

# Paramagnetic Resonance of the Cobalt Ion in Rutile Single Crystal\*

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The electron paramagnetic resonance of  $\text{Co}^{2+}$  in single-crystal rutile ( $\text{TiO}_2$ ) has been investigated at 3-cm wavelength and 4.2°K. The angular dependence of the resonance pattern indicates that the  $\text{Co}^{2+}$  ion enters substantially for the  $\text{Ti}^{4+}$  ion in the lattice. Strongly anisotropic values of the splitting factor  $g$  and hfs constant  $A$  are obtained, which may be understood in terms of a fairly large charge transfer to the surrounding ions.

THE sevenfold degenerate  $^4F$  state of the free  $\text{Co}^{2+}$  ion is split into two orbital triplets and one singlet by an octahedral crystal field, one triplet lying lowest. Because of this orbital degeneracy, both the electronic spin and orbital motion contribute to the magnetic moment, so that the paramagnetic resonance spectrum of  $\text{Co}^{2+}$  is of particular interest. If the spin-orbit coupling ( $\lambda \approx -180 \text{ cm}^{-1}$ ) and crystal field of lower symmetry are taken into account, the twelve-fold degeneracy (including the spin degeneracy) is replaced by six Kramers' doublets. Since only the lowest doublet is populated by electrons at low temperatures, the effective spin  $S'$  is taken to be  $\frac{1}{2}$ . Abragam and Pryce<sup>1</sup> have given a theoretical interpretation of the spin and orbital components of the splitting factor  $g$  and hfs constant  $A$  of  $\text{Co}^{2+}$  in tetragonal or trigonal symmetry using parameters for  $\text{Co}^{2+}$  based on crystal field theory. Tinkham<sup>2</sup> has extended this to the orthorhombic case of  $\text{ZnF}_2$ . This note presents results on the paramagnetic resonance spectrum of  $\text{Co}^{2+}$  in rutile ( $\text{TiO}_2$ ) single crystal, which has the same crystal structure as  $\text{ZnF}_2$ .

Crystalline  $\text{TiO}_2$  shows macroscopic tetragonal symmetry. This is because each unit cell contains two  $\text{Ti}^{4+}$  ions whose local symmetry is orthorhombic and whose symmetry axes differ by a  $90^\circ$  rotation about the  $c$  axis.<sup>3</sup> This configuration causes the resonance lines to have a  $90^\circ$  rotation period when the magnetic field is perpendicular to the  $c$  axis (see Fig. 1), and to coincide when the field is parallel to the  $c$  axis. The orthorhombic local symmetry arises from six  $\text{O}^{2-}$  ions, the four nearest neighbors being arranged in a rectangle (its long edge parallel to the  $c$  axis), and the other two lying on an axis normal to the rectangle. We have chosen the  $z$  axis parallel to the  $c$  axis, and the  $x$  axis normal to the rectangle, and the  $y$  axis parallel to the short edge of the rectangle. The symmetry around the  $x$  axis is nearly tetragonal, and this, with the aid of crystal field theory, can be used to distinguish the resonance pattern along the  $x$  axis from that along the  $y$  axis, as shown below, although the experimental data alone do not distinguish these.

The experiments were performed at 3-cm wavelength

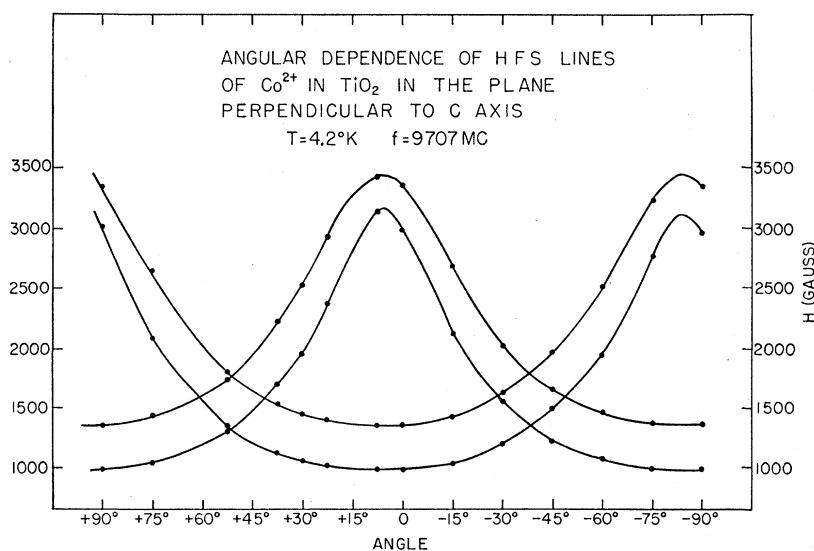


FIG. 1. Dependence of the hyperfine structure lines of  $\text{Co}^{2+}$  in single crystal rutile on angular orientation in the  $a$ - $b$  plane. The pairs of lines indicate the positions of the outer members of the eight-line hyperfine pattern.

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<sup>1</sup> A. Abragam and M. H. Pryce, Proc. Roy. Soc. (London) **A206**, 173 (1951).

<sup>2</sup> M. Tinkham, Proc. Roy. Soc. (London) **A236**, 549 (1956).

<sup>3</sup> R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1948).

TABLE I. Values of the splitting factor  $g$  and hfs constant  $A$  for the case of  $\text{Co}^{2+}$  in  $\text{TiO}_2$ . The decomposition into spin and orbital  $g$ -value contributions is also given, and for comparison, the corresponding values obtained by Tinkham<sup>a</sup> in the case of  $\text{Co}^{2+}$  in  $\text{ZnF}_2$  are included.

	$\text{TiO}_2$				$\text{ZnF}_2$			
	$g$	$g_s$	$g_L = kg_L^0$	$A$ ( $10^{-4} \text{ cm}^{-1}$ )	$g$	$g_s$	$g_L$	$A$ ( $10^{-4} \text{ cm}^{-1}$ )
$x$	$2.19 \pm 0.005$	2.13	0.06	$(-)^b 40 \pm 2$	$(2.6)^b$	2.33	0.22	$(-43)^b$
$y$	$5.88 \pm 0.02$	4.67	1.21	$150 \pm 2$	$6.05 \pm 0.01$	4.42	1.63	$217 \pm 2$
$z$	$3.75 \pm 0.01$	3.20	0.55	$26 \pm 1$	$4.1 \pm 0.1$	3.25	0.85	$(67)^b$

<sup>a</sup> See reference 2.

<sup>b</sup> Values enclosed in parentheses are obtained from theory.

at  $4.2^\circ\text{K}$ . The eight hfs lines of the  $\text{Co}^{2+}$  ion were well separated along all directions, although the intensity of the signal was much smaller than that of  $\text{Cr}^{3+}$ ,<sup>4</sup> or  $\text{Fe}^{3+}$ .<sup>5</sup> Peak-to-peak separation of the derivative of the absorption curve was about  $1.7 \pm 0.2$  oe for each hfs line, and the absorption signal was very easily saturated. Since the signals had a  $90^\circ$  period for the field normal to the  $c$  axis, and coincided for the field along the  $c$  axis, we conclude that the  $\text{Co}^{2+}$  ion substitutes for the  $\text{Ti}^{4+}$  ion in the rutile lattice. The  $g$  and  $A$  values obtained are listed in Table I.

The low symmetry of the orthorhombic environment equires other experimental data, as from optical absorption, in order to decompose the  $g$  and  $A$  values into spin and orbital contributions, as in the case of  $\text{Co}^{2+}$  in  $\text{MgO}$ .<sup>6</sup> The broad absorption band, however, with no peak in the visible and infrared region, is partially due to overlap of the  $\text{Fe}^{3+}$  and  $\text{Cr}^{3+}$  bands. For this reason, the rather small admixture (perhaps less than 10%)<sup>6</sup> of the higher level must be neglected. This approach gives the form<sup>2</sup>

$$g_x = g_{sx} + kg_{Lx}^0 = (10 - 8a)/3 + k(1 - 2a),$$

$$g_y = g_{sy} + kg_{Ly}^0 = (10 + 4a + 4r)/3 + k(1 + a + r),$$

$$g_z = g_{sz} + kg_{Lz}^0 = (10 + 4a - 4r)/3 + k(1 + a - r),$$

where  $a$  and  $r$  are due to the axial and rhombic components of the crystal field, respectively, and  $k$  is called the orbital reduction factor ( $k \leq 1$ ) showing charge transfer from the paramagnetic ion to the surrounding ions. The values of  $a$ ,  $r$ , and  $k$  obtained are 0.45, 0.55, and 0.61, respectively.  $k=0.61$  is considerably smaller than the values obtained for  $\text{Co}^{2+}$  in  $\text{MgO}$  ( $\approx 0.89$ )<sup>6</sup> and  $\text{ZnF}$  ( $\approx 0.9$ ).<sup>2</sup> Such a large charge transfer can possibly be explained by the larger  $\text{Co}^{2+}$  ionic radius (0.78 Å) compared to the  $\text{Ti}^{4+}$  radius (0.60 Å).<sup>3</sup> The spin and orbital contributions to the splitting factor are also given in Table I.

The hfs constant  $A$  can be written in terms of spin and orbital  $g$  values in the form<sup>2</sup>

$$A_i = N^2 P[(g_L^0)_i - \frac{1}{2} K(g_s)_i], \quad i = x, y, z,$$

if we neglect the small, uncertain contribution of the  $3d$  electrons. The two unknown factors,  $N^2$  (normalizing factor) and  $K$  (admixture of unpaired  $s$  electron to the  $\text{Co}^{2+}$  ion) cannot satisfy the three  $A$  components, but the best-fitting values are 0.56 and 0.42, respectively, where we have assumed that  $P = (2\gamma\beta\beta_N \langle r^{-3} \rangle) = 0.0225 \text{ cm}^{-1}$ .<sup>1</sup> Although these values are only roughly estimated, their relative magnitude will be correct, and the  $N^2 < k$  relation<sup>2,6</sup> appears to hold.

Pairs of so-called forbidden transitions of weak intensity were recorded between the main hfs lines around the  $x$  axis.<sup>7</sup> They appear to be  $\Delta m = \pm 1, \pm 2$  lines due to quadrupole interaction as studied by Bleaney,<sup>8</sup> but their angular dependence and relative intensity for different  $m$  values do not follow his equations. Forbidden transitions due to the rf magnetic field parallel to the static field<sup>9</sup> could also be observed. Another group of weak hfs signals, having different angular dependence from that of the main group, was recorded in the sample of highest Co concentration (doping being 0.05%). However, these were so close to the main lines and so weak that accurate  $g$  and  $A$  values were not obtained. Study of their origin is now in progress, and it appears that they are due to  $\text{Co}^{2+}$  combined with an oxygen vacancy.

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<sup>7</sup> We have observed the super hfs of the main (allowed) and forbidden lines of  $\text{V}^{4+}$  in  $\text{TiO}_2$  which is presumably caused by charge transfer from the  $\text{V}^{4+}$  ion to the nearest  $\text{Ti}^{4+}$  ion (to be published). In the present case, no super hfs was observed, possibly because of very weak signals.

<sup>8</sup> B. Bleaney, Phil. Mag. **42**, 44 (1951).

<sup>9</sup> C. D. Jeffries, Phys. Rev. **117**, 1056 (1960).

<sup>4</sup> H. J. Gerritsen, Phys. Rev. Letters **2**, 153 (1959).

<sup>5</sup> D. L. Carter and A. Okaya, Phys. Rev. **118**, 1485 (1960).

<sup>6</sup> W. Low, Phys. Rev. **109**, 256 (1958).