

ELECTRON PARAMAGNETIC RESONANCE SPECTRUM OF  $V^{3+}$  IN CORUNDUM

G. M. ZVEREV and A. M. PROKHOROV

Institute of Nuclear Physics, Moscow State University

Submitted to JETP editor September 10, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) **38**, 449-454 (February, 1960)

Electron-spin paramagnetic resonance has been investigated in a corundum single crystal with 0.13%  $V^{3+}$ . The experimental results are interpreted with the aid of the spin Hamiltonian, for which the following parameters were determined:  $g_{\parallel} = 1.915 \pm 0.002$ ;  $D = 7.0 \pm 0.3 \text{ cm}^{-1}$ ;  $|A| = (0.959 \pm 0.005) \times 10^{-2} \text{ cm}^{-1}$ ;  $|E| < 10^{-2} \text{ cm}^{-1}$ .

WE have previously<sup>1</sup> reported the detection of the electron paramagnetic resonance spectrum of  $V^{3+}$  in corundum.\* The present paper presents results obtained in a more detailed investigation.

The free  $V^{3+}$  ion, which has a  ${}^3F_2$  ground level, contains two unpaired 3d electrons. A vanadium ion replaces an aluminum ion isomorphically in a corundum ( $Al_2O_3$ ) single crystal, where it is surrounded by six oxygen ions forming a slightly deformed octahedron.<sup>3</sup> At the center of the octahedron, where the paramagnetic ion is located, the crystal electric field possesses basically cubic symmetry with a small admixture of fields having a lower order of symmetry. Figure 1 shows how fields with different symmetries split the F ground level of the free ion.

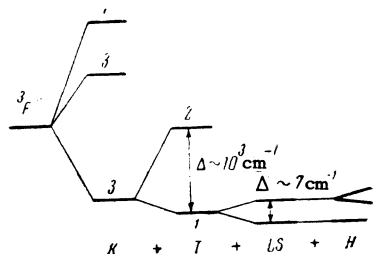


FIG. 1

The field of the corundum lattice is similar in character to the field of hydrated alum resulting from the octahedron of molecules of crystallization water. The splitting of the lowest energy level of  $V^{3+}$  in fields with different symmetries has been studied by Siegert<sup>4</sup> and Van Vleck<sup>5</sup> for the purpose of explaining the magnetic behavior of vanadium alum. The ground level of free  $V^{3+}$  possesses sevenfold orbital degeneracy ( $L = 3$ ). A cubically symmetric field removes the orbital

degeneracy and converts this level into a singlet (lying uppermost) and two triplets (Fig. 1). The components of a crystal field having trigonal symmetry further split the lower triplet into a singlet and a doublet, with a separation  $\Delta$  on the order of  $10^3 \text{ cm}^{-1}$ . Thus in the corundum lattice field the lowest vanadium ion level will be a singlet with triple spin degeneracy.

The lower triplet is further split into a singlet and a doublet through spin-orbit interaction. Van den Handel and Siegert<sup>6</sup> in analyzing the magnetic susceptibility of vanadium-ammonium alum found a separation of  $5 \text{ cm}^{-1}$  between the higher-lying doublet and the singlet. The degeneracy of the triplet is completely removed by the admixture of a field with orthorhombic symmetry; this occurs in corundum.

Since at low temperatures and even at room temperature practically only the lowest energy levels are occupied, in the study of paramagnetic resonance we are interested in only the three lowest spin levels, with which we can associate the effective spin  $S' = 1$  (Fig. 2). The singlet level corresponds to  $S'_z = 0$  and is nonmagnetic, while the doublet corresponds to  $S'_z = \pm 1$ .

Paramagnetic resonance can be used to observe transitions between these three spin levels. Because of the large initial splitting of levels  $\epsilon_1$  and  $\epsilon_{2,3}$  observation of absorption lines representing the transitions  $\epsilon_1 \leftrightarrow \epsilon_2$  and  $\epsilon_1 \leftrightarrow \epsilon_3$  ( $|\Delta M| = 1$ ) would require  $7\text{-cm}^{-1}$  quanta. For  $1\text{-cm}^{-1}$  quanta a magnetic field of  $\sim 60$  kilo-oersteds is required. With the usual range of frequencies and magnetic fields we can expect to observe the transition between levels  $\epsilon_2$  and  $\epsilon_3$  ( $|\Delta M| = 2$ ).

The detection of electron-spin resonance may be hindered by short spin-lattice relaxation times resulting in extreme line broadening. In the case of the vanadium ion the spin-lattice relaxation time

\*The paramagnetic resonance of  $V^{3+}$  in corundum has recently been detected also by Lambe, Ager and Kikuchi.<sup>2</sup>

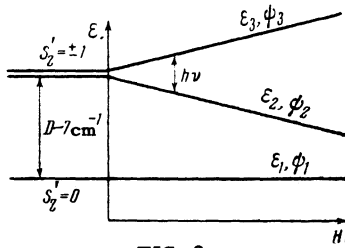


FIG. 2

is very short at room temperature because of closely higher orbital levels. Therefore resonance can be observed only at low temperatures.

The resonance spectrum was investigated in corundum single crystals containing 0.13% vanadium together with  $Cr^{3+}$  and  $Fe^{3+}$  impurities not exceeding 0.001%. Measurements were performed in the frequency range 9000–39,000 Mcs at liquid-helium temperature. For the 25,000–39,000 Mcs range we used a microwave spectrograph with a reentrant-type cavity resonator. For the 9000- and 15,000-Mcs ranges superheterodyne spectrographs with reflecting resonators were used.

At  $T = 290^\circ$  and  $77^\circ$  K we did not succeed in detecting paramagnetic resonance of  $V^{3+}$ . At liquid-helium temperature one line with eight hyperfine components was observed, corresponding to the nuclear spin  $I = 7/2$  of  $V^{51}$  (Fig. 3).

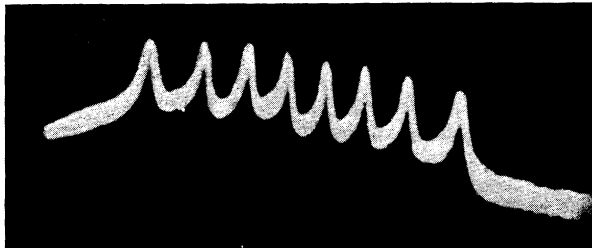


FIG. 3. Electron paramagnetic resonance line of  $V^{3+}$  in corundum,  $\nu = 37,450$  Mcs,  $T = 4.2^\circ$  K,  $\theta = 0$ .

The positions and widths of the line components were measured as functions of the angle  $\theta$  between the trigonal crystal axis (the  $z$  axis) and the direction of the static magnetic field  $H$ . We also studied the frequency dependence of line position for different  $\theta$  and the temperature dependence of intensity at 1.6–4.2° K. Intensities were compared for different relative orientations of the static magnetic field  $H$  and radio-frequency field  $H_1$ .

The results were interpreted by means of the spin Hamiltonian for the three lowest levels in a magnetic field:

$$\hat{\mathcal{H}} = D\hat{S}_z^2 + g_{\parallel}\beta H_z\hat{S}_z + g_{\perp}\beta(H_x\hat{S}_x + H_y\hat{S}_y) + A\hat{S}_z\hat{I}_z + B(\hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y) + E(\hat{S}_x^2 - \hat{S}_y^2), \quad (1)$$

where  $\hat{S}_x, \hat{S}_y, \hat{S}_z$  are the projections of the effective electron spin,  $\hat{I}_x, \hat{I}_y, \hat{I}_z$  are the nuclear-spin projections,  $H_x, H_y, H_z$  are the magnetic field components,  $g_{\parallel}$  and  $g_{\perp}$  are the spectroscopic splitting factors,  $\beta$  is the Bohr magneton,  $D$  is the initial splitting factor,  $E$  is the orthorhombic field constant,  $A$  and  $B$  are the hyperfine structure constants. The Hamiltonian (1) resembles that proposed for  $V^{3+}$  by Abragam and Pryce,<sup>7</sup> differing by the addition of the term containing  $E$ .

By means of perturbation theory with the conditions  $D \gg g_{\parallel}\beta H, g_{\perp}\beta H; g_{\parallel}\beta H \gg E, A, B$  we calculate the following energy levels from the Hamiltonian:

$$\begin{aligned} \epsilon_1 &= (g_{\perp}\beta H \sin \theta)^2 D^{-1}; \\ \epsilon_2 &= D + g_{\parallel}\beta H \cos \theta + \frac{1}{2} \frac{(g_{\perp}\beta H \sin \theta)^2}{D + g_{\parallel}\beta H \cos \theta} \\ &\quad + \frac{E^2}{2g_{\parallel}\beta H \cos \theta} + Am; \\ \epsilon_3 &= D - g_{\parallel}\beta H \cos \theta + \frac{1}{2} \frac{(g_{\perp}\beta H \sin \theta)^2}{D - g_{\parallel}\beta H \cos \theta} \\ &\quad - \frac{E^2}{2g_{\parallel}\beta H \cos \theta} - Am, \end{aligned} \quad (2)$$

where  $m$  is the  $z$  projection of the nuclear spin.

Transitions with  $|\Delta M| = 1$  ( $\epsilon_1 \leftrightarrow \epsilon_2; \epsilon_1 \leftrightarrow \epsilon_3$ ) are not observed since  $h\nu \ll D$ . For the  $|\Delta M| = 2$  transition we have

$$\begin{aligned} h\nu &= \left( 2 - \frac{(g_{\perp}\beta H \sin \theta)^2}{D^2} \right) [g_{\parallel}\beta H \cos \theta + Am] \\ &\quad + \frac{E^2}{g_{\parallel}\beta H \cos \theta}. \end{aligned} \quad (3)$$

Figure 4a shows the angular dependence of the vanadium line center for different frequencies. The position of the line center was calculated by averaging all hyperfine components.

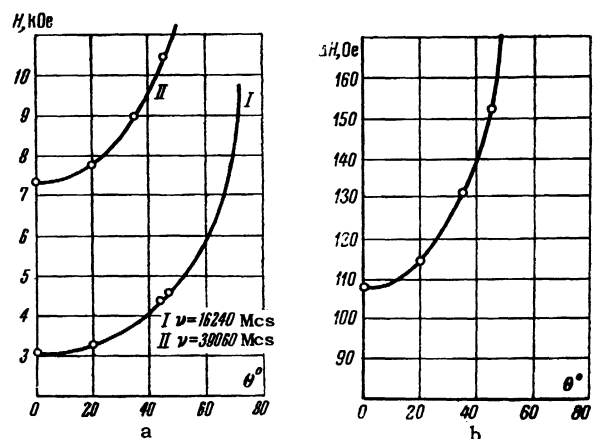


FIG. 4. Center of  $V^{3+}$  line (a) and hyperfine splitting (b) as functions of the angle  $\theta$ . Circles represent experimental values; the solid curves were calculated.

Both for parallel orientation ( $\theta = 0$ ) and for nonzero values of  $\theta$  the frequency was found to be proportional to the magnetic field within experimental error (0.1%). Second-order corrections are therefore not required in (3). We also obtained  $g_{\parallel} = 1.915 \pm 0.002$ .

The hyperfine components were equidistant at all angles  $\theta$  for which measurements were obtained. The angular dependence of the hyperfine splitting is shown in Fig. 4b and is in good agreement with the theoretical relation calculated from (3), neglecting second-order terms, for  $|A| = (0.959 \pm 0.005) \times 10^{-2} \text{ cm}^{-1}$ .\*

For the purpose of determining  $D$  we used the temperature dependence of line intensities in the range 1.6–4.2° K. Relative intensities were measured for the lines of  $V^{3+}$  and of  $Cr^{3+}$  and  $Fe^{3+}$ , which were present in the single crystal as impurities. In order to obviate errors due to saturation the experiments were performed at minimum power levels in the microwave spectrometer resonator; lines were registered by a superheterodyne detector. The temperature dependence of the  $Cr^{3+}$  and  $Fe^{3+}$  line intensities was calculated using known values of the constants in the spin Hamiltonians of these ions.<sup>8-11</sup>  $D = 7.0 \pm 0.3 \text{ cm}^{-1}$  was obtained with accuracy limited by the accuracy with which the relative intensities were measured. At low temperatures, because of the competition between two processes, — the increasing difference between the populations of levels 2 and 3 and the actual decrease of these populations because of the existence of level 1 — the vanadium line maximum should appear at  $T \sim 7^{\circ} \text{ K}$ .

Experiments performed with parallel orientation showed that the  $\epsilon_2 \leftrightarrow \epsilon_3$  transition is induced by the  $z$  component of the radio-frequency magnetic field. For this reason the term  $E(\hat{S}_x^2 - \hat{S}_y^2)$  was introduced into the Hamiltonian to represent the interaction between the spin and the orthorhombic component of the crystal field. The Hamiltonian proposed for  $V^{3+}$  by Abragam and Pryce<sup>7</sup> does not account for the fact that the line representing the  $|\Delta M| = 2$  transition does not vanish in the parallel orientation. In reference 1 the present authors introduced the term  $\Delta \hat{S}_x^2$  into the Hamiltonian to represent an interaction that removes the degeneracy of the doublet  $S'_z = \pm 1$  in zero magnetic field, while the  $|\Delta M| = 2$  transition in parallel orientation is allowed with the probability  $\Delta/D$ . However, the latter transition should be induced by the  $x$  component of the radio-frequency field, which disagrees with experiment. The Hamiltonian is more properly corrected by the addition

of the term  $E(\hat{S}_x^2 - \hat{S}_y^2)$ , which appears in second order in (3) and thus has practically no effect on either the line position or the hyperfine splitting. The term is required in order to account correctly for line intensities.

The wave functions for the different levels are

$$\begin{aligned}\psi_1 &= \frac{\sqrt{2} g_{\perp} \beta H \sin \theta}{D} \psi^{-1} + \psi^0 + \frac{\sqrt{2} g_{\perp} \beta H \sin \theta}{D} \psi^{+1}; \\ \psi_2 &= \frac{E}{2g_{\parallel} \beta H \cos \theta} \psi^{-1} + \frac{\sqrt{2} g_{\perp} \beta H \sin \theta}{D} \psi^0 + \psi^{+1}; \\ \psi_3 &= \psi^{-1} + \frac{\sqrt{2} g_{\perp} \beta H \sin \theta}{D} \psi^0 - \frac{E}{2g_{\parallel} \beta H \cos \theta} \psi^{+1},\end{aligned}\quad (4)$$

where  $\psi^{-1}$ ,  $\psi^0$ ,  $\psi^{+1}$  are the wave functions of the states with  $S'_z = -1$ ,  $S'_z = 0$  and  $S'_z = +1$ , respectively. The matrix elements for the  $\epsilon_2 \leftrightarrow \epsilon_3$  transition are

$$\begin{aligned}\langle 2 | \hat{S}_x' | 3 \rangle &= g_{\perp} \beta H \sin \theta / D; \\ \langle 2 | \hat{S}_y' | 3 \rangle &= -i g_{\perp} \beta H \sin \theta / D; \\ \langle 2 | \hat{S}_z' | 3 \rangle &= -E / g_{\parallel} \beta H \cos \theta.\end{aligned}\quad (5)$$

Thus the  $z$  component of the radio-frequency field will give a nonvanishing line intensity in parallel orientation. The experimentally observed constancy of the integral intensity with varying  $\theta$  while the radio-frequency field has a fixed orientation with respect to the  $z$  axis indicates that for nonzero values of  $\theta$  the principal contribution to line intensity comes from the matrix element of  $\hat{S}_z'$ , which does not vary with  $\theta$ .

In parallel orientation the width of a single component is 24 oersteds. Upon rotation of the crystal the width increases with  $\theta$  more rapidly than the hyperfine splitting  $\Delta H$  ( $\Delta H \approx \Delta H_0 / \cos \theta$ ), and at angles greater than 70° it is practically impossible to resolve the components.

This effect probably results from smearing of the trigonal crystal axis direction through an angle  $\Delta\theta$  because many microdomains with slightly different axial directions are present. In this case the additional line broadening should be  $\delta H = H \tan \theta \Delta\theta$ . This is insignificant in the case of parallel orientation, for which the line width will be determined by other factors such as spin-spin interaction, random inhomogeneities of the crystal field and interactions of ions with the magnetic moments of aluminum nuclei.

The foregoing hypothesis is in agreement with experiment; additional broadening associated with  $\Delta\theta$  varies from sample to sample. For example, at  $\theta = 36^{\circ}$  the width of a hyperfine component was 71 oersteds and 38 oersteds, respectively, in two different samples, although in parallel orientation the corresponding widths were 25 and 24 oersteds.

\*In reference 1 we gave erroneously  $2|A|$  instead of  $|A|$ .

$\Delta\theta$  was calculated to be  $0.5^\circ$  and  $0.2^\circ$  for these samples.

No temperature dependence of line width was detected in the range  $1.6 - 4.2^\circ\text{K}$ , thus indicating the absence of broadening due to spin-lattice relaxation.

Corundum is still the only single crystal in which a paramagnetic resonance spectrum of  $V^{3+}$  has been detected. This may result from the fact that the trigonal component of the crystal field is stronger in corundum than in other commonly used substances such as alum; the splitting  $\Delta$  of orbital levels of the lower triplet would thus be greater, making the spin-lattice relaxation time  $T_1$  for  $V^{3+}$  in corundum longer than in alum. This may possibly account for the failure to detect electron paramagnetic resonance of vanadium in alum.

From our study of the  $V^{3+}$  spin resonance spectrum we were able to determine only the parameters  $g_{\parallel}$ ,  $A$  and  $D$  in the spin Hamiltonian.  $E$  might possibly be determined from measurements of absolute line intensities or relative intensities at different frequencies. Our present estimate,  $|E| < 10^{-2} \text{ cm}^{-1}$ , is based on the fact that the term containing  $E$  in (3) may be neglected to within experimental accuracy.  $g_{\perp}$  might be determined from the detailed angular dependence of line intensities; it would be difficult to determine  $B$  at present. The detection of  $|\Delta M| = 1$  lines would be of considerable interest but would require the con-

struction of a microwave spectrometer for the  $150 - 250 \times 10^3 \text{ Mc}$  range.

The authors are indebted to A. A. Popova, R. P. Bashuk, and A. S. Bebchuk, who prepared the corundum-vanadium samples.

<sup>1</sup>G. M. Zverev and A. M. Prokhorov, JETP **34**, 1023 (1958), Soviet Phys. JETP **7**, 707 (1958).

<sup>2</sup>Lambe, Ager, and Kikuchi, Bull. Am. Phys. Soc. Ser. II, **4**, 261 (1959).

<sup>3</sup>E. S. Rudnitskaya, Тр. Ин-та кристаллографии (Trans. Inst. of Crystallography) **8**, 13 (1953).

<sup>4</sup>A. Siebert, Physica **4**, 138 (1937).

<sup>5</sup>J. H. Van Vleck, J. Chem. Phys. **7**, 61 (1939).

<sup>6</sup>J. van den Handel and A. Siebert, Physica **4**, 871 (1937).

<sup>7</sup>A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

<sup>8</sup>A. A. Manenkov and A. M. Prokhorov, JETP **28**, 762 (1955), Soviet Phys. JETP **1**, 611 (1955).

<sup>9</sup>L. S. Kornienko and A. M. Prokhorov, JETP **33**, 805 (1957), Soviet Phys. JETP **6**, 620 (1958).

<sup>10</sup>G. M. Zverev and A. M. Prokhorov, JETP **34**, 513 (1958), Soviet Phys. **7**, 354 (1958).

<sup>11</sup>G. S. Bogle and H. F. Symmons, Proc. Phys. Soc. (London) **73**, 531 (1959).

Translated by I. Emin