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ELECTRON PARAMAGNETIC RESONANCE OF THE V^{+++} ION IN SAPPHIRE

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THE electronic paramagnetic resonance (epr) spectrum of the V^{+++} ion has been investigated in a sapphire single crystal Al_2O_3.

The ground state of this ion is $^3F_2$. The sevenfold degeneracy of the orbital energy level is split by a crystalline electric field of cubic symmetry into a singlet and two triplets with the triplet found at the lower level. A crystalline field of trigonal or tetragonal symmetry splits this orbital triplet into a doublet and a singlet. The lowest energy level of the V^{+++} ion in a crystalline field of trigonal symmetry is the singlet, which has a triple degeneracy ($S = 1$). In work by Siegert[1] and van Vleck[2] it has been shown that at zero magnetic field the levels with $S_Z = 0$ and $S_Z = \pm 1$ should be separated by approximately 10 cm^{-1}. Hence one would expect to see a line corresponding to the transition from the $S_Z = +1$ level to the $S_Z = -1$ level. Since the number of unpaired electrons is even the $S_Z = +1$ and $S_Z = -1$ levels should be slightly split at zero magnetic field.

To observe the line it is necessary that its width be small, i.e., the spin-lattice relaxation time must be greater than 10^{-11} sec. In the sapphire lattice there is a strong electric field of trigonal symmetry which produces a wide separation in the lower orbital levels of the V^{+++} ion. Hence one would expect that the spin-lattice relaxation time should be sufficiently long at low temperatures. In those crystal lattices in which the axial component of the electric field is weaker there is not much hope of seeing epr lines for V^{+++}. It is for this reason that the V^{+++} spectrum has probably not been studied up to this time.

We have observed one line of the V^{+++} ion in a sapphire single crystal at $T = 4.2°K$ at frequencies ranging from 14 to 38 kilomegacycles/sec. There was a sharp reduction in line intensity when the temperature was reduced to 2°K. When the temperature was increased the line became smeared out and vanished. The line could not be observed at $T = 77°K$. The line comprises eight equidistant components corresponding to a nuclear spin $I = 7/2$ for V^{51}.

The line was observed in the parallel orientation, i.e., with the fixed magnetic field parallel to the z axis of the crystal and vanished, becoming broadened, when the crystal was rotated through an angle greater than 60° with respect to the parallel orientation. The half-widths of the individual components in the parallel orientation were 20 oersteds; the components were 108 oersteds apart.

The spectrum was interpreted by means of the spin Hamiltonian:[3]

$$\hat{\mathcal{H}} = DS_z^2 + g_\parallel \beta H_z S_z + g_\perp \beta (H_x S_x + H_y S_y) + \Delta S_x + AS_z I_z + B(S_x I_x + S_y I_y),$$

where S_X, S_Y and S_Z are the electron spin projections, I_X, I_Y, and I_Z are the nuclear spin projections, H_X, H_Y and H_Z are the projections of the magnetic field vector, β is the Bohr magneton, D is the spacing between the $S_Z = 0$ and $S_Z = 1$ levels, $g_\parallel$ and $g_\perp$ are the g-factors for the two orientations, A and B are the hyperfine-splitting constants for the various orientations and the term ΔS_X denotes the small splitting of the $S_Z = +1$ and $S_Z = -1$ levels at zero magnetic field. The spectrum was interpreted under the assumption that $D \gg \Delta$ and $g_\parallel \beta H$ and $g_\perp \beta H$ were each greater than A or B.

$\Delta M = 1$ transitions were not observed since $D \gg h\nu$. In the case of a $\Delta M = 2$ transition we have:

$$h\nu = (2 - D^{-2}(\Delta + g_\perp \beta H \sin\alpha)^2)(g_\parallel \beta H \cos\alpha + Am),$$

where α is the angle between the magnetic field and the trigonal axis of the crystal and m is the projection of the nuclear spin on the z axis.

The formula which has been obtained is in good agreement with all the experimental results; the effect of the term $(\Delta + g_\perp \beta H \sin\alpha)^2 D^{-2}$ can be neglected for the experimental errors reported here. Hence we can only determine $g_\parallel$ and A in the spin Hamiltonian:

$$g_\parallel = 1.92 \pm 0.01; \quad A = (1.93 \pm 0.02) \cdot 10^{-2}\ \text{cm}^{-1}.$$

Measurement of the line intensities at various temperatures indicates that $D > 0$ and is approximately $10\ \text{cm}^{-1}$.

The results which have been obtained are in agreement with the values $g_\parallel = 1.98$, $g_\perp = 1.82$ and $D = 5.0\ \text{cm}^{-1}$, obtained by van der Handel and Siegert[4] from measurements from the susceptibility of vanadium — ammonium alums.

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DISPERSION OF SOUND IN METALS IN A MAGNETIC FIELD

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DISPERSION effects in the velocity of sound in solid metals, predicted by Alpher and Rubin,[1] have not been observed at the present time; this situation is probably a result of the fact that the effect is so small. In the present paper experiments in which this effect was observed are reported.

A special system was designed and built to investigate small changes in the velocity of acoustic vibrations; under favorable conditions this instrument makes it possible to measure changes of approximately 10^{-6} in the velocity of sound. The operation of the instrument is based on a comparison and measurement of the phase difference between vibrations which pass through the sample being investigated and those which are transmitted directly from an ultrasonic generator.

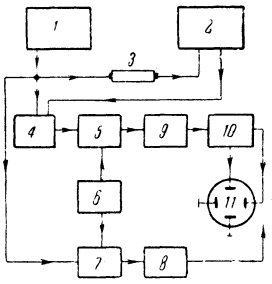

FIG. 1. Diagram of the measuring instrument. 1) 7 mc/sec crystal oscillator, 2) tuned amplifier, 3) sample, 4) electronic switch, 5) mixer, 6) quartz-crystal heterodyne unit, 7) mixer, 8) peeking amplifier, 9) frequency multiplier, 10) circular sweep generator, 11) cathode ray oscilloscope.

A block diagram of the measurement scheme is shown in Fig. 1. The high-frequency voltage from a quartz-crystal oscillator is applied to a quartz radiator which is fastened to one side of the cylindrical sample. A quartz detector is fastened to the second face of the sample; the voltage from the detector is then passed through a tuned amplifier to the phase meter.[2] A voltage obtained directly from the crystal radiator is also applied to the phase meter. Using a frequency multiplication factor of 18, phase differences of the order of 0.2 degrees can be measured.

X-cut quartz slabs 10 mm in diameter were used as ultrasonic radiators. The samples were cylindrical rods 20 cm long and 1.4 cm thick. Because of the high acoustic absorption in polycrystalline tin there was no need to take account of standing waves which could distort the results of the measurements; similarly there was no need to consider reflections from the side surfaces of the sample, produced by the cone-shaped radiation pattern of the quartz radiator. To avoid these effects in aluminum the surface was roughened by cutting to enhance scattering; the face at the receiving end was also cut at a small angle with respect to the axis.

The velocity of sound in a magnetic field is given by the expression:*

$$c_l = c_{l0}\left(1 + \frac{s^2}{2c_{l0}^2}\sin^2\vartheta\right), \qquad c_t = c_{t0}\left(1 + \frac{s^2}{2c_{t0}^2}\cos^2\vartheta\right).$$

Here c_l is the velocity of longitudinal wave while c_t is the velocity of the transverse wave, $s^2 = \mu H^2/4\pi\rho$, ρ is the density, ϑ is the angle between