ACOUSTIC PARAMAGNETIC RESONANCE OF Mn^{3+} IN CORUNDUM

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With V^{3+} and Fe^{2+} in an Al_2O_3 lattice as an example, it was shown that acoustic paramagnetic resonance (APR) is an effective method of investigating the spin system of ions with an even number of electrons [1]. We report here the observation of the APR spectrum of the Mn^{3+} ion in corundum, which has a strong spin-phonon interaction.

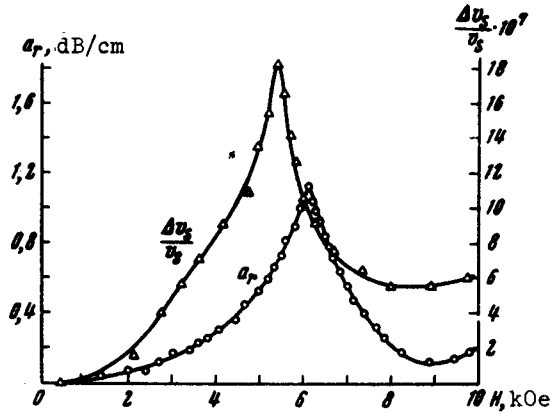
The experimental conditions were as follows: The resonant absorption and dispersion of a longitudinal hypersonic wave of 9.4 GHz frequency, propagating in corundum along a twofold symmetry axis (x axis) was investigated at the temperature of liquid helium (4.2°K). The concentration of the manganese impurity in the corundum crystal was 0.01%. The crystal had the form of a cylinder of 2.6 mm diameter and 15 mm length, with optically flat and parallel end faces perpendicular to the x axis. To excite the hypersound, a CdS converter film with an aluminum substrate was deposited on one of the end faces by vacuum sputtering. The axis of the film texture was perpendicular to the substrate. The method of exciting and receiving the hypersound, with the aid of a point-like microwave-field concentrator, was described earlier.

A hypersonic interferometer was developed for the measurement of the resonant absorption and dispersion of the hypersound velocity. The interferometer had two channels of equal acoustic path length. The corundum crystal with the manganese impurity was located in the first measuring channel, whereas in the second, reference channel the hypersound propagated in corundum containing no paramagnetic impurities. The corundum crystal in the reference channel had the same form and orientation as the measurement crystal. Owing to simultaneous optico-mechanical finishing of these crystals, their lengths did not differ by more than 0.5 μ. To exclude the temperature effect in the velocity measurements, both crystals were mounted in an acoustic head having a construction similar to that described in [2], and were placed in liquid helium. The first interferometer channel was used to measure the resonant absorption of the hypersound. The interpretation of the hypersonic echo signals was by the paired-pulse method [2]. The resonant dispersion was measured by comparing the phases of the hypersonic echo signals in the reference and measurement channels with passage of the magnetic field over the resonance line. The sensitivity of the interferometer has made it possible to measure relative hypersound-velocity changes $\Delta v_s/v_s < 10^{-7}$.

If a magnetic field $H \leq 12$ kOe is directed along the threefold symmetry axis (z axis), a broad resonant-absorption line is observed with a maximum at a field $H_r = 6.1$ kOe and a width 2.2 kOe (see the figure). The deviation of the direction of H from the z axis leads to an increase of the resonant field H_r for this line, and when $\theta > 10°$ there appears a second resonance in strong fields. When $\theta = 15°$, the hypersound absorption has maxima near 7 and 11 kOe. The two resonances coalesce at $\theta = 45°$ and $H_r = 8.9$ kOe. With further increase of θ, the resonances again separate, but the magnitude of the absorption at the maximum decreases. When $\theta > 60°$ the absorption exhibits a monotonic decrease with the magnetic field, without any resonances. At $\theta = 90°$, no dependence of the absorption on the magnetic field is observed. The resonant absorption decreases when the crystal is cooled to 1.8°K. For $\theta = 0$ we have $\alpha_r(4.2°K)/\alpha_r(1.8°K) = 5.5$. The resonant absorption is accompanied by a change of the phase velocity of the hypersound wave (see the figure). The difference between the resonant fields for $\Delta v_s/v_s(H)$ and $\alpha_r(H)$, and also the relative magnitude of the velocity change

$$\frac{\Delta v_s}{v_s}(H_r')|\simeq\frac{1}{2}\alpha_r(H_r)k_s^{-1}$$

(k_s is the hypersound wave vector) agree with the theory of resonant dispersion in APR [3]. The absence of a sharp maximum on the $\Delta v_s/v_s(H)$ curve is apparently connected with the inhomogeneous broadening of the resonance line and the influence of the second resonance.



Resonant absorption and dispersion of the hypersound velocity at T = 4.2°K and θ = 0.

The observed broad resonance curve of the hypersound absorption and the large value of the absorption at the maximum of the curve point to the presence of a spin-phonon coupling for the impurity paramagnetic center. This allows us to state that the observed resonant absorption is due to transitions in the spectrum of the trivalent manganese, since manganese impurity ions with a different valence (Mn^{2+} or Mn^{4+}) in corundum, which have previously been investigated by the EPR method [4, 5], have narrow absorption lines corresponding to Kramers doublets with weak spin-phonon coupling. The Mn^{3+} entering the corundum lattice replaces isomorphically the Al^{3+} ion. The ground state of the free ion is ^5D. In the cubic field of the oxygen octahedron, this state splits into the lower state ^5E_g and an excited state $^5T_{2g}$ lying $10D_q \simeq 2 \times 10^5$ cm^{-1} higher. An important fact is that the orbital doublet ^5E_g is not split by the crystal field of cubic and trigonal symmetry of the rigid oxygen octahedron in corundum. Such a situation was considered theoretically in [6]. It was shown that in the case of a strong spin-phonon coupling the degeneracy is lifted when account is taken of the vibrations of the ions of the octahedron (the dynamic Jahn-Teller effect). Of importance in lifting the degeneracy are deformations that lead to tetragonal or rhombic distortions of the octahedron (for example, displacements in the direction of the twofold symmetry axis). The joint action of the lattice deformation and of the spin-orbit coupling lead to a splitting of the 10-fold degenerate orbital level ^5E_g. On the basis of the angular and temperature dependences of α_r it can be concluded that the resonant absorption is due to transitions between the levels of the doublet with $M_s = \pm 1$. Since α_r decreases with temperature, the lower level is a singlet level, and the levels of the $M_s = \pm 1$ doublet are located a distance D away from it. The initial splitting D can be readily determined from the temperature dependence of the APR, which yields D = 5.7 cm^{-1}. The peculiar angular dependence of the APR and the presence of two resonances can be explained as being due to the presence in the corundum lattice of two non-equivalent Mn^{3+} ions, the spectra of which intersect at θ = 45°. The measured values of the absorption coefficient and of the width of the resonance line make it possible to estimate the elements of the spin-phonon interaction tensor for Mn^{3+} in corundum. On the basis of calculations analogous to those in [1], we obtain

$$\left[\frac{1}{4}(G_{1111}-G_{2211})^2+G_{1112}^2\right]^{1/2}\geqslant 5\cdot 10^2\,\mathrm{cm}^{-1}.$$

The nonlinear value exceeds by 2×10^2 times the corresponding components of the tensor $G_{ik\ell m}$ for Cr^{3+} in corundum.

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[1] E.M. Ganapol'skii, Fiz. Tverd. Tela 11, 3679 (1969), 12, 2606 (1970) [Sov. Phys.-Solid State 11, 2938 (1970); 12 (1971)].
[2] E.M. Ganapol'skii, Prib. Tekh. Eksper. No. 6, 214 (1969).
[3] E.H. Jacobsen and K.W.H. Stevens, Phys. Rev. 129, 2036 (1963).
[4] W. Low and J.T. Suss, Phys. Rev. 119, 132 (1960).
[5] S. Geschwind, P. Kisliuk, M.P. Klein, J. Remeika, and D.L. Wood, Phys. Rev. 126, 1684 (1962).
[6] C. Bates, J.M. Dixon, J.R. Fletcher, and K.W.H. Stevens, J. Phys. C. 1, 859 (1968).