PARAMAGNETIC ABSORPTION OF SOUND

S. A. AL'TSHULER, B. I. KOCHELAEV, and A. M. LEUSHIN

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1. INTRODUCTION

IN recent years, in addition to the wide range of investigations of the behavior of paramagnets in variable magnetic fields, there has also been successfully developed the study of the absorption of energy from a sound field by bodies containing paramagnetic particles. Initially the resonance absorption of sound was treated theoretically,[1] as an analog of paramagnetic resonance.* Later on there were detailed computations made of the magnitude of this effect for various types of paramagnets[3,18] (crystals containing ions of the iron group, rare earth compounds, metals) on the assumption of different mechanisms of interaction of the paramagnetic particles with the sound field. The computations were also extended to nuclear paramagnets.[31-33]

In a series of papers[55-58] there was given a theoretical explanation of some interesting features of the

pulse methods for studying acoustic paramagnetic resonance. Some authors[50-51,53-54] discussed the shape of the line from acoustic paramagnetic resonance and calculated the moments of the absorption curves.

The first experimental results on the observation of acoustic paramagnetic resonance are due to Proctor and Tanttila,[40] who observed the effect on the spins of Cl^{35} nuclei in crystals of $NaClO_3$. Later on these investigations were continued using various experimental methods and in different substances.[41-49] The transition from nuclear to electron spins was made difficult by the need to use sound oscillations of much higher frequency. This problem was successfully solved in 1959 by Jacobson, Shiren, and Tucker,[26] who first observed electron acoustic paramagnetic resonance due to the spins of manganese ions and F-centers embedded in a quartz lattice. The continuation of these investigations gave much valuable information concerning the properties of lattice vibrations and their interaction with the spin system of paramagnets. Altogether, the first experimental results on acoustic paramagnetic resonance confirm the existing theories of the phenomenon, but at various points there have appeared serious discrepancies which await their explanation.

In addition to acoustic paramagnetic resonance there should also be a nonresonant absorption of sound which is the analog of paramagnetic absorption

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*The initiative in starting studies of resonance absorption of sound is due to E. K. Zavoĭskiĭ, who shortly after the discovery of paramagnetic resonance proposed to some physicists to study the theory of this phenomenon and to calculate the possibilities of observing it experimentally. The first results of the theoretical treatment of this phenomenon and its quantitative estimate were published by Al'tshuler in 1952.[1] In this same year, Kastler[2] treated qualitatively the problem of the effect of ultrasonics on nuclear paramagnetic resonance. Kastler reported the unsuccessful attempt to Grievet and Soutif to discover this effect in 1949.

in parallel magnetic fields.[64] The problem of nonresonant acoustic paramagnetic absorption was recently treated theoretically;[65,66] it was shown that present day experimental techniques permit one relatively easily to observe this effect. Nonresonant paramagnetic absorption is a maximum at relatively low frequencies, which should significantly simplify its experimental investigation.

Acoustic paramagnetic resonance appears to have interesting applications. Kastler[60] has proposed to use the acoustical effect for polarization of nuclei. Townes et al.[59,63] have established the conditions for the appearance of an acoustical "maser effect," the achievement of which would make possible the development of generators and amplifiers of supersonics.

2. RESONANT PARAMAGNETIC ABSORPTION OF SOUND

Resonant paramagnetic absorption of sound, or acoustic paramagnetic resonance, consists in the selective absorption of sound energy by a system of magnetic particles which occurs when the quanta of energy of the sound vibrations become equal to the intervals between magnetic energy levels. Thus, the distinction between the acoustic effect and ordinary paramagnetic resonance consists in the fact that the variable magnetic field is replaced by a sound field of the same frequency. In ordinary paramagnetic resonance, the energy accumulated in the spin system is transmitted to the lattice vibrations via the mechanism of spin-lattice relaxation. Acoustic resonance consists in the transfer of energy of sound vibrations of the lattice to the spin system, which occurs once again because of the existence of a spin-phonon interaction. It should, however, be remembered that paramagnetic spin-lattice relaxation even at the very lowest temperatures is usually due to a second order process, namely, combination scattering of phonons. The resonance absorption of ultrasound is obviously a one-phonon process.* The energy stored in the spin system after sound absorption will, by virtue of relaxation processes, be transferred back to the lattice in exactly the same way as under conditions of ordinary paramagnetic resonance.

Let us find the general expression for the coefficient of paramagnetic resonance absorption of sound.[3] The probability per second that a paramagnetic particle undergoes a transition between magnetic levels α and β, absorbing one quantum of the lattice oscillations, is equal to

$$A_{\alpha,\beta} = \frac{2\pi}{\hbar^2} \varrho_\omega |\langle \alpha, n_\omega | \mathcal{H}_{\text{s-p}} | \beta, n_\omega - 1 \rangle|^2, \qquad (2.1)$$

where $\langle \alpha, n_\omega | \mathcal{H}_{\text{s-p}} | \beta, n_\omega - 1 \rangle$ is the matrix element of the Hamiltonian for the spin-phonon interaction, n_ω is the number of phonons with the resonance frequency

*In paramagnets there will also be a combination scattering of sound, but the magnitude of this effect is very small.

ω, and $\rho_\omega = \omega^2 V / 2\pi^2 v^3$ is the spectral density of longitudinal or transverse plane polarized phonons propagating in a crystal of volume V with velocity v. If the sound vibrations are almost monochromatic, with a mean spread of frequency equal to $\Delta\omega$, then the intensity of the sound wave, that is the energy passing per second through unit area, is equal to $I = I_\omega \Delta\omega$, where $I_\omega = v\rho_\omega n_\omega \hbar\omega / V$.

Let us assume that the interval $\Delta\omega$ is much smaller than the line width of paramagnetic resonance absorption $\omega_{1/2}$. Then the energy of the sound waves absorbed per second per unit volume of the paramagnet, which contains N particles, at temperature T is equal to

$$E = NA_{\alpha,\beta} \frac{(\hbar\omega)^2}{kT} g(\omega) \Delta\omega, \qquad \int_0^\infty g(\omega) d\omega = 1. \qquad (2.2)$$

Here $g(\omega)$ gives the shape of the absorption line. The factor $\hbar\omega/kT$ determines the difference in occupation numbers of the pair of magnetic levels, and thus determines the excess of absorption acts over acts of emission of phonons. From (2.1) and (2.2) we get for the sound absorption coefficient

$$\sigma_{\alpha,\beta} = \frac{E}{I} = \frac{2\pi}{\hbar^2} \frac{N\hbar\omega V}{kTvn_\omega} g(\omega) |\langle \alpha, n_\omega | \mathcal{H}_{\text{s-p}} | \beta, n_\omega - 1 \rangle|^2. \qquad (2.3)$$

The calculation of matrix elements of the spin-phonon interaction requires a knowledge of the structure of the energy levels of the magnetic particles and the mechanism responsible for the coupling of the spin system to the lattice vibrations. In the following paragraphs we shall deal with the computation of the sound absorption coefficient for different types of paramagnets. The overwhelming majority of studies of paramagnetic properties have been on crystals whose paramagnetism is due to ions of the iron group. We shall deal in most detail with the acoustic effect in such crystals. We note that all the computations have been carried out without taking into account local disturbances of the lattice vibrations resulting from the injected paramagnetic ions.

3. CRYSTALS CONTAINING IONS OF THE IRON GROUP

The ions of the iron group usually are introduced in a crystal lattice so that they are in an octahedral surrounding of identical diamagnetic particles—molecules of water, oxygen ions, etc. Therefore the crystalline electric field acting on the paramagnetic ion consists of a strong component having cubic (octahedral) symmetry and a weak component of lower symmetry (cf. reference 4). Except for special cases, the crystalline field is weaker than the forces which cause the formation of the paramagnetic ion term, but is stronger than the spin-orbit interaction of the electrons. Because of this, the orbital motion is suppressed, and paramagnetism in first approximation has purely spin form. The calculation of the energy levels of the paramagnetic ion is accomplished

using the following Hamiltonian:

$$\mathcal{H}_{ion} = \mathcal{H}_0 + \mathcal{V}_0 + \lambda LS + 2\beta SH + \beta LH, \qquad (3.1)*$$

where λ is the spin-orbit coupling constant, β is the Bohr magneton, S and L are the spin and orbital angular momenta, H is the strength of the external magnetic field. In formula (3.1), $\mathcal{H}_0$ is the Hamiltonian of the free ion, including all interactions which do not depend on the spin variables; $\mathcal{V}$ is the energy of the ion in the crystalline electric field for the case of a rigid lattice; the third term is the operator of the spin-orbit coupling; the fourth and fifth terms are the energy in the external magnetic field of the spin and orbital angular momenta respectively. If we do not make the assumption of a rigid lattice and take into account the changes which are produced by the sound, then in place of (3.1) we have, for a paramagnetic ion interacting with lattice vibrations, the following Hamiltonian:

$$\mathcal{H} = \mathcal{H}_{ion} + \mathcal{H}_{latt} + (\mathcal{V} - \mathcal{V}_0). \qquad (3.2)$$

The Hamiltonian describing the lattice vibrations has the form

$$\mathcal{H}_{latt} = \sum_\omega \hbar\omega \left(a_\omega^+ a_\omega^- + \frac{1}{2} \right), \qquad (3.3)$$

where a_ω^+ and a_ω^- are the operators for creation and annihilation of phonons of frequency ω, having the properties

$$a_\omega^+ | \ldots n_\omega \ldots > = (n_\omega + 1)^{1/2} | \ldots n_\omega + 1 \ldots >,$$
$$a_\omega^- | \ldots n_\omega \ldots > = n_\omega^{1/2} | \ldots n_\omega - 1 \ldots >. \qquad (3.4)$$

By $| \ldots n_\omega \ldots \rangle$ we denote the eigenfunctions of the phonon system. The third term in the Hamiltonian, $\mathcal{V} - \mathcal{V}_0$, which represents the difference in energy of the ion in the crystalline electric field with a vibrating and a rigid lattice, couples the spin of the paramagnetic ion to the lattice vibrations. Here we assume that the main role in the spin-phonon interaction is played by the Kronig–Van Vleck mechanism,† which consists in the following: the vibrations of the lattice modulate the electrostatic interaction of the paramagnetic ion with the neighboring diamagnetic particles,

as a result of which there is a periodic variation of the orbital motion of the electrons which, for the most part to be sure, is "frozen in." The periodic changes in spin-orbit coupling lead to a reorientation of the electron spin with respect to the external magnetic field.

For further computations we expand V in the normal coordinates Q of the octahedral complex:

$$\mathcal{V} = \mathcal{V}_0 + \sum_p \mathcal{V}^p Q_p + \ldots, \qquad (3.5)$$

where $\mathcal{V}^p = \partial V / \partial Q_p$ are certain functions of the coordinates of the 3d-electrons which have been calculated by Van Vleck.[5]* We can limit ourselves to the linear terms in the expansion in Q_p, since we are interested only in one-phonon processes. If we expand Q_p in the normal coordinates of the whole crystalline lattice, then regarding $\mathcal{V} - \mathcal{V}_0$ as a perturbation we obtain for the matrix element of the spin-phonon interaction operator in which we are interested[6]

$$\langle a, n_\omega | \mathcal{H}_{s\text{-}p} | \beta, n_\omega - 1 \rangle = u \sum_{p, k \geq n} a_p \langle a | \lambda b_{kk}^p \hbar\omega S_k$$

$$+ \lambda b_{kn}^p [2\beta H (l_k S_n + l_n S_k) + \lambda (S_k S_n + S_n S_k)] | \beta \rangle. \qquad (3.6)$$

Here $k, n = x, y, z$, $u = n_\omega^{1/2} (\hbar\omega / dVv^2)^{1/2} \sin \varphi \cdot R$, d is the density of the crystal, φ is a phase constant, R is the equilibrium distance from the nucleus of the paramagnetic ion to the nearest diamagnetic particle. The coefficients a_p are determined by the direction cosines λ_m and Φ_m of the velocity and polarization of the sound wave:

$$a_1 = \sqrt{\frac{2}{3}} (\lambda_x \Phi_x + \lambda_y \Phi_y + \lambda_z \Phi_z),$$
$$a_2 = (\lambda_x \Phi_x - \lambda_y \Phi_y),$$
$$a_3 = \sqrt{\frac{1}{3}} (\lambda_x \Phi_x + \lambda_y \Phi_y - 2\lambda_z \Phi_z),$$
$$a_4 = (\lambda_x \Phi_y + \lambda_y \Phi_x),$$
$$a_5 = (\lambda_z \Phi_x + \lambda_x \Phi_z),$$
$$a_6 = (\lambda_y \Phi_z + \lambda_z \Phi_y). \qquad (3.7)$$

Finally,

$$b_k^p = - \sum_{i \neq 0}' \frac{\langle 0 | \mathcal{V}^p | i \rangle \langle i | L_k | 0 \rangle}{(E_i - E_0)^2},$$

$$b_{kn}^p = \sum_{i, j \neq 0}' \frac{\langle 0 | L_k | i \rangle \langle i | L_n | j \rangle \langle j | \mathcal{V}^p | 0 \rangle + \langle 0 | L_k | i \rangle \langle i | \mathcal{V}^p | j \rangle \langle j | L_n | 0 \rangle + \langle 0 | \mathcal{V}^p | i \rangle \langle i | L_k | j \rangle \langle j | L_n | 0 \rangle}{(E_i - E_0)(E_j - E_0)}, \qquad (3.8)$$

where by E_0 and $| 0 \rangle$ we mean the energy and wave function of the ground orbital level, while the energies E_i, E_j, and the functions $| i \rangle$, $| j \rangle$, refer to excited orbital states. The complicated expressions (3.8) are obtained because in the ground state the orbital magnetic moment is equal to zero, and one must use higher

approximations of perturbation theory. We note that in (3.6) we have not taken into account the Zeeman splitting of the higher orbital levels, which gives significant additional terms which are linear in the spin variables.

*Here we also include $\mathcal{V}^1$, which was not included in reference 5; but in cases where the symmetry of the crystalline field at the paramagnetic ion is lower than cubic and the lowest orbital level in the cubic field is a triplet, it may give a contribution to the spin-phonon interaction.

*$LS = L \cdot S$.

†We shall consider later on other relaxation mechanisms, which are significant in certain cases.

If we substitute (3.6) in (2.3) and average over phases,* then we obtain for the coefficient of sound absorption

$$\sigma_{\alpha,\beta} = P\omega^2 \left| \sum_{p=1}^{6} a_p \langle \alpha | \mathscr{H}_p | \beta \rangle \right|^2, \qquad (3.9)$$

where $P = \pi N R^2 g(\omega)/kTv^3 d$, and $\mathscr{H}_p$ is a certain combination of spin operators which in general is different for different ions.

The representation of the coefficient of sound absorption as a function of matrix elements of certain spin operators is very convenient for the following reason: the experimental investigation of the spectrum of paramagnetic resonance makes it possible to establish the form of the so-called spin Hamiltonian. Finding the eigenvalues and eigenfunctions of this Hamiltonian gives a system of spin energy levels and enables one to calculate the probability of magnetic dipole transitions between them. By means of these same eigenfunctions, by calculating the matrix elements of the spin operators $\mathscr{H}_p$, we can easily compute the coefficient of resonance absorption of sound for each pair of spin levels.

In the following we shall establish the form of the operators $\mathscr{H}_p$ for all possible configurations of 3d-electrons. Here we shall divide the ions into two groups, depending on whether the system of spin levels is a Kramers doublet (effective spin $S' = \frac{1}{2}$) or a multiplet $(S' > \frac{1}{2})$. The point is that in the first case no electric fields can eliminate the degeneracy of the energy level, and consequently changes in the crystalline field due to the sound vibrations are less effective than in the second case.

4. IONS WITH EFFECTIVE SPIN $S' > \frac{1}{2}$

The theory of acoustic paramagnetic resonance for ions of this type has been treated in references 3, 7, and 8. The computations show that for all ions with $S' > \frac{1}{2}$ the spin operators $\mathscr{H}_p$ have the following form:

$$\mathscr{H}_1 = \varepsilon_1 (S_x^2 + S_y^2), \qquad \mathscr{H}_4 = \varepsilon_4 (S_x S_y + S_y S_x),$$
$$\mathscr{H}_2 = \varepsilon_2 (S_y^2 - S_x^2), \qquad \mathscr{H}_5 = \varepsilon_5 (S_z S_x + S_x S_z),$$
$$\mathscr{H}_3 = \sqrt{\tfrac{1}{3}}\,\varepsilon_3 (S_x^2 + S_y^2 - \eta S_z^2), \qquad \mathscr{H}_6 = \varepsilon_6 (S_y S_z + S_z S_y). \quad (4.1)$$

The values of the parameters ε_k will be established later for each kind of ion. We note that in obtaining formulas (4.1) from the general expression (3.6) for the Hamiltonian of spin-phonon interaction, we have neglected the term proportional to $\lambda\beta H$ since it is small compared to the term proportional to λ^2 over the whole range of practically applicable magnetic fields.

In obtaining (4.1) it was assumed that the coordinate axes x, y, z coincide with the tetragonal axes of the octahedron. Such a choice of coordinate axes is con-

venient if the field of lower symmetry is tetragonal. If, however, it has trigonal symmetry, then it is more convenient to go over to a new system of coordinates x', y', z' with the z' axis along the trigonal axis of the octahedron and the y' axis located in the xOy plane. Now the operators take the form:

$$\mathscr{H}_1' = \varepsilon_1' (S_{x'}^2 + S_{y'}^2),$$

$$\mathscr{H}_2' = \sqrt{\tfrac{1}{3}}\,\varepsilon_2' [(S_{x'}S_{y'} + S_{y'}S_{x'}) - \sqrt{2}(S_{y'}S_{z'} + S_{z'}S_{y'})],$$

$$\mathscr{H}_3' = \sqrt{\tfrac{1}{3}}\,\varepsilon_3' [\sqrt{2}(S_{z'}S_{x'} + S_{x'}S_{z'}) - (S_{y'}^2 - S_{x'}^2)],$$

$$\mathscr{H}_4' = \sqrt{\tfrac{1}{3}}\,\varepsilon_4' (S_{x'}^2 + S_{y'}^2 - \eta S_{z'}^2),$$

$$\mathscr{H}_5' = \sqrt{\tfrac{1}{3}}\,\varepsilon_5' [\sqrt{2}(S_{x'}S_{y'} + S_{y'}S_{x'}) + (S_{y'}S_{z'} + S_{z'}S_{y'})],$$

$$\mathscr{H}_6' = \sqrt{\tfrac{1}{3}}\,\varepsilon_6' [\sqrt{2}(S_{y'}^2 - S_{x'}^2) + (S_{z'}S_{x'} + S_{x'}S_{z'})].$$

$$(4.2)$$

One must remember that, because of the rotation of the coordinate axes, the coefficients a_p in the fundamental formula (3.9) must be replaced by coefficients a_p', which are given as follows:

$$a_1' = \sqrt{\tfrac{2}{3}}\,(\lambda_{x'}\Phi_{x'} + \lambda_{y'}\Phi_{y'} + \lambda_{z'}\Phi_{z'}),$$

$$a_2' = \sqrt{\tfrac{1}{3}}\,[\sqrt{2}(\lambda_{y'}\Phi_{z'} + \lambda_{z'}\Phi_{y'}) - \lambda_{x'}\Phi_{y'} - \lambda_{y'}\Phi_{x'}],$$

$$a_3' = -\sqrt{\tfrac{1}{3}}\,[\lambda_{x'}\Phi_{x'} - \lambda_{y'}\Phi_{y'} + \sqrt{2}(\lambda_{z'}\Phi_{x'} + \lambda_{x'}\Phi_{z'})],$$

$$a_4' = -\sqrt{\tfrac{1}{3}}\,(\lambda_{x'}\Phi_{x'} + \lambda_{y'}\Phi_{y'} - 2\lambda_{z'}\Phi_{z'}),$$

$$a_5' = \sqrt{\tfrac{1}{3}}\,[\sqrt{2}(\lambda_{x'}\Phi_{y'} + \lambda_{y'}\Phi_{x'}) + \lambda_{y'}\Phi_{z'} + \lambda_{z'}\Phi_{y'}],$$

$$a_6' = \sqrt{\tfrac{1}{3}}\,[\lambda_{z'}\Phi_{x'} + \lambda_{x'}\Phi_{z'} - \sqrt{2}(\lambda_{x'}\Phi_{x'} - \lambda_{y'}\Phi_{y'})].$$

$$(4.3)$$

We proceed to consider individual ions.

1) $3d^2\ {}^3F,\ V^{3+}$. The successive splittings of the orbital levels by the strong field of cubic symmetry and the weak field of tetragonal or trigonal symmetry are shown in Fig. 1. States arising in the field of cubic symmetry are classified according to the irreducible representations of the octahedral group, Γ_k in the notation introduced by Bethe.[9] Since $\delta \ll \Delta$, we can restrict ourselves to considering that the level Γ_4
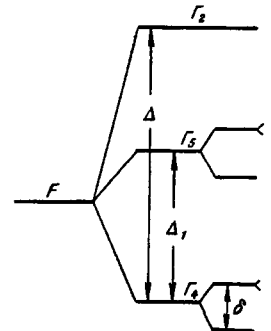

FIG. 1. Diagram showing successive splitting of an F-term in a strong electric field of cubic symmetry and a weak field of tetragonal or trigonal symmetry.

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*Such an averaging is admissible if the length of the sound wave is much smaller than the linear dimensions of the crystal.

alone participates in the spin-phonon interaction. The computations show that

$$\varepsilon_1 = \varepsilon_1' = -\frac{15\sqrt{6}}{8}\left(\frac{ee'}{R^2}\right)\left(\frac{\lambda}{\delta}\right)^2\frac{\bar{r}_0^4}{R^4},$$

$$\varepsilon_2 = \varepsilon_2' = \varepsilon_3 = \varepsilon_3' = \frac{27}{56}\left(\frac{ee'}{R^2}\right)\left(\frac{\lambda}{\delta}\right)^2\left(\frac{12}{5}\frac{\bar{r}_0^2}{R^2} - \frac{25}{6}\frac{\bar{r}_0^4}{R^4}\right),$$

$$\varepsilon_4 = \varepsilon_4' = \varepsilon_5 = \varepsilon_5' = \varepsilon_6 = \varepsilon_6' = -\frac{27}{28}\left(\frac{ee'}{R^2}\right)\left(\frac{\lambda}{\delta}\right)^2\left(\frac{1}{5}\frac{\bar{r}_0^2}{R^2} - \frac{5}{3}\frac{\bar{r}_0^4}{R^4}\right),$$

$$\eta = 0,$$

(4.4)

where e is the elementary charge, e' is the effective charge of the diamagnetic particle which is nearest to the paramagnetic ion, $\bar{r}_0^2$ and $\bar{r}_0^4$ are the mean square and mean fourth power of the distance of the 3d-electron from the nucleus of the paramagnetic ion.

2) $3d^3 \; {}^4F$, V^{2+}, Cr^{3+}; $3d^8 \; {}^3F$, Ni^{2+}. The diagram of the splitting of orbital levels is obtained by inverting the picture shown in Fig. 1. The lowest orbital level is the singlet Γ_2. The computations give:

$$\varepsilon_1 = \varepsilon_1' = 0,$$

$$\varepsilon_2 = \varepsilon_2' = -\varepsilon_3 = \varepsilon_3' = \frac{25}{3}\left(\frac{ee'}{R^2}\right)\left(\frac{\lambda}{\Delta_1}\right)^2\frac{\bar{r}_0^4}{R^4},$$

$$\varepsilon_4 = -\varepsilon_4' = \varepsilon_5 = \varepsilon_5' = \varepsilon_6 = \varepsilon_6'$$

$$= -\frac{2}{21}\frac{\lambda^2}{\Delta_1}\left(\frac{ee'}{R^2}\right)\left[15\left(\frac{2}{\Delta} + \frac{1}{\Delta_1}\right)\frac{\bar{r}_0^2}{R^2} + 5\left(\frac{3}{\Delta} - \frac{2}{\Delta_1}\right)\frac{\bar{r}_0^4}{R^4}\right],$$

$$\eta = 2.$$

(4.5)

3) $3d^4 \; {}^5D$, Cr^{2+}, Mn^{3+}. The picture of the splitting of the orbital levels is shown in Fig. 2. The computations lead to:

$$\varepsilon_1 = 0,$$

$$\varepsilon_2 = -\frac{12}{7}\left(\frac{ee'}{R^2}\right)\left(\frac{\lambda^2}{\Delta\delta_1}\right)\left(3\frac{\bar{r}_0^2}{R^2} + \frac{25}{12}\frac{\bar{r}_0^4}{R^4}\right),$$

$$\varepsilon_3 = \varepsilon_4 = \varepsilon_5 = \varepsilon_6 = 0.$$

(4.6)

It should be remembered that a field of trigonal symmetry does not split the doublet Γ_3, and therefore the crystalline field has a lower symmetry, because of the Jahn-Teller[10] effect. We shall not consider this case.

4) $3d^6 \; {}^5D$, Fe^{2+}. The pattern of splitting of the orbital levels is obtained by inverting the picture shown in Fig. 2. In a cubic field the lowest orbital level is the triplet Γ_5. The computations give:

$$\varepsilon_1 = \varepsilon_1' = -\frac{5\sqrt{6}}{9}\left(\frac{ee'}{R^2}\right)\left(\frac{\lambda}{\delta_2}\right)^2\frac{\bar{r}_0^4}{R^4},$$

$$\varepsilon_2 = \varepsilon_2' = \varepsilon_3 = \varepsilon_3' = -\frac{1}{7}\left(\frac{ee'}{R^2}\right)\left(\frac{\lambda}{\delta_2}\right)^2\left(9\frac{\bar{r}_0^2}{R^2} - \frac{25}{3}\frac{\bar{r}_0^4}{R^4}\right),$$

$$\varepsilon_4 = \varepsilon_4' = \varepsilon_5 = \varepsilon_5' = \varepsilon_6 = \varepsilon_6'$$

$$= \frac{2}{7}\left(\frac{ee'}{R^2}\right)\left(\frac{\lambda}{\delta_2}\right)^2\left(3\frac{\bar{r}_0^2}{R^2} - \frac{5}{3}\frac{\bar{r}_0^4}{R^4}\right),$$

$$\eta = 0.$$

(4.7)

Let us consider some general conclusions which follow from these results for resonance absorption of sound in crystals containing ions with $S' > \frac{1}{2}$.

Because of the quadratic dependence of $\mathcal{H}_p$ on the spin variables, the selection rule for allowed transi-
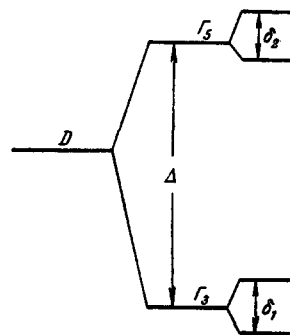

FIG. 2. Diagram showing the successive splitting of a D-term in a strong electric field of cubic symmetry and a weak field of tetragonal symmetry.

tions between spin levels under the action of sound has quadrupole character for ions with half-integral S. For example, the transition $M = -\frac{1}{2} \to M = \frac{1}{2}$ is much less probable than the transition $-\frac{1}{2} \to \frac{3}{2}$ (M is the magnetic spin quantum number). In the approximation which we are using, since we have neglected in the Hamiltonian (3.6) the term which is proportional to H, the probability of the transition $-\frac{1}{2} \to \frac{1}{2}$ is zero.

To a high degree of accuracy we may assume that the matrix elements $\langle \alpha |\mathcal{H}_p| \beta \rangle$ do not depend on frequency ω, and therefore, according to (3.9), the coefficient of sound absorption is $\sigma \sim \omega^2$. From (3.9) it also follows that the coefficient σ is inversely proportional to the temperature T of the crystal; this is valid if the differences in occupation of the levels α and β have the same dependence on T.

The spin variables appear to the fourth power in the expression for σ. Therefore simply because of the magnitude of the spin, the absorption resulting from the ions Fe^{2+}, Cr^{2+} may be greater than in crystals with Ni^{2+} ions by a whole order of magnitude. But the coefficient σ will, for the most part, be determined by the nature of the splitting of the ground energy level of the paramagnetic ion in the crystalline field and by the magnitude of the spin-orbit coupling. Thus, for example, because of the fact that for Cr^{3+} and Ni^{2+} ions in a cubic field the lowest orbital level is a singlet, the coefficient σ may be several orders of magnitude smaller than for other ions. In Table I, which is taken from reference 8, we give the results of approximate numerical estimates of σ, which are made for identical values of N, v, etc. for all the ions.

The velocity of propagation of the sound is very important since $\sigma \sim 1/v^3$. Already for this reason the absorption of longitudinal and transverse sound waves will be different. This difference can be much more important if we look at the values of a_p which, according to (3.7) and (3.9), determine the dependence of σ on the direction of propagation and the polarization character of the sound wave. We must, however, remember that the expressions given in (3.9) for a_p are obtained on the assumption that the neighborhood of the paramagnetic ion is octahedral.

The coefficient σ can change markedly as a function of the direction of the magnetic field H, but to exhibit this dependence without detailed computation is difficult,

Table I. Coefficient of sound absorption for ions with $S' > \frac{1}{2}$.

$\sigma = A(\omega^2/4\pi^2 T) \times 10^{-19}$ cm^{-1}

Configuration and term of ion	Spin	Ion	A
$d^2\,{}^3F$	1	V^{3+}	10^6
$d^3\,{}^4F$	$^3/_2$	Cr^{3+}, V^{2+}	1
$d^4\,{}^5D$	2	Cr^{2+}, Mn^{3+}	10^5
$d^6\,{}^5D$	2	Fe^{2+}	10^6
$d^8\,{}^3F$	1	Ni^{2+}	10^3

since it is determined by the eigenfunctions of the spin Hamiltonian.

5. EFFECT ON Ni^{2+} IONS IN AN MgO CRYSTAL

As an example, we give a detailed computation of the sound absorption coefficient σ for Ni^{2+} (S = 1) ions, which isomorphically replace some of the Mg^{2+} ions in the cubic lattice of the MgO crystal. In this case the spin-Hamiltonian has a completely simple form:[11]

$$\mathcal{H}_s = g\beta HS, \tag{5.1}$$

since a crystalline field of cubic symmetry does not split the energy levels of particles with S < 2. The energy E_M of the spin levels in the magnetic field H is equal to

$$E_{-1} = -g\beta H, \quad E_0 = 0, \quad E_1 = g\beta H. \tag{5.2}$$

We restrict ourselves to the following special cases: a) field H parallel to the tetragonal axis of the crystal, and b) field H parallel to the trigonal axis.

a) H ‖ Oz. In this case, according to (4.1), the Hermitian spin operators $\mathcal{H}_p$ have the following non-zero, non-diagonal matrix elements:

$$\begin{aligned}
&\langle M-2\,|\,\mathcal{H}_2\,|\,M\rangle \\
&\quad = -\frac{1}{2}\,\varepsilon_2\,\sqrt{(S+M)(S+M-1)(S-M+1)(S-M+2)}, \\
&\langle M-2\,|\,\mathcal{H}_4\,|\,M\rangle \\
&\quad = \frac{i}{2}\,\varepsilon_4\,\sqrt{(S+M)(S+M-1)(S-M+1)(S-M+2)}, \\
&\langle M-1\,|\,\mathcal{H}_5\,|\,M\rangle = \frac{1}{2}\,\varepsilon_4(2M-1)\sqrt{(S+M)(S-M+1)}, \\
&\langle M-1\,|\,\mathcal{H}_6\,|\,M\rangle = \frac{i}{2}\,\varepsilon_4(2M-1)\sqrt{(S+M)(S-M+1)}.
\end{aligned} \tag{5.3}$$

Then

$$\langle -1\,|\,\mathcal{H}_2\,|\,1\rangle = -\varepsilon_2, \quad \langle 0\,|\,\mathcal{H}_5\,|\pm 1\rangle = \frac{1}{\sqrt{2}}\,\varepsilon_4,$$

$$\langle -1\,|\,\mathcal{H}_4\,|\,1\rangle = i\varepsilon_4, \quad \langle 0\,|\,\mathcal{H}_6\,|\pm 1\rangle = \frac{i}{\sqrt{2}}\,\varepsilon_4. \tag{5.4}$$

In the further computation of the coefficient σ we shall consider the cases of sound waves propagating along the field and perpendicular to it. In order to indicate the direction of the sound wave and its polarization, we shall put two superscripts on the coefficient σ. Sub-

stituting the quantities (5.4) in (3.9) and using (3.7), we get non-zero values of $\sigma^{mn}_{\alpha,\beta}$ in the following cases:

1. Transition $-1 \to 1$ ($\Delta M = 2$):

$$\sigma^{xx}_{-1,1} = \sigma^{yy}_{-1,1} = P\varepsilon_2^2\omega^2,$$

$$\sigma^{xy}_{-1,1} = \sigma^{yx}_{-1,1} = P\varepsilon_4^2\omega^2. \tag{5.5}$$

As we see, sound absorption occurs if the direction of propagation and the polarization of the wave are perpendicular to the magnetic field H.

2. Transition $0 \to \pm 1$ ($\Delta M = 1$):

$$\sigma^{xz}_{0,\pm1} = \sigma^{zx}_{0,\pm1} = \sigma^{yz}_{0,\pm1} = \sigma^{zy}_{0,\pm1} = P\varepsilon_4^2\omega^2. \tag{5.6}$$

For this transition one has absorption only of transverse waves whose direction of propagation or polarization is parallel to the magnetic field H.

Let us proceed to a numerical estimate of σ. From the value of the splittings in the crystalline field[11] $\Delta = 14800$ cm^{-1}, $\Delta_1 = 8600$ cm^{-1}, it follows that ee$'/R^2 \sim 3.27 \times 10^{-3}$ erg-cm^{-1}; for the Ni^{2+} ion in an MgO crystal, $\lambda = -245$ cm^{-1}. Using the radial functions of 3d-electrons of a free ion of Ni^{2+}, one can easily calculate[12] $\overline{r_2^2} = 0.31 \times 10^{-16}$ cm^2, $\overline{r_0^4} = 0.29 \times 10^{-32}$ cm^4. From x-ray structure data[13] it is known that $R = 2.1 \times 10^{-8}$ cm, and consequently the density of the crystal is d = 3.5 g-cm^{-3}.

If we set $N \sim 1.5 \times 10^{19}$ ion/cm^3, $g(\omega) \sim 1/\omega_{1/2} \sim 10^{-8}$ sec, and assume for the longitudinal vibrations $v_l = 3 \times 10^5$ cm-sec^{-1}, and for the transverse vibrations $v_t = 2 \times 10^5$ cm-sec^{-1}, then for T = 300° K we have:

$$\begin{aligned}
&\sigma^{xx}_{-1,1} = \sigma^{yy}_{-1,1} = 5.5 \cdot 10^{-21}\omega^2, \\
&\sigma^{xy}_{-1,1} = \sigma^{yx}_{-1,1} = 0.5 \cdot 10^{-21}\omega^2, \\
&\sigma^{xz}_{0,\pm1} = \sigma^{zx}_{0,\pm1} = \sigma^{yz}_{0,\pm1} = \sigma^{zy}_{0,\pm1} = 0.5 \cdot 10^{-21}\omega^2.
\end{aligned} \tag{5.7}$$

b) H ‖ Oz'. For the matrix elements of the operators $\mathcal{H}'_p$ (4.2), we have, using (5.3):

$$\begin{aligned}
&\langle -1\,|\,\mathcal{H}'_2\,|\,1\rangle = \frac{i}{\sqrt{3}}\,\varepsilon_2, & &\langle 0\,|\,\mathcal{H}'_2\,|\mp 1\rangle = -\frac{i}{\sqrt{3}}\,\varepsilon_2, \\
&\langle -1\,|\,\mathcal{H}'_3\,|\,1\rangle = \frac{1}{\sqrt{3}}\,\varepsilon_2, & &\langle 0\,|\,\mathcal{H}'_3\,|\mp 1\rangle = \frac{1}{\sqrt{3}}\,\varepsilon_2, \\
&\langle -1\,|\,\mathcal{H}'_5\,|\,1\rangle = i\sqrt{\frac{2}{3}}\,\varepsilon_4, & &\langle 0\,|\,\mathcal{H}'_5\,|\mp 1\rangle = -\frac{i}{\sqrt{6}}\,\varepsilon_4, \\
&\langle -1\,|\,\mathcal{H}'_6\,|\,1\rangle = -\sqrt{\frac{2}{3}}\,\varepsilon_4, & &\langle 0\,|\,\mathcal{H}'_6\,|\mp 1\rangle = \frac{1}{\sqrt{6}}\,\varepsilon_4.
\end{aligned} \tag{5.8}$$

Substituting these values of $\langle\alpha\,|\,\mathcal{H}_p\,|\,\beta\rangle$ in (3.9), we find non-zero coefficients in the following cases:

1. Transition $-1 \to 1$ ($\Delta M = 2$):

$$\begin{aligned}
&\sigma^{x'x'}_{-1,1} = \sigma^{y'y'}_{-1,1} = \frac{1}{9}\,P(2\varepsilon_4 - \varepsilon_2)^2\,\omega^2, \\
&\sigma^{x'y'}_{-1,1} = \sigma^{y'x'}_{-1,1} = \frac{1}{9}\,P(2\varepsilon_4 + \varepsilon_2)^2\,\omega^2, \\
&\sigma^{z'x'}_{-1,1} = \sigma^{x'z'}_{-1,1} = \sigma^{y'z'}_{-1,1} = \sigma^{z'y'}_{-1,1} = \frac{2}{9}\,P(\varepsilon_2 - \varepsilon_4)^2\,\omega^2.
\end{aligned} \tag{5.9}$$

2. Transition $0 \to \pm 1$ ($\Delta M = 1$):

$$\sigma_{0,\pm1}^{x'x'} = \sigma_{0,\pm1}^{y'y'} = \sigma_{0,\pm1}^{x'y'} = \sigma_{0,\pm1}^{y'x'} = \frac{2}{9} P(\varepsilon_2 + \varepsilon_4)^2 \omega^2,$$

$$\sigma_{0,\pm1}^{z'x'} = \sigma_{0,\pm1}^{x'z'} = \frac{1}{9} P(2\varepsilon_2 + \varepsilon_4)^2 \omega^2,$$

$$\left.\begin{array}{l}\\ \\ \\ \end{array}\right\} \quad (5.10)$$

$$\sigma_{0,\pm1}^{y'z'} = \sigma_{0,\pm1}^{z'y'} = \frac{1}{9} P(2\varepsilon_2 - \varepsilon_4)^2 \omega^2.$$

Numerical evaluations for the same parameter values as in a) give

$$\sigma_{-1,1}^{x'x'} = \sigma_{-1,1}^{y'y'} = 1.05 \cdot 10^{-21} \omega^2,$$

$$\sigma_{-1,1}^{x'y'} = \sigma_{-1,1}^{y'x'} = 1.03 \cdot 10^{-21} \omega^2,$$

$$\sigma_{-1,1}^{z'x'} = \sigma_{-1,1}^{x'z'} = \sigma_{-1,1}^{y'z'} = \sigma_{-1,1}^{z'y'} = 5.6 \cdot 10^{-21} \omega^2,$$

$$\sigma_{0,\pm1}^{x'x'} = \sigma_{0,\pm1}^{y'y'} = 0.8 \cdot 10^{-21} \omega^2, \qquad (5.11)$$

$$\sigma_{0,\pm1}^{x'y'} = \sigma_{0,\pm1}^{y'x'} = 3.0 \cdot 10^{-21} \omega^2,$$

$$\sigma_{0,\pm1}^{x'z'} = \sigma_{0,\pm1}^{z'x'} = 7.0 \cdot 10^{-21} \omega^2,$$

$$\sigma_{0,\pm1}^{y'z'} = \sigma_{0,\pm1}^{z'y'} = 9.6 \cdot 10^{-21} \omega^2.$$

We see that in the case of a magnetic field directed along the trigonal axis one can have absorption of both longitudinal and transverse waves for all transitions.

6. IONS WITH EFFECTIVE SPIN $S' = \frac{1}{2}$

The theory of acoustic paramagnetic resonance for ions of this type has been treated in references 3, 7, and 8. In Secs. 3 and 4 we have seen that the operators $\mathcal{H}_p$ in which we are interested consist of two parts:
1) a term linear in the spin variables S_k and proportional to the small quantity $w = 2\beta H = 2\hbar\omega/g$, and
2) a term quadratic in the S_k and proportional to $\lambda \gg w$. For ions with $S' > \frac{1}{2}$ we neglected the linear term. But for the case of $S' = \frac{1}{2}$ the matrix elements of quadratic combinations of the spin components are equal to zero, so that for ions considered in this paragraph we must include the term proportional to w.

First we consider ions with $S = S' = \frac{1}{2}$. From the calculations it follows that if the field with lower symmetry is tetragonal, then

$$\mathcal{H}_1 = w\varepsilon_1 (l_x S_x + l_y S_y), \qquad \mathcal{H}_4 = w\varepsilon_4 (l_x S_y + l_y S_x),$$

$$\mathcal{H}_2 = w\varepsilon_2 (l_y S_y - l_x S_x), \qquad \mathcal{H}_5 = 2w\varepsilon_5 l_x S_z,$$

$$\mathcal{H}_3 = \sqrt{\frac{1}{3}} w\varepsilon_3 (l_x S_x + l_y S_y), \qquad \mathcal{H}_6 = 2w\varepsilon_6 l_y S_z.$$

$$(6.1)$$

If the field of lower symmetry is trigonal,

$$\mathcal{H}_1' = w\varepsilon_1 (l_{x'} S_{x'} + l_{y'} S_{y'}),$$

$$\mathcal{H}_2' = w\varepsilon_2 \sqrt{\frac{1}{3}} \left[(l_{x'} S_{y'} + l_{y'} S_{x'}) - 2\sqrt{2} l_{y'} S_{z'} \right],$$

$$\mathcal{H}_3' = -w\varepsilon_3 \sqrt{\frac{1}{3}} \left[(l_{y'} S_{y'} - l_{x'} S_{x'}) - 2\sqrt{2} l_{x'} S_{z'} \right],$$

$$\mathcal{H}_4' = w\varepsilon_4 \sqrt{\frac{1}{3}} (l_{x'} S_{x'} + l_{y'} S_{y'}),$$

$$\mathcal{H}_5' = \omega\varepsilon_5 \sqrt{\frac{2}{3}} \left[(l_{x'} S_{y'} + l_{y'} S_{x'}) + \sqrt{2} l_{y'} S_{z'} \right],$$

$$\mathcal{H}_6' = \omega\varepsilon_6 \sqrt{\frac{2}{3}} \left[(l_{y'} S_{y'} - l_{x'} S_{x'}) + \sqrt{2} l_{x'} S_{z'} \right].$$

$$(6.2)$$

As already stated in Sec. 4, in the case of a field of trigonal symmetry, the coefficients a_p in formula

(3.9) should be replaced by coefficients a_p' [cf. (4.3)].

We proceed to consider individual ions.

1) $3d^1$ ^2D, Ti^{3+}. The picture of the splitting of the orbital levels is inverted relative to the scheme shown in Fig. 2. Calculations including the contribution to the spin-phonon interaction of only the levels of the lowest triplet Γ_5 give

$$\varepsilon_i (Ti^{3+}) = \frac{1}{\lambda} \varepsilon_i (Fe^{2+}). \qquad (6.3)$$

The values of the parameters ε_i for Fe^{2+} are given in (4.7).

2) $3d^9$ ^2D, Cu^{2+}. The picture of the splitting of the orbital levels is given in Fig. 2. The field of trigonal symmetry does not split the lowest orbital doublet. Therefore our computations apply only to the tetragonal field of the crystal. The computations show that

$$\varepsilon_i (Cu^{2+}) = \frac{1}{\lambda} \varepsilon_i (Cr^{2+}). \qquad (6.4)$$

3) $3d^7$ ^4F, Co^{2+}. The Co^{2+} ion is a special case. The point is that in all crystals investigated up to now, which contain the Co^{2+} ion, the effect of the field of lower symmetry is of the same order as the spin-orbit interaction. Therefore the system of energy levels of this ion is a collection of Kramers doublets separated by intervals ~ 200—300 cm^{-1}. Thus, even though the free ion Co^{2+} has spin $S = \frac{3}{2}$, in a crystal the effective spin is $S' = \frac{1}{2}$. The computation of the spin-phonon interaction for an arbitrary direction of the magnetic field is extremely complicated. Calculations made for a field H, parallel to the tetragonal z axis, including only the Kramers doublet which is closest to the ground state have shown that the absorption coefficient of sound is equal to

$$\sigma = P \frac{\hbar^2 w^4}{4\pi^2 g^2} q^2 (a_5^2 + a_6^2), \qquad (6.5)$$

where the parameter $q \sim 10^9$ cm^{-1}.

The most characteristic feature of the group of ions considered in this section is the different frequency dependence of the magnitude of the effect: for ions with $S' > \frac{1}{2}$, $\sigma \sim \omega^2$; for ions with $S' = \frac{1}{2}$, $\sigma \sim \omega^4$. Aside from this, these two groups of ions differ very little from one another. In Table II we give the results of approximate numerical calculations[8] made for certain values of N, v, ..., which are the same for all ions.

7. CRYSTALS CONTAINING IONS OF THE RARE-EARTH ELEMENTS

The most characteristic feature of the paramagnetic properties of crystals of this type is the large contribution to the magnetic susceptibility of both the orbital and the spin moments, which is explained by the fact that the crystalline field cannot disturb the spin-orbit coupling in the electron shells of the rare-earth ions.[4] Unlike the ions of the iron group, the rare-earth ions in most cases do not have a simple octahedral coordination. The symmetry of the crys-

Table II. Coefficients of sound absorption for ions with $S' = \frac{1}{2}$.
$\sigma = A(\omega^4/16\pi^4 T) \times 10^{-40}$ cm^{-1}

Configuration and term of ion	Spin	Ion	A
$d^1 {}^2D$	$S' = S = \frac{1}{2}$	Ti^{3+}	10^4
$d^7 {}^4F$	$S' = \frac{1}{2},\ S = \frac{3}{2}$	Co^{2+}	10^2
$d^9 {}^2D$	$S' = S = \frac{1}{2}$	Cu^{2+}	1

talline field acting on the rare earth ions usually is trigonal. In this field, the energy level of a free paramagnetic ion which contains an odd number of electrons is split into a series of Kramers doublets; if, however, the number of electrons is even, we get singlet and doublet sublevels. As an example, we show in Figs. 3 and 4 the patterns of splitting of the energy levels of the ions Pr^{3+}, Ho^{3+}; Ce^{3+}, Nd^{3+} in the ethylsulfates. The intervals Δ between levels are equal on the average to $10-100$ cm^{-1}.
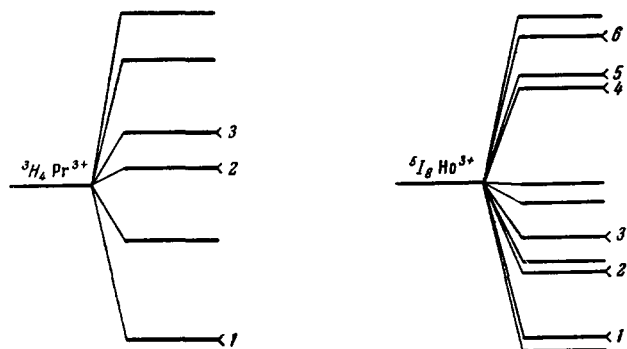

FIG. 3. Diagram of splitting of ground states of Pr^{3+} and Ho^{3+} ions in the crystalline field of ethylsulfates.
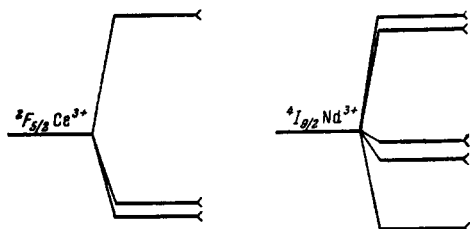

FIG. 4. Diagram of the splitting of ground states of Ce^{3+} and Nd^{3+} ions in the crystalline field of ethylsulfates.

The mechanism of spin-phonon interaction in crystals with rare earth ions has been treated in references 14 and 15. The lattice vibration, by modulating the crystalline field, can directly change the orientation of the magnetic moment of the rare-earth ion, since in the case considered by us the coupling between the spin and orbital moments of the electron shells is stronger than the effect of the crystalline field.

After preliminary estimates of the magnitude of resonance absorption of sound by rare earth elements,[3] detailed computations were made for the ethylsulfates

of all the rare earth elements.[16] It turned out that there was an enormous difference in the magnitude of the effect for ions with an even number and for ions with an odd number of electrons. The point is that in the case of ions with an even number of electrons, the degeneracy of the energy levels can be completely raised by a crystalline field of sufficiently low symmetry. Therefore in calculations by perturbation methods the spin-phonon interaction already appears in first approximation. The coefficient of absorption of sound associated with transitions between sublevels, which arise as the result of splitting of a non-Kramers doublet by the external magnetic field, is equal to

$$\sigma = \alpha P \left(\frac{ee'}{R} \right)^2 \left(\frac{\bar{r}_0^3}{R^2} \right)^2 \omega^2, \qquad (7.1)$$

where α is a numerical coefficient which depends strongly on the direction of propagation of the sound. The absorption is maximum for a sound wave moving perpendicular to the trigonal axis of the crystal; for sound propagating along the crystalline axis, $\alpha = 0$. In Table III we give results of computations of the absorption coefficient σ_l for a longitudinal sound wave propagating perpendicular to the crystal axis. For transverse waves, the absorption coefficient can be calculated from the formula

$$\sigma_{tr} = \frac{4}{9} \left(\frac{v_1}{v_{tr}} \right)^3 \sigma_l, \qquad (7.2)$$

where v_l and v_{tr} are the velocities of longitudinal and transverse waves. It should be remembered that for ions of the type we are considering $g_\perp = 0$.[15]

The possibility of observing acoustic paramagnetic resonance in the substances we are considering is essentially related to the following facts.

First, the degeneracy of the energy levels of ions with an even number of electrons is completely removed, because of the Jahn-Teller effect. True, the Jahn-Teller splitting for the rare earths is small, being of the order of $0.01-0.1$ cm^{-1}, but all the same to obtain a clearly expressed resonance effect one needs to use frequencies which are greater than 1000 Mc. Secondly, the spin-phonon interaction in rare-earth compounds is so large that at normal temperatures the paramagnetic resonance lines merge together completely. Therefore, the measurements must be carried out at liquid helium temperature; in certain cases one can use liquid hydrogen temperatures. Thirdly, for the rare earth ions with an even number of electrons the lowest level may be a singlet. But the doublet levels which are of interest for the paramagnetic resonance effect may be extremely weakly populated at low temperatures. Thus, for the Eu^{3+} ion the ground state corresponds to an angular momentum quantum number $I = 0$; the first excited level is 270 cm^{-1} higher. For ions of the rare-earth elements with an odd number of electrons, the energy levels in the crystalline field are Kramers doublets, so that the matrix elements of the spin-phonon inter-

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Table III. Coefficients of absorption of longitudinal sound waves in ethylsulfates of rare-earth ions with an even number of electrons $\sigma_l = A(\omega^2/4\pi^2 T) \times 10^{-13}$ cm^{-1}

Ion	No. of doublet	Interval between doublet and ground state (in cm^{-1})	A	Ion	No. of doublet	Interval between doublet and ground state (in cm^{-1})	A
Pr^{3+}	1	0	1.7	Ho^{3+}	1	4	7.3
	2	170	8.8		2	47	15.8
	3	212	1.7		3	60	150.1
Eu^{3+}	1	270	800.7		4	139	0
					5	141	1.5
	1	7	3.7		6	197	150.1
Tb^{3+}	2	24	10.5	Tm^{3+}	1	14	5.6
	3	26	60.8		2	26	12.0
	4	50	10.5		3	98	49.4
					4	129	13.4

action are different from zero only in the second approximation of perturbation theory. Thus, the absorption coefficient σ differs from the value given by formula (7.1) by a factor $(\hbar\omega/\Delta)^2$. Thus, for Nd^{3+} the interval $\Delta = 170$ cm^{-1} and at T = 20° K the calculations give $\sigma = 3 \times 10^{-39} (\omega/2\pi)^4$ cm^{-1}. The frequency dependence is the same as for ions of the iron group with S' = $\frac{1}{2}$. The magnitude of the absorption is obviously very sensitive to the location of the nearest energy levels. Thus, for cerium ethylsulfate the interval between the lowest two doublets is only 3 cm^{-1}, which increases the coefficient σ to a value $\sim 10^{-35}$ $(\omega/2\pi)^4$ cm^{-1}.

The results given in this section of computations of the acoustical effect are quite crude for the following reasons. First, in the calculations one has used a simplified picture of the normal vibrations of the crystal. A more precise inclusion of the nature of the vibrations of the particles surrounding the paramagnetic ion is difficult to carry out because of the complex structure of the crystalline unit cell. Therefore, conclusions regarding the dependence of the absorption coefficient on direction and polarization of the sound waves are extremely rough.

Second, the spin-phonon interaction in many cases is so large that one is hardly justified in using perturbation methods.

8. CRYSTALS CONTAINING PARAMAGNETIC IONS IN S-STATES

Among paramagnets, those crystals which contain Mn^{2+}, Fe^{3+}, Eu^{2+}, Gd^{3+}, Cm^{3+} occupy a special position. All these ions are in S-states and therefore the crystalline field gives rise to extremely small splittings of their ground states, usually not exceeding 1 cm^{-1}. The calculations of the value of resonance absorption of sound have been done for the ions Mn^{2+} and Fe^{3+} (S = $\frac{5}{2}$) on the assumption that the splitting of the lowest energy level under the action of the crystalline and external magnetic fields is given by a spin-

Hamiltonian of the following simple "cubic" type:[3]

$$\mathscr{H}_s = \frac{1}{6} a \left[S_x^4 + S_y^4 + S_z^4 - \frac{1}{3} S (S+1)(3S^2 + S - 1) \right]$$

$$+ g\beta HS. \tag{8.1}$$

Just as for the other ions with S' > $\frac{1}{2}$, considered by us in Sec. 4, the coefficient σ can be calculated from formula (3.9). The spin operators $\mathcal{H}_p$ have the same form (4.1), the expressions for the parameters ϵ_i are very complicated, and we shall not reproduce them here. The general properties of resonance absorption of sound which were established in Sec. 4 also apply to ions in S-states. The magnitude of the effect can be estimated from the formula

$$\sigma = \alpha P a^6 \omega^2, \tag{8.2}$$

where α is a numerical factor.

The detailed computations show that in a strong magnetic field $g\beta H \gg a$, transitions M $\rightarrow$ $-$M are forbidden, where the magnetic quantum number is M = $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$. Other transitions are possible between neighboring levels under the influence of transverse vibrations and between levels with $\Delta M = 2$ under the action of longitudinal waves.

9. THE WALLER MECHANISM

If the orbital magnetism of the atoms is quenched then, as shown by one of the authors,[17] in paramagnetic materials with large magnetic moments of the atoms and with a large density of paramagnetic particles the main role in the spin-phonon interaction may be played by the modulation by the lattice vibrations of the magnetic dipole interactions of the atoms (the Waller mechanism). Resonance absorption of sound resulting from this mechanism has been considered in reference 18.

Let us assume for simplicity that the paramagnetic particles form a simple cubic lattice, and let the lattice constant be R. Using the usual expression for the operator of magnetic dipole interaction,

$$U_{kl} = g^2\beta^2 \left(\frac{(S_k S_l)}{r_{kl}^3} - \frac{3(S_k \cdot r_{kl})(S_l \cdot r_{kl})}{r_{kl}^5} \right) \qquad (9.1)$$

and assuming that the sound wave propagates along the x axis, we can bring the square of the matrix element of the spin-phonon interaction, which appears in (2.3), to the following form:

$$|\langle \alpha, n_\omega | \mathcal{H}_{s-p} | \beta, n_\omega - 1 \rangle| = \frac{\hbar n_\omega}{dV\omega} \sum_l \left(\frac{\omega r_{kl}}{v} \right)^2 |\langle \alpha | U_{klx} | \beta \rangle|, \qquad (9.2)$$

where

$$U_{klx} = \frac{\partial U_{kl}}{\partial x_{kl}}, \qquad (9.3)$$

and the summation extends over all paramagnetic particles. We shall use a representation in which S_{kz} and S_{lz} are diagonal; the corresponding magnetic quantum numbers are denoted by M_k and M_l. For transitions with $\Delta M_k = 1$, $\Delta M_l = 0$, using (9.1) and (9.3), we find the square of the corresponding matrix element U_{klx}:

$$\langle M_k, M_l | U_{klx} | M_k + 1, M_l \rangle |^2 = \frac{9g^4\beta^4}{4r_{kl}^{14}} z_{kl}^2 [2x_{kl}^2 (x_{kl}^2 + y_{kl}^2)$$

$$- 10x_{kl}^2 r_{kl}^2 + r_{kl}^4] M_l^2 (S + M_k)(S - M_k + 1). \qquad (9.4)$$

Carrying out an average over different directions of propagation of the sound with respect to the crystal axes, and also over all possible values of M_k and M_l, we find

$$|\langle M_k, M_l | U_{klx} | M_k + 1, M_l \rangle|^2 = \frac{253}{84} \frac{g^4\beta^4}{r_{kl}^9} S(S+1)^2(2S+1). \qquad (9.5)$$

Substituting this expression in (9.2) and then in (2.3) and considering only the effect of nearest neighbors, we find for the absorption coefficient

$$\sigma = \gamma_\perp PZ \left(\frac{g^2\beta^2}{R^4} \right)^2 S(S+1)^2(2S+1)\omega^2, \qquad (9.6)$$

where Z is the number of nearest neighbors of the ion in the crystal lattice and $\gamma_\perp = 253/42$.

Our computations apply to the absorption of sound vibrations propagating perpendicular to the applied magnetic field. If we make an analogous calculation for waves parallel to the magnetic field, we obtain the same expression (9.6), but with a different coefficient $\gamma_\| = 8/21$.

For the absorption coefficient due to double transitions ($\Delta M_k = +1$, $\Delta M_l = +1$), we get

$$\sigma = \gamma PZ \left(\frac{g^2\beta^2}{R^4} \right)^2 (S+1)^2(2S+1)^2\omega^2, \qquad (9.7)$$

where $\gamma_\perp = 20/7$, $\gamma_\| = 20/21$. Thus it appears that the line corresponding to the resonance condition

$$\hbar\omega = 2g\beta H, \qquad (9.8)$$

should have approximately the same intensity as the ordinary line, whose position is determined by the condition

$$\hbar\omega = g\beta H. \qquad (9.9)$$

An estimate of σ from formula (9.6) for MnF_2 at a temperature T = 300° K, $\omega_{1/2}/2\pi = 10^9$ sec^{-1}, gives $\sigma \sim 10^{-21} \omega^2$ cm^{-1}.

In materials with a high density of magnetic ions, in addition to dipole-dipole interaction there will also be large exchange forces. The role of these forces in spin-phonon interaction can be very significant since they fall off rapidly with distance. However, if the exchange interaction has the isotropic form $\mathcal{H}_{ex} = \sum_l I(r_{kl})(S_l \cdot S_k)$ then it cannot give rise to transitions between Zeeman levels through the lattice vibrations, since the matrix $\mathcal{H}_{ex}$ is diagonalized simultaneously with the matrix of the Zeeman energy $g\beta H \sum_k S_{zk}$. Inclusion of spin-orbit coupling leads to the appearance of anisotropic exchange forces. Assuming that these forces have the dipole form[19]

$$\mathcal{H}_{ex} = \sum_l I(r_{kl})[(S_k S_l) - 3r_{kl}^{-2}(S_k r_{kl})(S_l r_{kl})], \qquad (9.10)$$

it has been shown in reference 18 that they can increase the values of σ obtained above, which were due to dipole-dipole interaction alone, by one to two orders of magnitude.

10. ACOUSTIC PARAMAGNETIC RESONANCE AND SPIN-LATTICE RELAXATION IN IONIC CRYSTALS

Acoustic paramagnetic resonance and paramagnetic spin-lattice relaxation are very closely connected with one another, since both phenomena are the result of spin-phonon interaction. This relation becomes especially simple and direct if we consider the relaxation at sufficiently low temperatures to guarantee a predominant role for one-phonon processes. In this section when we speak of spin-lattice relaxation, we shall assume that it is accomplished by one-phonon processes.

Let us establish the relation between the time of spin-lattice relaxation τ and crystal temperature T_0 and the coefficient of resonant sound absorption σ at temperature T. First let us assume that S' = $\frac{1}{2}$; then the probability of absorption of a phonon per second under the influence of the thermal vibrations of the lattice is $A = 1/2\tau$. This probability is proportional to the Debye density of phonon states ρ_l and the average value of the quantum number $\bar{n}_l$ at temperature T_0, so that

$$A = A_0 \rho_l \bar{n}_l, \qquad (10.1)$$

$$\rho_l = \frac{\omega^2 V}{\pi^2 v^3}, \quad \bar{n}_l = \frac{kT}{\hbar\omega}.$$

In the expression for ρ_l we include only transverse vibrations, since $A \sim v^{-5}$ and the velocity of transverse waves is much smaller than that of longitudinal waves.

By the coefficient σ we shall mean the coefficient of absorption of transverse sound waves averaged over the different directions of propagation and all possible

polarizations. The intensity of the sound wave is equal to $I = I_\omega \Delta\omega$, where $I_\omega = v\rho_\omega \bar{n}_\omega \hbar\omega/V$, and ρ_ω and $\bar{n}_\omega$ have the same meaning as ρ_l and $\bar{n}_l$, but refer to sound vibrations. Furthermore using formulas (2.1), (2.2), and (2.3), we easily obtain

$$\sigma = \frac{\pi^2}{2} \frac{\hbar^2 N v^2}{k^2 T T_0 \tau} g(\omega). \qquad (10.2)$$

If $S' > \frac{1}{2}$, and consequently the number of spin levels is greater than 2, then to each pair of spin levels α, β there corresponds a certain probability of a spin-phonon transition $A_{\alpha,\beta}$ and a certain coefficient of sound absorption $\sigma_{\alpha,\beta}$. The relaxation time which is measured by the method of parallel fields or the relaxation times $\tau_{\alpha,\beta}$ obtained by saturating different lines of paramagnetic resonance are complicated functions of the transition probabilities $A_{\alpha,\beta}$. It is therefore impossible to establish a simple relation between the relaxation times $\tau_{\alpha,\beta}$ and the coefficients $\sigma_{\alpha,\beta}$. Nevertheless, in the case of $S' > \frac{1}{2}$, formula (10.2) is approximately valid, in particular if by σ and τ we mean the average values of the coefficients of absorption $\sigma_{\alpha,\beta}$ and relaxation times $\tau_{\alpha,\beta}$.

Because magnetic dipole transitions are not possible for each pair of spin levels, data concerning $\tau_{\alpha,\beta}$ obtained by the saturation method are in general insufficient for a unique determination of the quantities $A_{\alpha,\beta}$. Besides, the ratios of the probabilities of spin-phonon transitions are given most accurately by theory, and it is therefore very important to have the possibility of an experimental determination of these ratios. From a knowledge of the transition probabilities $A_{\alpha,\beta}$ for each pair of spin levels we can also find the best conditions of polarization of the nuclei by means of certain dynamical methods, and in particular we can raise the efficiency of paramagnetic amplifiers (masers).

In obtaining relation (10.2) we have tacitly assumed that both the resonance absorption of sound and the spin-lattice relaxation are due to the same mechanism of spin-phonon interaction. But it is well known that the theory of spin-lattice relaxation in ionic crystals at low temperatures is fraught with difficulties. The results of measurements of the dependence of relaxation times on the concentration of paramagnetic ions, on the intensity of the external magnetic field, and on temperature, very often are in explicit contradiction to theoretical predictions. In Van Vleck's opinion[20] all these facts can be explained if one assumes that the energy of exchange between the spins of the ions and the phonons occurs not directly, but via irregularities of the lattice ("exchange pockets" etc). This point of view has found a certain amount of experimental confirmation. Experimental studies of acoustic paramagnetic resonance, in particular the determination of the extent to which relation (10.2) is correct, should be of great importance for clarifying the nature of spin-lattice relaxation. In this connection it will be

of great interest to get the results of measurements of the dependence of the coefficient of sound absorption on the concentration of paramagnetic ions, on the frequency of the sound, and on the temperature of the crystal.

Kochelaev[21,22] pointed out the following two facts, which may be important both for acoustic paramagnetic resonance and for processes of spin-lattice relaxation.

In certain crystals there are separate paramagnetic complexes, for example, six water molecules with a paramagnetic ion at the center. The particles within a complex are coupled to one another much more strongly than with other atoms in the crystal. Because of this, the displacement of the paramagnetic ion with respect to some particle near to it becomes much smaller than the average value of the relative displacement of neighboring atoms for the whole crystal. As a consequence, the spin-lattice interaction is reduced, and, as the computations show,[21] relaxation and acoustic effects may be reduced by several orders of magnitude.

Defects of the crystal lattice, which give rise to scattering of elastic waves, may have a serious influence on the nature of the spin-phonon interaction. As computations have shown,[22] if the amplitude of the scattered waves does not depend on frequency, then elastic vibrations of the lattice due to scattered waves are coupled more strongly with the spin system than vibrations which are produced by plane waves. Consequently, in the formulas for the absorption coefficients, there appears a factor $\eta N^{-4/3} \omega^{-2}$; by η we denote a parameter which characterizes the lattice defect. For ions with $S' > \frac{1}{2}$ the dependence of σ on the sound frequency ω disappears; in the case of $S' = \frac{1}{2}$ this dependence becomes weaker, $\sigma \sim \omega^2$. We also note that if acoustic paramagnetic resonance is mainly the result of absorption of scattered waves, then the dependence of σ on the direction of the incident sound waves which we have found in the preceding sections should disappear as a result of averaging over all possible values of the direction cosines λ_i.

11. METALS

The study of acoustic resonance on electron spins in metals is of especial interest. The reason for this is that the study of absorption of electromagnetic waves in metals is extremely difficult because of the skin effect.

The possibility of observing acoustic resonance on the spins of conduction electrons in metals was considered in reference 23. As the fundamental cause of interaction of the spins with the sound field, it is assumed that one has a modulation of the internal crystalline field by the sound vibrations, thus influencing the spins through the spin-orbit coupling. The problem is solved by investigation of the magnetization M

of an electron gas in the presence of sound

$$M = \frac{\beta}{(2\pi\hbar)^3} \int Sp(\sigma\varrho)\,d\mathbf{p}. \qquad (11.1)$$

Here ρ is a single-particle operator for the density of the electron gas, σ is a Pauli operator, and the integration extends over the electron momentum space. The motion of the electrons is described phenomenologically by introducing a time of free flight of the electrons t_l and a time of paramagnetic relaxation τ_{sp}. After solving the kinetic equation for ρ, one easily finds the magnetization M which has resonance character. The width of the resonance line was equal to

$$\omega_{1/2} = \frac{1}{\omega\tau_{sp}} + \omega\left(\frac{u}{v}\right)^2 t_l, \qquad (11.2)$$

where u is the electron velocity. Since the resonance is noticeable only for $\omega_{1/2} \ll \omega$, the resonance frequencies must satisfy the condition

$$\tau_{sp}^{-1} \ll \omega \ll t_l^{-1}\left(\frac{v}{u}\right)^2. \qquad (11.3)$$

In particular, for Li and Be in which the time of paramagnetic relaxation τ_{sp} is determined by impurities ($\tau_{sp} \gtrsim 10^{-7}$ sec), at high temperatures (when $t_l \sim 10^{-13}$–10^{-14} sec) a numerical estimate gives $\omega \sim 10^8$–10^9 sec^{-1}. From this we see that the resonance value of the magnetic field should be small. This justifies the neglect of quantization of the orbital motion of the electrons in finding the density operator. From the conditions of possibility of observation of the resonance, it also follows that one cannot succeed in polarizing nuclei by acoustic resonance on the spins of free electrons for to obtain a significant polarization one requires strong magnetic fields and low temperatures.

For an estimate of the order of magnitude of the coefficient of sound absorption near resonance, one has the following formula:

$$\sigma = 48\ln 2 \frac{\Omega^2}{\omega^2} \frac{\chi\Delta g\varepsilon u a q^2 k\,\overline{(\mathbf{q}\mathbf{u})^2}}{\beta\,\overline{dv\,[(\Omega-\omega)^2+\omega_{1/2}^2]}}, \qquad (11.4)$$

where Ω is the Larmor frequency, χ is the paramagnetic susceptibility of the metal, Δg is the difference in g-factors for the free electron and an electron in the lattice, a is the lattice constant, and ϵ and u are the energy and velocity of the electron at the Fermi surface, and the prime denotes an average over it; q and k are the wave vectors of the sound and the electron respectively. A numerical estimate shows that $\sigma \lesssim 10^{-5}$ cm^{-1}. This value for the absorption coefficient shows that the effect of acoustic resonance on spins of conduction electrons far exceeds the effect on nuclei ($\sigma \sim 10^{-8}$–10^{-9} cm^{-1}), which has already been observed experimentally.

Let us consider the possibility of observing paramagnetic acoustic resonance in rare-earth metals.[18] Paramagnetism of these metals is due to the 4f-electrons which lie deep within the atoms; the effect of conduction electrons is insignificant. Therefore there

is a great similarity between the magnetic properties of the rare-earth metals and the salts of these elements. By comparing theoretical computations with experimental data on paramagnetic resonance in metallic cerium, praseodymium, and neodymium, it was established[24] that the atoms of these metals are three-fold ionized and that the splitting of their energy levels is determined by an electric field having the same symmetry as the crystal lattice. In this connection it is reasonable to assume that the spin-phonon interaction in rare-earth metals is determined by the same mechanism as in the salts of these elements, namely by a modulation of the electric field by the lattice vibrations. Therefore the calculation of the coefficient of absorption of sound energy is done in the same way as in Sec. 7. Differences arise only because of the different symmetry of the crystalline field. Let us first consider metals having a cubic lattice, which includes β-cerium, β-praseodymium, europium, and ytterbium. Their common property is that the crystalline field of cubic symmetry does not completely split the energy levels of the ions, and there remains a non-Kramers degeneracy which can be lifted by a field of lower symmetry. Such a field occurs in particular when one perturbs the crystal by sound vibrations; from this it is clear that the spin-phonon interaction will be different from zero even in the first approximation of perturbation theory. Therefore the coefficient of sound absorption in this case will again be given by formula (7.1).

Let us give as an example a numerical estimate of the coefficient of absorption of sound in β-cerium. If the effective charge e' = e and if we choose the maximum possible value of α (which corresponds to the perpendicular orientation of the magnetic field with respect to the direction of the sound wave), then at T = 300° K we obtain $\sigma \sim 10^{-18}\omega^2$ cm^{-1}.

Let us discuss the possibility of observing the effect in rare-earth metals with a hexagonal lattice. In metals whose ions contain an even number of electrons (α-Pr, Tb, Ho, Pm), the coefficient of sound absorption may be of the same order of magnitude as in metals with cubic symmetry, since some of the energy levels of these ions retain their twofold (non-Kramers) degeneracy in an electric field of hexagonal symmetry. The situation is different for metals whose ions have an odd number of electrons. In this case the electric field of hexagonal symmetry causes a complete splitting of the energy levels, keeping only the twofold Kramers degeneracy. Since this degeneracy cannot be removed by any electric field, the spin-lattice coupling can manifest itself only in second approximation. Therefore the resonance absorption of sound in these metals will be approximately a factor $(g\beta H/\Delta)^2$ smaller than in metals with a cubic lattice (where Δ is the splitting of the energy levels in the electric field). The same also applies to samarium, whose lattice is tetragonal.

A special case is that of gadolinium, whose ion is in an S-state. Spin-lattice interaction in Gd^{3+} apparently is determined by magnetic and exchange interactions.

12. EXPERIMENTAL INVESTIGATION OF ELECTRONIC ACOUSTIC PARAMAGNETIC RESONANCE

To obtain a clear effect of electronic acoustic paramagnetic resonance, it is necessary that the resonance frequencies be much greater than the width of the absorption line. In most cases achieving this condition requires the use of hypersonics. At the same time, it is clear that the magnitude of the effect increases significantly at high frequencies. The technique of generation of hypersonics has as yet not been very well developed.[25] Especial difficulties are the transmission of hypersonics from a generator to the material under investigation. Therefore it was natural to try first to obtain an effect on piezoelectric crystals containing paramagnetic centers in the form of impurities or lattice defects. Actually the first successful attempts were on quartz crystals, in which one has detected resonance absorption of hypersonics on impurity ions of Mn^{2+} and in F-centers.[26]

We note that the difficulties associated with the need for applying microwave frequencies can be avoided sometimes if one uses transitions between spin levels which approach one another (and almost cross) in large magnetic fields (for example, in the Cr^{3+} ion, the transition $-\frac{3}{2} \rightarrow +\frac{1}{2}$). The possibility of such experiments has been discussed in reference 7. Up to now, for the experimental study of acoustic paramagnetic resonance, two methods have been applied:
1) measurement of the absorption coefficient, and
2) measurement of the saturation factor.

Measurements of the coefficient σ give direct information concerning spin-phonon interaction. But the application of this method requires absolute measurements of the loss of acoustic power resulting both from the resonance effect in which we are interested as well as from other causes. In order to avoid the difficulties associated with such measurements Shiren[27] recently proposed the use of double phonon-photon quantum transitions. The probability of such a double quantum transition is proportional to the product of the energy densities of the phonons and photons. From the absorbed photon energy, whose measurement is simple, one can deduce the absolute value of the absorbed sound energy.

In the method of saturating the usual paramagnetic resonance, which is widely used for measuring spin-lattice relaxation times, one uses the following formula for the saturation factor q:

$$q_{\alpha, \beta} = \frac{N_\alpha - N_\beta}{N_\alpha^0 - N_\beta^0} = [1 + 2\tau_{\alpha, \beta} A_{\alpha, \beta}]^{-1}, \qquad (12.1)$$

where $N_\alpha^0 - N_\beta^0$ is the difference in population of levels α and β if the paramagnet is in its equilibrium

state; $N_\alpha - N_\beta$ is the same quantity under saturation conditions; $A_{\alpha, \beta}$ is the probability of the transition $\alpha \rightarrow \beta$ under the influence of an rf magnetic field, and $\tau_{\alpha, \beta}$ is the relaxation time characterizing the process of establishment of equilibrium if it is disturbed by a change in the populations of levels α and β. By measuring $q_{\alpha, \beta}$ and $A_{\alpha, \beta}$ one finds $\tau_{\alpha, \beta}$. Formula (12.1) will also apply to the saturation fator of acoustic paramagnetic resonance if we understand by $A_{\alpha, \beta}$ the probability of the transition $\alpha \rightarrow \beta$ under the influence of sound vibrations. In acoustic experiments (assuming that one knows the relaxation time $\tau_{\alpha, \beta}$) one measures $q_{\alpha, \beta}$ and thus finds $A_{\alpha, \beta}$. A defect of the saturation method is the necessity for auxiliary measurements to determine $\tau_{\alpha, \beta}$.

In the majority of the experimental work done up to now, the saturation factors were measured, or one simply noted the fact that there was an influence of sound of the resonance frequency on the ordinary electron paramagnetic resonance. In the first experiments on resonance absorption of sound, Jacobsen, Shiren, and Tucker[26] observed the influence of sound, of double the resonance frequency, generated in a quartz crystal, on the signals of the ordinary paramagnetic resonance resulting from impurity ions Mn^{2+} and from paramagnetic centers which are formed as a result of irradiation of a quartz crystal by neutrons, electrons, or γ rays. A partial saturation of the line occurred both under the influence of longitudinal and of transverse sound waves.

Mattuck and Strandberg[28,6] observed how signals of ordinary paramagnetic resonance on Cr^{3+} ions in corundum and MgO and F-centers in quartz were saturated when one applied ultrasonics of frequency 13 Mc. They verified the selection rules established in Sec. 3 on ions of Cr^{3+} in corundum. For the transition between sublevels of the Kramers doublet $\pm \frac{1}{2}$, which is forbidden under the influence of sound, the applying of the ultrasonics had no effect to an accuracy of 1% on the magnitude of the ordinary resonance signal. For the allowed transitions they succeeded in getting practically complete saturation by using ultrasonics.

For Cr^{3+} in an MgO crystal, because of the absence of any significant fine structure splittings of the spin levels, saturation of the ordinary resonance signal under the influence of ultrasonics should have been achieved very easily. The experimental data turned out to be in complete contradiction to the predictions of the theory. From measurements of the magnitude of the saturation it follows that the spin-phonon interaction is 10^7 times smaller than expected. In the opinion of Mattuck and Strandberg such a marked discrepancy between theory and experiment is related to the fact that the introduction of the triply charged Cr^{3+} ion in place of the doubly charged Mg^{2+} ion gives rise to strong local changes of the lattice.

The work of Shiren[29] was devoted especially to testing the validity of the quadrupole selection rules for Cr^{3+} ions in corundum and Mn^{2+} and Fe^{3+} ions

in MgO. He generated longitudinal sound vibrations of frequency 9000 Mc in the crystals. For all three ions the results of the measurements turned out to be in good agreement with the selection rules.

Tucker,[30] by exciting longitudinal vibrations of frequency 9100 Mc along the trigonal axis of ruby, studied the dependence of the absorption coefficient σ on the orientation of the static magnetic field. The experimental data were in good agreement with the theoretical curves. When the magnetic field was directed parallel to the trigonal axis of the crystal, there was no sound absorption, as expected. For this case the theory predicts that absorption is possible only for transverse phonons.

In this same work the first absolute measurements of absorption coefficients were made, showing that $\sigma = 4 \times 10^{-2}$ cm^{-1} both for the transition $1 \rightarrow 2$ at $\theta = 20°$, as well as for the transition $3 \rightarrow 4$ at $\theta = 70°$ (the levels are numbered from top to bottom, θ is the angle between the magnetic field and the trigonal axis of the crystal), which in order of magnitude is in agreement with the theoretical values of σ given in Table I.

An interesting result was obtained by Jacobsen and co-workers.[26] The value of the spin-phonon interaction in their acoustic experiments was three orders of magnitude smaller than the magnitude of the coupling of the spins with phonons observed in low temperature relaxation measurements. Apparently spin-lattice relaxation at low temperature is achieved not by direct processes, but by some other means, possibly via irregularities of the crystals.[20]

13. ACOUSTIC PARAMAGNETIC RESONANCE ON NUCLEI

Resonance absorption of sound occurs not only in electronic paramagnets, but also in substances having nuclear paramagnetism. A preliminary estimate of the coefficients of sound absorption on nuclei was made by Al'tshuler.[18] Later detailed calculations of σ were carried out by Kraus and Tanttila,[31] Kessel',[32] and Bolef and Menes.[33]

In crystalline nuclear paramagnets the dominant role in spin-phonon interaction is played by one of the following mechanisms. If the nuclear spin $I = \frac{1}{2}$, the spin-phonon coupling results from magnetic interaction of the nuclei with the paramagnetic particles.[34] The value of the absorption coefficient σ can be estimated from formulas (9.6) and (9.7), if we replace $(g\beta)^4$ by $(g_n\beta\beta_n)^2$, where β_n is the nuclear magneton and g, g_n are the g-factors of the paramagnetic atom and the nucleus respectively. Such an estimate carried out[35] for protons in $CuSO_4 \cdot 5H_2O$ gave $\sigma \sim 10^{-23}\omega^2$ at T = 1° K, which is an entirely observable effect, since Bolef and Menes[33] measured $\sigma \sim 10^{-9}$ cm^{-1}. In the case of nuclei with spin $I > \frac{1}{2}$, the coupling of the spin system to phonons is the result of electric quadrupole interaction of the nuclei with the crys-

talline fields modulated by the lattice vibrations.[36] The existing theoretical treatment of resonance absorption of sound via quadrupole interaction refers only to cubic crystals of the NaCl type, in which most experimental work has been carried out. The most general form of the Hamiltonian for quadrupole interaction of a nucleus with the internal crystalline electrical field is

$$\mathcal{H}_Q = \frac{1}{6} \sum_{jk} Q_{jk} \nabla_j \nabla_k \varphi, \tag{13.1}$$

$$\nabla_j \nabla_k \varphi = \nabla_j \nabla_k \varphi_0 + \sum_{il} S_{jkil} \varepsilon_{il}, \quad j, k, i, l = x, y, z, \tag{13.2}$$

$$Q_{jk} = -\frac{3eQ}{2I(2I-1)} \left\{ I_j I_k + I_k I_j - \frac{2}{3} \delta_{jk} I^2 \right\}. \tag{13.3}$$

Here eQ is the value of the quadrupole moment, φ and φ_0 are the potentials of the crystalline electric field of the vibrating and rigid lattices, ε_{il} are the components of the deformation tensor, S_{jkil} is a fourth-rank tensor which characterizes the coupling of the crystal deformation with the electric field gradient.

In the following, to calculate the components of the tensor of the electric field gradient, we use a point model of the lattice. In order to take into account: 1) the amplification of the interaction because of the large quadrupole moments induced in the electron shells of the atom by the nuclear quadrupole moment, 2) the reduction of the interaction because of the polarization of the atoms by the crystalline field, 3) the increase of the interaction because of covalent binding and other effects, we introduce, as usual, an effective charge $\gamma e'$ for ions surrounding the nucleus under consideration (e' is the charge of the ion). The nature and properties of the factor γ have been discussed in detail by Cohen and Reif.[37] In an ideal rigid cubic lattice $\nabla_j \nabla_k \varphi = 0$ because of the symmetry of the crystal.[38] Sound vibrations destroy the cubic symmetry, and in (13.1) there appear terms different from zero.

Since the deviations of the ions from their equilibrium positions are much less than their separations, $\nabla_j \nabla_k \varphi$ in the presence of the sound can be calculated by expanding in a series in these displacements and stopping with linear terms, since only they are responsible for the direct processes of interaction of phonons with the spin system.

One can give the expression for the coefficient of sound absorption the same form as for crystals with ions of the elements of the iron group, (3.9). Taking into account the interaction of the nucleus only with ions of the first coordination sphere, we get

$$\mathcal{H}_1 = 0, \qquad \mathcal{H}_4 = 2\varepsilon (I_x I_y + I_y I_x),$$
$$\mathcal{H}_2 = 3\varepsilon (I_y^2 - I_x^2), \qquad \mathcal{H}_5 = 2\varepsilon (I_z I_x + I_x I_z),$$
$$\mathcal{H}_3 = \sqrt{3} \, \varepsilon [3I_z^2 - I(I+1)], \quad \mathcal{H}_6 = 2\varepsilon (I_y I_z + I_z I_y). \tag{13.4}$$

$$\varepsilon = 3 \left(\frac{e'}{R} \right)^2 \frac{1}{2I(2I-1)} \gamma \frac{Q}{R^2}, \tag{13.5}$$

R is the equilibrium distance from the nucleus to the nearest ion.

Numerical estimates of the values of σ for the case of a strong magnetic field applied along the [100] direction are given in Table IV (cf. reference 32).

Table IV. Coefficient of sound absorption on nuclei in cubic crystals.
$$\sigma = A(\omega^2/4\pi^2 T)\gamma^2 \times 10^{-22} \text{ cm}^{-1}$$

Nucleus	Spin	Material	$A_{1z}^{\perp}$	$A_{2x}^{\perp}$	$A_{2y}^{\perp}$	$A_{1x}^{\parallel}$	$A_{1y}^{\parallel}$
Br^{79}	$3/2$	LiBr	1.96	4.2	1.96	1.96	1.96
Br^{79}	$3/2$	KBr	0.76	1.64	0.76	0.76	0.76
Br^{79}	$3/2$	AgBr	1.5	3.4	1.5	1.5	1.5
I^{127}	$5/2$	KI	12.6	28.6	12.9	12.6	12.6

Here $A_{kl}^{\perp(\parallel)}$ refers to sound which is propagating perpendicular (parallel) to the magnetic field and polarized along the axis $l = x, y, z$, and absorbed as a result of transitions $\Delta m = \pm k$. By using the theoretically computed[39] values of γ we obtain: $\sigma_{Br^{79}}(KBr) \sim 10^{-20} \omega^2$ cm^{-1}, $\sigma_{I^{127}}(KI) \sim 10^{-20} \omega^2$ cm^{-1}. We note that acoustical investigation of nuclear paramagnets can be an excellent method for experimentally determining the factor γ.

The nuclear absorption of sound can be observed not only on nuclear magnetic levels, but also on the hyperfine components of singlet electron levels of paramagnetic ions. The coefficients of sound absorption in such sublevels have been calculated for the lowest simple level of Pr^{3+} and for the ground level of Ho^{3+} in ethylsulfates.[16] For Pr^{3+}, $\sigma_l = (v_l/v_t)^3\sigma_t \sim 10^{-21} \omega^2$ cm^{-1}, where absorption occurs only for sound propagating perpendicular to the crystal axis. For Ho^{3+}, $\sigma_l = (v_l/v_t)^3\sigma_t \sim 10^{-17} \omega^2$ cm^{-1}, where there is absorption of transverse waves in the case where the direction of propagation of the sound is parallel to the crystal axis, but when the sound propagates perpendicular to the crystal axis the absorption occurs only for longitudinally polarized waves. It is interesting to note that the selection rules for the acoustical effect are the same as for ordinary paramagnetic resonance.

14. EXPERIMENTAL INVESTIGATIONS OF ACOUSTIC PARAMAGNETIC RESONANCE ON NUCLEI

In 1955, Proctor and Tanttila[40] reported that by using a long ultrasonic pulse at the resonance frequency corresponding to the quadrupole splitting of Cl^{35} nuclei in sodium chlorate ($NaClO_3$), they had succeeded in reducing the difference in population of the degenerate spin states ($m = \pm \frac{1}{2}$, $m = \pm \frac{3}{2}$, where m is the magnetic quantum number of the nuclear spin), which was easily detected by standard methods of nuclear magnetic resonance. Soon thereafter, Proctor and Robinson[41] completed similar investigations on the magnetic nuclear levels of Na^{23} in a single crystal of NaCl.

The experimental study of the time for nuclear spin-lattice relaxation as a result of one-phonon processes apparently have not been done since they require extremely low temperatures. Experiments on acoustic paramagnetic resonance permit one to study one-phonon processes at room temperature. A series of detailed studies of this type have been carried out on crystals containing nuclei with large quadrupole moments. In these experiments there were great complications because of the difficulty in determining the density of energy of the ultrasonics acting on the spin system. Proctor and Tanttila,[42] continuing their work with Cl^{35} nuclei in sodium chlorate, attempted to estimate the dynamic quadrupole coupling factor γ of Kranendonk[36] (cf. Table IV), by using data concerning the time of phonon relaxation for the determination of the density of sound energy. The inadequacy of these data, however, did not permit them to draw any definite conclusions from a comparison with the theory. For Na^{23} nuclei in a NaCl crystal, Proctor and Robinson[43] obtained $\gamma = 1.4$, which almost agrees with Kranendonk's theory, omitting the anti-shielding effects; an estimate of the absorption coefficient gave $\sigma \sim 10^{-10}$ cm^{-1}.

Jennings, Tanttila, and Kraus[44] avoided the difficulty of finding the sound energy density by restricting themselves to a determination of the ratio of the strengths of dynamical quadrupole couplings of Na and I nuclei in a single crystal of NaI. They found $\gamma_I/\gamma_{Na} = 10.9$. Taylor and Bloembergen[45] determined the density of sound energy of a wave in a crystal of NaCl by measuring the magnitudes of displacements produced by the sound wave. They obtained a serious discrepancy with the simple point model, not taking into account anti-shielding factors: $\gamma = 5$ for Na and $\gamma = 9$ for Cl.

All the experiments cited above were based on measurements of the degree of saturation due to the ultrasound. Menes and Bolef[46] first carried out direct measurements of the coefficient of absorption of energy from an ultrasonic wave of resonance frequency by nuclei of In^{115} in a single crystal of InSb. The absorption of sound in the sample results in a change of its mechanical Q-value, which is determined from the change in the electrical impedance of the generator of sound waves. For the absorption resulting from transitions $\Delta m = \pm 1$ and $\Delta m = \pm 2$, the observed dependence of the absorption on the direction of propagation of sound was in good agreement with the theoretical predictions. Continuing their investigations,[33] they measured the coefficients of absorption σ on nuclei of I^{127} in KI and Br^{79} in KBr: $\sigma_I = 1.4 \times 10^{-8}$ cm^{-1}, $\sigma_{Br} = 0.6 \times 10^{-9}$ cm^{-1}. This enabled them to determine the factors $\gamma = 38$ for I^{127} and $\gamma = 26$ for Br^{79}. The values obtained, as one sees immediately by comparison with the data of Sec. 13, are much smaller than the theoretical values.

By making a series of measurements of absorption coefficients for the same nucleus I^{127} in different

crystals (CsI, RbI, KI, NaI), Menes and Bolef[47] came to the conclusion that the values of the factors γ obtained by them can be explained as follows: Because of the overlapping of the iodine ion with neighboring atoms, there is a significant admixture of states arising from a transition of an electron in the outer p-shell to excited levels. This assumption also gives a good explanation of the data concerning the chemical shift.

Interesting work using resonance absorption of sound was carried out by Abragam and Proctor.[48,49] These authors carried out an extensive study of the concept of temperature of a spin system. For this purpose, in order to prove experimentally the applicability of the concept of spin temperature to nuclei with equidistant magnetic levels, it was necessary to destroy the Boltzman distribution of populations of these levels. This cannot be done by using a varying magnetic field, since it acts equally on all neighboring levels. The application of ultrasound, which enables one to act on levels with $\Delta m = \pm 2$, destroys the equilibrium distribution. As the measurements showed, equilibrium is reestablished over the spin-spin relaxation time T_2, which speaks in favor of the applicability of the concept of spin temperature.

15. SHAPE OF THE ACOUSTIC PARAMAGNETIC RESONANCE LINE

In investigating acoustic paramagnetic resonance, as in any other resonance phenomenon the sources of information are the location of the absorption line, its intensity, and its shape. The spectra and line intensities from acoustic resonance have been discussed in detail above. Let us now proceed to look at the shape of the absorption curve.

If the incident sound wave is monochromatic and the lifetime of the phonons in the material is not too small, the shape of the acoustic paramagnetic resonance line is determined by those same causes as in ordinary magnetic resonance. The distinction consists in the fact that although the system of energy levels is the same in both cases, the properties of acoustic perturbations giving rise to transitions between these levels are different. In this connection the study of the absorption line shape for acoustic paramagnetic resonance can give additional information concerning the structure of the spin system.

In ideal crystals the main quantity determining the shape of the acoustic resonance line is spin-spin interaction. This problem was studied in references 50 and 51. Let us consider a system of identical interacting spins in the presence of a constant magnetic field directed along the z axis. The Hamiltonian of such a system has the following form:

$$\mathcal{H} = g\beta H \sum_j S_z^j + \mathcal{H}_{s\text{-}s} \, , \quad \mathcal{H}_{s\text{-}s} = \sum_{\substack{j > k \\ \alpha, \beta}} P_{\alpha\beta} S_\alpha^j S_\beta^k,$$

$$\alpha, \beta = x, \, y, \, z. \tag{15.1}$$

The second term on the right is the Hamiltonian of the spin-spin interactions which includes magnetic dipole-dipole and exchange interactions. Let us assume that the magnitude of the magnetic field H is so large that $\mathcal{H}_{s\text{-}s}$ can be treated as a perturbation on the Zeeman energy operator $\mathcal{H}_z$. In the absence of spin-spin interactions all of the levels of the spin system are equidistant. When one includes $\mathcal{H}_{s\text{-}s}$ each Zeeman energy level is converted to a band whose width is determined by the magnitude of the spin-spin interaction. In principle the shape of the absorption curve can be found by calculating its moments, where for symmetric curves all the odd moments are equal to zero. We shall find the second moment of the curve which, at least in order of magnitude, determines the width of the absorption line. Since we are interested in the shape of a definite line lying at a definite frequency $\omega_0 = ng\beta H/\hbar$ $(n = 1, 2, \ldots)$, we should take into account in the spin-phonon interaction operator $\mathcal{H}_{s\text{-}p}$ only the part which gives rise to transitions between the energy bands noted above, which are separated by a distance $ng\beta H$ from one another. We shall denote this part of the operator by $\tilde{\mathcal{H}}_{s\text{-}p}$.

Since the probability of transitions between a pair of levels of the spin system, p and q, under the influence of ultrasound is proportional to $|\langle p|\mathcal{H}_{s\text{-}p}|q\rangle|^2$, we get

$$\langle \omega^2 \rangle = \frac{\sum_{p, q} \{\omega_{pq}^2 \, | \langle p | \tilde{\mathcal{H}}_{s\text{-}p}| q \rangle |^2\}}{\sum_{p, q} | \langle p | \tilde{\mathcal{H}}_{s\text{-}p} | q \rangle |^2} \, . \tag{15.2}$$

Here p and q run through the labels of the energy levels in the bands between which the transitions occur. Formula (15.2) can be written in a form which is more compact and convenient for computation:

$$\langle \omega^2 \rangle = -\frac{\mathrm{Sp}\,(\tilde{\mathcal{H}}\, \tilde{\mathcal{H}}_{s\text{-}p} - \tilde{\mathcal{H}}_{s\text{-}p}\,\tilde{\mathcal{H}})^2}{\hbar^2 \,\mathrm{Sp}\,(\tilde{\mathcal{H}}_{s\text{-}p})^2} \, . \tag{15.3}$$

The tilde means that we include in the Hamiltonian $\mathcal{H}$ only the part which commutes with $\mathcal{H}_z$. We emphasize that if the Hamiltonian $\mathcal{H}$ is not cut off in this fashion, formula (15.2) cannot be represented in the form (15.3) and will represent a mean squared frequency of an absorption curve including all the satellite peaks, which are separated from the line in which we are interested by frequencies which are multiples of ω/n. The mean square deviation of the absorption frequency from the center of the line (or, what is the same thing, the second moment of the curve divided by its area, i.e., the reduced moment) is

$$\langle (\Delta\omega)^2 \rangle = \left\langle \left(\omega - \frac{ng\beta H}{\hbar} \right)^2 \right\rangle \tag{15.4}$$

which, as we have mentioned, characterizes the width of line. However, the width of the line cannot be determined uniquely from $\langle (\Delta\omega)^2 \rangle$; to do this we must make some assumption concerning the shape of the absorption curve. For example, for a Gaussian curve the width of the line at half maximum is given by

$$\omega_{1/2} = 2 \sqrt{2 \ln 2 \langle (\Delta\omega)^2 \rangle}. \qquad (15.5)$$

The specific form of the spin-phonon interaction operator depends on the type of paramagnet.

In the case of spin $S = \frac{1}{2}$, the Hamiltonian of the spin-phonon interaction in its general form can be represented as a linear function of the spin projection operators S_x, S_y, S_z. Obviously the resonance frequency for absorption of ultrasound will be the same as in ordinary paramagnetic resonance. It is not difficult to see that the width of the line of resonance absorption of ultrasound will in this case also coincide with the width of the magnetic resonance line.

In the case of spin $S > \frac{1}{2}$, for the majority of paramagnets the Hamiltonian of the spin-phonon interaction is a quadratic function of the spin projection. The most general form of the spin-phonon interaction in this case is the following:

$$\mathcal{H}_{s\text{-}p} = \sum_j [A(S_z^j S_z^j - S^{j2}) + B(S_z^j S_+^j + S_+^j S_z^j)$$
$$+ B^*(S_z^j S_-^j + S_-^j S_z^j) + C S_+^j S_+^j + C^* S_-^j S_-^j], \qquad (15.6)$$

where $S_\pm^j = S_x^j \pm i S_y^j$ and A, B, C, are linear functions of the operators for creation and annihilation of phonons. The absorption lines lie at frequencies $g\beta H/\hbar$ and $2g\beta H/\hbar$. A computation using formulas (15.3) and (15.4) for the line at frequency $g\beta H/\hbar$ (corresponding to the transition $\Delta M = \pm 1$) gives the following result for the second moment of the absorption curve:

$$\langle (\Delta\omega)^2 \rangle_{\Delta M=1} = \frac{1}{12} S(S+1) \sum_{j(\neq k)} [5(P_{xx}^{jk} + P_{yy}^{jk})^2 + 4(P_{zz}^{jk})^2].$$
$$(15.7)$$

If the spin-spin interactions are determined by magnetic dipole-dipole and isotropic exchange interactions, then

$$P_{xx}^{jk} + P_{yy}^{jk} = -g^2\beta^2 r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}) + 2J_{jk},$$
$$P_{zz}^{jk} = g^2\beta^2 r_{jk}^{-3}(1 - 3\cos^2\theta_{jk}) + J_{jk}, \qquad (15.8)$$

where J_{jk} is the exchange integral, and θ_{jk} is the angle between r_{jk} and the z axis.

The second moment for the line at frequency $2g\beta H/\hbar$ is equal to

$$\langle (\Delta\omega)^2 \rangle_{\Delta M=2} = \frac{1}{6} S(S+1) \sum_{j(\neq k)} [(P_{xx}^{jk} + P_{yy}^{jk})^2 + 8(P_{zz}^{jk})^2]. \quad (15.9)$$

In reference 51 formulas were also obtained for the fourth moment of the absorption curve, but we shall not bother to give them here because of their complexity.

From formulas (15.7) and (15.9), taking account of (15.8), we arrive at the following important conclusions:

a) When only magnetic dipole-dipole interactions are present, the second moment of the line of paramagnetic resonance absorption for the transition $|\Delta M| = 2$ is twice as large as the second moment of the line of magnetic resonance absorption (cf. reference 52). For the transition $|\Delta M| = 1$ the second

moment of the absorption curve is the same in both cases.

b) The second moment of the curve of acoustic paramagnetic resonance depends on isotropic exchange interactions, in contrast to the case for magnetic resonance.

This last point gives one hope that a study of the shape of the acoustic resonance line will give additional information concerning the properties of exchange interactions. In particular, in acoustic resonance the well-known effect in magnetic resonance of exchange narrowing of the absorption line is absent (or is small).

As already stated, all the formulas given above apply only for the case where all the spin levels are equidistant. However, this is not the case, with rare exceptions, in electronic and nuclear paramagnets with a non-cubic lattice. In this connection, in reference 53 there was recently calculated the second moment for the absorption curve resulting from transitions between Zeeman levels shifted as a result of the action of the crystalline field of axial symmetry (magnetic field directed along the symmetry axis). The reduced second moment of the absorption curve for the transition $M \rightleftharpoons M + 2$ is

$$\langle (\Delta\omega)^2 \rangle = \sum_{j(\neq k)} \frac{4}{3} (P_{zz}^{jk})^2 S(S+1)(2S+1)$$
$$+ \frac{1}{16} (P_{xx}^{jk} + P_{yy}^{jk})^2 \{4(M+1)^2 + [S(S+1) - M(M-1)]^2$$
$$+ [S(S+1) - (M+2)(M+3)]^2\}. \qquad (15.10)$$

In the case of the transition $|\Delta M| = 1$, $\langle (\Delta\omega)^2 \rangle$ for nonequidistant levels always coincides with the formula for magnetic resonance. We note that if the resonance lines caused by the fine and hyperfine structure of the level are not resolved (as a result of spin-spin interactions), then this may be regarded as an additional cause of line broadening. This question has still not been investigated in acoustic resonance.

In non-ideal crystals there may be a spread in values of the crystal field constants from atom to atom, which gives rise to a broadening of the resonance line. This effect was investigated theoretically in reference 54. It was assumed that the cause of the spread in values of the field constant is the presence of dislocations in the crystal. It was shown, in particular, that if the width of the line is determined by dislocations, then the ratio of the second moments of the ultrasonic (transition $\Delta M = 2$) and magnetic resonance for spins $S = \frac{3}{2}$ and $S = \frac{5}{2}$ are equal respectively to $\delta(\frac{3}{2}) = \frac{5}{3}$ and $\delta(\frac{5}{2}) = \frac{12}{5}$.

As yet only very little experimental data have been obtained concerning the line width of paramagnetic acoustic resonance (Table V).

From the available data one can conclude that in most cases the line width is apparently determined

Table V

Paramagnetic particle	Transition	$\omega_{1/2}/2\pi$ (in kc)	Literature
Na^{23} in NaI	$\Delta M = 2$	4.65	44
I^{27} in NaI	$\Delta M = 2$	4.49	44
Na^{23} in NaCl	$\Delta M = 2$	4	43
Mn^{2+} in quartz		3000	26
F-centers in quartz	$\Delta M = 1$	10^6	26

by lattice defects. In particular the experimental ratio of the squares of the widths of acoustic and magnetic resonances do not contradict the theory [$\delta(\frac{3}{2})$ = 1.7 in reference 43 and $\delta(\frac{5}{2}) > \delta(\frac{3}{2})$ in reference 33]. Such a comparison can be made only when the shapes of the curves of acoustic and magnetic resonance coincide, which cannot of course be guaranteed beforehand.

In connection with the material presented, it is of great interest to investigate the line shape in crystals with a minimum number of defects.

16. PULSE METHODS FOR INVESTIGATING ACOUSTIC PARAMAGNETIC RESONANCE

Paramagnetic resonance absorption of sound in the stationary state, as we have mentioned, is the analog of ordinary paramagnetic resonance. In recent years there have been discovered and widely investigated effects of magnetic induction and spin echoes, which result from irradiation of a paramagnet by pulses and by electromagnetic fields of definite duration. A study of these effects gives important information concerning the kinetics of magnetization and the structure of the spin system. There is unquestionably interest in the examination of the possibilities of observing similar effects with pulse application of ultrasonics to paramagnets and the understanding of their properties by this method. This problem has been treated theoretically in papers 55—58.

Here we shall show how, as a result of the influence of ultrasonic pulses, the magnetization of a paramag-

netic crystal is changed. Suppose that the spin system of a paramagnet is described by the Hamiltonian $\mathcal{H}_0$. At the moment of switching on of the ultrasonic generator (t = 0), the density matrix of the system is given by the usual canonical distribution

$$\varrho(0) = \frac{\exp(\mathcal{H}_0/kT)}{\mathrm{Sp}\exp(-\mathcal{H}_0/kT)}, \qquad (16.1)$$

and the magnetization of the crystal is equal to

$$\langle M(0) \rangle = \mathrm{Sp}[\varrho(0)M], \qquad (16.2)$$

where **M** is the operator for the magnetic moment of the sample. The further change of the density matrix in time is given by the equation

$$ih\frac{\partial\varrho}{\partial t} = -\varrho(\mathcal{H}_0 + \mathcal{H}_{\text{s-p}}) + (\mathcal{H}_0 + \mathcal{H}_{\text{s-p}})\varrho$$
$$= -[\varrho, (\mathcal{H}_0 + \mathcal{H}_{\text{s-p}})], \qquad (16.3)$$

where $\mathcal{H}_{\text{s-p}}$ again is the Hamiltonian for the interaction of the spin system with the sound field; the magnetization M(t) is determined by the formula (16.2) with the appropriate density matrix $\rho(t)$. To solve the problem it is convenient to go over to the interaction representation. We introduce a density matrix $\rho'(t)$:

$$\varrho(t) = \exp\left(\frac{i}{h}\mathcal{H}_0 t\right)\varrho'(t)\exp\left(-\frac{i}{h}\mathcal{H}_0 t\right). \qquad (16.4)$$

It is not difficult to show that $\rho'(t)$ satisfies the equation

$$ih\frac{\partial\varrho'}{\partial t} = -[\varrho', \mathcal{H}'_{\text{s-p}}], \qquad (16.5)$$

where

$$\mathcal{H}'_{\text{s-p}} = \exp\left(-\frac{i}{h}\mathcal{H}_0 t\right)\mathcal{H}_{\text{s-p}}\exp\left(\frac{i}{h}\mathcal{H}_0 t\right). \qquad (16.6)$$

The formal solution of equation (12.5) is

$$\varrho'(t) = \exp\left(\frac{i}{h}\mathcal{H}'_{\text{s-p}}t\right)\varrho'(0)\exp\left(-\frac{i}{h}\mathcal{H}'_{\text{s-p}}t\right). \qquad (16.7)$$

Now using (16.1), (16.4), (16.7) and the property Sp(AB) = Sp(BA), we get the following formula for the magnetization of the paramagnet t seconds after the switching on of the sound generator:

$$\langle M(t) \rangle = \mathrm{Sp}\{\varrho(t)M\} = \frac{\mathrm{Sp}\left\{\exp(-\mathcal{H}_0/kT)\exp\left(-\frac{i}{h}\mathcal{H}'_{\text{s-p}}t\right)M'\exp\left(\frac{i}{h}\mathcal{H}'_{\text{s-p}}t\right)\right\}}{\mathrm{Sp}\exp(-\mathcal{H}_0/kT)}, \qquad (16.8)$$

where $M' = \exp\left(-\frac{i}{h}\mathcal{H}_0 t\right) M \exp\left(\frac{i}{h}\mathcal{H}_0 t\right)$.

Let us apply this general formula to the case of nuclear paramagnets. We shall consider the case where the Zeeman levels of an individual spin are equidistant. (This means that in the absence of the sound field the gradient of the electric field at the nucleus is equal to zero, i.e., we are restricting ourselves to cubic crystals.) Suppose that a longitudinal sound wave propagates along the [110] direction; we choose it as the x' axis (in this case we do not get simultaneously a wave with transverse polarization).

Then the operator for interaction with the sound field of the spin system of a layer of matter of thickness much less than the wave length and situated perpendicular to the direction of propagation of the sound is given for cubic crystals on the basis of (13.1) by the following expression:

$$\mathcal{H}_{\text{s-p}}(t) = h\cos(\omega t)\sum_j \{\omega_1(I_{y'}^j I_{z'}^j + I_{z'}^j I_{y'}^j) + \omega_2(I_{x'}^{j2} - I_{y'}^{j2})\};$$

$$\omega_1 = \gamma\frac{eQS_{11}\varepsilon_0}{4I(2I-1)}\left[\left(\frac{3}{4} - \frac{S_{44}}{S_{11}}\right)\sin\theta\cos\theta\right],$$

$$\omega_2 = -\gamma\frac{eQS_{11}\varepsilon_0}{4I(2I-1)}\left[\left(\frac{3}{4} + \frac{S_{44}}{S_{11}}\right) - \left(\frac{3}{4} - \frac{S_{44}}{S_{11}}\right)\sin^2\theta\right],$$

$$\varepsilon_{x'x'} = \varepsilon_0\cos(\omega t). \qquad (16.9)$$

Here we have introduced the usual notation for the components of the tensor S_{ijkl}: $S_{11} = S_{xxxx}$, $S_{44} = S_{yzyz}$, and the unprimed coordinate axes are drawn along the cubic axes of the crystal. The magnetic field vector ($\parallel z'$) makes an angle θ with the [1$\bar{1}$0] direction. The summation extends over all nuclei in the particular layer of matter. Assuming that the spin-spin interactions are small compared to the Zeeman energy,

$$\mathscr{H}_0 = -\gamma_0 \hbar H \sum_j I_{z'}^j = -\omega_0 \hbar \sum_j I_{z'}^j, \qquad (16.10)$$

where γ_0 is the gyromagnetic ratio and H the magnetic field intensity. It is not difficult to see that if the sound frequency is equal to the Larmor frequency ω_0, then only the first term in the Hamiltonian (16.9) (with factor ω_1) can give rise to resonance transitions; if, however, $\omega = 2\omega_0$ then only the second term (we denote them by $\mathscr{H}_1$ and $\mathscr{H}_2$ respectively) can give resonance. Therefore in each of these cases we can substitute in formula (16.8) in place of $\mathscr{H}_{s-p} = \mathscr{H}_1 + \mathscr{H}_2$ only the resonant part (either $\mathscr{H}_1$ or $\mathscr{H}_2$). It should be noted that when we go over from $\mathscr{H}_1$ and $\mathscr{H}_2$ to operators in the interaction representation, $\mathscr{H}_1'$ and $\mathscr{H}_2'$ are operators which are independent of time plus additional terms which oscillate in time with a frequency which is a multiple of the Larmor frequency; these latter terms will be ineffective for pulse lengths $t_0 \gg 2\pi/\omega_0$ and can be neglected.

A specific calculation for the cases I = 1 and I = $\frac{3}{2}$ leads to the following result for the macroscopic magnetization of the layer of matter after the passage of an ultrasonic pulse of duration t_0 (in the first non-vanishing approximation in the quantity $\xi = \hbar\gamma_0 H/kT$ for the components of M):

Spin I = 1:

$$\langle M \rangle_{\omega=\omega_0} = \frac{N\gamma\hbar\xi}{6} \left\{ \xi \sin(\omega_1 t_0) [x_0' \cos(\omega_0 t) - y_0' \sin(\omega_0 t)] + \right.$$
$$\left. + z_0' 4 \cos\frac{(\omega_1 t_0)}{2} \right\},$$

$$\langle M \rangle_{\omega=2\omega_0} = \frac{2N\gamma\hbar\xi}{3} z_0' \cos(\omega_2 t_0).$$

$$(16.11)$$

Spin I = $\frac{3}{2}$:

$$\langle M \rangle_{\omega=\omega_0} = \frac{\sqrt{3}N\gamma\hbar\xi}{4} \left\{ \xi \sin(\sqrt{3}\omega_1 t_0) [x_0' \cos(\omega_0 t) - y_0' \sin(\omega_0 t)] \right.$$
$$\left. + \frac{z_0'}{\sqrt{3}} [\cos(\sqrt{3}\omega_2 t_0) + 4] \right\},$$

$$\langle M \rangle_{\omega=2\omega_0} = N\gamma\hbar\xi z_0' [\cos(\sqrt{3}\omega_2 t_0) + 1].$$

$$(16.12)$$

Here N is the number of nuclei in the particular sample volume, x_0', y_0', z_0' are unit vectors along the x', y', z' axes. From formulas (16.11) and (16.12) we see that:

a) As a result of the action of the sound pulse with frequency $\omega = \omega_0$, there appear in the x'y' plane oscillating components of the macroscopic magnetic moment, i.e., we get an effect of free magnetic induction which can be investigated by standard methods.

The maximum value of the amplitude of the induction signal is reached if the duration of the pulse t_0 satisfies the relation $\omega_1 t_0 = \pi/2$ for I = 1 and $\sqrt{3}\,\omega_1 t_0 = \pi/2$ for I = $\frac{3}{2}$ (see below concerning the order of magnitude of the effect). The ultrasonic pulse at frequency $\omega = 2\omega_0$ does not excite oscillating components of the magnetization vector.

b) The ultrasonic pulse at both frequencies (ω_0 and $2\omega_0$) results in a change of the z' component of the macroscopic magnetic moment. Curiously, for integer spin, I = 1, the extremal values of the components $\langle M_{z'} \rangle$ and $\langle M_{x'} \rangle$, $\langle M_{y'} \rangle$ are not reached simultaneously. In the case of half-integral spin, I = $\frac{3}{2}$, this phenomenon does not occur.

c) If the spin-spin relaxation time T_2 is sufficiently long, then one can have a spin-echo effect produced as usual by two pulses of definite duration (cf. in this connection references 57 and 58). We should immediately make the following remark. The nuclear induction signal cannot last indefinitely, its duration being limited principally by the spin-spin relaxation time T_2. Therefore in order to succeed in observing a signal we must impose another requirement on the duration of the sound pulse: $t_0 \ll T_2$. The shape of the drop-off of the decaying induction signal was investigated theoretically in reference 56.

An important question arises concerning the order of magnitude of the effect. From formulas (16.12) and (16.13) we see that the amplitude of the nuclear induction signal A_s produced by the ultrasound is less than the amplitude for the usual effect A_M for two reasons: First of all, A_s is proportional to ξ^2 whereas A_M is proportional to ξ; secondly, because of the fact that $\epsilon_0 \approx \omega B \cos(qx)/v$, where B is the amplitude of the sound vibrations and q is the wave vector, in summing the effect over all sample layers it turns out that the components of the macroscopic vector in neighboring antinodes of the standing sound wave are rotated in opposite directions and the total signal is equal to zero. For this last reason only those layers of material can be effective whose thickness is $l < 1/q$. A rough estimate shows that if A_M refers to induction on Br[79] nuclei in KBr observed at room temperature and in a field of H = 3000 oe, then in order for $A_s \sim A_M$ we must have T = 1.4° K and H = 10,000 oe (for the same number of nuclei).

However, one can avoid these difficulties. In reference 58 it was shown that if one uses two pulses, one at frequency ω_0 and the other at $2\omega_0$, then $A_s \sim \xi$, i.e., the first reason for the small signal is removed.

One can get rid of both difficulties in studying the effect of ultrasonic pulses on paramagnets by following the change in $\langle M_{z'} \rangle$.[56] This change can be detected if we flip $\langle M_{z'} \rangle$ with a variable magnetic field pulse through an angle $\pi/2$, which results in a precession of $\langle M_{z'} \rangle$ in the x'y' plane, and consequently produces a signal in the pick-up loop.

Finally, there remains for us to discuss what information can be obtained by such experiments. The most interesting results which have so far been obtained in experiments on observation of sound resonance in paramagnets using a continuous method of operation are measurements of the magnitude of spin-phonon interaction. However, these measurements can be made only with an accuracy determined by the shape of the absorption curve and, if there is saturation of the magnetic resonance by the sound, with an accuracy of the order of the spin-lattice relaxation time. In observing the signal from free induction caused by an ultrasonic pulse, the magnitude of the spin-phonon interaction is measured independently of any parameters, by determining the duration of the pulse t_0 for which the induction signal has its extreme value. In addition, one gets further information concerning the spin-system structure by studying the shape of the curve of decay of the induction signal.

Of course, it is not possible beforehand to guess all the possible applications of this method, since the effect considered here has as yet not been detected experimentally. One can, however, hope that this will be done in the near future.

17. DOUBLE RESONANCE. POSSIBLE APPLICATIONS OF ACOUSTIC PARAMAGNETIC RESONANCE

Everybody knows the extensive use that has been made of double paramagnetic resonance. First, it makes possible a very great increase in sensitivity of radiospectroscopic measurements; second, it has also made possible the proposal of new dynamical methods for polarization of nuclei; third, it has led to the production of low-noise, paramagnetic amplifiers (masers). The application of the method of double resonance is possible if the paramagnetic particles have more than two spin levels. A simple case of three spin levels is shown in Fig. 5. We say that we have double resonance if the paramagnet is subjected to the action of oscillating fields at two resonance frequencies; for example, ω_{31} and ω_{32}. The existence of resonant paramagnetic absorption of sound opens the possibility of applying both combined magnetoacoustic double resonce (where one of the oscillating fields is magnetic and the other acoustic), as well as double acoustic resonance (where both of the oscillating fields are acoustic).

Combined double resonance has been used in practice in some of the experiments described in Secs. 12 and 14. The idea of these experiments is simple: the change in occupation of level E_3 occuring as the re-
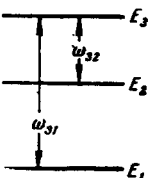

FIG. 5. Diagram of double resonance.

sult of resonance absorption of sound of frequency ω_{31} is observed by detecting the usual paramagnetic resonance at frequency ω_{32}. The usefulness of this method consists in the fact that while magnetic dipole transitions are often allowed only between neighboring spin levels, under the action of ultrasonics one also has allowed double transitions. This latter fact makes it very convenient to use ultrasonics for obtaining "maser-effects."[59] The necessary condition for this effect is a negative resonance absorption, resulting when the population of a certain spin level can be made greater than the population of any lower-lying level. For example, if we saturate the transition $E_3 \rightarrow E_1$, then we obtain either $N_3 > N_2$ or $N_2 > N_1$. The sound field can be a very convenient "intensifier," enabling one easily to obtain saturation of the transition $E_3 \rightarrow E_1$.

Kastler[60] proposed the use of double magnetoacoustic resonance for polarization of nuclei in metals. Unfortunately, as the detailed investigation showed (cf. Sec. 11), this idea is not feasible. However, in nonmetallic paramagnets orientation of nuclear spins by using resonance absorption of sound is entirely possible. The advantages of such a method of orientation of nuclei have as yet not been studied.

Because of the possibility of negative resonance absorption of sound, in principle we can have, in addition to the usual (photon) maser effect, the occurrence of a phonon maser effect. Obtaining a photon maser effect would make possible the production of generators (and amplifiers) of coherent sound vibrations in the region of microwave and even higher frequencies. According to Townes[59] the condition for production of a phonon maser effect can be found as follows.

Let us assume that the system of spins is in a state with a negative temperature, where the excess of spins in the upper level is n. The spins relax via one-phonon processes with a lifetime $\tau = \tau_0/(\bar{n}_p + 1)$, where $\bar{n}_p$ is the average quantum number of the lattice oscillator, and τ_0 is the relaxation time of the spins for a lattice temperature equal to zero. Then the rate of increase in number of phonons N_p with frequencies ω to $\omega + \Delta\omega$ is given by the equation

$$\frac{dN_p}{dt} = -\frac{\varrho_\omega \Delta\omega \bar{n}_p}{\tau_p} + \frac{n}{\tau}, \qquad (17.1)$$

where ρ_ω is the number density of lattice oscillators and τ_p is the lifetime of a phonon of frequency $\sim \omega$. Obviously in order that dN_p/dt be positive it is necessary that one satisfy the condition

$$\frac{(\bar{n}_p + 1)}{\tau_0} n > \frac{\varrho_\omega \Delta\omega \bar{n}_p}{\tau_p}. \qquad (17.2)$$

For $kT \gg \hbar\omega$ this relation, which is the condition for the occurrence of a maser effect, takes the form*

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*Note added in proof. Relation (17.3) is the condition for the generation of sound. Analogously, one can obtain the condition for sound amplification, which has the form $\sigma_{\alpha,\beta}/\sigma_0 > (-q_{\alpha,\beta})^{-1}$; here $\sigma_0 = 1/v\tau_p$ is the coefficient of absorption of sound associated with nonmagnetic losses.

$$\frac{n\tau_\Phi}{\varrho_\omega \Delta\omega\tau_0} > 1. \qquad (17.3)$$

If (17.3) holds, the number of phonons with frequency ω will increase so long as no important non-linear effects appear.* The question of the possibility of producing a sound maser is treated in detail in papers 61—63.

18. NONRESONANT PARAMAGNETIC ABSORPTION OF SOUND

So far we have considered the most interesting type of paramagnetic absorption of ultrasonics—acoustic paramagnetic resonance. There is also another important aspect of this phenomenon—the nonresonant paramagnetic absorption of sound. The reasons for this absorption are, from the thermodynamic point of view, relaxation processes both of the spin system as well as between it and the thermal oscillations of the lattice. If we extend the analogy between paramagnetic absorption of sound and of an electromagnetic field, then the relaxation absorption of sound in a paramagnet is the analog of the well-known phenomenon of absorption of electromagnetic energy for parallel orientation of a constant and a variable magnetic field.[64]

First let us consider the absorption of sound in a paramagnet resulting from interaction of the spin system with the thermal vibrations of the lattice. The theory of this problem was developed by Kochelaev.[65] We shall make the computation in a semi-phenomenological manner following his paper.

We shall consider a small volume V of a crystal, whose linear dimensions are much smaller than the sound wave length. We may then assume that the crystal deformation is constant over its extent; this volume should, however, contain a sufficiently large number of atoms so that one can have a macroscopic description. Let us assume that this volume of the paramagnet can be divided into two subsystems which interact weakly with one another—the spin system and the thermal lattice vibrations. We assume that equilibrium in the spin system is established instantaneously. In other words, the time for intra-spin relaxation τ_s shall be much smaller than the time of spin lattice relaxation τ, and $\omega\tau_s \ll 1$. Furthermore, as shown in reference 65, we may neglect the deviation of the lattice from thermodynamic equilibrium in the presence of the sound field, and we can also neglect thermal conductivity of the spin system.

In the presence of the sound field the state of the spin system, taking into account all the preceding statements, can be characterized completely by the temperature T, the value of the magnetic field H, and the components of the deformation tensor of the

*Noted added in proof. Recently Tucker[66] reported on a phonon maser, by means of which he has succeeded in obtaining amplification of hypersonics of frequency $\sim 10^{10}$ cps by using synthetic ruby as the working material.

crystal. If the vibrations are longitudinal, then the number of components of the deformation tensor can be reduced to one:

$$\varepsilon = \varepsilon_0 \cos(qz) \exp(i\omega t) = \varepsilon' \exp(-i\omega t). \qquad (18.1)$$

The work done by the spin system when the external parameter ε is changed is:

$$\delta W = Fd\varepsilon, \quad F = F(T, H, \varepsilon) = -\left(\frac{\partial\psi}{\partial\varepsilon}\right)_{T,H}. \qquad (18.2)$$

Here ψ is the free energy of the spin system in the presence of the external magnetic field, and F is the generalized force corresponding to the coordinate ε. If ε is small, we may assume that the deviation of the state of the spin system from equilibrium is negligible. Therefore all the equations can be written in the linear approximation in the small quantities ε, $\xi = F - F_0$, $\theta = T - T_0$ (where F_0 and T_0 are the equilibrium values of F and T). The dissipative properties of the spin system are conveniently described by introducing a "sound susceptibility of the spin system" by the following equation:

$$\zeta = \xi/\varepsilon = \zeta' - i\zeta'', \qquad (18.3)$$

where ζ' and ζ'' are real. It is easily seen that damping of the sound wave in the paramagnetic, resulting from the dissipative properties of the spin system, is determined by the imaginary part of ζ. One can also see that the energy absorbed per unit time is

$$\dot{E} = \frac{\omega}{2}\zeta''(\varepsilon')^2. \qquad (18.4)$$

Expanding F in a series in powers of θ and ε and using the heat balance equation, we find

$$\zeta'' = \frac{T(\Psi_{T\varepsilon})_0^2}{C_H}\frac{\omega\tau}{1+\omega^2\tau^2}, \quad \Psi_{T\varepsilon} = \frac{\partial^2\Psi}{\partial T\,\partial\varepsilon}. \qquad (18.5)$$

Here C_H is the specific heat of the spin system in unit volume of the paramagnet and $\Psi = \psi/V$.

In order to express ζ'' in terms of known quantities, we must find the explicit form of $(\Psi_{T\varepsilon})_0$. By definition,

$$\psi = -kT \ln[\mathrm{Sp}\exp(-\mathscr{H}/kT)]. \qquad (18.6)$$

The Hamiltonian of the spin system, because of the smallness of the parameter ε, can be written as a power series in ε:

$$\mathscr{H} = \sum_{n=0}^{\infty} \mathscr{H}_n\varepsilon^n. \qquad (18.7)$$

Further expanding (18.6) in powers of $1/kT$ and using (18.4) and (18.5), we get the coefficient of absorption of sound in the first non-vanishing approximation in ε and $1/kT$, after averaging over the whole volume of the crystal:

$$\sigma = \frac{1}{dv^3k^2T^3C_H\eta}\left[\mathrm{Sp}\,\mathscr{H}_0\mathscr{H}_1 - \frac{1}{\eta}\mathrm{Sp}\,\mathscr{H}_0\mathrm{Sp}\,\mathscr{H}_1\right]^2\frac{\omega^2\tau}{1+\omega^2\tau^2}, \qquad (18.8)$$

where η is the number of possible states of the spin system. This formula solves our problem. Let us

make it more specific for some typical paramagnets.

First let us consider paramagnets whose magnetic particles have a spin $S > \frac{1}{2}$. We make the calculation for salts of elements of the iron group, whose ions are located in an octahedral surrounding where the crystalline field has a weak trigonal component. The Hamiltonian for such a spin system in the absence of sound has the form:

$$\mathcal{H}_0 = \sum_j \left[\beta g_\| S_z H_z + \beta g_\perp (S_x H_x + S_y H_y) \right.$$
$$\left. + \frac{1}{6} D (S_x^j + S_y^j + S_z^j)^2 \right] + \mathcal{H}_{s-s}. \quad (18.9)$$

Here D is the splitting of the spin levels in the electric field of a crystal of trigonal symmetry, $\mathcal{H}_{s-s}$ is the Hamiltonian for spin-spin interaction. The operator $\mathcal{H}_1 \epsilon$ is the Hamiltonian for spin-phonon interaction [cf. formulas (3.6), (4.1), and (4.5)]. Substituting these operators in (18.8), we obtain

$$\sigma = \frac{AN^2}{T^3 C_H} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2},$$
$$A = 2 \cdot 10^{-3} \frac{\epsilon_1^2 D^2 R^2}{dv^3 k^2} [4S^2 (S+1)^2 - 3S (S+1)]^2 \quad (18.10)$$
$$\times (\lambda_x \lambda_y + \lambda_x \lambda_z + \lambda_y \lambda_z)^2,$$

where ϵ_4 is defined in (4.4)—(4.7) for the corresponding ions, and λ_x, λ_y, λ_z are the cosines of the angles between the direction of propagation of the sound and the coordinate axes. From this formula it follows that:

a) One should observe a strong anisotropy in the sound absorption coefficient. (In particular, σ takes on its maximum value if the sound propagates along the trigonal symmetry axis of the crystalline field, and goes to zero if it is directed along a cubic axis.)

b) The absorption coefficient is proportional to the square of the fine structure constant of the spin levels. This result apparently is a general one for all paramagnets.

c) With increasing magnetic field, sound absorption disappears. This is also a general result if the fine structure constants are not small.

Let us make a numerical estimate of the absorption coefficient for chromium-potassium alums. If the sound is directed along the trigonal symmetry axis of the crystalline field of one of the nonequivalent Cr^{3+} ions (in the unit cell of alums there are four nonequivalent ions and the trigonal symmetry axes of the electric field are directed along the space diagonals of the cube) and we use $\omega = 2\pi \cdot \times 10^7$ cps, $T = 300°$ K and (4.5), then we obtain $\sigma \sim 10^{-5}$ cm^{-1}.

In the case of $S = \frac{1}{2}$ the Hamiltonian $\mathcal{H}_0$ consists solely of the Zeeman energy operator and $\mathcal{H}_{s-s}$. Using the explicit form of the operator for spin-phonon interaction (3.6) and (6.1), we obtain for a crystal with paramagnetic ions in an octahedral surrounding with a weak component of a crystalline field of tetragonal symmetry:

$$\sigma = \frac{A'N^2}{T^3 C_H} \frac{\omega^2 \tau}{1 + \omega^2 \tau^2},$$
$$A' = \frac{\epsilon_2^2 \beta^4}{dv^3 k^2} \left[(\alpha_x^2 - \alpha_y^2)^2 H^4 + \frac{4}{3} (\alpha_x^2 + \alpha_y^2) H^2 K^2 + \frac{4}{9} K^4 \right] (\lambda_x^2 - \lambda_y^2). \quad (18.11)$$

Here ϵ_2, for example, in the case of Cu^{2+}, was determined in (6.4), while α_x, α_y, α_z are the direction cosines of the external magnetic field. The spin-spin interaction is included here by introducing a local magnetic field distributed in Gaussian fashion, with a constant effect field equal to K. We see that in the case of $S = \frac{1}{2}$ sound absorption increases with increasing magnetic field intensity (for $H \to \infty$, $\sigma \sim H^2$).

We estimate σ for copper salts. Let $H = 10^4$ oe, $\omega = 2\pi \times 10^7$ cps, $T = 300°$ K, $(\lambda_x^2 - \lambda_y^2) = 1$, $(\alpha_x^2 - \alpha_y^2) = 1$. Then $\sigma \sim 10^{-4}$ cm^{-1}.

The estimates given here show that this effect can easily be detected. The dependence of σ on the magnitude of the magnetic field enables one to separate paramagnetic absorption of sound from other effects.

Let us go on to consider nonresonant paramagnetic absorption of sound resulting from intraspin relaxation.[66] The calculation from the very start will be carried out quantum mechanically. For simplicity we choose the case where the spectrum of the spin system is determined solely by the spin-spin interactions (magnetic dipole-dipole and isotropic exchange interactions). Again we consider a small volume of the paramagnet. The energy of the sound field absorbed by the spin system of this volume in a transition between levels p and q is proportional to the quantum of energy $\hbar\omega = E_p - E_q$, the difference in population of these levels $\hbar\omega/kT$ (we assume $kT \gg \hbar\omega$) and the corresponding transition probability. Assuming all this, we write the coefficient of absorption of the ultrasound, averaging over the whole volume of the crystal:

$$\sigma(\omega) = \frac{\omega^2 f(\omega)}{4kT dv^3}, \quad (18.12)$$

$$f(\omega) \Delta\omega = \sum_{\omega - \frac{\Delta\omega}{2}}^{\omega + \frac{\Delta\omega}{2}} |\langle p | \mathcal{H}_{s-p} | q \rangle|^2.$$

The summation is extended over a small interval of the spectrum of the spin system, but one which contains a large number of discrete levels. It is not difficult to see that the moments of the function $f(\omega)$ can be expressed in terms of $Sp\,\mathcal{H}_{s-p}^2$, $Sp\,\dot{\mathcal{H}}_{s-p}^2$, etc. Since we are interested only in the order of magnitude of the effect, we shall limit ourselves to calculating the zero'th and second moments of $f(\omega)$. Assuming that $f(\omega)$ is a Gaussian, we obtain the following formula for the coefficient of absorption of sound (where the vibrations are polarized longitudinally) for spin $S > \frac{1}{2}$ [cf. (3.6), (4.1), and (4.5)]:

$$\sigma(\omega) = \frac{\sqrt{2}\pi}{15} \frac{N\epsilon_1^2 R^2}{dv^3 kT\omega_0} S(S+1) [4S(S+1) - 3] \omega^2 \exp\left(-\frac{\omega^2}{2\omega_0^2}\right), \quad (18.13)$$

$$\omega_0^2 = \langle \omega^2 \rangle = \frac{2g^4\beta^4}{\hbar^2} S(S+1) \sum_j \{(5r_{ij}^{-6} - 3z_{ij}^2 r_{ij}^{-8}) + 2J_{ij}^2\}. \quad (18.14)$$

The maximum of the absorption lies in the frequency region $\omega_{max} = \sqrt{2}\,\omega_0$. An important consequence of this formula is that ω_{max} depends on the isotropic exchange interactions, whereas ω_{max} for the absorption of an electromagnetic field does not depend on them. The numerical estimate of σ for MgO with Ni^{2+} impurities gives (concentration 1%): $\omega_{max} \sim 10^9$ cps, $\sigma \sim 10^{-5}$ cm^{-1}.

We note that with increasing magnetic field H the absorption due to spin-spin interactions disappears. As a result, the effect will be small in salts whose magnetic particles have a spin $S = \frac{1}{2}$, since in this case the spin-phonon interaction itself is proportional to H.

Experimentally there has as yet been no investigation of nonresonant paramagnetic absorption of sound. These experiments could give valuable information concerning the magnitude of spin-phonon interaction and concerning the structure of spin systems. Besides, the carrying out of such experiments is much simpler than the observation of resonance; in particular, one does not require such high sound frequencies.

19. CONCLUSION

We have treated paramagnetic absorption of sound in the principal types of paramagnets and discussed the available experimental data. Throughout we have pointed to the analogy between the effects considered here and the action on paramagnets of radiofrequency electromagnetic fields. From the presentation we see that all the fundamental effects which are produced in paramagnets by an electromagnetic field (resonance, spin induction and echoes, relaxation phenomena), which have already received extensive and intense application to the investigation of materials, can also be carried out using sound fields. We may assert that paramagnetic absorption of sound is possible in almost all substances in which paramagnetic absorption of rf electromagnetic fields has been observed. We have not touched on questions of semi-conductors, crystals with color centers, solid free radicals, and gases and liquids. As for the first two materials, effects are possible in them (they have been observed on F-centers[26]) as is indicated by the existing theory of spin lattice relaxation.[67] There is no information concerning spin-phonon interactions in solid free radicals since, in experiments on the saturation of paramagnetic resonance, the spin-phonon part does not manifest itself, but one sees only the coupling of the spins with the reservoir of energy of exchange interaction. The investigation of paramagnetic absorption of sound in this kind of material will give a fundamental answer concerning the type of spin-phonon coupling in it. Liquid and gaseous paramagnets occupy a special position since the effect of paramag-

netic absorption of sound in them will probably be small.[35] The reason for this is that the change in interaction of a given particle with its surroundings comes mainly not from sound vibrations, but from diffusion displacements. For example, in water with a sound strength of $I = 1$ watt/cm^2 and frequency $\omega = 6\pi \times 10^7$ sec^{-1}, the amplitude of the vibrational motion is $A_s \sim 2 \times 10^{-7}$ cm, whereas the diffusion displacement is $A_d \sim 3 \times 10^{-6}$ cm.

Of course, acoustic paramagnetic resonance will probably not be so widely applied as ordinary paramagnetic resonance, since to demonstrate it experimentally is more complicated. Nevertheless, the investigation of paramagnetic absorption of sound may give additional information concerning the properties of materials which are difficult or impossible to obtain from experiments on absorption of an electromagnetic field. This applies primarily to the question of the properties of spin-phonon interaction. The point is that this interaction is usually investigated by measuring times for spin-lattice relaxation. However, such a method gives little information concerning spin-phonon interactions because of the great difficulty in theoretical interpretation of the measurements, especially as the measured time is, as a matter of fact, the time for establishment of equilibrium of the distribution of populations of levels of the spin system, which generally speaking is not necessarily determined by the interaction of the spins with the lattice vibrations. Obviously in studying the interaction of spins with a sound field the spin-phonon interaction is investigated directly. There are very great possibilities in studying acoustic resonance on electron spins in metals, since such experiments with an electromagnetic field are extremely difficult because of the skin effect. Further possibilities of acoustic paramagnetic resonance are indicated by the fact that transitions produced by a sound field are subjected to different selection rules than those stimulated by electromagnetic fields. Finally, by comparing the absorption coefficients in a paramagnet of sound and of an electromagnetic field, one can conclude that as a rule effects due to sound are several orders of magnitude greater.

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