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On the Theory of Electronic and Nuclear Paramagnetic Resonance under the Action of Ultrasound

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The theory of resonance absorption of ultrasound in different classes of paramagnetic substances (salts, rare-earth metals, salt solutions, and gases) is presented. We consider the different mechanisms of the spin-lattice interaction, and discuss the cause of the effect. The magnitude of the calculated coefficient shows that for a series of substances the effect can easily be observed, in other cases it is possible to use an indirect method of observation.

1. INTRODUCTION

IN the work of the author[1] on the theory of resonance absorption of ultrasound in different paramagnetic salts, there is an assumption that the spin-lattice interaction is caused by the modulation of the internal electric field of the crystal by the elastic vibrations of the lattice.

In this paper we consider, in the case of the absorption of ultrasound in salts, an assumption that the spin-lattice interaction is due to magnetic and exchange forces. In certain cases it turns out that this mechanism causes the greatest effect. We also calculate the resonance absorption effect of ultrasound in rare-earth metals, in some of which it proves to be extremely important. We also consider the resonance absorption of ultrasound caused by nuclear paramagnetism. As has been made clear this often gives a large effect that is observed directly, as well as by indirect methods*.

In our calculation we proceed from the following general formula for the sound absorption coefficient [1]:

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

Where N is the number of magnetic atoms per unit volume, ν and v are the frequency and the velocity of propagation of sound, V and T are the volume and temperature of the paramagnetic body, $\nu_{1/2}$ is the half-width of the absorption line, $\mathscr{H}_{\alpha, \beta; n_a-1, n_a}$ is the matrix element of the spin-lattice interaction, acting between the magnetic sublevels α and β and the vibration state of the lattice characterized by the quantum numbers $n_a - 1$ and n_a.

The calculation of the absorption of sound starts from the assumption that the resonance condition is satisfied; this in the simplest case has the form

$$h\nu = g\beta H, \tag{2}$$

where g is the spectroscopic splitting factor, β is the magneton, H is the intensity of the applied magnetic field.

2. MAGNETIC AND EXCHANGE INTERACTIONS

The first theory of paramagnetic relaxation was developed [2] by building from the assumption that the spin-lattice coupling is brought about by means of magnetic forces acting between the atoms of the crystal. Later, in samples of several paramagnetic salts[3] it was demonstrated that this mechanism was completely inadequate in explaining the observed values of the relaxation times. Another mechanism was introduced which we too used in a previous paper [1]. However, in certain paramagnetic substances the mechanism considered by Waller[2] played an essential role. Waller considered the case in which the atomic spin $S = \frac{1}{2}$. In addition it was easily seen, that the probability of the change of the spin orientation under the action of the oscillations of the internal magnetic field was proportional to the fourth power of the atomic magnetic moment. However, this probability was also

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*Resonance absorption of ultrasound occurs not only in paramagnetic, but also in ferromagnetic and anti-ferromagnetic substances. The absence of a satisfactory theory of the spin-lattice interaction for ferro and anti-ferromagnetic substances makes it difficult to give a quantitative determination of the acoustic effect. It is known that the usual effect of the ferro and anti-ferromagnetic resonances is not less than the resonance absorption in paramagnetic substances. Hence we may expect that the resonance absorption of ultrasound in ferro and anti-ferromagnetic substances is also significant.

[1] S. A. Al'tshuler, J. Exper. Theoret. Phys. USSR **28**, 38 (1955)

[2] J. Waller, Z. Phys. **79**, 370 (1932)

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

inversely proportional to a^9, where a denotes the equilibrium spacing between the magnetic atoms of the crystal. Hence it was clear that the magnetic forces could determine spin-lattice interactions in substances with large atomic magnetic moments and with a large density of magnetic atoms.

We take the usual expression for the atomic magnetic dipole interaction operator:

$$U_{kl} = g^2\beta^2\left[\frac{(S_k S_l)}{r_{kl}^3} - \frac{3(S_k r_{kl})(S_l r_{kl})}{r_{kl}^5}\right]. \tag{3}$$

To determine the absorption coefficient of sound we start from formula (1). Substituting in (1) the square of the spin-lattice interaction matrix element, if it is assumed that the sound wave is propagated along the x axis, one easily obtains the following formula[2].

$$\begin{aligned}&|\mathscr{H}_{\alpha,\beta;\,n_a-1,\,n_a}|^2\\ &= \frac{hn_a}{4\pi^2 M\nu}\sum_l\left(\frac{2\pi\nu r_{kl}}{v}\right)^2 |(U_{klx})_{\alpha,\beta}|^2,\end{aligned} \tag{4}$$

where

$$U_{klx} = \partial U_{kl}/\partial x_{kl}, \tag{5}$$

the summation being carried out over all the magnetic atoms of the crystal. As usual, we apply this formula where the atoms comprise a simple cubic lattice. We are going to make use of the representation in which S_{kz} and S_{lz} are diagonal, and we denote by M_k and M_l the magnetic quantum numbers of the appropriate atoms. The operator U_{klx} will contain various terms of the type $S_{kq}S_{lp}$, non-diagonal matrix elements which differ from zero only in the following case:

$$\begin{aligned}&(S_{kx}S_{lz})_{M_k,M_k+1;\,M_l,\,M_l} = \tfrac{1}{2}\sqrt{S(S+1)-M_k(M_k+1)}\,M_l \equiv t,\\ &(S_{ky}S_{lz})_{M_k,\,M_k+1;\,M_l,M_l} = it;\end{aligned} \tag{6}$$

$$\begin{aligned}&(S_{kx}S_{lx})_{M_k,M_k+1;\,M_l,M_l+1}\\ &= \tfrac{1}{4}\sqrt{S(S+1)-M_k(M_k+1)}\\ &\times\sqrt{S(S+1)-M_l(M_l+1)} \equiv p,\\ &(S_{kx}S_{ly})_{M_k,M_k+1;\,M_l,\,M_{l+1}}\\ &= (S_{ky}S_{lx})_{M_k,\,M_k+1;\,M_l,\,M_l+1} = ip,\\ &(S_{ky}S_{ly})_{M_k,\,M_k+1;\,M_l,\,M_l+1} = -p.\end{aligned} \tag{7}$$

At first we consider the absorption of sound by the allowed transition $\Delta M_k = 1$ and $\Delta M_l = 0$. With the aid of (3), (4), and (6) we find the absolute square of the matrix element U_{klx}:

$$\begin{aligned}&|(U_{klx})_{M_k,\,M_k+1;\,M_l,\,M_l}|^2\\ &= 9\frac{g^4\beta^4}{r_{kl}^{14}}\,z_{kl}^2\,[2x_{kl}^2(x_{kl}^2+y_{kl}^2)\\ &-10x_{kl}^2r_{kl}^2+r_{kl}^4]\,t^2.\end{aligned} \tag{8}$$

We carry out the averaging for various directions of propagation of sound relative to the axes of the crystal, and also for all values of M_k and M_l. Then we obtain

$$\begin{aligned}&|(U_{klx})_{M_k,\,M_k+1;\,M_l,\,M_l}|^2\\ &= \frac{759}{7}\frac{g^4\beta^4}{r_{kl}^8}\frac{1}{36}S(S+1)^2(2S+1).\end{aligned} \tag{9}$$

We substitute this expression into (4) and then into (1) and taking into account the action of nearest neighbors only, we obtain for the absorption coefficient

$$\sigma = \gamma PZ(g^2\beta^2/a^3)^2 S(S+1)^2(2S+1)\nu^2, \tag{10}$$

where Z is the number of nearest neighbor atoms in the crystal lattice, $\gamma\perp = 253/21$, d is the density of the substance, and $P = \pi^2 N/kTv^3\nu_{1/2}d$. Our calculation pertains to the absorption of sound vibrations, propagated perpendicular to the applied magnetic field, along the z axis. If we carry out the analogous calculation for waves that are parallel to the magnetic field then we obtain the same expression as (1) only with the coefficient $\gamma\parallel = 16/21$.

For the absorption coefficient, in the coupled double transition ($\Delta M_k = +1$; $\Delta M_l = +1$), we obtain

$$\sigma = \gamma PZ(g^2\beta^2/a^3)^2(S+1)^2(2S+1)^2\nu^2, \tag{11}$$

where $\gamma\perp = 40/7$, $\gamma\parallel = 40/21$. In this way it is found that the line-width which corresponds to the resonance condition

$$h\nu = 2g\beta H, \tag{12}$$

yields approximately the same intensity as for the usual normal line which is specified by condition (2).

As an example, we estimate the absorption coefficient σ from formula (10) for MnF_2. For a temperature $T = 300\,^\circ K$, assuming $\nu_{1/2} = 10^9$ sec^{-1}, we obtain

$$\sigma = 0.7\cdot 10^{-19}\,\nu^2\ \text{см}^{-1}. \tag{10'}$$

The action of a magnetic force in the spin-lattice interaction is appreciable in substances with large densities of magnetic atoms. But in these substances there is also a large exchange force. The usual operator of the exchange interaction gives the following isotropic form:

$$\sum_l I(r_{kl})\,(S_k\,S_l).$$

This matrix does not have non-diagonal elements, and therefore isotropic exchange forces cannot directly influence a spin-lattice interaction**. However there are found in certain paramagnetic substances anisotropic exchange forces[4] that are able to play an essential role. For example, these forces are involved in the explanation of the magnetic substance $NiSiF_6\cdot 6H_2O$[5], where the exchange interaction operator has the dipole form

$$\mathscr{H}_{\text{об}} = \sum_l A(r_{kl}) \times [(S_k\,S_l) - 3\,r_{kl}^{-2}(S_k\,r_{kl})(S_l r_{kl})]. \tag{13}$$

Then the calculation is precisely analogous to the calculation we employed in the magnetic case . We only know the dependence of the integral A on the atomic spacing. If we make the natural assumption that $A(r) = A_0\,(a)\,e^{-r/r_0}$ where $r_0 \sim a$, then the matrix element of the disturbance goes over to the expression $[\,(2/a) + (1/r_0)\,]$. If we assume that it equals $3/a$ we obtain for the coefficient of sound absorption the same formulas (10) and (11), but $(g^2\beta^2/a^3)$ is replaced by $[\,A(a)\,]^2$. For the transition between neighboring energy levels the coefficient γ is equal to

$$\gamma_\perp = 391/105, \qquad \gamma_\parallel = 8/21.$$

The detailed comparison of the experiments for paramagnetic resonance and the theoretical calculations carried out by Glebashev[6], for a wide range of substances, showed that the exchange integral lies between the limits 10^{-17}– 10^{-18} erg. In such a case the exchange force may increase the value of the calculated absorption coefficient over the action of magnetic interaction alone by one or two orders of magnitude.

3. RARE-EARTH METALS

The paramagnetism of the rare-earth metals depends on the deep lying internal atomic $4f$ electrons; the action of the conduction electrons is insignificant. Hence there exist great similarities between the magnetic properties of rare-earth metals and the salts of these elements. The author[7] by means of a comparison of the theoretical calculations with the experiments for the paramagnetic resonance in metallic cerium, praseodymium and neodymium has established that the atoms of these metals are triply ionized and the splitting of their energy levels is determined by electric fields having the same symmetry as the crystal lattice.

We carry out the calculation of the absorption coefficient of sound in rare-earth metals assuming that the spin-lattice interaction definitely modulates the electrical field of the vibrating lattice. At first we confine ourselves to the metals possessing cubic lattices, of which there are β- cerium, β-praseodymium, europium and ytterbium. For calculating the absorption coefficient we must use formulae (1), (4) and (5), only it is neccessary to understand that by U_{kl} is meant the energy of $4f$ electrons in electric fields, created by neighboring metallic ions. Taking into account the interaction of the six nearest neighbors and considering that the sound waves are propagated along the x axis, we find for U_{klx} the following expression:

$$U_{klx} = \frac{3ee'}{a^4} \times [u_x(r^2 - 3x^2) + 2u_y\,xy + 2u_z\,xz]\ , \tag{14}$$

where $\mathbf{r}$ is the radius vector connecting $4f$ electron to the nucleus, x, y, z are components of this vector e' is the effective ionic charge, a is the lattice constant, $\mathbf{u}$ is the unit vector, along the direction of the atomic vibrations.

β-cerium. The energy levels and wave functions found in an electric field of cubic symmetry and an external magnetic field are specified in formula (26) of reference 1, for Ce^{+++} and Fe^{+++} which have total angular momentum of 5/2. This formula allows

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** The average internal magnetic fields of crystals, and consequently the resulting absorption line-width $\nu_{1/2}$ is highly dependent on isotropic exchange forces. Hence this force indirectly influences the absorption of ultrasound and the spin-lattice interaction.

[4] W. Opechowski, Physica **14**, 234 (1948)

[5] J. F. Ollom and J. H. Van Vleck, Physica **17**, 205 (1951)

[6] G. Y. Glebashev, Dissertation, Kazan State University, 1954

[7] S. A. Al'tshuler, J. Exper. Theoret. Phys. USSR **26**, 439 (1954)

us to simplify the calculation, if we take into account that the Zeeman splitting is by far weaker than that caused by the electric field. We calculate with the aid of the given functions and show that in first approximation only the following nondiagonal matrix elements differ from zero:

$$(U_{klx})_{ac} = (U_{klx})_{bd} = \frac{4\sqrt{3}}{105}(-3u_x + 2iu_y)\left(\frac{ee'}{a^2}\right)\frac{\overline{r^2}}{a^2}, \qquad (15)$$

$$(U_{klx})_{ad} = (U_{klx})_{bc} = \frac{4\sqrt{3}}{105}u_z\left(\frac{ee'}{a^2}\right)\frac{\overline{r^2}}{a^2}.$$

Hence when we average for different directions of polarization, we find

$$|(U_{klx})_{ac}|^2 = 13\,|(U_{klx})_{ad}|^2 = 13\left(\frac{4}{105}\frac{ee'}{a^2}\frac{\overline{r^2}}{a^2}\right)^2. \qquad (16)$$

Substituting (16) into (4) and (1) we find the absorption coefficient of sound in a magnetic field perpendicular to the direction of propagation of the waves

$$\sigma = \gamma P\left(\frac{ee'}{a}\right)^2\left(\frac{\overline{r^2}}{a^2}\right)^2\nu^2, \qquad (17)$$

where

$$\gamma_{cc} = \gamma_{bd} = 13\,(8/105)^2, \quad \gamma_{ad} = \gamma_{bc} = (8/105)^2.$$

If the sound wave is parallel to the magnetic field, then $\gamma_{ac} = \gamma_{bc} = \gamma_{ad} = \gamma_{bd} = 2(8/105)^2$. This formula is correct for any metal having a cubic lattice, except that the γ factors have different values. The numerical value of the coefficient σ is difficult to obtain since as yet we have not given the magnitude of the effective charge. If we assume $e' = e$ and for γ we take the maximum value, then for $T = 300\,°\mathrm{K}$ we find

$$\sigma \sim 10^{-16}\nu^2\ \mathrm{cm}^{-1}. \qquad (17')$$

The differences $E_a - E_c$ and $E_b - E_d$ are equal and fit a single absorption line, whose position is necessarily strongly dependent on the direction of the external magnetic field relative to the axes of the crystal. On turning the magnetic field from the [100] direction to along the [111] direction, the value of the spacing $E_a - E_c = E_b - E_d$ is changed from $4/3g\beta H$ to $1/3g\beta H$. Hence in polycrystalline samples this absorption line has a half-width of the order of $g\beta H$.

The position of other absorption lines is slightly dependent on the direction of the magnetic field relative to the crystal axes, because the change of the interval $E_a - E_d = E_b - E_c$ goes only from $7/3g\beta H$ to $8/3g\beta H$.

β-praseodymium. In an electric field of cubic symmetry the energy levels of praseodymium split into four components: one singlet, one doublet and two triplets. The resultant splitting in a magnetic field does not depend on the direction of this field relative to the crystal axes. The perturbation method leads to the following values for the energy and wave functions:

$$E^{(\alpha)}_{1,3} = \frac{7}{27}\Delta \pm \frac{1}{2}G + \frac{189}{80}\frac{G^2}{\Delta}; \qquad (18)$$

$$\Psi^{(\alpha)}_{1,3} = \frac{1}{\sqrt{8}}(\Phi_{\mp 3} + \sqrt{7}\,\Phi_{\pm 1});$$

$$E^{(\alpha)}_{2} = \frac{7}{27}\Delta + \frac{864}{35}\frac{G^2}{\Delta};$$

$$\Psi^{(\alpha)}_{2} = \frac{1}{\sqrt{2}}(\Phi_{-4} - \Phi_4);$$

$$E^{(\beta)} = \frac{14}{27}\Delta + \frac{180}{7}\frac{G^2}{\Delta};$$

$$\Psi^{(\beta)} = \frac{1}{\sqrt{24}}(\sqrt{5}\Phi_{-4} + \sqrt{14}\,\Phi_0 + \sqrt{5}\,\Phi_4);$$

$$E^{(\gamma)}_{1,2} = \frac{2}{27}\Delta \pm \frac{36}{5}\frac{G^2}{\Delta};$$

$$\Psi^{(\gamma)}_{1} = \frac{1}{\sqrt{24}}(\sqrt{7}\,\Phi_{-4} - \sqrt{10}\,\Phi_0 + \sqrt{7}\,\Phi_4);$$

$$\Psi^{(\gamma)}_{2} = \frac{1}{\sqrt{2}}(\Phi_{-2} + \Phi_2);$$

$$E^{(\delta)}_{1,3} = -\frac{13}{27}\Delta \pm \frac{5}{2}G + \frac{189}{80}\frac{G^2}{\Delta};$$

$$\Psi^{(\delta)}_{1,3} = \pm\frac{1}{\sqrt{8}}(\sqrt{7}\,\Phi_{\mp 3} - \Phi_{\pm 1});$$

$$E^{(\delta)}_{2} = -\frac{13}{27}\Delta - \frac{36}{5}\frac{G^2}{\Delta};$$

$$\Psi^{(\delta)}_{2} = \frac{1}{\sqrt{2}}(\Phi_{-2} - \Phi_2).$$

Here Δ is the total value of the splitting of the main energy levels of Pr^{+++} in the electric field of the crystal. In a magnetic field perpendicular to the propagation direction of the sound

$$\gamma_{\alpha_1\alpha_3} = \frac{13}{3}\left(\frac{182}{275}\right)^2, \quad \gamma_{\alpha_1\alpha_2} = \gamma_{\alpha_2\alpha_3} = \frac{8}{27}\left(\frac{182}{275}\right)^2,$$

$$\gamma_{\delta_1\delta_3} = \frac{13}{27}\left(\frac{208}{275}\right)^2, \quad \gamma_{\delta_1\delta_2} = \gamma_{\delta_2\delta_3} = \frac{2}{3}\left(\frac{338}{825}\right)^2,$$

$$\gamma_{\gamma_1\gamma_2} = 13\left(\frac{416}{33\cdot 225}\right)^2.$$

If the direction of the field is parallel to the direction of motion of the sound wave then the only difference is in the following factors

$$\gamma_{\alpha_1\alpha_2} = \gamma_{\alpha_2\alpha_3} = \frac{16}{27}\left(\frac{182}{275}\right)^2, \quad \gamma_{\delta_1\delta_2} = \gamma_{\delta_2\delta_3} = \frac{4}{3}\left(\frac{338}{825}\right)^2.$$

Particular interest exists in the absorption of sound in the resulting transition between the above levels γ_1 and γ_2, as the magnetic field splits the level γ only in the second approximation. The location of the absorption peak in this case is determined by the value of Δ. In this way the observation of this line allows an immediate evaluation of the magnitude of the electric field inside the crystal. We notice that with the aid of the ordinary paramagnetic resonance this is impossible since the magnetic dipole transition between the sublevels γ_1 and γ_2 is forbidden.

Europium. The angular momentum of triply ionized atoms of europium in the ground state is zero. At room temperature, however, there is a noticeable polulation of the first excited state with $J = 1$ separated from the ground state by 214 cm^{-1}. It is well known that the energy level $J = 1$ does not split in an electric field of cubic symmetry. Hence the splitting in an external magnetic field is the same as for the free atom.

The factor γ has the following values

$$(\gamma_\perp)_{-1,1} = 0.52; \ (\gamma_\perp)_{-1,0} = (\gamma_\perp)_{0,1} = 0.08;$$
$$(\gamma_\parallel)_{-1,0} = (\gamma_\parallel)_{0,1} = 0.16;$$
$$(\gamma_\parallel)_{-1,1} = 0.$$

Ytterbium. In the ground state the ytterbium ion has $J = 7/2$, the same as ionic gadolinium. Hence we take advantage of the calculated energy and wave functions for gadolinium[8]:

$$E^{(a)}_{1,2} = \pm \frac{3}{2} G;$$
$$\Psi^{(a)}_{1,2} = \frac{1}{2} (\sqrt{3}\, \Phi_{\pm 5/2} - \Phi_{\mp 3/2});$$
$$E^{(b)}_{1,4} = \frac{5}{8} \Delta \pm \frac{11}{6} G;$$
$$\Psi^{(b)}_{1,4} = \sqrt{\frac{7}{2}} \left(\Phi_{\pm 7/2} - \sqrt{\frac{5}{7}}\, \Phi_{\mp 1/2} \right);$$
$$E^{(b)}_{2,3} = \frac{5}{8} \Delta \pm \frac{1}{2} G;$$
$$\Psi^{(b)}_{2,3} = \frac{1}{2} (\Phi_{\pm 5/2} + \sqrt{3}\, \Phi_{\mp 3/2});$$
$$E^{(c)}_{1,2} = \Delta \pm \frac{7}{6} G;$$
$$\Psi^{(c)}_{1,2} = \sqrt{\frac{5}{12}} \left(\Phi_{\pm 7/2} + \sqrt{\frac{7}{5}}\, \Phi_{\mp 1/2} \right).$$

With the aid of these wave functions the factors that are non-zero are found to have the following values

$$(\gamma_\perp)_{b_1 b_3} = (\gamma_\perp)_{b_2 b_4} = 13 / (21)^2;$$
$$(\gamma_\parallel)_{b_1 b_2} = (\gamma_\parallel)_{b_3 b_4} = (4 / 7)^2.$$

We now consider metals with hexagonal lattices. At first we concern ourselves with α-Ce, Nd, Dy and Er whose ions have an odd number of electrons. In these ions electric fields of hexagonal symmetry cause complete splitting of the energy levels, retaining only the Kramers degeneracy. Since this degeneracy is not removed by the electric field the spin-lattice coupling can only emerge in second approximation. Hence the effect of paramagnetic resonance in ultrasound in these metals is $(g\beta H/\Delta)^2$ times weaker than in metals with cubic lattices. All that we have said also applies to samarium whose lattice is tetragonal.

A special case is presented by gadolinium whose ions are in the S state. The spin-lattice interaction in Gd^{+++} appears to depend on magnetic and exchange forces.

The ions of metallic α-Pr, Tb, Ho, Pm contain even numbers of electrons. Certain energy levels of these ions retain their double (non-Kramers) degeneracy in an electric field of hexagonal symmetry, which may be removed in a field of lower symmetry. In this case the spin-lattice interaction is different from zero in the first approximation. The effect on the absorption of sound will be of the same order as in metals of cubic lattices.

The study of the resonance absorption of ultrasound in rare-earth metals has a special interest, as the investigation of the absorption of electromagnetic waves in metals is extremely difficult to carry out because of the skin-effect.

4. NUCLEAR PARAMAGNETIC RESONANCE IN ULTRASOUND

Resonance absorption of ultrasound obviously takes place not only in "electronic" paramagnetics but also in substances possessing nuclear paramagnetism. We attempt to estimate the magnitude of this effect.

To begin with, we will consider solid bodies (non-metallic). The exchange of energy between the elastic vibrations of the lattice and the system of nuclear spins, due to a magnetic nuclear interaction, gives an effect whose value can be calculated from formula (10). Thereby it is only necessary to keep in mind that in the first place β is the nuclear magneton; this decreases the absorption coefficient by $\sim 10^{12}$. In the second place, $\nu_{1/2}$ now means the line-width of the nuclear resonance, which causes an increase of approximately 10^5. A more careful numerical calculation

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[8] C. Kittel and J. M. Guttinger, Phys. Rev. 73,162 (1948)

carried out for the NaBr, gives $\sigma \sim 10^{-25}\nu^2$cm^{-1}. Thus the absorption of ultrasound by the action of magnetic fields is extremely slight.

It is known that in many cases the spin-lattice coupling is caused by a quadrupole interaction[9]. The order of magnitude of the absorption coefficient of sound, caused by quadrupole forces, may be determined from formula (10) if we replace $g^2\beta^2$ by e^2Q. If we take into account that $\beta \sim 10^{-23}$G/cm^3, and $Q \sim 10^{-25}$cm^2, then for some substances the resulting $\sigma = 10^{-20}\nu^2$cm^{-1}. This value is exceedingly small since for an applied static magnetic field $\sim 10^4$ oersteds, as is seen from condition (2), we are obliged to employ an alternating field of frequency 10^7 cycles per sec.

We may expect a large effect in liquids . As is known from the theory of spin-lattice interactions in liquids[10], it follows that whereas in solid bodies the spectrum of thermal vibration frequencies determines a correspondingly small intensity from condition (3), in liquids the thermal motion contains oscillations of these frequencies with enormous intensities. In the case of solids we could, in comparison with the intensity of sound vibrations, neglect the thermal oscillations of these frequencies. Now we must properly reject this assumption, and then the probability of absorbing energy quanta of sound vibrations has an order of magnitude equal to $\frac{1}{2}\tau$ (τ is the time of spin-lattice relaxation).

The energy of sound waves, absorbed per unit volume of a substance in one second is obviously equal to

$$\frac{1}{2\tau} N h\nu \frac{h\nu}{kT} \frac{\Delta\nu}{\nu_{1/2}},$$

and hence for the absorption coefficient we have (I is the intensity of sound vibrations)

$$\sigma = N(h\nu)^2 \Delta\nu / 2\tau k T I \nu_{1/2}. \qquad (19)$$

We check, as an example, the proton resonance in water. By means of the addition of a paramagnetic salt the time of the spin-lattice relaxation may easily be brought to 10^{-4} seconds.

If $\nu = 3 \times 10^7$ cycles per sec. and the frequency interval and half-width $\nu_{1/2}$ are approximately the same, then in one second the energy absorbed ~ 360 ergs. It is easily calculated that the intensity of sound and thermal vibrations are comparable, if $I \approx 10^5$ ergs/cm^{3}sec; and therefore we find $\sigma \sim 0.01$ cm^{-1}. An increase in the sound intensity causes a disappearance of the effect because of saturation (cf. below). It is necessary to keep in mind that in so far as the spin-lattice interaction in water is produced by magnetic forces, then we have two absorption lines, whose locations are determined by equations (2) and (12), wherein the second line, as was easily derived in reference (10), has twice the intensity of the first.

It is well known that in the usual phenomenon of nuclear magnetic resonance we frequently observe a saturation effect, which consists in the fact that the spin-lattice interaction does not enable a transfer of all of the energy, absorbed by the spin system, to the thermal vibrations of the lattice. Consequently the population of the upper magnetic levels increases and the absorption of energy from the electromagnetic field decreases. An analogous effect is possible in the case of paramagnetic resonances for ultrasound. For simplicity we assume that we have only two magnetic levels and let A stand for the transition probability between them per second under the action of ultrasound. We denote by n the excess population of the lower level and let n_0 stand for the excess which corresponds to thermal equilibrium for the lattice temperature. In the absence of ultrasound, as is well known, the process of establishing equilibrium is set forth in the equation

$$dn/dt = (n_0 - n)/\tau,$$

where we may consider that τ determines the time of spin-lattice relaxation. If there is a sound field in the substance, then the equation takes the form

$$\frac{dn}{dt} = \frac{n_0 - n}{\tau} - 2nA, \qquad (20)$$

from which it follows that in the stationary state ($dn/dt = 0$)

$$n/n_0 = 1/(1 + 2A\tau). \qquad (21)$$

This value is usually called the saturation factor. If $n/n_0 \gg 1$, it is clear that the absorption of ultrasound is vanishingly small.

In liquids $A = (1/2\tau)(\Delta\nu/\nu_{1/2})$, the factor n/n_0 is nearly ½ and consequently saturation is feeble. In solids it is easy to calculate the following expression for the transition probability:

$$A = I\sigma kT / N(h\nu)^2. \qquad (22)$$

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[9] R. V. Pound, Phys. Rev. 79, 585 (1950)

[10] N. Blombergen, E. M. Purcell and R. V. Pound, Phys. Rev. 73, 678 (1948)

The numerical value shows that with an intensity of the order of $1 \mathrm{W/cm}^2$ for a frequency 10^7 cycles per sec. we obtain a strong saturation. This fact may be used for the indirect detection of the absorption of ultrasound by nuclei. Suppose that we are observing the usual effect of the resonance absorption of an electromagnetic field of frequency ν. Then we superimpose a sufficiently strong acoustic field of the same frequency and the effect may be canceled.

With the aid of formulae (21) and (22) the possibility of the saturation effect for electric paramagnetic resonance for ultrasound can also be explained. In certain substances, which possess a large sound absorption coefficient σ, saturation may be approached under experimental conditions.

5. CONCLUSION

We have considered the resonance absorption of ultrasound in the main types of paramagnetic substances. For metals we considered only the rare-earths. In other metals the effect we have investigated is small. In metals that do not have available deep lying f-electrons with uncompensated spins, paramagnetism is due to the outer atomic electrons, which participate in conduction. In consequence of this the translational motion will also participate in the exchange of energy between the lattice vibrations and the electronic spins, observed in an applied magnetic field. Since the average energy of translational motion far exceeds the magnetic energy of the electrons, then clearly the absorption of sound cannot substantially depend on the magnetic field intensity; it will not have the sharply defined resonance character.

In the foregoing section we considered the nuclear effect in liquids. Formula (19) can only be applied for estimating the electronic resonance absorption of sound in liquid solutions of paramagnetic salts. In this case the number of absorbing atoms N is considerably smaller than in the case of nuclear resonances, the half width of the absorption line is on the other hand much larger. Hence the absorption coefficient is comparatively small, in spite of the considerably much shorter time of spin-lattice relaxation ($\tau \sim 10^{-8}$sec). In truth electronic resonance permits the use of very high frequencies, which may make the effect observable, at the present time,by a sensitive arrangement.

The theory of spin-lattice interaction,developed for liquids, may be applied also to gases. With the aid of formula (20) of reference (10) we find that the time of paramagnetic relaxation for gases for atmospheric pressure and for room temperature is equal to $\tau \sim 10^{-6}$ sec. From formula (19) it follows that the absorption coefficient is very small [order of magnitude $10^{-20} (\nu^2/l) \mathrm{cm}^{-1}$], if we take advantage of what is known from experiments on paramagnetic resonance in oxygen[11] where the value of $\nu_{1/2} = 0.05 \mathrm{~cm}^{-1}$.

It is of interest to compare these considerations to the paramagnetic resonances for electromagnetic waves.

1. To begin with, we compare the magnitudes of both effects. The coefficient of absorption of energy in an electromagnetic field[12] is equal. to

$$\sigma_e = \frac{8\pi^2}{c} \nu \chi''. \tag{23}$$

Where χ'' is the imaginary part of the complex magnetic susceptibility. If by χ_0 we denote the static susceptibility, then for maximum absorption $\chi'' \approx \chi_0 \nu / \nu_{1/2}$,and consequently,

$$\sigma_e = \frac{8\pi^2}{c\nu_{1/2}} \chi_0 \nu^2. \tag{24}$$

At "electronic" paramagnetic frequencies $\nu_{1/2} \sim 10^9$ cycles per sec, $\chi_0 \sim 10^{-5}$ and hence $\sigma \sim 10^{-22} \nu^2 \mathrm{~cm}^{-1}$. For the absorption coefficient of ultrasound for many substances we also derive the expression, proportional to ν^2, in which the proportionality factor is strongly dependent on the magnitude of the matrix element of the spin-lattice interaction. If this matrix element differs from zero in the first approximation, the for the coefficient of sound absorption σ we obtain a value exceeding σ_e . Under the requirements of higher approximations then usually σ_e and σ have values of the same order.

We make the observation, that throughout we calculated the average absorption coefficient for solids for longitudinal and transverse waves. Generally speaking, the transition probabilities between magnetic sublevels under the action of acoustic vibrations of the first type are very greatly surpassed by those for vibrations of the second type. Thus, for example, if the magnetic field is perpendicular to the direction of propagation of sound waves, then the absorption of sound in the resulting transition between sublevels *ad* and *bc of* β- cerium is possible only

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[11] R. Beringer and J. G. Castle, Phys. Rev. **78**, 581 (1950); **81**, 82 (1951)

[12] J. C. Gorter, *Paramagnetic Relaxation* (1949), pg. 41

under the action of transverse oscillations.

2. In the case of the usual paramagnetic resonance the probability of absorbing a photon is a maximum if the alternating magnetic field is perpendicular to the static field; this probability decreases to zero if the magnetic fields are set parallel to one another. The probability of absorbing phonons is slightly dependent on the direction of the magnetic field. All the changes in the direction of this field may vary the order of magnitude of the effect.

3. The absorption of ultrasonic frequencies is a possible result of transitions between those sublevels for which the magnetic dipole transitions are forbidden. Hence, for example, in substances with pure spin paramagnetism the probability of absorbing photons is large only for transitions coupled by changes of the magnetic quantum numbers of the atoms by unity, where we know that only one resonance line appears. The probability of absorbing phonons has the same order both for transitions in which the magnetic quantum numbers of two interacting atoms change by unity, and those which are connected with changes of the quantum numbers of single atoms. Hence two observable absorption lines exist here.

4. The line widths of paramagnetic resonances both for ultrasound as well as for electromagnetic waves depend on the same factors. If the spin-lattice interaction is stronger than the spin-spin interaction, the half-width is of the order of $\sim 1/2\pi\tau$ and hence is strongly temperature dependent. If the spin coupling is stronger than the coupling to the lattice vibrations, then the line-width depends on the magnetic dipole interaction, exchange forces, electric fields of the ions and is not temperature dependent. Although the broadening of the absorption line in both phenomena is explained by the same forces, the form of one line can differ considerably from the other in the second case considered. This is explained by the fact that for the two phenomena we deal with one and the same band of energy levels, which produce magnetic and other interactions. However, the rules which determine the transition probability between these levels, under the action of ultrasound and under the action of an external alternating magnetic field, are completely different in nature. Thus, for example, the resonance line for the absorption of an electromagnetic field narrows under the action of an isotropic exchange force, as is well known [13]. Proof of this narrowing is based upon the fact that the second moment of the absorption line does not depend on the exchange force; this follows from the fact that the matrix S_x, which determines the probability of the magnetic dipole transition, commutes with the exchange interaction operator $A\Sigma S_i S_k$.

Evidently, the transition under the action of ultrasound may lead to an absorption line, the second moment of which depends on exchange forces. Nevertheless, the order of the absorption line-width is the same in both effects.

We note still another case in what follows. Comparatively small sensitivity of the ultrasonic method of investigation makes it desirable to use an indirect method of detecting paramagnetic resonances in ultrasound. Some of these were discussed in a previous section. We indicate one possibility. Paramagnetic resonance absorption of ultrasound will be accompanied by magnetization of substances which may be evaluated with the help of the coefficient of high frequency susceptibility χ'. From the investigation of the usual paramagnetic resonances it is known, that if the static magnetic field is changed, then the maximum change χ' is approximately equal to the value χ'', for maximum absorption. However with the help of (23) and (24) we at once find $\chi' \sim c\sigma/8\pi^2\nu$. The change in magnetization under the action of ultrasound may probably be observed by the use of the usual method of measuring χ' of Zavoiskii[14] or by nuclear induction[15].

In conclusion we note that the calculation of the spin-lattice interaction, which determines the magnitude of the effect of resonance absorption of ultrasound in paramagnetic substances can not lay claim to any great precision. The purpose was to arrange the calculation as an estimate of the order of magnitude of the effect and to establish the essential mechanism. The most interesting result which permits investigation is the explanation of the nature of the determinable characteristic constant of the spin-lattice interaction in various classes of paramagnetic bodies.

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[13] J. H. Van Vleck, Phys. Rev. 74, 1168 (1948)

[14] E. K. Zavoiskii, J. Exper. Theoret. Phys. USSR 17, 155 (1947)

[15] F. Bloch, W. W. Hansen, and M. Packard, Phys. Rev. 70, 474 (1946)

Translated by B. Hamermesh
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