

Spin Resonance of  $\text{SnO}_2:\text{V}$  and the Vanadium  $3d$  Electron Orbital

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(Received 31 July 1964)

The ESR spectrum of  $\text{SnO}_2$  containing about 0.5% vanadium observed in K band at liquid-nitrogen temperature shows two sets of shfs. Relative intensity measurements show that the large shfs (168 G) is due to the two tins located along the  $c$  axis and the small shfs (28 G) due to the four tins lying in a diagonal plane of the unit cell containing four oxygens. The large shfs is largely isotropic, with an axial maximum along the  $c$  axis. This suggests that the ground electron level is  $3d(x^2-y^2)$ . The next level is  $3d(xz)$ . This is deduced from the  $g$  values ( $g_{zz}=1.939$ ,  $g_{yy}=1.903$ , and  $g_{xx}=1.943$ ).

## I. INTRODUCTION

IN reporting the ESR (electron spin resonance) properties of vanadium in corundum,<sup>1</sup> the possible usefulness of vanadium to probe electron interactions in solids was pointed out. This suggestion stemmed from the fact that the odd proton isotope,  $^{51}\text{V}$ , is essentially 100% having  $I=\frac{7}{2}$  with a large hfs (hyperfine structure) characteristic of odd proton nuclei and that the different vanadium electron configuration states can be produced with relative ease. As a part of this program, Borcherts and Kikuchi investigated  $\text{VO}^{2+}$  in zinc ammonium Tutton salt to establish the nature of the impurity defect complex formed by the vanadyl ion.<sup>2</sup>

We have investigated vanadium in tin oxide as a part of the program. A strikingly large shfs (superhyperfine structure) was observed. From this structure, the symmetry of the ground state molecular orbital was deduced, and the ordering of the energy levels of the low-lying  $t_{2g}$  triplet was determined. Furthermore, evidence is given that the direct interaction between the vanadium and tin has, perhaps, a much more important role than the indirect interaction via the nearest oxygen ligands. Some of these results have been reported briefly.<sup>3,4</sup>

The importance of vanadium in  $\text{SnO}_2$  and in other crystals having the rutile structure stems from the fact that the electron configuration of the impurity vanadium is  $3d^1$ . By means of this "simple," one-magnetic-electron system, the hope is to obtain infor-

mation about the "molecular electron energy shells," analogous to the atomic electron energy shells of hydrogen and other "one-electron" systems of atomic spectroscopy. This information, makes it possible to construct a filling-up scheme for the various molecular orbitals and thus account for more complex electron configurations. Another objective is to delineate some of the subtle electron interactions in solids that cannot be conveniently studied in more complex configurations.

Historically, the study of the iron group elements in rutile-type structures was initiated by M. Tinkham.<sup>5</sup> Following his observation of the  $3d^5 \text{Mn}^{2+}$  ion shfs due to the nearest-neighbor fluorine ligands in  $\text{ZnF}_2$ , the theory for this structure was developed by Keffer, Oguchi, O'Sullivan, and Yamashita<sup>6</sup> and also by Clogston, Gordon, Jaccarino, Peter, and Walker.<sup>7</sup> Attention to vanadium in  $\text{TiO}_2$  was drawn by the experimental studies of Gerritsen and Lewis<sup>8</sup> and the initial theoretical investigation by Rei.<sup>9</sup> Later Yamaka and Barnes<sup>10</sup> reported the shfs stemming from the odd titanium isotopes and recently Yamaka<sup>11</sup> has obtained some results on the multiple quantum transitions by the ENDOR technique. Similar studies for the molybdenum  $4d^1$  electron in  $\text{TiO}_2$  have been carried out by Kyi<sup>12</sup> and by Chang.<sup>13</sup> The latter has also reported

<sup>5</sup> M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535, 549 (1956).

<sup>6</sup> F. Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, Phys. Rev. **115**, 1553 (1959).

<sup>7</sup> A. M. Clogston, J. P. Gordon, V. Jaccarino, M. Peter, and L. R. Walker, Phys. Rev. **117**, 1222 (1960).

<sup>8</sup> H. J. Gerritsen and H. R. Lewis, Phys. Rev. **119**, 1010 (1960).

<sup>9</sup> D. K. Rei, Soviet Phys.—Solid State **3**, 1845 (1962) [Fiz. Tver. Tela **3**, 2535 (1961)].

<sup>10</sup> E. Yamaka and R. G. Barnes, Phys. Rev. **135**, A144 (1964).

<sup>11</sup> E. Yamaka (private communication).

<sup>12</sup> R. T. Kyi, Phys. Rev. **128**, 151 (1962).

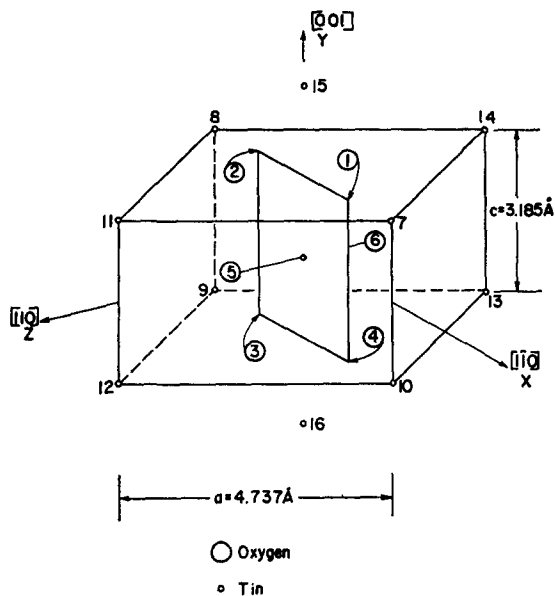
<sup>13</sup> T. Chang, Bull. Am. Phys. Soc. **8**, 464 (1963).

<sup>1</sup> J. Lambe and C. Kikuchi, Phys. Rev. **118**, 71 (1960).

<sup>2</sup> R. H. Borcherts and C. Kikuchi, J. Chem. Phys. **40**, 2270 (1964).

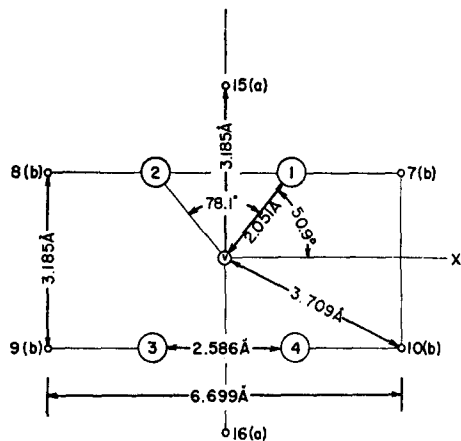
<sup>3</sup> W. H. From, C. Kikuchi, and P. Dorain, Bull. Am. Phys. Soc. **9**, 37 (1964).

<sup>4</sup> I. Chen, C. Kikuchi, and H. Watanabe, Bull. Am. Phys. Soc. **9**, 38 (1964).

FIG. 1. Unit cell of  $\text{SnO}_2$  rutile structure.

measurements on the tungsten  $5d^1$  electron in the same host crystal.<sup>14</sup> I. Siegel investigated vanadium in  $\text{GeO}_2$ , which exhibits both the crystalline and glassy states.<sup>15</sup>

Other iron group ions for which the ESR properties in  $\text{TiO}_2$  have been reported are nickel,<sup>16</sup> manganese,<sup>17</sup> iron,<sup>18</sup> cobalt,<sup>19</sup> and chromium.<sup>20</sup> The last, as is well known, has been extensively studied because of its importance as a maser material. For  $\text{SnO}_2$ , the ESR

FIG. 2. Bond distances and angles of atoms in the diagonal ( $XY$ ) plane of  $\text{SnO}_2$  unit cell.

properties of chromium,<sup>21</sup> manganese,<sup>22</sup> and vanadium<sup>23</sup> have been reported.

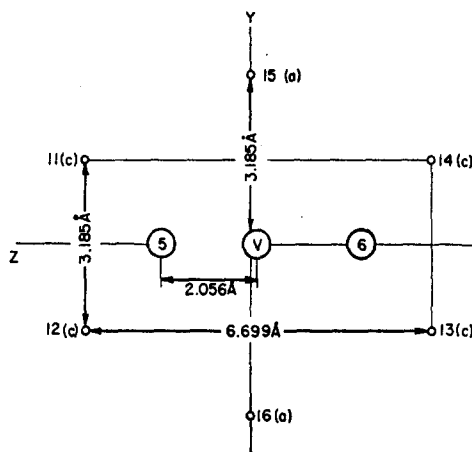
## II. STRUCTURE

The crystal of  $\text{SnO}_2$ , known as cassiterite,<sup>24</sup> has atoms in the following positions of tetragonal  $D_{4h}$ :

$$\text{Sn: } 000; \frac{1}{2} \frac{1}{2} \frac{1}{2},$$

$$\text{O: } \pm(uu0; u - \frac{1}{2}, \frac{1}{2} - u, \frac{1}{2}).$$

The lattice parameters are  $a = 4.737 \pm 0.001 \text{ \AA}$ ,  $c = 3.185 \pm 0.001 \text{ \AA}$ , and  $u = 0.307 \pm 0.001$ , with  $c/a = 0.672$ . The  $c$  axis is the fourfold axis, and this was taken as the  $y$  axis. The values for  $\text{TiO}_2$  are  $a = 4.594 \pm 0.003 \text{ \AA}$ ,  $c = 2.959 \pm 0.002 \text{ \AA}$ ,  $u = 0.306 \pm 0.001$ , and  $c/a = 0.644$ . The flat unit cell contains two molecules of  $\text{SnO}_2$ .

FIG. 3. Bond distances and angles of atoms in the diagonal ( $YZ$ ) plane of  $\text{SnO}_2$  unit cell.

The site symmetry is  $D_{2h}$ , as can be seen from the unit cell shown in Fig. 1. A vanadium occupying the center of such a cell is surrounded immediately by a slightly distorted octahedron of oxygens, and then farther out  $3.708 \text{ \AA}$  away by eight tins, which outline the unit cell. In addition, important for the interpretation of the experimental results are the two tins along the  $c$  axis ( $y$  axis) only  $3.185 \text{ \AA}$  away. These are referred to as the  $a$  tins, which, as we show, give rise to a large superhyperfine structure (shfs). Furthermore, the oxygens and the tins of the unit cell lie on two diagonal planes of the unit cell. The bond distances and angles computed from x-ray data are shown in Figs. 2 and 3. The four tins shown in Fig. 2, lying in the plane of the four oxygens are called the  $b$  tins. It is shown that these four structurally equivalent tins account for the observed small shfs.

<sup>14</sup> T. Chang, *Bull. Am. Phys. Soc.* **9**, 568 (1964).

<sup>15</sup> I. Siegel, *Phys. Rev.* **134**, A193 (1964).

<sup>16</sup> H. J. Gerritsen and E. S. Salisky, *Phys. Rev.* **125**, 1853 (1962).

<sup>17</sup> H. G. Andresen, *Phys. Rev.* **120**, 1606 (1960).

<sup>18</sup> D. L. Carter and A. Okaya, *Phys. Rev.* **118**, 1485 (1960).

<sup>19</sup> E. Yamaka and R. G. Barnes, *Phys. Rev.* **125**, 1568 (1962).

<sup>20</sup> H. J. Gerritsen, S. E. Harrison, H. R. Lewis, and J. R. Wittke, *Phys. Rev. Letters* **2**, 153 (1959).

<sup>21</sup> W. H. From, *Phys. Rev.* **131**, 961 (1963).

<sup>22</sup> W. H. From, P. B. Dorain, and C. Kikuchi, *Bull. Am. Phys. Soc.* **9**, 244 (1964).

<sup>23</sup> P. H. Kasai, *Phys. Letters* **7**, 5 (1963).

<sup>24</sup> R. Wyckoff, *Crystal Structure* (Interscience Publishers, Inc., New York, 1958).

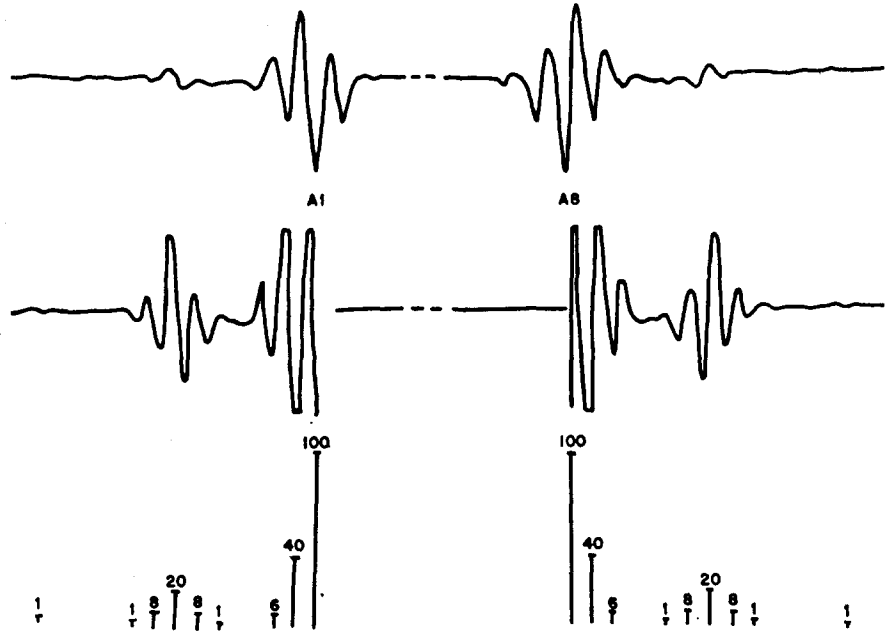


FIG. 4. Portions of the ESR spectra of SnO<sub>2</sub>:V<sup>4+</sup> at low and high gain. The magnetic field is along the *A*-site *Z* axis. Calculated relative intensities of the lines are indicated at the bottom.

The symmetry operations of the *D*<sub>2h</sub> group are *C*<sub>2</sub>, *C*<sub>2</sub><sup>'</sup>, and *C*<sub>2</sub><sup>''</sup> representing 180° rotations about the *z*, *y*, and *x* axes respectively, the reflections  $\sigma_v$ ,  $\sigma_v'$ , and  $\sigma_v''$  in the *xy*, *xz*, and *yz* planes, respectively, and the inversion *I*. The character table for this group, and some of the typical functions and operators that transform as the irreducible representations are given in Table I. The character table was taken from Koster's paper.<sup>25</sup> The particular notation for the double representations was chosen to display their relations to the irreducible representations of the double cubic group.

An examination of the crystal structure shows that there are two nonequivalent sites, one with the site *z* axis along the [110] direction, and for the other along the [1 $\bar{1}$ 0] direction. These are referred to as the

*A* and *B* sites, respectively. A consequence of this fact is that when the magnetic field is along the [110] direction, the magnetic field will be along the site *z* axis for the vanadiums in the *A* sites but along the site *x* axis for those in the *B* sites.

III. EXPERIMENTAL PROCEDURE AND RESULTS

Measurements were made with a K-band ESR spectrometer at liquid nitrogen temperature. Single crystals of SnO<sub>2</sub> containing about 0.5% vanadium were grown by T. Reed of the MIT Lincoln Laboratory. A portion of the ESR spectrum, taken with the magnetic field along the *A*-site *z* axis is shown in Fig. 4. The striking characteristic of the spectrum is that each hfs line is split into a number of components and furthermore flanked by two prominent groups of lines with two more groups at twice the separation that can be seen under higher spectrometer gain. The groups are separated by about 88 G. Figure 5 shows the positions of the *B*-site lines relative to those of *A* sites.

TABLE I. Character table of Group *D*<sub>2h</sub>.

	E	<i>C</i> <sub>2</sub>	<i>C</i> <sub>2</sub> <sup>'</sup>	<i>C</i> <sub>2</sub> <sup>''</sup>	<i>I</i>	$\sigma_v$	$\sigma_v'$	$\sigma_v''$		
<i>N</i> <sub>1</sub>	1	1	1	1	1	1	1	1	$3x^2 - r^2$	$x^2 - y^2$
<i>N</i> <sub>2</sub>	1	-1	1	-1	1	-1	1	-1	<i>zx</i>	$\cdot L_y$
<i>N</i> <sub>3</sub>	1	1	-1	-1	1	1	-1	-1	<i>xy</i>	$\cdot L_x$
<i>N</i> <sub>4</sub>	1	-1	-1	1	1	-1	-1	1	<i>yz</i>	$\cdot L_z$
<i>N</i> <sub>1</sub> <sup>'</sup>	1	1	1	1	-1	-1	-1	-1		
<i>N</i> <sub>2</sub> <sup>'</sup>	1	-1	1	-1	-1	1	-1	1	<i>y</i>	
<i>N</i> <sub>3</sub> <sup>'</sup>	1	1	-1	-1	-1	1	1	1	<i>z</i>	
<i>N</i> <sub>4</sub> <sup>'</sup>	1	-1	-1	1	-1	-1	1	-1	<i>x</i>	
	E	<i>C</i> <sub>2</sub>	<i>C</i> <sub>2</sub> <sup>'</sup>	<i>C</i> <sub>2</sub> <sup>''</sup>	<i>I</i>	$\sigma_v$	$\sigma_v'$	$\sigma_v''$		
$\Gamma_4^+$	2	-2	0	0	0	2	-2	0	0	0
$\Gamma_4^-$	2	-2	0	0	0	-2	2	0	0	0

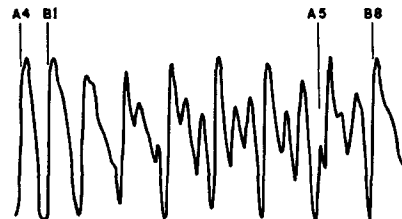


FIG. 5. Positions of the *B*-site ESR lines relative to those of *A* sites. The magnetic field is along the *Z* axis for *A* sites, but along the *X* axis for the *B* sites.

<sup>25</sup> G. F. Koster, Solid State Phys. 5, 173 (1957).

TABLE II. Experimental results.

	x	y	z
g	1.939	1.903	1.943
A(gauss)	23.3	47.03	154.4
a(gauss)	~ 166	172.6	165.2
b(gauss)	~ 28	28	28

Only one group of eight hfs lines centered about  $g$  approximately equal to two is observed, so that the electron spin is  $\frac{1}{2}$ . The observed spectrum is described by the spin Hamiltonian

$$\mathcal{H} = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + \mathbf{S} \cdot \mathbf{A} \cdot \mathbf{I} + \sum_{a\text{-tins}} \mathbf{S} \cdot \mathbf{a}_i \cdot \mathbf{I}_i + \sum_{b\text{-tins}} \mathbf{S} \cdot \mathbf{b}_i \cdot \mathbf{I}_i,$$

where the first and the second term represent the Zeeman and the hyperfine interaction terms. The last terms represent the electron interaction with the  $a$  and  $b$  tins, respectively. The measured values of the spin Hamiltonian are presented in Table II. It is noted that the  $a$  tensor is largely isotropic with a small but definite axial maximum along the  $y$  axis (crystal  $c$  axis). This indicates that the ground state molecular orbital contains the  $s$  and the  $p_y$  atomic orbitals of the  $a$  tins. We return to this point presently.

The difference in the relative intensities of the groups of lines as compared to the relative intensities of lines in a group provides the necessary information to assign the large and small shfs. Tin consists of the odd isotopes  $^{115}\text{Sn}$  (0.35%),  $^{117}\text{Sn}$  (7.54%), and  $^{119}\text{Sn}$  (8.62%), all with spin  $\frac{1}{2}$ . Because of the low abundance, the effects of  $^{115}\text{Sn}$  can be neglected. The last two isotopes have the nuclear  $g$  values of 1.9898 and 2.0818, respectively, so that for our purposes both isotopes can be considered equivalent. The combined isotope abundance is 16.7%, or about  $\frac{1}{6}$ . This leads to the relative intensity ratio of 1:20:100:20:1 for two structurally equivalent tins and 6:40:100:40:6 for four structurally equivalent tins. Inspection of the spectrum then shows that the large shfs is due to two structurally equivalent tins and the small shfs to the four structurally equivalent tins.

#### IV. DISCUSSION

We now show that the  $a$ -tin shfs and the  $g$  values provide important information about the electron orbital energy level scheme. The vanadium is bonded to six oxygens, which to the first approximation form a regular octahedron. The perturbation from such an environment causes the splitting of the  $3d$  level into a doublet  $e_g$  and a triplet  $t_{2g}$  of the  $O_h$  group, with the latter lying lower. The orbitals belonging to  $e_g$  are  $3z^2-r^2$  and  $xy$ , and those for  $t_{2g}$  are  $x^2-y^2$ ,  $zx$ ,

and  $zy$ . The interchanging of the roles of the orbitals  $x^2-y^2$  and  $xy$  should be noted. This arises from the difference in the choice of the coordinate axes.

Referring to Table II we note that the components of the  $a$ -tensor consist of a large isotropic part with a smaller anisotropic part, with an axial maximum along the  $y$  axis. This suggests that the  $s$  and the  $p_y$  atomic orbitals of the  $a$  tins overlap directly and/or indirectly with the central metal orbital. Because of structural equivalence of the tins, the linear combinations that need be taken are  $s_{15} \pm s_{16}$ ,  $y_{15} \pm y_{16}$  where we simply write  $y$  for the  $p_y$  atomic orbital. From the group character table, it can be shown that  $s_{15} + s_{16}$ ,  $y_{15} - y_{16}$  transform like  $N_1$ , and that  $s_{15} - s_{16}$ ,  $y_{15} + y_{16}$  transform like  $N_2'$ , an odd representation. Since the central metal orbital is even, the symmetry of the ground-state orbital must be  $N_1$ . From the table it is seen that there are two such functions, namely  $3z^2-r^2$  and  $x^2-y^2$ . The first has its lobes along the site  $z$  axis, whereas the second has lobes along the  $x$  and  $y$  axes. Consequently, the metal orbital contributing to the ground state is mainly  $x^2-y^2$ .

The positions of the remaining two levels  $N_2$  and  $N_4$  of  $t_{2g}$  relative to  $N_1$  can be inferred from the  $g$  values. Theory shows that  $\Delta g_i$  is given by<sup>26</sup>

$$\Delta g_i \equiv g_i - g_0 = -2\lambda \sum_{\alpha} \frac{|\langle N_{\alpha} | L_i | N_1 \rangle|^2}{(E_{\alpha} - E_1)},$$

in which  $E_1$  is the energy of the ground state  $N_1$ ,  $E_{\alpha}$  is the energy of the level  $N_{\alpha}$  contributing to  $\Delta g$  through the spin-orbit interaction, and  $\lambda$  is the usual spin-orbit coupling constant. From the character table it is easy to see that the following relations for the product representations hold:

$$\begin{aligned} N_1 N_2 &= N_2, & N_2 N_3 &= N_4, \\ N_1 N_3 &= N_3, & N_3 N_4 &= N_2, \\ N_1 N_4 &= N_4, & N_4 N_2 &= N_3. \end{aligned}$$

Furthermore, according to the character table, the

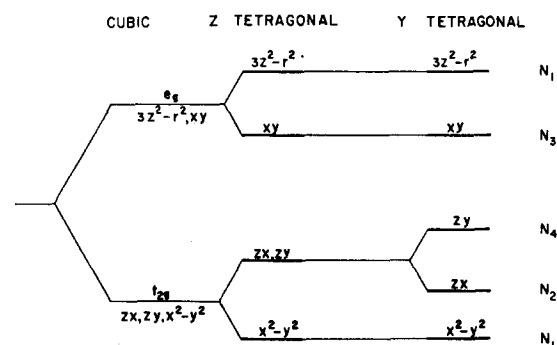


FIG. 6. Splitting of  $3d$  orbital levels in crystalline field of  $\text{SnO}_2$ .

<sup>26</sup> B. Bleaney and K. W. H. Stevens, Rept. Progr. Phys. **16**, 108 (1953).

TABLE III. Irreducible representations of the central and ligand orbitals in  $\text{SnO}_2:\text{V}^{4+}$ .

	Central	O in xy-plane	b-Tins	O on z-axis	c-Tins	d-Tins
$N_1$	$x^2 - y^2$	$s_1 + s_2 + s_3 + s_4$	$s_7 + s_8 + s_9 + s_{10}$	$s_5 + s_6$	$s_{11} + s_{12} + s_{13} + s_{14}$	$s_{15} + s_{16}$
		$x_1 - x_2 - x_3 + x_4$	$x_7 - x_8 - x_9 + x_{10}$	$z_5 - z_6$	$y_{11} - y_{12} - y_{13} + y_{14}$	$y_{15} - y_{16}$
		$y_1 + y_2 - y_3 - y_4$	$y_7 + y_8 - y_9 - y_{10}$		$z_{11} + z_{12} - z_{13} - z_{14}$	
$N_2$	$zx$	$z_1 - z_2 - z_3 + z_4$	$z_7 - z_8 - z_9 + z_{10}$	$x_5 - x_6$	$x_{11} + x_{12} - x_{13} - x_{14}$	
$N_3$	$xy$	$x_1 + x_2 - x_3 - x_4$	$x_7 + x_8 - x_9 - x_{10}$			
		$y_1 - y_2 - y_3 + y_4$	$y_7 - y_8 - y_9 + y_{10}$		$x_{11} + x_{12} - x_{13} + x_{14}$	$x_{15} - x_{16}$
		$s_1 - s_2 + s_3 - s_4$	$s_7 - s_8 + s_9 - s_{10}$			
$N_4$	$zy$	$z_1 + z_2 - z_3 - z_4$	$z_7 + z_8 - z_9 - z_{10}$	$y_5 - y_6$	$s_{11} - s_{12} + s_{13} - s_{14}$	
					$y_{11} + y_{12} - y_{13} - y_{14}$	$z_{15} + z_{16}$
					$z_{11} - z_{12} - z_{13} + z_{14}$	

operators  $L_x$ ,  $L_y$ , and  $L_z$ , which contribute to  $\Delta g_x$ ,  $\Delta g_y$ , and  $\Delta g_z$  respectively, transform like  $N_4$ ,  $N_2$  and  $N_3$ . Table II gives  $g_x=1.939$  and  $g_y=1.903$ . Therefore if it is assumed that only one level gives an appreciable contribution to  $\Delta g$ ; as is the case for one crystal-field theory, one is led to the conclusion that  $N_2$  lies below  $N_4$  for  $\text{SnO}_2$ . However, more detailed molecular orbital calculations suggest that  $N_4$  lies next to  $N_1$ . The details are to be presented in a later paper. Figure 6 shows the complete removal of the orbital degeneracies as the result of symmetry reduction from  $O_h$  to  $D_{2h}$ .

The electron spin resonance of the  $3d^3$  configuration,  $\text{Cr}^{3+}$  and  $\text{Mn}^{4+}$ , have been reported by us. These studies indicate that the  $a$ -tin shfs's are appreciably smaller, about 31.3 and 38 G for  $\text{Mn}^{4+}$  and  $\text{Cr}^{3+}$ , respectively, in comparison to 168 G for  $\text{V}^{4+}$ . A part of the cause for the reduction in the shfs can be seen from the

energy level diagram and the combining orbitals given in Table III. If the level separations of  $N_1$ ,  $N_2$ , and  $N_4$  are small in comparison to the electron electrostatic interaction the three electrons can be expected to occupy the levels  $N_1$ ,  $N_2$ , and  $N_4$ . However, as pointed out earlier, only the  $N_1$  molecular orbital contains the  $s$  atomic orbitals of the  $a$  tins. Consequently, the isotropic shfs of the  $3d^3$  is expected to be about  $\frac{1}{3}$  that of the  $3d^1$  configuration.

#### ACKNOWLEDGMENTS

We are indebted to Dr. T. Reed (MIT Lincoln Laboratory) and A. Mariano (Copper Research Laboratory, Lexington, Massachusetts) for technical assistance and to Dr. R. Tucker (Corning Glass), Dr. P. H. Kasai (Union Carbide), Professor H. Watanabe, and Mr. S. Karavelas for many helpful discussions.