SHIFT OF THE COMPONENTS OF THE FINE STRUCTURE OF THE RAYLEIGH LINE FOR LIGHT SCATTERING IN PARAMAGNETS

S. A. AL'TSHULER and B. I. KOCHELAEV

Kazan' State University

Submitted to JETP editor March 18, 1965

J. Exptl. Theoret. Phys. (U.S.S.R.) 49, 862-866 (September, 1965)

It is shown that it is possible to observe the shift of the fine structure components of the Rayleigh line which occurs when the frequency of the phonon which participates in the light scattering coincides with one of the splittings of the spin levels of the paramagnetic ion. Possible experiments for observing the scattering of light with simultaneous saturation of the paramagnetic resonance lines are discussed.

1. Under certain conditions the absorption of sound in paramagnets as a function of magnetic field has sharp maxima corresponding to the sound frequency coinciding with the intervals between spin levels (cf., for example, the summary [1]). It is obvious that in the absorption region the relation between the sound frequency and the wave vector changes and thus becomes dependent on the magnetic field. This effect results, in particular, in a shift of the fine structure components of the Rayleigh line for definite values of the magnetic field.[1)] Since the frequency of the phonons participating in the scattering of light in crystals is of order 10^{10}—10^{11} cps, the investigation of Rayleigh scattering in paramagnets offers the possibility of studying the spin-phonon interaction without having to contend with the difficulties of exciting sound at such high frequencies. In the present note we discuss the possibilities for doing such an experiment.

2. The change of the sound velocity as a result of spin-phonon interaction has been detected experimentally,[2] and a qualitative explanation of the effect has been given.[3] we shall give a more detailed examination of this question. The Hamiltonian of the system can be written in the form

$$\mathcal{H} = \mathcal{H}_s + \mathcal{H}_p + \mathcal{H}_{sp}; \quad \mathcal{H}_p = \sum_{q\lambda} \hbar\omega_{q\lambda} b^+_{q\lambda} b_{q\lambda},$$

$$\mathcal{H}_{sp} = i \sum_{jm} \sum_{q\lambda} (-1)^m \varepsilon_{2\lambda}{}^m Y_{2j}{}^{-m} \left(\frac{\hbar q}{2Mv_\lambda}\right)^{1/2} \times (b^+_{q\lambda} e^{iqr_j} - b_{q\lambda} e^{-iqr_j}). \quad (1)$$

Here $\mathcal{H}_s$, $\mathcal{H}_p$ and $\mathcal{H}_{s-p}$ are the respective Hamiltonians for the spin system, the phonon field, and the spin-phonon interaction; $b^+_{q\lambda}$ and $b_{q\lambda}$ are the operators for the creation and annihilation of phonons with wave vector q and polarization λ; $\omega_{q\lambda}$ is the phonon frequency; M is the mass of the crystal; v_λ is the sound velocity in the absence of spin-phonon interaction; Y^{-m}_{rj} is a function of the operators of the angular variables of the "magnetic" electrons of the j-th paramagnetic ion; $\epsilon^m_{2\lambda}$ are the components of the spherical tensor of second rank constructed from the unit vectors u and e^λ of the wave vector and the polarization vector:

$$\varepsilon_{2\lambda}{}^0 = 6^{-1/2}\{u_x e_x{}^\lambda + u_y e_y{}^\lambda - 2u_z e_z{}^\lambda\},$$

$$\varepsilon_{2\lambda}{}^{\pm 1} = \pm 1/2\{u_x e_z{}^\lambda + u_z e_x{}^\lambda \pm i(u_z e_y{}^\lambda + u_y e_z{}^\lambda)\},$$

$$\varepsilon_{2\lambda}{}^{\pm 2} = -1/2\{u_x e_x{}^\lambda - u_y e_y{}^\lambda \pm i(u_x e_y{}^\lambda + u_y e_x{}^\lambda)\}. \quad (2)$$

We write the equation of motion for the phonon Green function

$$D_{q\lambda}(t-t') = i\theta(t-t')\langle [b_{q\lambda}(t),\ b_{q\lambda}{}^+(t')]\rangle = \langle\langle b_{q\lambda} | b_{q\lambda}{}^+\rangle\rangle.$$

We have:

$$\left(i\frac{\partial}{\partial t} - \omega_{q\lambda}\right) D_{q\lambda}(t-t') = -\delta(t-t')$$

$$- i\sum_{jm} (-1)^m \varepsilon_{2\lambda}{}^m \left(\frac{q}{2M\hbar v_\lambda}\right)^{1/2} \exp[-iqr_j] \langle\langle Y_{2j}{}^{-m} | b_{q\lambda}{}^+\rangle\rangle,$$

$$\left(i\frac{\partial}{\partial t'} + \omega_{q\lambda}\right) \langle\langle Y_{2j}{}^{-m} | b_{q\lambda}{}^+\rangle\rangle$$

$$= -i\sum_{j'm'} (-1)^{m'} \varepsilon_{2\lambda}{}^{m'} \left(\frac{q}{2M\hbar v_\lambda}\right)^{1/2} \times \exp[iqr_{j'}] \langle\langle Y_{2j}{}^{-m} | Y_{2j'}{}^{-m'}\rangle\rangle. \quad (3)$$

[1)] This was first pointed out by V. L. Ginzburg.

We neglect the interaction between different normal modes of the lattice. The brackets $\langle \ldots \rangle$ denote a statistical average; [A, B] is the commutator of the operators A and B; $\theta(t - t')$ is a step function, equal to one for $t > t'$ and zero for $t < t'$.

Changing to the time Fourier transform in (3) and introducing the polarization operator $P_{q\lambda}(\omega)$ (cf., for example, [4]) according to the equation

$$\{\omega - \omega_{q\lambda} - qP_{q\lambda}(\omega)\} D_{q\lambda}(\omega) = -1/2\pi, \quad (4)$$

we find in first approximation in $\mathcal{H}_{s\text{-}p}$:

$$P_{q\lambda}(\omega) = \frac{\pi N}{\hbar \rho v_\lambda} \sum_{j, m, m'} (-1)^{m+m'} \varepsilon_{2\lambda}{}^{m} \varepsilon_{2\lambda}{}^{m'} \langle\langle Y_{2j}{}^{-m} | Y_{2j'}{}^{-m'} \rangle\rangle_\omega \times \exp[-iq(\mathbf{r}_j - \mathbf{r}_{j'})]. \quad (5)$$

Here ρ is the density of the crystal and N the number of paramagnetic particles per unit volume.

If we search for the poles of the function $D_{q\lambda}(\omega)$, which determine the phonon frequencies, we find

$$\omega = \omega_\lambda + qP_{q\lambda}(\omega). \quad (6)$$

The real part of this equation determines the dependence of the phonon frequency on the wave vector, and the imaginary part determines the phonon absorption.

We note that the polarization operator is practically independent of the modulus of the wave vector for values corresponding to sound vibrations, since the spin correlations fall off rapidly with distance. The observed sound velocity is now

$$v_{q\lambda}{}^{H} = v_\lambda + \mathrm{Re}\, P_{q\lambda}(\omega).$$

Let us consider $P_{q\lambda}(\omega)$ in more detail. Introducing the single-particle statistical operator $\rho_{kk'}$, diagonal in the energy representation of the unperturbed spin system, we have:

$$P_{q\lambda}(\omega) = \frac{\pi N}{\hbar \rho v_\lambda} \sum_{\substack{jkl \\ k'l'}} \Lambda_{kk'} \Lambda_{l'l} \langle\langle \rho_{kk'} | \rho_{l'l} \rangle\rangle_\omega \exp[-iq(\mathbf{r}_j - \mathbf{r}_{j'})],$$

$$\Lambda_{kk'} = \sum_m (-1)^m \varepsilon_{2\lambda}{}^{m} (Y_{rj}{}^{-m})_{kk'}. \quad (7)$$

We shall first assume that there are no interactions in the spin system. Writing the equation of motion for the spin retarded Green function, we get:

$$\langle\langle \rho_{kk'} | \rho_{l'l} \rangle\rangle_\omega = \frac{\langle \rho_{k'k'} - \rho_{kk} \rangle}{2\pi} \left\{ \frac{P}{\omega - \omega_{k'k}} - i\pi\delta(\omega - \omega_{k'k}) \right\} \delta_{kl}\delta_{k'l'},$$

$$P_{q\lambda}(\omega) = \frac{N}{2\hbar \rho v_\lambda} \sum_{jkk'} |\Lambda_{kk'}|^2 \langle \rho_{k'k'} - \rho_{kk} \rangle \times \left\{ \frac{P}{\omega - \omega_{k'k}} - i\pi\delta(\omega - \omega_{k'k}) \right\} \quad (8)$$

where the symbol P denotes the principal value.

We then see that in the equilibrium state, when the difference in spin level occupation numbers

$$N_{k'} - N_k = \langle \rho_{k'k'} - \rho_{kk} \rangle < 0 \text{ for } \omega_{k'k} > 0,$$

the imaginary part of (8) is positive; this causes the appearance in the phonon correlation function of a factor which falls of exponentially with time, as it should. If the spin system is not in an equilibrium state and

$$N_{k'} - N_k > 0 \text{ for } \omega_{k'k} > 0,$$

then Im $P_{q\lambda}(\omega)$ changes sign and the sound wave is amplified in passing through the crystal (cf. [1]). The presence of interactions in the spin system causes the delta function in Im $P_{q\lambda}(\omega)$ to be replaced by some curve $g(\omega - \omega_{k'k})$ with a finite width.

Using the analytic properties of Green functions, the change in the spin velocity can be expressed in terms of the phonon damping:

$$\mathrm{Re}\, P_{q\lambda}(\omega) - \mathrm{Re}\, P_{q\lambda}(\infty) = \frac{P}{\pi} \int_{-\infty}^{\infty} d\omega' \frac{\mathrm{Im}\, P_{q\lambda}(\omega')}{\omega' - \omega}. \quad (9)$$

In particular, if the curve $g(\omega - \omega_{k'k})$ has the Lorentz shape with a width equal to Δ, the maximum value of the sound velocity at frequencies in the vicinity of resonance will be:

$$\left[\frac{\delta v_\lambda}{v_\lambda}\right]_{\omega = \Omega_0 \mp \Delta} = \pm v_\lambda \frac{\sigma_{q\lambda}(\Omega_0)}{2\Omega_0}, \quad \sigma_{q\lambda}(\omega) = \frac{\omega}{v_\lambda{}^2} \mathrm{Im}\, P_{q\lambda}(\omega). \quad (10)$$

Here $\sigma_{q\lambda}(\omega)$ the coefficient for paramagnetic absorption of sound and Ω_0 is the resonance frequency.

3. Let us make some numerical estimates and discuss the possibility of observing this effect. As an example we consider the MgO crystal with impurities of Ni^{2+} and Fe^{2+}, whose spin-phonon interaction has been well investigated. [2] For both ions the ground state in a field of cubic symmetry is a triplet with effective spin S = 1, which is split only by a magnetic field. The velocity of longitudinal sound waves along the (100) axis in MgO is 9.25×10^5 cm/sec. Consequently in the scattering of light from a mercury arc ($\omega/2\pi = 7 \times 10^{14}$ cps) at right angles, the distance between fine structure components, according to the Mandel'shtam-Brillouin formula, is $\Omega/2\pi$

$= 6 \times 10^{10}$ cps. The coefficient of paramagnetic resonance absorption of sound in MgO with a concentration of Ni^{2+} ions equal to $c = 5 \times 10^{-6}$, at a frequency $\Omega/2\pi = 9.225 \times 10^9$ cps was [2] $\sigma = 0.25$ cm^{-1} for the transition with a change of spin projection $\Delta M = 2$ at liquid helium temperatures. For this transition σ depends on the angle φ between the direction of propagation of the sound (100) and the direction of the external magnetic field as $\sin^4\varphi$; in this case $\varphi = 90°$. According to (8), the maximum change in the velocity of the phonons participating in the light scattering is equal in our example to $\delta v/v = 4 \times 10^{-5}$ (we have assumed the absorption coefficient $\sigma(\Omega) \sim \Omega^2$). We then see that the effect is observable in a MgO crystal with a concentration of Ni^{2+} ions of order $c \sim 10^{-2}$—10^{-3}.

In the case of the Fe^{2+} ion the absorption coefficient was $\sigma = 0.44$ at a frequency $\Omega/2\pi = 9.46 \times 10^9$ cps and a concentration $c = 7.5 \times 10^{-5}$ and $\varphi = 16.5°$, other conditions being the same. Consequently the change in the velocity of phonons of frequency $\Omega/2\pi = 3 \times 10^{10}$ also at $\varphi = 90°$ will be $\delta v/v = 0.01$, which seems to indicate a considerable shift of the fine structure components of the Rayleigh line in such a crystal.

Other suitable objects for study might be crystals containing paramagnetic ions of elements of the iron group, like V^{3+}, Cr^{4+}, and Ti^{3+}. We may anticipate an especially large effect in crystals containing paramagnetic ions of the rare earths with an even number of electrons. In this case, in particular, there is no need to satisfy the resonance conditions between phonon and spin frequencies, and one will see a dispersion of the sound caused by the relaxation processes in the spin system.[1] Moreover, even in the absence of a magnetic field there should be considerable damping of the sound and a dependence of its velocity on frequency in paramagnetic crystals of the rare earths, in contrast to diamagnetic crystals (for example in praseodymium ethyl sulfate as compared to lanthanum ethyl sulfate). This effect might also be detectable in liquids, but the dependence on magnetic field should be weak because of broadening of the line shape $g(\omega)$ by Brownian motion.

We should mention the following point. Because the change of the sound velocity, according to (8), is proportional to the difference in occupations of the spin levels, one should expect the largest shift to occur at low temperatures when the intensity of the Rayleigh scattering is greatly reduced. It is therefore desirable to use a laser as the light source. The width of the fine structure components will apparently be of the same order as these shifts, and the precision in measuring the latter will be low. Besides, the value of the spin-phonon interaction which one gets from relaxation measurements in most cases claims only to give the order of magnitude. The question of the line shape under resonance conditions will be treated elsewhere.

It would be of great interest to observe Rayleigh scattering with inverted spin level occupations (for example by using maser action). If the rate of energy transfer from the spin system to the resonant phonons is greater than that from these phonons to others, the temperature of the resonant phonons will increase sharply, which will lead to a corresponding increase in the light scattering. According to (8) the sign of the shifts then changes. For saturation of the paramagnetic resonance by equating the populations of the spin levels, the shifts and broadening of the lines disappear, but the scattered intensity still increases. Such experiments enable one to study the dynamics of the establishment of equilibrium in the system of spins and phonons.

In conclusion we should like to mention that the study of the Rayleigh scattering of light in paramagnets is of particular interest for the case of strong spin-phonon interaction, when the observation of acoustic paramagnetic resonance is impossible because of the broadening of the absorption line. The widths of the Mandel'shtam-Brillouin components can be varied by changing the concentration of paramagnetic ions.

[1] S. A. Al'tshuler, B. I. Kochelaev and A. M. Leushin, UFN 75, 459 (1961), Soviet Phys. Uspekhi 4, 880 (1962).

[2] N. S. Shiren, Phys. Rev. 128, 2103 (1962).

[3] E. H. Jacobsen and K. W. H. Stevens, Phys. Rev. 129, 2036 (1963).

[4] S. V. Tyablikov and V. L. Bonch-Bruevich, The Green Function Method in Statistical Mechanics, New York, Interscience, 1962.

Translated by M. Hamermesh
114