ELECTRONIC PARAMAGNETIC RESONANCE IN THE V^{3+} ION IN CORUNDUM

G. M. ZVEREV and A. M. PROKHOROV

Institute for Nuclear Physics, Moscow State University

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The spin Hamiltonian constant $g_\perp$ has been determined experimentally. A theoretical interpretation of the spin Hamiltonian constants D, $g_{||}$ and $g_\perp$ is presented. The value of the trigonal crystal field parameter is found to be $\Delta = -280\ \mathrm{cm}^{-1}$ and the spin-orbit coupling constant $\lambda = +38\ \mathrm{cm}^{-1}$.

WE published earlier[1,2] the main results of a study of the electron paramagnetic resonance spectrum of the V^{3+} ion in corundum. The aim of the present work is the determination of $g_\perp$ and a theoretical analysis of the values of the constants of the spin Hamiltonian.

1. We expressed the positions of the lines of the spectrum by the formula[2]

$$h\nu = \left[2 - \frac{(g_\perp \beta H \sin\theta)^2}{D^2}\right](g_{\parallel}\beta H\cos\theta + Am) + \frac{E^2}{g_{\parallel}\beta H\cos\theta}, \tag{1}$$

derived on the assumption that $D \gg g_{||}\beta H$, $g_\perp\beta H$; $g_{||}\beta H \gg E, A, B$. When the trigonal crystal axis lies perpendicular to the direction of the external magnetic field ($\theta = 90°$), the line position corresponds, according to (1), to an effective field $H = \infty$. However, (1) does not apply for large fields since the assumption $D \gg g_{||}\beta H$, $g_\perp\beta H$ is no longer valid.

We calculate the spin energy levels of the V^{3+} ion for $\theta = 90°$ on the assumption that D and $g_\perp\beta H$ are of the same order of magnitude. For $\theta = 90°$ the spin Hamiltonian takes the form

$$\begin{aligned}\hat{\mathcal{H}} &= D\hat{S}_z'^2 + g_\perp\beta H\hat{S}_x' + E(\hat{S}_x'^2 - \hat{S}_y'^2)\\ &+ A\hat{S}_z'\hat{I}_z + B(\hat{S}_x'\hat{I}_x + \hat{S}_y'\hat{I}_y).\end{aligned} \tag{2}$$

The terms describing the hyperfine structure will be accounted for later by perturbation theory.

Solution of the secular equation gives the following expressions for the energy levels

$$\varepsilon_1 = \tfrac{1}{2}(D+E) - \left[\tfrac{1}{4}(D+E)^2 + (g_\perp\beta H)^2\right]^{1/2}, \quad \varepsilon_2 = D - E,$$

$$\varepsilon_3 = \tfrac{1}{2}(D+E) + \left[\tfrac{1}{4}(D+E)^2 + (g_\perp\beta H)^2\right]^{1/2}. \tag{3}$$

The dependence of the positions of the energy levels on the magnitude of the applied magnetic field is shown in Fig. 1.

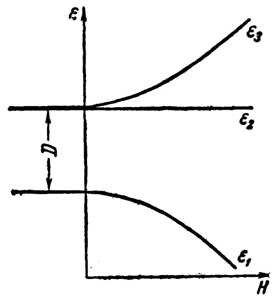

FIG. 1. Energy levels of the V^{3+} ion as a function of magnetic field perpendicular to the trigonal crystal axis.

The energy of the transition $\epsilon_3 \longleftrightarrow \epsilon_2$ is equal to

$$\begin{aligned}h\nu &= \tfrac{1}{2}(3E - D) + \left[\tfrac{1}{4}(D+E)^2 + (g_\perp\beta H)^2\right]^{1/2}\\ &\approx (g_\perp\beta H)^2 D^{-1}.\end{aligned} \tag{4}$$

The approximate equality applies for small $g_\perp\beta H/D$ and for E neglected. We can estimate for what value of the magnetic field the resonance line for $\theta = 90°$ can be observed. Taking $g_\perp \sim 1.6$, as predicted by theory, the field H should be ~ 40 koe in an experiment at a frequency of 37 500 Mc/sec. The line would be observed in a field ~ 20 koe at 9000 Mc/sec. Calculation of the matrix elements of the transition $\epsilon_2 \longleftrightarrow \epsilon_3$ leads to the following result:

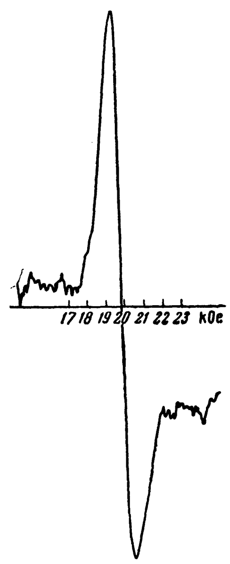

FIG. 2. Electronic paramagnetic resonance line of the V^{3+} ion in corundum with magnetic field perpendicular to the trigonal axis.

$$\langle \varepsilon_2 | \hat{S}'_x | \varepsilon_3 \rangle = 0,$$
$$\langle \varepsilon_2 | \hat{S}'_y | \varepsilon_3 \rangle = -ih\nu [(h\nu)^2 + (g_\perp \beta H)^2]^{-1/2} \approx -i (g_\perp \beta H) D^{-1},$$
$$\langle \varepsilon_2 | \hat{S}'_z | \varepsilon_3 \rangle = -(g_\perp \beta H) [(h\nu)^2 + (g_\perp \beta H)^2]^{-1/2} \approx -1. \quad (5)$$

Since the matrix element $\hat{S}'_Z$ has the largest value, the high frequency field must be in the direction of the trigonal crystal axis in order to observe the resonance line.

The line in the perpendicular orientation should show a hyperfine structure with eight equidistant components, differing in energy by an amount

$$\Delta\varepsilon = 2h\nu g_\perp \beta HB / [(h\nu)^2 + (g_\perp \beta H)^2]. \quad (6)$$

2. The experimental determination of $g_\perp$ was made at 9300 Mc/sec at a temperature of 4.2° K. The corundum crystal, containing 0.13% vanadium impurity, was oriented so that its trigonal axis was perpendicular to the steady magnetic field and parallel to the high frequency magnetic field in the resonator. A very broad line was found with its peak at 19 800 oe. The value of the field strength was measured with a magnetometer using a Hall probe. Using the value[2] $D = 7.0 \pm 0.3\ \text{cm}^{-1}$ and putting $E = 0$, the value derived from (4) is $g_\perp = 1.63 \pm 0.05$.

Using (4), the constants D and $g_\perp$ can in principle be determined from the position of the line in the perpendicular orientation for various frequencies. However, the position of its peak cannot be determined with sufficient accuracy because of the large line width, and the error in determining D by this method would be extremely large.

The line width is associated mainly with the unresolved hyperfine structure. Besides, since in the accessible range of fields the energy of the ϵ_3 level depends weakly on magnetic field, while the energy of level ϵ_2 does not change, the line for the transition $\epsilon_2 \longleftrightarrow \epsilon_3$ is appreciably field broadened. The effect of scatter in the directions of the trigonal axis also contributes a certain amount to the line width.[2] Calculation shows that hyperfine structure should contribute ~1000 oe to the line width (if we put $B \approx A$).

3. The constants D, $g_{||}$ and $g_\perp$ of the spin Hamiltonian can be derived theoretically. In a crystal field of cubic symmetry, the sevenfold degeneracy of the F ground level of the V^{3+} ion is partly lifted. The lowest level becomes an orbital triplet. Further splitting of this level takes place under the influence of spin-orbit coupling and the crystalline field of trigonal symmetry. This splitting is described by the fine structure Hamiltonian:[3]

$$\hat{W} = \Delta (1 - \hat{l}'^2_z) - \alpha\lambda \hat{l}'_z \hat{S}_z - \alpha'\lambda (\hat{l}'_x \hat{S}_x + \hat{l}'_y \hat{S}_y), \quad (7)$$

where $\hat{\mathbf{l}}'$ is the effective orbital momentum operator $l' = 1$, $\hat{\mathbf{S}}$ is the spin operator $S = 1$, Δ is the parameter of the crystal field of trigonal symmetry, λ is the spin-orbit coupling constant and α and α' are constants close to $3/2$. We have here neglected the contribution of spin-spin interaction between the electrons of the paramagnetic ions, since this is insignificant.

We can find the energy level scheme by solving the secular equation. In order to obtain two closely spaced levels (singlet and doublet) at the bottom, we have had to put $\Delta < 0$. The distance between the singlet and doublet, corresponding to the constant D of the spin Hamiltonian is equal to

$$D = \tfrac{1}{2} \{[(\Delta + \alpha\lambda)^2 + 8\alpha'^2\lambda^2]^{1/2} - [\Delta^2 + 4\alpha'^2\lambda^2]^{1/2} - \alpha\lambda\} \approx \alpha'^2\lambda^2/|\Delta|. \quad (8)$$

This approximate expression is valid for small λ/Δ.

In order to find the g-factors one must find the wave functions of the lowest energy states, and calculate the matrix elements of the interaction operator of the ion with the external magnetic field. We obtain the result[3,5]

$$g_{\|} \approx 2 - (\alpha + 2)\alpha'^2\lambda^2/\Delta^2, \qquad g_\perp \approx 2 - 2\alpha'^2\lambda/|\Delta|. \quad (9)$$

Expressions (8) and (9) enable us to determine from the constants of the spin Hamiltonian ($D = 7.0\ \text{cm}^{-1}$, $g_{||} = 1.915$, $g_\perp = 1.63$) the values $\Delta = -280\ \text{cm}^{-1}$, $\lambda = 38\ \text{cm}^{-1}$, $\alpha = 1.40$ and $\alpha' = 1.17$.

Pryce and Runciman[6] studied corundum with vanadium optically and calculated the energy level scheme for this ion. The values $\Delta = -1200\ \text{cm}^{-1}$ and $\lambda \approx 70\ \text{cm}^{-1}$ which they chose could not explain the experimental g-factor values. We obtained considerably smaller values of the spin-orbit coupling constant than for the free ion ($\lambda = 104\ \text{cm}^{-1}$). The reduction in λ indicates the presence of covalent binding between the d-electrons of the paramagnetic ion and the electrons of the surrounding oxygen ions.

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