Letters to the Editor

ELECTRON-NUCLEAR PARAMAGNETIC RESONANCE OF V^{3+} IONS IN CORUNDUM

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Submitted to JETP editor April 22, 1964

J. Exptl. Theoret. Phys. (U.S.S.R.) **47**, 382-383 (July, 1964)

IF paramagnetic particles, for example ions of elements of the intermediate groups, are introduced into a crystalline lattice, and if the number of electrons in these particles is even, then the lowest electronic level induced by the crystalline electric field can be a singlet. The state of the paramagnetic ion in this level will nevertheless be degenerate if the nuclear spin $I \neq 0$. The character and magnitude of the splitting of the lowest level under the influence of the internal crystalline electric and external magnetic fields will be determined not only by the nuclear moments but also by a contribution made to the electric quadrupole and the magnetic dipole moments by the electrons of the unfilled shell. The role of the electrons can be very much larger than that of the nucleus. Hence both the magnitude of the resonance frequencies and also in the intensity of magnetic resonance will be intermediate between the usual effects of electron and nuclear resonance. The calculation of spectra of this kind of "electron-nuclear resonance" was carried out by Zaripov.[1] Because of the absence of sufficient experimental data at the present time, however, one cannot indicate particular objects suitable for experimental investigation.

With an aim at discovering electron-nuclear paramagnetic resonance in an experiment, we settled on corundum containing V^{3+} as an impurity, because the EPR investigation of Zverev and Prokhorov[2] definitely established that the lowest electronic level was a singlet and was separated from the upper level by an interval $\Delta \approx 8\ cm^{-1}$. This small separation evinced fears that the resonance lines would be excessively broadened by dipole-dipole interactions with ions in the excited level. The calculations of Minaeva[3] showed that at a temperature $\sim 1°K$ the lines should be sufficiently narrow.

The measurements were carried out in a nuclear resonance spectrometer of increased sensitivity, which allowed us to obtain a signal from the aluminum nuclei with a signal-to-noise ratio of several thousand at helium temperatures. An improved Pound circuit and synchronous detection were used in the spectrometer. The corundum sample we studied had a volume of 0.1 cm^3 and a V^{3+} concentration of $\sim 0.5\%$ relative to the number of Al^{3+} ions. If the crystal is so oriented that the angle θ between its trigonal axis and the external magnetic field H lies between 20 and 45°, then a distinct resonance line, corresponding to the transition $\pm 1/2$, is observed at 1.5°K. The width of the line is 0.2 to 0.3 Mc. When the temperature is increased to 4.2°K, the line broadens and the effect disappears, in agreement with the predictions of the theory.[3] In exactly the same way at angles $< 20°$ and $> 45°$ observation of the effect becomes impossible because of excessive line broadening. In the first case the reason for the broadening is the strong decrease in the gyromagnetic ratio γ at small θ (the measurements were carried out at constant generator frequency ~ 6 Mc by varying the field H); in the second case the reason is merging of the principal absorption line with subordinate ones. Because of the large width, we were barely able to establish the positions of only four secondary lines, corresponding to transitions $\pm 1/2 \rightarrow \pm 3/2$ and $\pm 3/2 \rightarrow \pm 5/2$.

The spectrum observed at various orientations of the crystal can be explained by the following spin Hamiltonian:

$$\mathcal{H} = d\{I_z^2 - 1/3 I(I+1)\} - \gamma_\perp \hbar (H_x I_x + H_y I_y) - \gamma_\parallel \hbar H_z I_z,$$

where $d/h = 0.40 \pm 0.07$ Mc, $\gamma_\parallel$ agrees with the gyromagnetic ratio for the nucleus of the free atom, and $|\gamma_\perp / \gamma_\parallel| = 3.72 \pm 0.03$. These values for the spin Hamiltonian constants are easily interpreted theoretically.

[1] M. M. Zaripov, Izv. AN SSSR, ser. fiz. **20**, 1220 (1956), Columbia Tech. Transl. p. 1110.

[2] G. M. Zverev and A. M. Prokhorov, JETP **40**, 1016 (1961), Soviet Phys. JETP **13**, 714 (1961).

[3] R. M. Minaeva, FTT **5**, 1403 (1963), Soviet Phys. Solid State **5**, 1020 (1963).

Translated by L. M. Matarrese
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