mechanism of spin-lattice interaction.

2. SALTS OF ELEMENTS OF THE IRON GROUP

First we introduce the usual formula for the coefficient of absorption. The probability per second that an atom undergoes transition from one magnetic level α to another level β, absorbing in this process one quantum of lattice vibration, is equal to

$$A = \frac{4\pi^2}{h^2}\rho_a \left|\mathcal{H}_{\alpha,\,\beta;\,n_a-1,\,n_a}\right|^2. \tag{5}$$

Here $\mathcal{H}_{\alpha,\,\beta;\,n_a-1,\,n_a}$ is the matrix element of excitation, consisting of spin-lattice and possibly other interactions. The energy absorbed per unit volume of the paramagnetic specimen is

$$E = AN\frac{(h\nu)^2}{kT}\frac{\Delta\nu}{\nu_{1/2}}. \tag{6}$$

Hence we obtain for the absorption coefficient

$$\sigma = \frac{4\pi^2}{h^2}\frac{Nh\nu V}{kTvn_a\nu_{1/2}}\left|\mathcal{H}_{\alpha,\,\beta;\,n_a-1,\,n_a}\right|^2. \tag{7}$$

We assume that the sound absorption is related to the periodic variations of the electric field of the crystal under the action of the elastic vibrations of the lattice. In many salts the magnetic ion is surrounded by six water molecules, placed at the corners of an octahedron. The normal vibrations of such a group of molecules were investigated by Van Vleck[3]. If we denote by Q_k the normal coordinates of the system $Me \times 6H_2O$, then it is shown that the energy of the spin-lattice interaction will depend linearly only on some 6 coordinates, so that, neglecting quadratic terms relative to Q_k, we can write

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[2] H. C. Kramers, D. Bijl, C. J. Gorter, Physica **16**, 65 (1950)

[3] J. H. Van Vleck, J. Chem. Phys. 7, 72 (1939)

$$\mathcal{H}_{\alpha,\beta;\,n_a-1,\,n_a}=\sum_{k=1}^{6}(\mathcal{H}_k)_{\alpha,\beta}(Q_K)_{n_a-1,\,n_a}. \qquad (8)$$

The quantities Q_k will be linear functions of all $3N$ normal coordinates q_i which characterize the elastic waves of the lattice:

$$Q_K=\sum_i a_{k_i}q_i, \qquad (9)$$

where

$$\begin{aligned}
a_{1i}&=0; \qquad (10)\\
a_{2i}&=u\,(\lambda_{x_i}\Phi_{x_i}-\lambda_{y_i}\Phi_{y_i});\\
a_{3i}&=u\,(\lambda_{x_i}\Phi_{x_i}+\lambda_{y_i}\Phi_{y_i}-2\lambda_{z_i}\Phi_{z_i})\,/\sqrt{3};\\
a_{4i}&=u\,(\lambda_{x_i}\Phi_{y_i}+\lambda_{y_i}\Phi_{x_i}+\lambda_{z_i}\Phi_{x_i}+\lambda_{x_i}\Phi_{z_i}\\
&\qquad+\lambda_{z_i}\Phi_{y_i}+\lambda_{y_i}\Phi_{z_i})\,/\sqrt{3};\\
a_{5i}&=u\,(\lambda_{x_i}\Phi_{z_i}+\lambda_{z_i}\Phi_{x_i}-\lambda_{y_i}\Phi_{z_i}\\
&\qquad-\lambda_{z_i}\Phi_{y_i})/\sqrt{2};\\
a_{6i}&=u\,(\lambda_{x_i}\Phi_{z_i}+\lambda_{z_i}\Phi_{x_i}+\lambda_{y_i}\Phi_{z_i}+\lambda_{z_i}\Phi_{y_i}\\
&\qquad-2\lambda_{y_i}\Phi_{x_i}-2\lambda_{x_i}\Phi_{y_i})/\sqrt{6},
\end{aligned}$$

and

$$u=(2\pi\nu R\,/\,v)\sin\delta_i. \qquad (11)$$

Here Φ_{x_i}, Φ_{y_i}, Φ_{z_i} and λ_{x_i}, λ_{y_i}, λ_{z_i} are the direction cosines of the polarization and the velocity of propagation of the wave, respectively, R is the equilibrium distance between the molecule of water and the magnetic ion, δ_i is a phase constant.

We assume that the magnetic field is parallel to the z axis and that the sound wave is propagated along the x axis. Then, substituting (8) in (7), and making use of (9), (10) and (11), we get, for the absorption coefficient of a wave propagated in a direction perpendicular to the magnetic field, the expression

$$\begin{aligned}
\sigma_{\perp}=\frac{2}{9}P\nu^2R^2\Big[&3|\mathcal{H}_2|^2+|\mathcal{H}_3|^2 \qquad (12)\\
&+\frac{1}{\sqrt{3}}(\mathcal{H}_2\mathcal{H}_3^*+\mathcal{H}_2^*\mathcal{H}_3)\\
&+2|\mathcal{H}_4|^2+\frac{3}{2}|\mathcal{H}_5|^2+\frac{5}{2}|\mathcal{H}_6|^2\\
&+\sqrt{\frac{3}{2}}(\mathcal{H}_4\mathcal{H}_5^*+\mathcal{H}_4^*\mathcal{H}_5)\\
&-\frac{1}{\sqrt{2}}(\mathcal{H}_4\mathcal{H}_6^*+\mathcal{H}_4^*\mathcal{H}_6)\\
&+\frac{\sqrt{3}}{2}(\mathcal{H}_5\mathcal{H}_6^*+\mathcal{H}_5^*\mathcal{H}_6)\Big]_{\alpha,\beta},
\end{aligned}$$

Here d is the density of the substance and P represents the factor $\pi^2N/kTv^3\nu 1/_2d$ which appears in all expressions for the coefficient of sound absorption in solids. We have carried out averages over all directions of polarization and over all possible values of δ_i. Similarly if the wave is propagated in a direction parallel to the magnetic field we obtain the expression*

$$\begin{aligned}
\sigma_{\parallel}=\frac{2}{9}P\nu^2R^2[&4|\mathcal{H}_3|^2+2|\mathcal{H}_4|^2+3|\mathcal{H}_5|^2 \qquad (12')\\
&+|\mathcal{H}_6|^2+2\sqrt{2}(\mathcal{H}_4\mathcal{H}_6^*+\mathcal{H}_6^*\mathcal{H}_6)]_{\alpha,\beta}.
\end{aligned}$$

We first consider the rather thoroughly investigated, (both theoretically and experimentally) titanium-cesium and chromium-potassium alums. The atom of titanium entering into the compounds $CsTi(SO_4)_2\cdot 12H_2O$ is found in the position ^2D. The strong field of cubic symmetry, created by the water molecules, splits the orbital energy level into a doublet and triplet, separated by an interval greater than 50, 000 cm^{-1}. The trigonal field created by the remaining atoms of the crystal and the spin-orbital interaction completely removes the orbital degeneracy. In the absence of an external magnetic field only the double spin degeneracy is preserved. We assume that the magnetic field is applied parallel to the trigonal axis of the crystal; the splitting of the lowest energy level will be defined by a g factor, equal to $5/4$ [4]. We are interested in the matrix element of excitation which combines these two magnetic sublevels. It is possible to obtain it by making use of the known calculations on the time of paramagnetic relaxation [5], if we include in the excitation operator the energy of the atom in the external magnetic field, the spin-orbit and orbit-lattice interactions. The first approximation shows this matrix element equal to zero. In the second approximation the matrix element of excitation is equal to

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* Henceforth we shall denote by $\perp$ and $\parallel$ quantities relating to waves propagated in directions perpendicular and parallel, respectively, to the applied magnetic field.

[4] B. Bleaney and K. W. H. Steevens, Ann. Rep. Prog. Phys. 16, 108 (1952)

[5] J. H. Van Vleck, Phys. Rev. 57, 426 (1940)

$$\mathscr{H}_{-^1/_2,+^1/_2;n_a-1,\,n_a} = \frac{3}{2}\frac{\lambda g\beta H}{\delta^2}\Big[\sqrt{6}a\,(iQ_2+Q_3) \qquad (13)$$

$$-\frac{1}{\sqrt{3}}b\,(iQ_5-Q_6)\Big]_{n_a-1,\,n_a},$$

where

$$a = -\frac{12}{7}\left(\frac{\overline{r^2}}{R^2}-\frac{25}{18}\frac{\overline{r^4}}{R^4}\right)\frac{e\mu}{R^3}; \qquad (14)$$

$$b = \frac{24}{7}\left(\frac{\overline{r^2}}{R^2}-\frac{5}{6}\frac{\overline{r^4}}{R^4}\right)\frac{e\mu}{R^3}.$$

Here r is the mean distance of the $3d$ electron from the nucleus, μ is the effective dipole moment of the water molecule, δ is the interval separating the two lowest orbit sublevels, λ is the constant of spin-orbit interaction. Hence we immediately obtain the value of $\mathscr{H}_k$, the substitution of which in (12) and (12′) gives us the following expression for the absorption coefficient .

$$\sigma = \alpha h^2 P\left(\frac{\lambda}{\delta^2}\right)^2\left(\frac{e\mu}{R^2}\right)^2\nu^4, \qquad (15)$$

where

$$\alpha = 3\left(\frac{8}{7}\right)^2\left[11\left(\frac{\overline{r^2}}{R^2}\right)^2-\frac{85}{3}\frac{\overline{r^2}\,\overline{r^4}}{R^6}+\frac{75}{4}\left(\frac{\overline{r^4}}{R^4}\right)^2\right].$$

The absorption coefficient does not depend on the angle between the constant magnetic field and the direction of propagation of the ultrasound. Making use of the following values for the quantities entering into this formula:

$\lambda = 154\ \text{см}^{-1}$; $\delta = 500\ \text{см}^{-1}$;
$v = 2.3\times10^5\ \text{см/сек.}$; $d = 2\ \text{г/см}^3$;
$R = 2\times10^{-8}\ \text{см}$; $\overline{r^2} = 1.23\times10^{-16}\ \text{см}^2$;
$\overline{r^4} = 2.46\times10^{-32}\ \text{см}^4$; $\mu = 2\times10^{-18}$ CGSE;
$\nu_{1/2} = 1.8\times10^8\ \text{сек.}^{-1}$; $T = 20°\text{K}$,

(taken in large part from Bleaney and Steevens [4] and Van Vleck [5]), we get for σ:

$$\sigma = 2.4\times10^{-38}\nu^4\ \text{см}^{-1}. \qquad (16)$$

In estimating σ, we have taken $T = 20°$, since titanium-cesium alum possesses an anomalously short time for spin-lattice relaxation, so that resonance absorption is found only at low temperatures.

We proceed to chromium alum. The basic state of the triply ionized atom of chromium is ^4F. The splitting scheme of the energy levels by the electric field of the crystal and the external magnetic field is shown in Fig. 1. The strong cubic field produces a splitting of the orbit energy level into three sublevels, the lowest of which is single. The overall splitting Δ, according to Bleaney and Bowers [6] is 50,000/cm. If electron spin is taken into account, the degeneracy of the basic energy level associated with it is preserved in a field of cubic symmetry. The trigonal field splits the spin quadruplet into two Kramers doublets, the interval δ between them lying in the range 0.12 to 0.18 cm^{-1} for chromium alums of various types. The magnetic spin quantum numbers $\pm 3/2$ correspond to the lower doublet, the numbers $\pm 1/2$ to the upper.

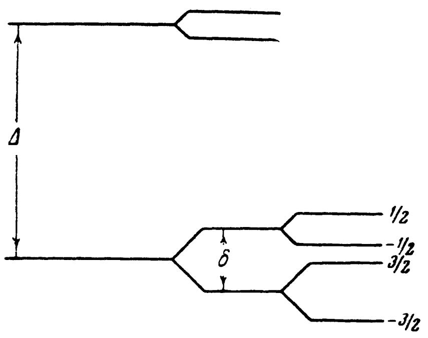

Fig. 1. Scheme of the successive splitting of the basic energy level of the Cr^{+++} ion because of its presence in the electric field of a crystal of cubic symmetry, in a weak field of trigonal symmetry and, in an external magnetic field.

The matrix element of excitation, which consists of spin-orbit and spin-lattice interaction, differs from zero only in the third approximation, and can be represented in the following form [5]:

$$\mathscr{H}_{\alpha,\,\beta;\,n_a-1,\,n_a} = \{\varepsilon_1[Q_3(2S_z^2-S_x^2-S_y^2) \qquad (17)$$

$$+\sqrt{3}Q_2(S_y^2-S_x^2)]+\varepsilon_2[Q_4(S_xS_y+S_yS_x)$$

$$+Q_5(S_xS_z+S_zS_x)$$

$$+Q_6(S_yS_z+S_zS_y)]\}_{\alpha,\,\beta;\,n_a-1,\,n_a},$$

where

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

$$\varepsilon_2 = \frac{12\cdot324}{175}\frac{\lambda^2}{\Delta^2}\left(\frac{e\mu}{R^3}\right)\left(\frac{\overline{r^2}}{R^2}-\frac{55}{36}\frac{\overline{r^4}}{R^4}\right),$$

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[6] B. Bleaney and K. D. Bowers, Proc. Phys. Soc. (London) 64A, 1135 (1951)

S is the spin moment operator, α, $\beta = \pm 1/2, \pm 3/2$.

In our approximation, only transitions between sublevels of different Kramers doublets are nonvanishing. Therefore the location of the absorption line will no longer be determined by Eq. (1), which refers to transitions between sublevels that are produced upon the imposition of an external magnetic field. With the help of (17) and (12), calculation leads to the following expression for the absorption coefficient:

$$\sigma = \alpha\left(\frac{e\mu}{R^2}\right)^2\left(\frac{\lambda}{\Delta}\right)^4 P\nu^2. \tag{18}$$

For transitions $-1/2 \rightarrow 3/2$ and $-3/2 \rightarrow 1/2$, the coefficient is equal to

$$\alpha'_\perp = 3\left(\frac{8\cdot 324}{175}\right)^2\left[\left(\frac{\overline{r^2}}{R^2}\right) - \frac{55}{18}\frac{\overline{r^2}\,\overline{r^4}}{R^6} + 82\left(\frac{\overline{r^4}}{R^4}\right)^2\right], \tag{19}$$

$$\alpha'_\parallel = 3\left(\frac{8\cdot 324}{175}\right)^2\left(\frac{\overline{r^2}}{R^2} - \frac{55}{36}\frac{\overline{r^4}}{R^4}\right)^2.$$

For transitions between sublevels $-3/2 \rightarrow -1/2$, $1/2 \rightarrow 3/2$, the coefficient α does not depend on the direction of the applied magnetic field, and is equal to $8\alpha'_\parallel$.

If, in estimating the numerical value of the absorption coefficient we assume that $\lambda = 88\ \text{cm}^{-1}$; $d = 1.7\ \text{gm/cm}^3$, $\nu_{1/2} = 1.03 \times 10^9\ \text{sec}^{-1}$, $T = 300^\circ$ K, and that the other quantities have the same values as for titanium-cesium alums, we get

$$\sigma'_\perp = 0.80\times 10^{-21}\nu^2\ \text{cm}^{-1};\ \sigma'_\parallel = 0.56\times 10^{-23}\nu^2\ \text{cm}^{-1}. \tag{20}$$

For salts of titanium and chromium we obtained a different dependence of the magnitude of the absorption on the frequency of the sound. This behavior is explained by the fact that in the case of chromium alums the spin degeneracy is partially removed even in the absence of any external magnetic field.

3. SALTS OF RARE EARTH ELEMENTS

Spin-lattice interaction in salts of rare earth elements possesses a number of peculiarities which were considered in an earlier work of the author[7]. As an example, we consider cerium nitrate. The free triply ionized atom of cerium is in the state ${}^2F_{5/2}$. The six molecules of water which surround the magnetic ion evidently produce a field of cubic symmetry. This field splits the fundamental energy level into a doublet and a quadruplet, separated by a difference Δ (Fig. 2). A weaker trigonal field, produced by the remaining atoms of the crystal, splits the quadruplet into two doubly degenerate sublevels. Further splittings of the levels ab, cd and fg in an external magnetic field, applied parallel to the axis of the octahedron, have the values $11/3\, g\beta H$, $g\beta H$, $5/3\, g\beta H$, respectively.

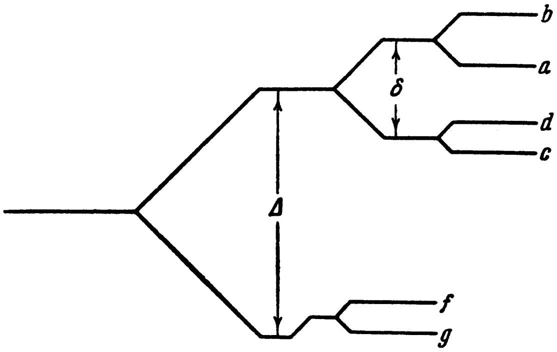

Fig. 2. Scheme of the successive splitting of the basic energy level of the Ce+++ ion because of its presence in the electric field of a crystal of cubic symmetry, in a weak field of trigonal symmetry, and in an external magnetic field.

We first consider absorption due to transitions between levels f and g. The matrix element of the interaction, which included the spin-lattice interaction and the potential of the trigonal field, differs from zero in the second approximation, and is equal to

$$\mathcal{H}_{f,\,g;\,n_a-1,\,n_a} = \frac{1}{8}\left(\frac{e\mu}{R^3}\right)\left(\frac{\overline{r^2}}{R^2} - \frac{9}{64}\frac{\overline{r^4}}{R^4}\right)^2 \tag{21}$$

$$\times\frac{(5/3\, g\beta H)\,\delta}{\Delta^2}(Q_5 + iQ_6)_{n_a-1,\,n_a}.$$

For absorption coefficients we get, by the usual method,

$$\sigma_\parallel = \frac{1}{18}\left(\frac{\overline{r^2}}{R^2} - \frac{9}{64}\frac{\overline{r^4}}{R^4}\right)^2\left(\frac{e\mu}{R^2}\right)^2\frac{h^2\delta^2 P}{\Delta^4}\nu^4, \tag{22}$$

$$\sigma_\perp = 1/4\,\sigma_\parallel.$$

If we take $\nu_{1/2} = 1.6 \times 10^9$/sec. as the half width of the absorption line, and use the values given in reference 7 for the other quantities, we get (at

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[7] S. A. Al'tshuler, J. Exper. Theoret. Phys. USSR 24, 681 (1953)

$T = 20^\circ$ K)

$$\sigma_{\parallel} = 3 \cdot 10^{-44}\, \nu^4 \text{см}^{-1}. \qquad (22')$$

The matrix element of excitation for transitions between the sublevels *ab* has the same form as that for *fg*. The only difference is that the interval *ab* is $^{11}/_5$ times larger than the interval *fg*. As a consequence the absorption coefficient obtained for *fg* must be multiplied by $(^5/_{11})^2$.

Calculation shows that the probabilities of transitions between levels *cd* are zero. This result is related to our choice of a field of low symmetry (relative to the fundamental cubic field). With a field of another type we would have obtained absorption of the same order as for the other pair of levels.

Thus the absorption coefficient for cerium nitrate is shown to be very small. Such a result is explained by the low symmetry of the electric field of the crystal, which leaves only the Kramers degeneracy of the energy level. This cannot be connected with changes in the electric field produced by the vibrations of the lattice. Otherwise it would be as if the electric field of the crystal had possessed such great symmetry that it could preserve the non-Kramers degeneracy of the energy levels. In such a case the spin-lattice interaction would differ from zero even in the first approximation and the absorption coefficient would be far larger.

Among the salts of the rare earths, most attention has thus far been given to the ethyl sulfates. In these cases the crystalline field possesses hexagonal symmetry. The Ian-Teller effect, which contributes to the low symmetry of the field, is so small [3] in the salts of the rare earths that it can be neglected. In atoms which have half integer spin, the field of hexagonal symmetry splits the energy levels so that only the Kramers degeneracy remains [8]. Therefore, in salts of cerium, neodymium and other elements, whose ions possess an odd number of electrons , the effect of resonance absorption of sound must be small. In atoms with an even number of electrons, the hexagonal field leaves certain energy levels doubly degenerate. For example, in praseodymium ethyl sulfate, the fundamental level of Pr^{+++} exhibits a non-Kramers doublet [9]. It is easy to estimate the sound absorption as a result of transitions between this pair of levels. If we assume that the matrix element of spin-lattice interaction for this doublet differs from zero in the first approximation, we get for the absorption coefficient,

$$\sigma = \gamma P \left(\frac{e\mu}{R^2}\right)^2 \left(\frac{\bar{r}^2}{R^2}\right)^2 \nu^2, \qquad (23)$$

where γ is a numerical coefficient of order unity. Taking $\nu_{1/2} = 2 \times 10^9$/sec as the width of the absorption line, we get, for 20°K,

$$\sigma \sim 10^{-15} \nu^2 \text{ см}^{-1}. \qquad (23')$$

We note that for salts of rare earth elements, the time of spin-lattice relaxation at room temperature appears to be very short [7]. Therefore observation of the sound absorption effect is possible only at low temperatures.

4. SALTS WITH MAGNETIC IONS IN THE *S* STATE

A special place is taken among paramagnetic salts by the salts of doubly ionized manganese and triply ionized iron and gadolinium. The magnetic ions of these salts are in the *S* state, for which reason the electric field of the crystal produces very small splitting of the fundamental level, not exceeding 1 cm^{-1}. It is also appropriate to consider the salts of iron whose ion is in the ^6S state. The Hamiltonian operator which gives the effect of the electric field of the crystal and the external magnetic field has the following form [10]:

$$\mathcal{H} = {}^1/_6 D [S_x^4 + S_y^4 + S_z^4 - {}^1/_3 S(S+1) \times (3S^2 + S - 1)] + g\beta H. \qquad (24)$$

For iron rubidium alums, $D = 0.0134$ cm^{-1} [11]. If the magnetic field is applied in the [100] direction, the non-vanishing matrix elements of $\mathcal{H}$ have the form

$$\begin{aligned}
\mathcal{H}_{\pm 5/2,\, \pm 5/2} &= D \pm {}^5/_2\, G, \\
\mathcal{H}_{\pm 3/2,\, \pm 3/2} &= -{}^3/_2\, D \pm {}^3/_2\, G, \\
\mathcal{H}_{\pm 1/2,\, \pm 1/2} &= D \pm {}^1/_2\, G, \\
\mathcal{H}_{-5/2,\, 3/2} = \mathcal{H}_{-3/2,\, 5/2} &= \frac{\sqrt{5}}{2} D.
\end{aligned} \qquad (25)$$

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[8] H. Bethe, Ann. Physik 3, 133 (1929)

[9] B. Bleaney and H. E. D. Scovil, Phil. Mag. **43**, 999 (1951)

[10] K. W. H. Steevens, Proc. Roy. Soc. **214**, 237 (1952)

[11] B. Bleaney and K. S. Trenar, Proc. Phys. Soc. (London) **65A**, 560 (1952)

Here $G = g\beta H$.

The solution of the secular equation leads to the following eigenvalues and wave functions:

$$E_a = -{}^1/_2 D - {}^1/_2 G + \sqrt{(D-2G)^2 + {}^5/_4 D^2};$$

$$\Psi_a = a_1\Phi_{-5/2} + a_2\Phi_{3/2}; \tag{26}$$

$$E_b = -{}^1/_2 D + {}^1/_2 G + \sqrt{(D+2G)^2 + {}^5/_4 D^2};$$

$$\Psi_b = b_1\Phi_{-3/2} + b_2\Phi_{5/2};$$

$$E_c = D - {}^1/_2 G;$$

$$\Psi_c = \Phi_{-1/2};$$

$$E_d = D + {}^1/_2 G;$$

$$\Psi_d = \Phi_{1/2};$$

$$E_f = -{}^1/_2 D - {}^1/_2 G - \sqrt{(D-2G)^2 + {}^5/_4 D^2};$$

$$\Psi_f = f_1\Phi_{-5/2} + f_2\Phi_{3/2};$$

$$E_g = -{}^1/_2 D + {}^1/_2 G - \sqrt{(D+2G)^2 + {}^5/_4 D^2};$$

$$\Psi_g = g_1\Phi_{-3/2} + g_2\Phi_{5/2}.$$

The triply ionized atoms of iron and cerium have a similar energy level structure, owing to the fact that in their ground state both ions have a quantum number of total angular momentum equal to $5/2$. Therefore, making use of Eqs. (8) and (9) of our work, which illustrates paramagnetic relaxation in cerium salts [7], we get for the matrix elements of the operator of spin-lattice interaction (with the help of the wave functions (26)):

$$\mathcal{H}_{ab} = -\frac{3}{2}\sqrt{5}\,(a_1b_1 - a_2b_2)\left(\frac{\bar{r}^2}{R^2} - \frac{9}{64}\frac{\bar{r}^4}{R^4}\right) \tag{27}$$

$$\times\left(\frac{e\mu}{R^3}\right)(Q_5 + iQ_6) \equiv F_1(a, b);$$

$$\mathcal{H}_{ac} = \frac{3}{8}\sqrt{2}\left\{3\,(\sqrt{5}\,a_1 + 3a_2)\left(\frac{\bar{r}^2}{R^2} + \frac{45}{32}\frac{\bar{r}^4}{R^4}\right)Q_2\right.$$

$$\left.-2i(\sqrt{5}\,a_1 - 3a_2)\left(\frac{\bar{r}^2}{R^2} + \frac{27}{32}\frac{\bar{r}^4}{R^4}\right)Q_4\right\}\frac{e\mu}{R^3}$$

$$\equiv F_2(a_1, a_2);$$

$$\mathcal{H}_{ad} = \frac{3}{2}\sqrt{2}\left\{a_2\frac{\bar{r}^2}{R^2} + \frac{9}{128}(7\sqrt{5}\,a_1 + 5a_2)\frac{\bar{r}^4}{R^4}\right\}$$

$$\times\left(\frac{e\mu}{R^3}\right)(Q_5 - iQ_6) \equiv F_3(a_2, a_1);$$

$$\mathcal{H}_{af} = -\frac{3}{4}\sqrt{3}\left\{(5a_1f_1 - a_2f_2)\frac{\bar{r}^2}{R^2}\right.$$

$$\left.-\frac{15}{64}[5a_1f_1 - 15a_2f_2 - 14\sqrt{5}(a_1f_2 + a_2f_1)]\frac{\bar{r}^4}{R^4}\right\}$$

$$\times\left(\frac{e\mu}{R^3}\right)Q_3 \equiv F_4(a, f);$$

$$\mathcal{H}_{ag} = F_1(a, g), \quad \mathcal{H}_{bc} = F_2(b_2, b_1);$$

$$\mathcal{H}_{bd} = F_3(b_1, b_2); \quad \mathcal{H}_{bf} = F_1(b, f);$$

$$\mathcal{H}_{bg} = F_4(b, g); \quad \mathcal{H}_{cd} = 0;$$

$$\mathcal{H}_{cf} = F_2(f_1; f_2); \quad \mathcal{H}_{cg} = F_3(g_1, g_2);$$

$$\mathcal{H}_{df} = F_3(f_2, f_1); \quad \mathcal{H}_{dg} = F_2(g_2, g_1).$$

With the help of (12), we get the sound absorption coefficient σ:

$$\sigma = \alpha P\,(e\mu\,/\,R^2)^2\nu^2. \tag{28}$$

If the magnetic field is applied perpendicularly to the direction of sound propagation, then the numerical coefficient will have the following values for the various pairs of levels:

$$\alpha_{ab} = 5\left[(a_1b_1 - a_2b_2)\left(\frac{\bar{r}^2}{R^2} - \frac{9}{64}\frac{\bar{r}^4}{R^4}\right)^2\right. \tag{29}$$

$$\equiv \alpha_1(a, b);$$

$$\alpha_{ac} = 2\left[a_2\frac{\bar{r}^2}{R^2} + \frac{9}{128}(7\sqrt{5}\,a_1 + 5a_2)\frac{\bar{r}^4}{R^4}\right]^2$$

$$\equiv \alpha_2(a_2, a_1);$$

$$\alpha_{ad} = \frac{3}{2}\left[\frac{3}{4}(\sqrt{5}\,a_1 + 3a_2)\left(\frac{\bar{r}^2}{R^2} + \frac{45}{32}\frac{\bar{r}^4}{R^4}\right)\right]^2$$

$$= \alpha_3(a_1, a_2);$$

$$\alpha_{af} = \frac{9}{16}\left\{(5a_1f_1 - a_2f_2)\frac{\bar{r}^2}{R^2}\right.$$

$$-\frac{15}{64}[5a_1f_1 - 15a_2f_2$$

$$\left.-14\sqrt{5}(a_1f_2 + a_2f_1)]\frac{\bar{r}^4}{R^4}\right\}^2 \equiv \alpha_4(a, f);$$

$$\alpha_{ag} = \alpha_1(a, g); \quad \alpha_{bc} = \alpha_2(b_2, b_1);$$

$$\alpha_{bd} = \alpha_3(b_2, b_1); \quad \alpha_{bf} = \alpha_1(b, f);$$

$$\alpha_{bg} = \alpha_4(b, g); \quad \alpha_{cd} = 0;$$

$$\alpha_{cf} = \alpha_3(f_1, f_2); \quad \alpha_{cg} = \alpha_2(g_1, g_2);$$

$$\alpha_{df} = \alpha_2(f_2, f_1); \quad \alpha_{dg} = \alpha_3(g_2, g_1);$$

$$\alpha_{fg} = \alpha_1(f, g).$$

If the magnetic field is applied parallel to the direction of sound propagation, then the numerical coefficient α, which we now denote by α', will be determined, according to Eqs. (27) by four functions α_i, if we give them the following values:

$$\alpha_1 = \alpha_1; \quad \alpha_2 = \frac{1}{2}(\sqrt{5}\,a_1 - 3a_2)^2 \tag{30}$$

$$\times\left(\frac{\bar{r}^2}{R^2} + \frac{27}{32}\frac{\bar{r}^4}{R^4}\right)^2;$$

$$\alpha_3' = \alpha_3; \quad \alpha_4' = 4\alpha_4.$$

In a strong magnetic field, which produces splittings much larger than does the electric field of the crystal, it is appropriate to characterize the energy levels by the values of the magnetic quantum number M. Thus, in this case,

$$a_1 = b_2 = f_2 = -g_1 = 1;$$
$$a_2 = b_1 = f_1 = g_2 = 0,$$

and for the coefficient α we have

$$\begin{aligned}
\Delta M = 1:\quad & \alpha_{-5/2,\,-3/2} = \alpha_{3/2,\,5/2} \\
& = 5\left(\frac{\bar{r}^2}{R^2} - \frac{9}{64}\frac{\bar{r}^4}{R^4}\right)^2; \\
& \alpha_{-3/2,\,-1/2} = \alpha_{1/2,\,3/2} = 2\left(\frac{\bar{r}^2}{R^2} + \frac{45}{128}\frac{\bar{r}^4}{R^4}\right)^2; \\
& \alpha_{-1/2,\,1/2} = 0; \\
\Delta M = 2:\quad & \alpha_{-5/2,\,-1/2} = \alpha_{1/2,\,5/2} \\
& = \frac{135}{2}\left(\frac{r^2}{R^2} + \frac{45}{32}\frac{\bar{r}^4}{R^4}\right)^2; \\
& \alpha_{-3/2,\,1/2} = \alpha_{-1/2,\,3/2} = \frac{9}{5}\alpha_{1/2,\,3/2}; \\
\Delta M = 3:\quad & \alpha_{-5/2,\,1/2} = \alpha_{1/2,\,5/2} = 10\left(\frac{63}{128}\frac{\bar{r}^4}{R^4}\right)^2; \\
& \alpha_{-3/2,\,3/2} = 0; \\
\Delta M = 4:\quad & \alpha_{-5/2,\,3/2} = \alpha_{-3/2,\,5/2} = 5\left(\frac{315}{128}\frac{\bar{r}^4}{R^4}\right)^2; \\
\Delta M = 5:\quad & \alpha_{-5/2,\,5/2} = 0.
\end{aligned} \tag{31}$$

It should be noted that transitions between neighboring sublevels are possible only under the action of transverse vibrations, and transitions for which $\Delta M = 2$ take place only under the action of longitudinal waves.

If a weak magnetic field is applied, then $a_1 = b_2 = -f_2 = -g_1 = \sqrt{5/6}$; $a_2 = b_1 = f_1 = g_2 = 1/\sqrt{6}$. In the limiting case of a vanishing magnetic field, the electric field splits the basic level of the iron ion into only two sublevels, for which the coefficient α is equal to

$$\alpha = 25\left[\left(\frac{\bar{r}^2}{R^2}\right)^2 - \frac{5}{6}\frac{\bar{r}^2\bar{r}^4}{R^6} + 36\left(\frac{\bar{r}^4}{R^4}\right)^2\right]. \tag{32}$$

In order to compute the absorption coefficient according to the formulas that we have developed, the following circumstances must be considered. In the previous cases, the energy of interaction of the magnetic ion with the water molecules is of the order of $e\mu/R^2$. The effect of the electric field of the crystal on the ion, which is in the S state, is even weaker. We take this circumstance into account by attaching correspondingly smaller values of the dipole moment μ. In iron-rubidium alums, the crystalline field produces energy splitting approximately 10^{-6} that in the same salts with another cation. Therefore, taking $\mu \sim 10^{-24}$, we get, for the absorption coefficient in the absence of a magnetic field,

$$\sigma = 10^{-24}\nu^2\,\text{cm}^{-1}. \tag{32'}$$

It is necessary to show that in some cases the crystalline field creates a much greater splitting. Thus, for the gadolinium ion [12], it is two orders larger, which increases the absorption coefficient σ by 10^4.

As we have seen, the probability of phonon absorption depends very critically upon the magnitude of the spin-orbit interaction of the electrons on the magnetic atom and, in particular, on the character of the splitting of the fundamental energy level of this atom by the electric field of the crystal. Therefore the magnitude of the effect of resonant absorption of sound can change over wide ranges in going from one substance to another. Contemporary ultrasonic techniques permit the obtaining of frequencies of 10^9 cps, which makes possible the observation of the resonance paramagnetic absorption of sound, at least in certain substances.

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[12] N. S. Garif'ianov, Doklady Akad. Nauk SSSR 84, 923 (1952)

Translated by R. T. Beyer
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