

# Paramagnetic Resonance of Iron Group Elements in Rutile. I. The $Ti^{47}$ and $Ti^{49}$ hfs Interaction\*

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The well-resolved structure of the electron spin resonance (ESR) of  $V^{4+}$  and  $Mn^{4+}$  in rutile ( $TiO_2$ ) is interpreted in terms of the hfs interaction of the  $Ti^{47}$  and  $Ti^{49}$  ions which occupy the nearest sites along the crystalline  $c$  axis. The absence of such structure in the cases of  $Cr^{3+}$  and  $Mn^{3+}$  is discussed in simple terms.

## INTRODUCTION

THE hfs interaction of a nonlocalized electron of a paramagnetic impurity with its surrounding nuclei gives a resolved structure of ESR lines if the interaction is larger than the linewidth. Studies of this structure, called a "super hfs" especially in the case of

the hfs lines, have been reported in the literature, e.g., by Tinkham in  $ZnF_2$ ,<sup>1</sup> by Dorain in  $CdS$ ,<sup>2</sup> by Lambe and Kikuchi in  $CdS$  and  $CdTe$ ,<sup>3</sup> by Bemski and by Watkins and Corbett in irradiated  $Si$ ,<sup>4,5</sup> and by several authors in alkali-fluorides.<sup>6</sup> Tinkham,<sup>1</sup> Clogston *et al.*,<sup>7</sup> and Watkins *et al.*<sup>5</sup> obtained the detailed electronic structure of the respective paramagnetic centers from analysis of the well-resolved structure of the absorption lines.

In this paper an investigation of the resolved structure of the ESR of the iron group elements in the diamagnetic  $TiO_2$  lattice to obtain the electronic structure of the paramagnetic ions is reported.

## EXPERIMENTAL APPARATUS

Single crystals doped with the iron group elements were grown by the Verneuil process by Dr. Nakazumi of Fuji Titanium Company, Ltd. The samples were sliced into approximately  $1 \times 5 \times 5$ -mm size, with the  $c$  axis lying in the  $5 \times 5$ -mm plane.

The experiments were performed with a bolometer balanced-type  $X$ -band apparatus at 77, 4.2, and 2.0°K. At times a narrower linewidth was obtained by pumping on liquid nitrogen until it solidified. The temperature of the sample was not measured but might have been at or near 60°K because of the poor contact of the solid nitrogen with the waveguide and cavity. The microwave signal generator (Laboratory for Electronics) has its frequency locked to a reference cavity, so that the absorption and dispersion signals were easily selected. A reflection-type sample cavity was used in the  $TE_{101}$  mode, with samples placed on its side wall. The magnet was rotated in the crystalline (110) and (001) planes. Magnetic field modulation was used at 70 cps, the signal was then narrow-band amplified, phase-sensitively detected, and traced on the chart recorder.

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<sup>2</sup> P. B. Dorian, Phys. Rev. **112**, 1058 (1958).

<sup>3</sup> J. Lambe and C. Kikuchi, Phys. Rev. **119**, 1256 (1960).

<sup>4</sup> G. Bemski, J. Appl. Phys. **30**, 1195 (1959).

<sup>5</sup> G. D. Watkins and J. W. Corbett, Phys. Rev. **121**, 1001 (1961); Phys. Rev. Letters **7**, 314 (1961).

<sup>6</sup> See, for example, W. C. Holton and H. Blum, Phys. Rev. **125**, 89 (1962); W. T. Doyle, Phys. Rev. **126**, 1421 (1962).

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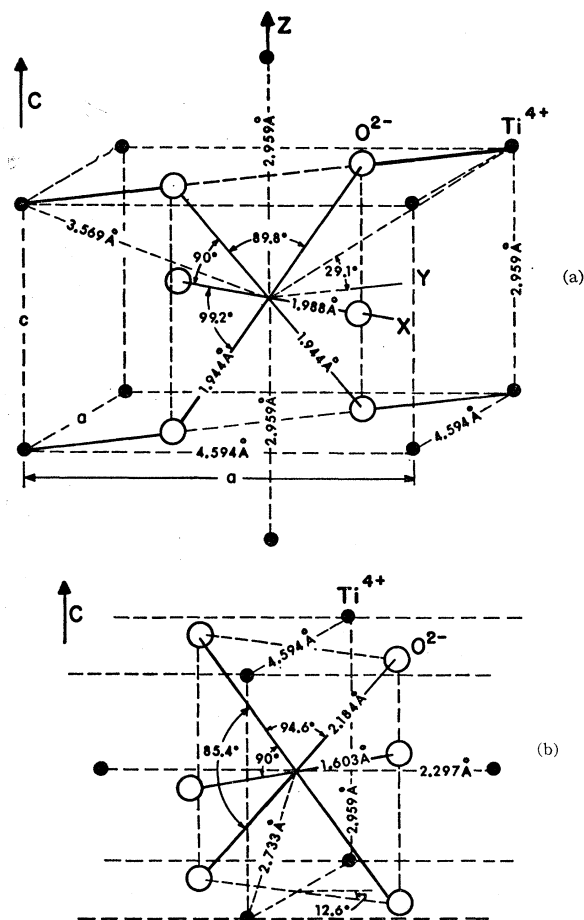


FIG. 1. Distorted octahedron of oxygens and the nearest and next-nearest  $Ti^{4+}$  sites for (a) substitutional and (b) interstitial sites of rutile.

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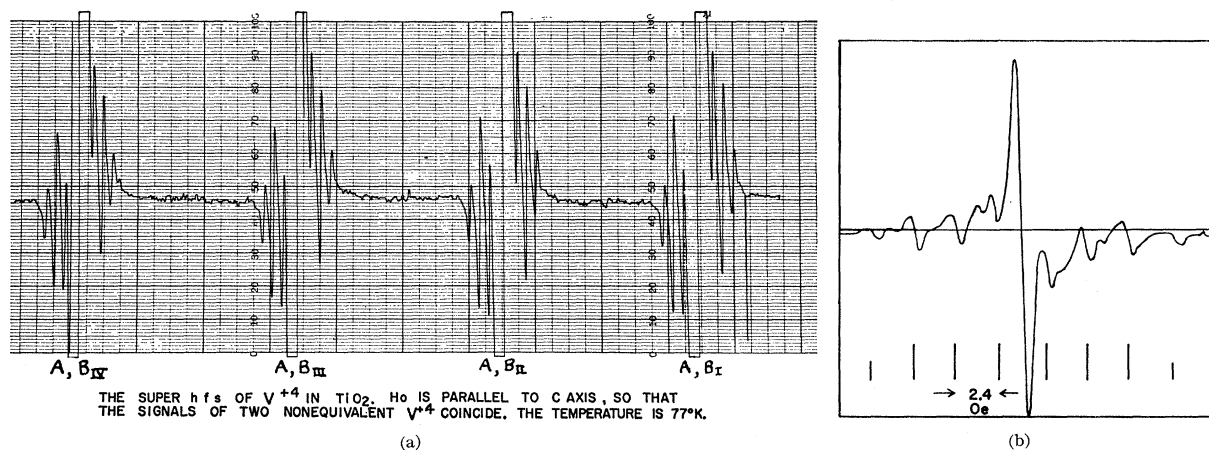


FIG. 2. ESR lines of V<sup>4+</sup> in TiO<sub>2</sub> for H<sub>0</sub> along the *c* axis. (a) Four lines of the hfs at 77°K. (b) Resolved structure of each hfs line at 4.2°K.

## RESOLVED STRUCTURE OF THE ABSORPTION LINES

### 1. Experimental Results

Rutile crystal shows macroscopic tetragonal symmetry, but each Ti<sup>4+</sup> site is surrounded by six oxygens of only orthorhombic symmetry, as shown in Fig. 1(a). The tetragonal symmetry results from having two Ti ions per unit cell, these being rotated by 90° about the *c* axis from each other. This feature gives rise to a characteristic angular dependence of the ESR lines at the substitutional site (*S* site), i.e., each line splits into two as H<sub>0</sub> is rotated from the *c* axis to the [110] axis.

On the other hand, as shown in Fig. 1(b), the rutile structure also possesses an interstitial cation site (*I* site)<sup>8</sup> surrounded by an oxygen octahedron, the shape of which is similar to the substitutional one. Since there are four different octahedra per unit cell, rotated about the *c* axis from each other, each resonance line for an *I* site splits into four instead of two as for the *S* site as H<sub>0</sub> is rotated from the *c* to the [110] axis. This characteristic angular dependence of the resonance line is used to distinguish between *S* and *I* sites as positions of paramagnetic centers in the rutile structure.

Among the impurities studied in this paper, V<sup>4+</sup>,<sup>9</sup> Cr<sup>3+</sup>,<sup>10</sup> Mn<sup>4+</sup>,<sup>11</sup> Fe<sup>3+</sup>,<sup>12</sup> Co<sup>2+</sup>,<sup>13</sup> Gd<sup>3+</sup>,<sup>14</sup> and a light-generated center of Ni (unknown valency)<sup>15</sup> occupy the

*S* site, whereas Ti<sup>3+</sup> (produced in reduction process)<sup>16,17</sup> and Ni<sup>3+</sup><sup>15</sup> occupy the *I* site.

For the hfs interaction with surrounding nuclei to give a resolved structure to the ESR lines the linewidth must be small. The iron group elements studied in TiO<sub>2</sub> had enough sharp lines at nitrogen and helium temperatures (e.g., Cr<sup>3+</sup>~1.2 to 3.0, Mn<sup>4+</sup>~0.8 to 1.2, V<sup>4+</sup>~1.0, Fe<sup>3+</sup>~0.6 to 2.0, at 77°K and Co<sup>2+</sup>~1.0 to 1.5, Ti<sup>3+</sup>~0.6 to 1.0 Oe at 4.2°K between inflection points of the absorption derivative) to yield the effect of such interaction. For example, each hfs line of V<sup>4+</sup> in TiO<sub>2</sub> with H<sub>0</sub> along the *c* axis had the same resolved structure,<sup>18</sup> as shown in Fig. 2. For H<sub>0</sub> not along the *c* axis, the resolved structures were similar, but with reduced separation between the satellites. In some directions the six inner hfs lines (i.e., except the outermost two lines) had a slightly deformed structure due to the forbidden lines  $\Delta M = \pm 1$ ,  $\Delta m = \pm 2$ . Furthermore, seven pairs of forbidden lines  $\Delta M = \pm 1$ ,  $\Delta m = \pm 1$ , showed the same structure as the allowed lines but with reduced intensity.

Mn<sup>4+</sup> and the *A* center<sup>12</sup> of Ti<sup>3+</sup> gave similar traces, the latter for the case of H<sub>0</sub> along the *c* axis as shown in Fig. 3. Cr<sup>3+</sup>, Fe<sup>3+</sup>,<sup>19</sup> Co<sup>2+</sup>, Gd<sup>3+</sup>, and Ni<sup>3+</sup> did not show such resolved structure.

The resonance lines shown in Figs. 2 and 3 have the main equidistant satellites, both outermost lines having one-half the intensity of the six remaining lines. This structure can be interpreted in terms of the neighboring Ti<sup>47</sup> and Ti<sup>49</sup> hfs interaction with the unpaired electron (see next section). Many other weak satellites were

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<sup>9</sup> H. J. Gerritsen and H. R. Lewis, Phys. Rev. **119**, 1010 (1960); G. M. Zverev and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **39**, 222 (1960) [English transl.: Soviet Phys.—JETP **12**, 160 (1961)].

<sup>10</sup> H. J. Gerritsen, S. E. Harrison, H. R. Lewis, and J. P. Wittke, Phys. Rev. Letters **2**, 153 (1959).

<sup>11</sup> H. G. Andresen, Phys. Rev. **120**, 1606 (1960).

<sup>12</sup> D. Carter and A. Okaya, Phys. Rev. **118**, 1485 (1960).

<sup>13</sup> E. Yamaka and R. G. Barnes, Phys. Rev. **125**, 1568 (1962).

<sup>14</sup> E. Yamaka, J. Phys. Soc. Japan **13**, 1557 (1963).

<sup>15</sup> H. J. Gerritsen and E. S. Sabisky, Phys. Rev. **125**, 1853 (1962).

<sup>16</sup> P. F. Chester, J. Appl. Phys. **32**, 866 (1961).

<sup>17</sup> E. Yamaka and R. G. Barnes, Ninth Annual Midwest Solid State Conference, Argonne, Illinois, 1961 (unpublished).

<sup>18</sup> Dr. Gerritsen has informed us that they observed the "dirt" lines of low intensity near the main lines, but did not pay much attention to them.

<sup>19</sup> We observed two hfs lines due to Fe<sup>57</sup> (2.245%,  $I = \frac{1}{2}$ ) and obtained  $A = 9.2 \pm 0.5 \times 10^{-4}$  cm<sup>-1</sup>, which was not reported in Ref. 12.

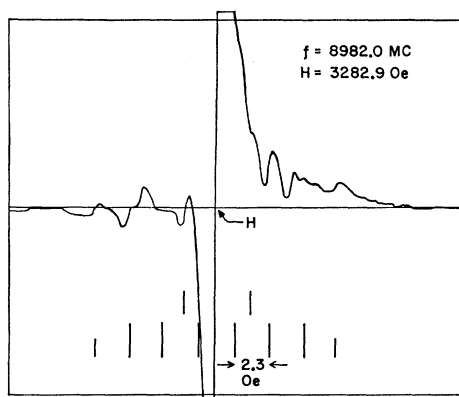


FIG. 3. ESR line of the *A* center (reduced) in  $\text{TiO}_2$  for  $H_0$  along the *c* axis at  $4.2^\circ\text{K}$ .

observed, especially at solid nitrogen temperature, at which temperature the linewidth and relaxation time were most favorable to obtaining a resolved structure. However, at this temperature it was rather difficult to keep the sample temperature constant, and the structure of the resonances was complicated, so that a detailed study was not attempted.

A phenomenological spin Hamiltonian for the  $\text{Ti}^{47}$  and  $\text{Ti}^{49}$  hfs interaction is

$$H = \sum_i \mathbf{S} \cdot \mathbf{A}^i \cdot \mathbf{I}^i, \quad (1)$$

where the summation is over the neighboring titanium sites. Since the main satellites seen in Fig. 2 come from the  $\text{Ti}^{47}$  or  $\text{Ti}^{49}$  occupying one of the two nearest sites along the *c* axis, as will be discussed in the next section, this spin Hamiltonian is simply written

$$H = A_x S_x I_x + A_y S_y I_y + A_z S_z I_z.$$

Table I shows the results obtained. The Ti hfs interaction in  $\text{Mn}^{4+}$  for  $H_0$  along (110) and (1 $\bar{1}$ 0) was small and a well-resolved structure was not observed. Also, four lines due to the nonequivalent sites of  $\text{Ti}^{3+}$  for the case of  $H_0$  along (110) and (1 $\bar{1}$ 0) were so close together that the satellites overlapped each other. Thus, *A* values could not be obtained for both cases.

## 2. Discussion

The regular satellites of the resonance lines seen in Figs. 2 and 3 show the existence of the hfs interaction

TABLE I. The  $\text{Ti}^{47}$  and  $\text{Ti}^{49}$  hfs interaction constants derived from the ESR of  $\text{V}^{4+}$  and  $\text{Mn}^{4+}$  in  $\text{TiO}_2$ . The values for  $\text{V}^{4+}$  in  $\text{SnO}_2$  are included for comparison. All values are in gauss.

	$A_x$	$A_y$	$A_z$	$A_{S^{II}}$	$A_{D^{II}+A_e^{II}}$
$\text{TiO}_2:\text{V}^{4+}$	2.0	2.0	2.4	2.13	0.13
$\text{TiO}_2:\text{Mn}^{4+}$	<0.5	<0.5	1.0		
$\text{SnO}_2:\text{V}^{4+}$ <sup>a</sup>	165.2	~166	172.6	167.9	2.33

<sup>a</sup> Reference 25.

of neighboring nuclei with the unpaired electron. Since the natural abundance of  $\text{O}^{17}$  is too small (0.029%) to account for this, the interacting nuclei might be the  $\text{Ti}^{47}$  ( $I = \frac{5}{2}$ , 7.75%) and  $\text{Ti}^{49}$  ( $I = \frac{7}{2}$ , 5.51%) of the neighboring cation sites. The *S* site is surrounded by two nearest Ti sites, 2.959 Å away along the *c* axis, and by eight next-nearest sites, 3.569 Å away, at the corners of the unit cell [Fig. 1(a)]. The *I* site also has two nearest Ti sites, 2.297 Å away at the centers of the two unit cells, and 2.733 Å away, at the corners of the unit cell. Thus, both the *S* and *I* sites have only two nearest Ti sites.

Since the local field symmetry arising from the distorted octahedron of oxygen is only orthorhombic ( $D_{2h}$ ), wave functions of the unpaired electrons have the symmetry property of  $D_{2h}$ . Clogston *et al.*<sup>7</sup> have given explicit expressions for 3d electrons augmented by the surrounding anions for the case of the rutile structure on the basis of group theory. It is a straightforward matter to include the Ti wave functions for our purposes. Group theory, of course, does not predict the eigenvalues of wave functions, and we have to solve a secular determinant by using the crystal field—including covalency with the ligands—this being a difficult problem.<sup>20</sup> However, the oxygen octahedron is distorted so little that the predominant symmetry will still be cubic. This means that  $d_e$ -type wave functions still have lower energies than  $d_\gamma$ -type wave functions, the former having lobes of high density which point between the attached oxygens. Thus,  $d_e$  ground states of  $\text{V}^{4+}$  ( $3d^1$ ) and  $\text{Mn}^{4+}$  ( $3d^3$ ) can easily bond with two nearest Ti ions located in the high-density direction in contrast to  $d_\gamma$  functions, whereas the latter can bond with the oxygens.

Here it is interesting to note that the fluorine hfs interaction in  $\text{ZnF}_2$  was observed only in  $d_\gamma$  electron cases whereas the Ti hfs interaction in  $\text{TiO}_2$  in this report was observed only for  $d_e$  electrons. This fact may be interpreted as due to the difference in bonding directions of the  $d_e$  and  $d_\gamma$  functions. On the other hand, the eight next-nearest sites are so far displaced ( $29.1^\circ$  away) from the high-density direction of the  $d_e$  functions, that bonding is expected to be quite small. Furthermore, following Tinkham,<sup>1</sup> the hfs interaction of neighboring nuclei depends strongly on the inter-nuclear distance. Thus, we can safely neglect the hfs interaction with the next-nearest sites for the *S* site in first approximation. This conclusion may also hold for the *I* site, although the oxygen octahedron of the *I* site is rotated  $12^\circ 35'$  around the *c* axis [Fig. 1(b)], and the nearest sites do not locate exactly along the direction of maximum density.

The  $\gamma$  values of the two titanium isotopes with non-zero spin,  $\text{Ti}^{47}$  and  $\text{Ti}^{49}$ , are fortunately nearly equal,<sup>21</sup>

<sup>20</sup> A. J. Leyendecker and A. H. Kahn calculated eigenvalues for the  $\text{V}^{4+}$  (*S* site) and  $\text{Ti}^{3+}$  (*I* site) by using a point-charge model NBS report 7434 (unpublished).

<sup>21</sup> C. D. Jeffries, Phys. Rev. **92**, 1212 (1953).

causing the six hfs lines of the former to coincide with the six inner lines of the latter. Therefore, *one* neighboring site gives rise to eight equidistant satellites, the two outermost lines having the intensity 0.69, the six inner lines 1.98, and the main line 86.7. Even if *two* sites (as in the present case) are taken into account, the main features will not be altered because the natural abundance is so small that the probability of occupation of both sites only by isotopes with spin is very small. An elementary calculation shows that the exact intensity ratio is 1.95:4.19:77.5 instead of 0.69:1.98:86.7, the other satellites having small intensities. The experimental ratio 2:4:48 does not agree with the predicted one for the main line.

The disagreement in the intensity ratios might be attributed to the following reasons: First, taking account of the contribution from the next-nearest ions will lower the intensity of the main line. However, this situation is rather complicated and the exact calculation has not been carried out. Second, since the main line has a longer relaxation time than the satellite lines,<sup>22</sup> the intensity of the former was reduced compared to that of the latter, even at  $10^{-3}$   $\mu$ W of microwave power (the limit of the attenuator in our apparatus) at 4.2°K. Indeed, it was possible that the main line had intensity of the same order as that of the satellites at higher power levels.

The above discussion leads to the conclusion that the resolved structure of the V<sup>4+</sup> and Mn<sup>4+</sup> absorption lines can be interpreted in terms of the hfs interaction of the two nearest Ti ions along the *c* axis.

To our knowledge, this is the first report of the hfs interaction of Ti isotopes in an ESR experiment.<sup>23</sup> However, the origin of the resolved structure of Ti<sup>3+</sup> (reduced), as shown in Fig. 3, cannot be clarified, since in this case both the hfs interaction of the paramagnetic center itself and of the nearest sites give similar structures, although the intensity ratios seem to make the former interaction more plausible.

The other small satellites which were most clearly seen at solid nitrogen temperature for V<sup>4+</sup> may be interpreted either by the combined hfs interaction of two isotopes occupying both nearest sites along the *c* axis, or by the interaction of the isotopes occupying the next-nearest sites.

The Hamiltonian for the titanium hfs interaction is

$$H = g\beta\gamma\beta_N \sum_a \left( \frac{\mathbf{S} \cdot \mathbf{I}_a}{r_a^3} + \frac{3(\mathbf{r}_a \cdot \mathbf{S})(\mathbf{r}_a \cdot \mathbf{I}_a)}{r_a^5} + \frac{8\pi}{3} \delta(\mathbf{r}_a) (\mathbf{S} \cdot \mathbf{I}_a) \right), \quad (3)$$

<sup>22</sup> In general, the relaxation time of a hfs line is shorter than that of a non-hfs line because of additional relaxation mechanisms ( $\Delta M = \pm 1$ ,  $\Delta m = \pm 1$  and  $\Delta M = 0$ ,  $\Delta m = \pm 1$ ). Indeed, it was clearly seen in TiO<sub>2</sub>:Cr<sup>3+</sup> that the main line was saturated to give the same order of intensity as the four hfs lines.

<sup>23</sup> Recently, the hfs interaction of the Ti isotopes in a liquid was reported. E. L. Walters and A. H. Maki, Phys. Rev. **125**, 233 (1962).

where  $r_a$  is the electron-nucleus distance and  $a$  is summed over the nuclei. The first two terms give the normal electron spin-nuclear spin coupling and the last term gives the *s*-electron contact interaction. The augmented ground-state wave functions to be used for this hfs energy can be written by combining with the wave functions of the impurity center the oxygen and titanium functions belonging to the  $\eta_1$  representation (invariant for all symmetry operations of  $D_{2h}$ ). We obtain, by using the symbols of Ref. 7, for V<sup>4+</sup>( $3d^1$ ),

$$D_2 = N_2 [d_2 + \alpha_2 \phi_{\eta_1} + (a_2/\sqrt{2})(s_1 + s_2) + (b_2/\sqrt{2})(\sigma_1 + \sigma_2)], \quad (4)$$

where  $d_2$  is the ( $z^2 - y^2$ ) type function of V<sup>4+</sup>,  $\phi_{\eta_1}$  is a linear combination of oxygen wave functions, in which the form of the linear combination of oxygen ions is omitted as these do not enter into the calculation.  $s_1$ ,  $s_2$  and  $\sigma_1$ ,  $\sigma_2$  are the 3*s* and 3*p* $\sigma$  functions of the two titanium sites, respectively.

For brevity, we introduce the definitions:

$$A_D^{\text{II}} = g\beta\gamma\beta_N \{1 - N_2^2(\alpha_2^2 + a_2^2 + b_2^2)\} R^{-3}, \quad (5)$$

$$A_S^{\text{II}} = g\beta\gamma\beta_N (8\pi/3) N_2^2 a_2^2 |s(0)|^2, \quad (6)$$

$$A_\sigma^{\text{II}} = g\beta\gamma\beta_N \langle r^{-3} \rangle N_2^2 b_2^2. \quad (7)$$

Here,  $R$  is the distance from the vanadium ion to the nearest titanium ion along the *c* axis. It is obvious that  $A_D^{\text{II}}$  is the dipole interaction of the paramagnetic ion magnetization,  $A_S^{\text{II}}$  is the isotropic contact interaction of the 3*s* orbitals occupied by electrons with unpaired spins, and  $A_\sigma^{\text{II}}$  is an anisotropic contribution of the magnetic dipole along the *c* axis.

We then obtain from the spin Hamiltonian that

$$A_x^{\text{II}} = A_y^{\text{II}} = A_S^{\text{II}} - A_D^{\text{II}} - A_\sigma^{\text{II}} \quad (8)$$

and

$$A_z^{\text{II}} = A_S^{\text{II}} + 2A_D^{\text{II}} + 2A_\sigma^{\text{II}}. \quad (9)$$

The equality of  $A_x$  and  $A_y$  is supported by the experimental results (Table I). It should be noted that it is not possible to separate  $A_D^{\text{II}}$  and  $A_\sigma^{\text{II}}$  because these have the same angular dependence. The values obtained are listed in Table I.

The interesting result that a well-resolved structure was obtained for Mn<sup>4+</sup>( $3d^3$ ) but not for Cr<sup>3+</sup>( $3d^3$ ) nor for Mn<sup>3+</sup>( $3d^4$ )<sup>24</sup> might be explained as follows: The central ion with smaller charge will tend to push away the ligand oxygen ions and pull in the titanium ions by Coulomb interaction, the former displacement being greater. At the same time, the titanium ions will receive a repulsive force from the movement of the large oxygen ions. The absence of resolved structure in Cr<sup>3+</sup> and Mn<sup>3+</sup> appears to indicate that the repulsive force exceeds the pulling force on the titanium ions.

While preparing this manuscript, we received an interesting preprint concerning V<sup>4+</sup> in SnO<sub>2</sub> (rutile

<sup>24</sup> H. J. Gerritsen (to be published).

structure) from W. H. From<sup>25</sup> of the Lincoln Laboratory. These authors observed large hfs interactions due to the two nearest tin ions along the  $c$  axis, with much smaller interactions due to the eight next-nearest tin ions, the former  $A$  values being included in Table I for comparison. The qualitative results and their interpretation agree with ours, but the  $A$  values are surprisingly large, because both  $\text{TiO}_2$  and  $\text{SnO}_2$  have nearly equal covalent character,<sup>26</sup> and the lattice parameter of  $\text{SnO}_2$  is slightly larger than that of  $\text{TiO}_2$ . A similar interpretation of the Ti hfs interaction was given very recently by Chang<sup>27</sup> for the ESR spectrum of  $\text{Mo}^{5+}$  in  $\text{TiO}_2$ , but the details are not yet available.

### CONCLUSIONS

We have observed well-resolved structure in each hfs line of  $\text{V}^{4+}$  and  $\text{Mn}^{4+}$  in rutile single crystals. This structure consists of eight equidistant satellites around the main line, the two outermost lines having one-half the intensity of the six remaining lines. This is interpreted in terms of the hfs interaction of the unpaired electron with  $\text{Ti}^{47}$  and  $\text{Ti}^{49}$  nuclei which occupy the two nearest ion sites along the  $c$  axis. This hfs interaction evaluated with the augmented wave function which includes the titanium ions also explains the anisotropic hfs constants.

The absence of structure in the ESR of  $\text{Cr}^{3+}$  and  $\text{Mn}^{3+}$  may indicate that the nearest titanium ions are moved away in these cases, because the movement of the large oxygen ions pushes away the titanium ions by overcoming the Coulomb force due to the smaller charges of the paramagnetic impurities.

It should be noted that the paramagnetic state of a single  $d$  electron has not yet been interpreted theoretically, especially in the covalently bonded case. Rei<sup>28</sup> calculated the so-called reduction factor ( $K$ ) due to covalent bonding for the  $g$  values<sup>9</sup> of  $\text{V}^{4+}(3d^1)$  in  $\text{TiO}_2$  and found that  $K_{\perp}$  (perpendicular to the nearly-tetragonal axis, i.e., the  $x$  axis) must be less than 0.3 in order that  $K_{\parallel}$  may be smaller than unity. This value is unusually small. He was also unable to explain the  $A$  values<sup>9</sup> by using these  $K$  values. Kyi<sup>29</sup> had interpreted

TABLE II. Summary of  $g$ -value results for the single  $d$ -electron case in crystals of the rutile structure.

Ion	Host crystal	Electron configuration	Tetragonal axis	$g_x(c)$	$g_y$	$g_z$	Ref.
$\text{Ti}^{3+}$	$\text{TiO}_2$	$3d^1$	$c$	1.940	1.972	1.975	a, b
$\text{V}^{4+}$	$\text{TiO}_2$	$3d^1$	$x$	1.913	1.915	1.956	c
$\text{V}^{4+}$	$\text{SnO}_2$	$3d^1$	$c$	1.903	1.939	1.943	d
$\text{Nb}^{4+}$	$\text{TiO}_2$	$4d^1$	$c$	1.948	1.973	1.981	e
$\text{Mo}^{5+}$	$\text{TiO}_2$	$4d^1$	$x$	1.788	1.812	1.912	f
$\text{Ta}^{4+}$	$\text{TiO}_2$	$5d^1$	$c$	1.945	1.979	1.979	g

<sup>a</sup> Reference 16.

<sup>b</sup> Reference 17.

<sup>c</sup> Reference 9.

<sup>d</sup> Reference 25.

<sup>e</sup> P. F. Chester, J. Appl. Phys. **32**, 866 (1961).

<sup>f</sup> Reference 29.

<sup>g</sup> P. F. Chester, J. Appl. Phys. **32**, 2233S (1961).

the  $g$  values of  $\text{Mo}^{5+}(4d^1)$  in  $\text{TiO}_2$  by assuming that they are negative, but this interpretation is dubious, and Chang<sup>27</sup> has reported them to be positive on the basis of experiments with a circularly-polarized microwave cavity.

The distorted octahedron of rutile has the nearly-tetragonal axis lying along the  $x$  direction. However, Andresen<sup>11</sup> first pointed out that the tetragonal axis for  $\text{Mn}^{4+}$  lies along the  $z$  axis in contrast with isoelectronic  $\text{Cr}^{3+}$ .<sup>10</sup> The  $g$  values and tetragonal axes for various paramagnetic impurities with single  $d$  electron in the rutile structure are summarized in Table II. We note that the  $g$  value is minimum in case the  $c$  axis is the tetragonal axis, whereas it is maximum when the  $x$  axis is the tetragonal axis. Any theoretical interpretation must reflect this aspect.

Thus, the situation of a single  $d$  electron with covalent bonding is still not settled, and further information regarding the bonding would be desirable. However, the  $\text{Ti}^{47}$  and  $\text{Ti}^{49}$  hfs interaction, as seen in this paper, is rather small, and little information concerning the unpaired electron is likely to be obtained from the usual ESR method. Experiments utilizing the ENDOR technique would be desirable, and such experiments are now being planned.

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