

tallic state of V_2O_3 may differ from its value in the insulating state because of a different degree of covalency of the vanadium ion in the two states.

Recent experiments by Gossard, McWhan, and Remeika³ have shown that no magnetic order occurs in the metallic state of V_2O_3 (under pressure) down to a temperature of 4.2 °K. It is, therefore, tempting to associate the moment reduction from the expected value of 2 to 1.2 μ_B with the fact that insulating V_2O_3 is close to being a metal, with large overlap between d states on neighboring vanadium ions by way of the intervening oxygen ions. This would imply that there is an increased probability of finding a d electron on its neighboring V site to which it is antiferromagnetically coupled so that

it reduces the net moment of the ion pair involved. However, before such speculations can be made, an experimental determination of the g value of the ordered moment seems necessary in order to substantiate the above estimate.

ACKNOWLEDGMENTS

I would like to thank A. M. Clogston, who initiated this work, for many stimulating and illuminating discussions. My thanks also go to J. P. Remeika, who kindly furnished the V_2O_3 crystals and to S. Geschwind, D. B. McWhan, and A. C. Gossard for interesting discussions and for letting me use some of their results prior to publication.

¹D. B. McWhan and T. M. Rice, Phys. Rev. Letters **22**, 887 (1969).

²D. B. McWhan, T. M. Rice, and J. P. Remeika, Phys. Rev. Letters **23**, 1384 (1969).

³A. C. Gossard, D. B. McWhan, and J. P. Remeika, Paper IV of this series, Phys. Rev. B **2**, 3762 (1970).

⁴E. D. Jones, Phys. Rev. **137**, A978 (1965).

⁵R. B. Moon, Phys. Rev. Letters **25**, 527 (1970).

⁶B. Alefeld, M. Birr, and A. Heidemann, Naturwissenschaften **56**, 410 (1969).

⁷G. M. Zverev and A. M. Prokhorov, Zh. Eksperim. i Teor. Fiz. **38**, 449 (1960) [Soviet Phys. JETP **11**, 330 (1960)].

⁸M. Sauzade, J. Poutnan, P. Leses, and D. Silhouette, Phys. Letters **19**, 617 (1966).

Crystal Structure of the Low-Temperature Antiferromagnetic Phase of V_2O_3

P. D. Dernier and M. Marezio

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

(Received 26 May 1970)

At ~ 155 °K, the metallic corundum structure of V_2O_3 distorts to an insulating monoclinic one. Structural refinements of this low-temperature phase by x-ray diffraction techniques show an increase in the nearest-neighbor vanadium - vanadium distances at the transition. This is in direct contrast to previously reported distortion models. In the a - c plane of the monoclinic structure, the vanadium - vanadium distance across the shared octahedral face increases from 2.697 to 2.745 Å, while the vanadium - vanadium distance across the shared octahedral edge increases from 2.882 to 2.987 Å when proceeding from the corundum structure to the monoclinic one. The oxygen octahedra become skewed about the central vanadium atom, while the average vanadium - oxygen distance remains essentially constant. The expansion of the vanadium - vanadium distances associated with this transition is similar to the Mott transition observed in the Cr_2O_3 - V_2O_3 system in which the conduction electrons localize on their ionic sites when proceeding from the metal phase, α - V_2O_3 , to the insulating one, α - $(V_{0.962}Cr_{0.038})_2O_3$.

INTRODUCTION

At room temperature V_2O_3 has the corundum structure, space group $R\bar{3}c$, with approximate hexagonal close packing of the oxygen atoms and the vanadium atoms occupying $\frac{2}{3}$ of the octahedral sites. The compound is unique among the isostructural sesquioxides with respect to its unusually high c/a ratio and metallic conductivity. Recently, one of us has reported the structural refinements of single crystals of V_2O_3 and $(V_{0.962}Cr_{0.038})_2O_3$

near the metal-insulator (M-I) transition.¹ It has been observed that this M-I transition in the Cr_2O_3 - V_2O_3 system² is accompanied by a discontinuous change in the c/a ratio while the nearest-neighbor vanadium - vanadium distances increase, and the vanadium - oxygen distances remain essentially unchanged.

At low temperature, 150-160 °K, the corundum V_2O_3 distorts to a structure with monoclinic symmetry,³ which has been reported as insulating and

antiferromagnetic.⁴⁻⁶ This symmetry change has been previously explained by Goodenough⁷ and more recently by Feinleib and Paul⁸ as the result of a pairing of vanadium ions along one of three equivalent basal-plane (hexagonal cell) axes and a simultaneous tilting of the c_H axis. In direct contrast to this, we have observed an expansion in all the short vanadium - vanadium distances associated with the M-I transition at room temperature, and it has been our belief that a similar expansion should occur also at the low-temperature transition. In order to clarify this point the crystal structure of the low-temperature phase of V_2O_3 has been refined from single-crystal x-ray diffraction data.

I. SYMMETRY AND TWINNING

The orthohexagonal cell originally proposed by Warekois³ for the low-temperature phase is sixfold primitive and therefore it is not a conventional monoclinic cell. This cell is derived from the hexagonal cell according to the matrix

$$\begin{pmatrix} \vec{a}_m \\ \vec{b}_m \\ \vec{c}_m \end{pmatrix} = \begin{pmatrix} 1 & 2 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \vec{a}_H \\ \vec{b}_H \\ \vec{c}_H \end{pmatrix}.$$

Abrahams⁹ proposed a new monoclinic cell which is derived from the hexagonal cell according to the matrix

$$\begin{pmatrix} \vec{a}_m \\ \vec{b}_m \\ \vec{c}_m \end{pmatrix} = \begin{pmatrix} \frac{1}{3} & \frac{2}{3} & \frac{2}{3} \\ 1 & 0 & 0 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} \vec{a}_H \\ \vec{b}_H \\ \vec{c}_H \end{pmatrix}.$$

The space group corresponding to this cell is $C2/c$ with four formulas per unit cell. The interaxial angle β for this cell is $\sim 165^\circ$.

Still another C -centered cell exists which has the following dimensions:

$$a = 8.600 \text{ \AA}, \quad b = 5.002 \text{ \AA}, \\ c = 5.548 \text{ \AA}, \quad \beta = 123.1^\circ.$$

It is derived from the hexagonal cell by the matrix

$$\begin{pmatrix} \vec{a}_m \\ \vec{b}_m \\ \vec{c}_m \end{pmatrix} = \begin{pmatrix} 1 & 2 & 0 \\ -1 & 0 & 0 \\ -\frac{1}{3} & -\frac{2}{3} & \frac{1}{3} \end{pmatrix} \begin{pmatrix} \vec{a}_H \\ \vec{b}_H \\ \vec{c}_H \end{pmatrix}.$$

However, since β is $> 120^\circ$, this also is not a conventional cell. The value of β just prior to the metal-antiferromagnetic insulator (M-AF) transition is 121.3° .

Recently, McWhan and Remeika¹⁰ have completely indexed the powder pattern on the basis of a more reasonable monoclinic cell which is obtained from the hexagonal cell by the matrix

$$\begin{pmatrix} \vec{a}_m \\ \vec{b}_m \\ \vec{c}_m \end{pmatrix} = \begin{pmatrix} \frac{2}{3} & \frac{4}{3} & \frac{1}{3} \\ 1 & 0 & 0 \\ \frac{1}{3} & \frac{2}{3} & -\frac{1}{3} \end{pmatrix} \begin{pmatrix} \vec{a}_H \\ \vec{b}_H \\ \vec{c}_H \end{pmatrix},$$

with

$$a_m = 7.255(3) \text{ \AA}, \quad b_m = 5.002(2) \text{ \AA},$$

$$c_m = 5.548(2) \text{ \AA}, \quad \beta = 96.75(2)^\circ.$$

The most symmetrical space group corresponding to this cell is $I2/a$ with four formula weights per unit cell. This body-centered cell was chosen to describe the structure of the monoclinic phase of V_2O_3 because it appears to be the correct conventional monoclinic cell. The lattice constants and the positional parameters for the distorted structure are generated from the corundum structure as follows:

α -corundum $R\bar{3}c$:

$$V(12c): \pm (0, 0, u; 0, 0, u + \frac{1}{2}) + rh,$$

$$O(18e): \pm (v, 0, \frac{1}{4}; 0, u, \frac{1}{4}; \bar{v}, \bar{v}, \frac{1}{4}) + rh;$$

distorted structure $I2/a$:

$$a_m \approx \frac{1}{3}(12a_H^2 + c_H^2)^{1/2}, \quad b_m \approx a_H, \quad c_m \approx \frac{1}{3}(3a^2 + c^2)^{1/2},$$

$$\beta \approx \langle ([2 \ 4 \ 1][1 \ 2 \ 1]) \rangle = \tan^{-1} \frac{3\sqrt{3} c/a}{6 - (c/a)^2};$$

$$V(8f): \pm (x, y, z; \frac{1}{2} - x, y, \bar{z}) + bc$$

$$\text{with } x = u, \quad y \approx 0, \quad z \approx -2u,$$

$$O(8f): x \approx \frac{1}{4} + v/2, \quad y \approx -v/2, \quad z \approx \frac{1}{2} + v/2,$$

$$O(4e): \pm (\frac{1}{4}, y, 0) + bc, \quad y \approx \frac{1}{2} - v.$$

From the stereographic projection in Fig. 1 (exaggerated for clarity), one can see that three equivalent monoclinic cells can be derived from the parent hexagonal cell, each with its own unique b_H^* axis lying in the basal plane of the hexagonal cell. Since in the distortion the c_H^* axis tilts slightly with respect to the basal plane, a reflection such as the $(116)_H$ splits into three monoclinic reflections arranged in the form of a spherical equilateral triangle, as seen experimentally by McWhan and Remeika.¹⁰ This arrangement has been experimentally confirmed with several different crystals each with their c_H^* axis oriented parallel to the φ axis of the goniostat. For any given hexagonal reflection one may derive the appropriate indexes of the monoclinic reflections by use of the previous matrix as well as the following:

$$\begin{pmatrix} \frac{4}{3} & -\frac{2}{3} & \frac{1}{3} \\ 0 & 1 & 0 \\ -\frac{2}{3} & -\frac{1}{3} & -\frac{1}{3} \end{pmatrix} \text{ and } \begin{pmatrix} \frac{2}{3} & -\frac{2}{3} & \frac{1}{3} \\ -1 & -1 & 0 \\ \frac{1}{3} & -\frac{1}{3} & -\frac{1}{3} \end{pmatrix}.$$

Assuming no external bias and no internal strain,

an ideal crystal should twin in terms of scattering volume precisely $\frac{1}{3} : \frac{1}{3} : \frac{1}{3}$. Actually, we have seen only one crystal in six approach these values.

II. EXPERIMENTAL

X-ray intensity measurements of three V_2O_3 single crystals were taken manually with a General Electric XRD-5 diffractometer. A scintillation counter and a decade scalar were used as the detection system. Single Ni-filtered $Cu K$ radiation was used with an 8° take-off angle. For each set of intensities collected the temperature was maintained at $-(125 \pm 5)^\circ C$ by blowing a cold stream of nitrogen gas directly on the crystal. A Varian control unit was used to monitor and control the proper gas flow. The $(\bar{4}04)_M$ reflection was frequently measured to check temperature, sample orientation, and ice buildup.

Two of the crystals measured were rhombohedra flattened along the c_H axis, while the third crystal was ground into a sphere of radius 0.015 cm. These single crystals were grown by a new technique.¹⁰ They were oriented with their c_H axes parallel with the φ axis of the goniostat. This was the $(\bar{1}10)_H$ direction in the case of the sphere. The procedure for collecting intensities was essentially the same for all samples. For each reflection, the approximate angles 2θ , χ , and φ as calculated by the program MARCAUTOSET were set semiautomatically.¹¹ Once a particular reflection was acquired each angle was then maximized by hand and the intensity measured at the peak height. The background was taken $\pm 2^\circ$ of 2θ off the peak

maximum. Later the background intensities were averaged and subtracted from the maximum value to yield a net intensity. Only those reflections in the upper hemisphere of reciprocal space in the region of $20^\circ \leq 2\theta \leq 103^\circ$ were measured. This set of hkl 's was further reduced to a set containing reflections with $|h - 2l| \geq 3$. For all $|h - 2l| < 3$, the triply twinned reflections could not be resolved, but instead were smeared over one another through a small solid angle of reciprocal space. The total number of well-resolved independent reflections for each of the crystals was 44. For the spherical sample this number was 41. Two sets of data were collected from the spherical sample. One set contained reflections belonging largely to the strongest or most predominant twin while the second set contained reflections belonging to all three twin cells. These latter two sets of data yielded the best individual refinements and their combination was used for the final refinement.

For the plane-faced crystals, two different absorption correction methods were utilized. For one of these, the x-ray absorption program ACAC was used.¹² A purely empirical method, based on structure-factor ratios of room-temperature data, was used for the other sample. The first crystal was 0.022 cm thick with the sides of the pinacoidal triangles measuring 0.053 cm. The second crystal had similar dimensions. The linear-absorption coefficient for V_2O_3 is 813.6 cm^{-1} . Table I lists the values of μ times the linear dimensions for the various samples. For the spherical sample the program XRAY was utilized.¹³ Scattering factors used were those for neutral atoms; $\Delta f'$ and $\Delta f''$ were those for $Cu K\alpha$ radiation.^{14,15} The starting positional parameters for each refinement were derived from the room-temperature hexagonal-cell data previously reported.¹ In each case complete convergence was reached after four cycles of refinement carried out by the program ORFLS.¹⁶

III. RESULTS

Table I lists the results of various least-squares refinements of the low-temperature phase of V_2O_3 . Trial 5 is a refinement of the room-temperature corundum data on the monoclinic cell. The positional parameters of this refinement can be used as a basis of comparison with those of the low-temperature distorted structure. The function minimized in each refinement was $\sum w(|F_{\text{obs}}| - |F_{\text{calc}}|)^2$, where F_{obs} and F_{calc} are the observed and calculated structure factors, and w is the weight for each observation. The value of w for the spherical sample was determined from a plot of ΔF_{obs} versus F_{obs} for all independent reflections. Although there was considerable scatter for large F_{obs} , it was clear that the correct value for w was $1/0.088F_{\text{obs}}$. The statistical residual or weighted and unweighted R

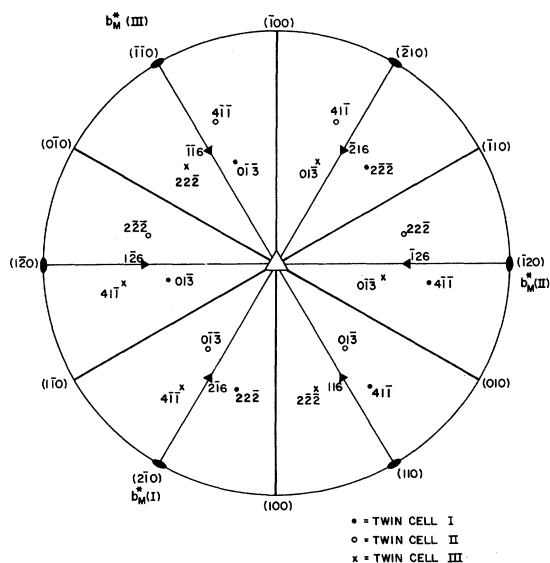


FIG. 1. Stereographic projection of the hexagonal cell and three equivalent monoclinic cells. The splitting of the $\{116\}_H$ into three monoclinic $(I2/a)$ reflections is exaggerated for clarity.

TABLE I. Refinements of V_2O_3 - space group $I2/a$.

Parameters		1	2	3	4	5
Scale	Factor	0.99(2)	6.03(11)	0.68(3)	0.73(3)	0.500(2)
V	x	0.3438(2) ^a	0.3439(3)	0.3450(9)	0.344(1)	0.3463(1)
	y	0.0008(10)	0.0012(12)	0.0021(32)	0.001(5)	0.0001(3)
	z	0.2991(2)	0.2993(3)	0.3000(9)	0.300(1)	0.3074(1)
	β	0.60(12)	0.67(12)	1.55(30)	1.84(27)	0.34(2)
O(1)	x	0.407(1)	0.406(2)	0.410(5)	0.410(5)	0.4058(5)
	y	0.845(2)	0.847(2)	0.850(6)	0.855(8)	0.8439(6)
	z	0.652(2)	0.651(2)	0.645(5)	0.646(6)	0.6556(5)
	β	0.80(19)	0.81(21)	1.77(60)	1.86(76)	0.45(5)
O(2)	x	0.250	0.250	0.250	0.250	0.250
	y	0.309(4)	0.304(5)	0.307(9)	0.299(11)	0.312(1)
	z	0.500	0.500	0.500	0.500	0.500
	β	0.87(28)	0.84(35)	0.60(73)	0.86(87)	0.36(8)
Unweighted R		0.028	0.025	0.087	0.086	0.007
Weighted R		0.036	0.033	0.104	0.090	0.009
μR^b		11.91	11.91	8.9-23.6	~9-24	...

^a0.3438(2) \equiv 0.3438 \pm 0.0002.

^bThis R represents the linear dimension.

values are listed in Table I for each trial. Unweighted R is based on the expression $\sum |F_{obs} - F_{calc}| / \sum F_{obs}$.

The greatest source of error in all trials was the uncertainty in the x-ray absorption coefficients. In the case of the unground crystals, this uncertainty resulted in relatively large standard deviations in positional parameters as well as unrealistic atomic temperature factors. In addition to the problem of deviations from ideal sample shape was that of variation of scattering volume of each twin cell with respect to a specific solid angle of reciprocal space. Apparently lattice strains resulting from the grinding operation caused considerable variation in this volume in the case of the spherical sample. The observed deviations in intensities of reflections belonging to the same crystallographic form were larger for the sphere as compared to the unground crystals. Despite these difficulties it was, nevertheless, possible to obtain relatively good refinements of the vanadium positions as shown in the final refinement (trial 1). It is important to note that the refinement of four independent sets of data resulted in a noticeable decrease in the vanadium z coordinate as compared to trial 5 (corundum data on monoclinic cell). Also, trials 1 and 2 show a statistically significant decrease in the vanadium x coordinate, while the y coordinate remains unchanged. Table II lists the

observed and calculated structure factors for trial 1.

The final refinement positional parameters together with the previously reported lattice pa-

TABLE II. Observed and calculated structure factors for V_2O_3 - space group $I2/a$.

h	k	l	F_0	$ F_c $	h	k	l	F_0	$ F_c $
0	0	2	107.3	108.0	-2	3	3	18.6	17.8
0	0	4	25.3	24.7	-2	4	2	79.5	78.8
0	1	3	117.9	113.5	3	2	3	26.6	25.4
0	1	5	76.4	73.8	-3	2	3	29.9	29.3
0	2	2	109.1	104.6	-4	0	0	90.0	88.6
0	2	4	27.7	26.7	-4	0	2	18.9	19.5
0	3	3	42.0	40.1	-4	0	4	65.1	65.4
-1	1	4	31.2	30.7	-4	1	1	118.9	121.4
-1	4	1	25.4	24.6	-4	1	3	88.5	93.3
-2	0	2	46.1	50.0	-4	2	0	73.8	74.0
2	0	4	38.7	35.7	-4	2	2	11.1	11.2
-2	0	4	94.7	98.7	-4	2	4	20.2	19.9
-2	1	1	102.0	102.3	-4	3	1	45.8	45.8
2	1	3	88.3	90.8	-4	3	3	72.4	73.9
-2	1	3	34.8	32.6	-5	1	2	31.2	30.3
2	1	5	33.5	33.9	5	2	1	24.4	25.1
-2	1	5	15.1	14.7	-6	0	2	72.6	76.9
-2	2	2	118.1	118.2	-6	1	3	24.9	25.0
2	2	4	70.9	71.7	-6	2	0	80.0	83.6
-2	2	4	74.8	78.3	-6	2	2	67.4	70.0
-2	3	1	80.7	79.2					

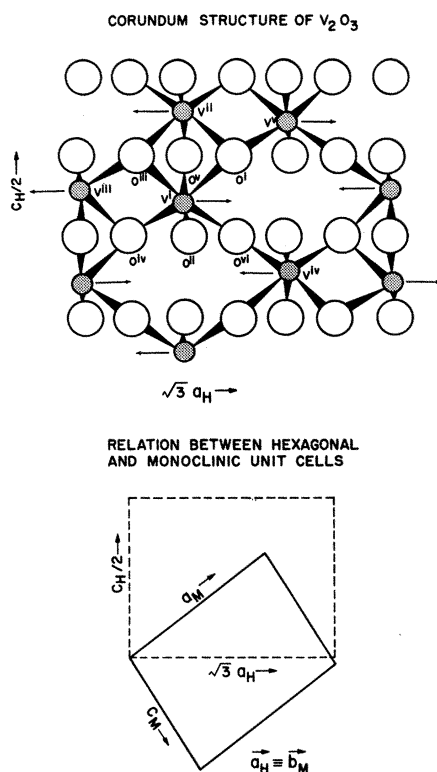


FIG. 2. A projection of the V_2O_3 structure on a plane perpendicular to the $[1\bar{1}0]$ axis. The vanadium atoms are at zero height and the oxygens are above and below the plane. The arrows indicate the direction of translation of the vanadium atoms at the M-AF transition.

rameters¹⁰ were used as input to the interatomic distances program ORFFE.¹⁷ Table III lists these distances and standard deviations as calculated by this program. For comparative purposes the equivalent distances in the corundum structures V_2O_3 and $(V_{0.962}Cr_{0.038})_2O_3$ are also listed. These interatomic distances were calculated by using the room-temperature positional parameters and the low-temperature lattice parameters. The atomic superscripts are those of the atoms in the projection of the corundum structure in Fig. 2.

IV. DISCUSSION

From Table III and Fig. 2 it can be seen that the monoclinic distortion of V_2O_3 involves an expansion of interatomic distances between pairs of vanadium atoms. At the M-AF transition, the $V^i - V^{ii}$ distance across the shared oxygen octahedral face increases from 2.700(1) to 2.745(2) Å. Simultaneously, the distance $V^i - V^{iii}$ across the shared octahedral edge (within the $a_M - c_M$ plane) increases from 2.872(1) to 2.987(4) Å. The $V^i - V^{iii}$ distances between vanadium atoms belonging to the $a_M - c_M$ plane and those belonging to adjacent layers do not appear to change significantly. It is of interest to note that those distances which increase correspond to pairs of vanadium atoms with parallel magnetic spins, whereas those which remain unchanged correspond to pairs with antiparallel spins.⁴ A simple view of the distortion mechanism is that of an abrupt rotation of vanadium pairs within the $a_M - c_M$ plane of approximately 1.8° . The sense of this rotation is such that the vanadium atoms always move toward

TABLE III. Interatomic distances in V_2O_3 .

	Monoclinic		Corundum	
	V_2O_3	V_2O_3	V_2O_3	$(V_{0.962}Cr_{0.038})_2O_3$
$V^i - V^{ii}$	2.745(2)	2.700(1)	2.745(1)	
$V^i - V^{iii}$	2.987(4)	2.872(1)	2.914(1)	
($a-c$ plane)				
$V^i - V^{iii}$	2.861(9)	2.872(1)	2.914(1)	
(adjacent layer)				
$V^i - V^{iii}$	2.876(9)	2.872(1)	2.914(1)	
(adjacent layer)				
$V^i - O^i$	2.028(9)	2.046(1)	2.059(1)	
$V^i - O^v$	2.065(14)	2.046(1)	2.059(1)	
$V^i - O^{iii}$	2.108(12)	2.046(1)	2.059(1)	
$V^i - O^{ii}$	1.989(10)	1.967(1)	1.974(1)	
$V^i - O^{iv}$	1.954(11)	1.967(1)	1.974(1)	
$V^i - O^{vi}$	1.963(11)	1.967(1)	1.974(1)	
$O^i - O^{ii}$	2.84(1)	2.803(1)	2.789(1)	
$O^i - O^{iii}$	2.87(3)	2.664(2)	2.659(2)	
$O^i - O^v$	2.68(2)	2.664(2)	2.659(2)	
$O^{iii} - O^v$	2.68(2)	2.664(2)	2.659(2)	
$O^i - O^{vi}$	2.83(1)	2.890(1)	2.894	
$O^{ii} - O^{vi}$	2.99(3)	2.947(1)	3.001	
$O^{ii} - O^{iv}$	2.99(3)	2.947(1)	3.001	
$O^{iv} - O^{vi}$	2.97(1)	2.947(1)	3.001	

the adjacent octahedral voids (see Fig. 2). In retrospect, the tilting of the c_H axis with respect to the a_M - c_M plane can now be understood in terms of this rotation of vanadium pairs. The pairs can rotate in three equivalent hexagonal-cell directions, e.g., $(1\bar{1}0)$, (010) , and $(\bar{1}00)$. This threefold degeneracy leads to the observed twinning of the monoclinic cell. Simple calculations based on this 1.8° tilt yield interatomic distances within the a_M - c_M plane of approximately 2.74 \AA for $V^i - V^{ii}$ and 2.97 \AA for $V^i - V^{iii}$. These are in good agreement with those from the least-squares refinement.

Although individual V - O distances vary considerably, the average V - O distance to oxygens of the shared octahedral face increases slightly from $2.046(1)$ to $2.07(1) \text{ \AA}$. The average V - O distance to oxygens of the unshared face appears nearly constant since this distance is $1.967(1) \text{ \AA}$ in the corundum structure and $1.97(1) \text{ \AA}$ for the monoclinic one. The overall average V - O distances are $2.007(1)$ and $2.02(1) \text{ \AA}$ for the two structures, respectively.

Unfortunately, it is difficult to make quantitative statements about the distortion of the oxygen octahedron at the M-AF transition since the standard deviations for the O - O distances are quite large. Qualitatively it can be seen that the $O^i - O^{ii}$ shared edge increases, while the $O^i - O^{vi}$ unshared edge decreases when proceeding from the M state to the AF state. By contrast, the distortion of the oxygen octahedron associated with the M-I transition in the Cr_2O_3 - V_2O_3 system is characterized by an umbrella-like expansion of O - O distances of the unshared face and a contraction of these distances in the shared face, while the O - O edges remain nearly constant. A crude picture of the octahedral distortion for the M-AF transition is one in which the octahedron becomes skewed about the cation so as to allow the V - V distances to expand in the a_M - c_M plane while leaving the average V - O distance unchanged. In the case of the M-I transition the octahedron distorts in an umbrella-like fashion

so as to allow all the nearest-neighbor V - V distances to expand while again leaving the average V - O distance nearly unchanged.

For both M-I and M-AF transitions the distortions consist essentially of the expansion of the short metal - metal distances. One would expect from a simple view of a Mott transition that the short V - V distances must necessarily expand resulting in a localization of electrons when proceeding from metal to insulator.¹⁸ The concept of an abrupt rotation of vanadium pairs at the M-AF transition agrees very well with the discontinuous nature of a Mott transition. It should be noted that while the M-I transition is accompanied only by a volume change, the M-AF transition involves both an increase in volume and a change in crystal symmetry.

V. CONCLUSION

It has been observed that the distortion of the corundum structure of V_2O_3 to the insulating antiferromagnetic monoclinic phase at low temperature involves a discontinuous expansion of nearest-neighbor V - V distances in the a_M - c_M plane, while the average V - O distance remains nearly constant. It has also been shown that the triply twinned monoclinic structure is a logical consequence of this distortion. Finally, the expansion of the V - V distances associated with this transition is similar to that of a Mott transition observed in the Cr_2O_3 - V_2O_3 system in which the conduction electrons localize on their ionic sites when proceeding from the metal to insulator.

ACKNOWLEDGMENTS

The authors wish to thank Mrs. R. C. Fulton for programming assistance. We especially thank J. P. Remeika for the excellent crystals, D. B. McWhan and W. H. Zachariassen for many helpful discussions concerning this work, and A. Santoro for helping us choose the conventional monoclinic cell.

¹P. D. Dernier, *J. Phys. Chem. Solids* (to be published).

²D. B. McWhan, T. M. Rice, and J. P. Remeika, *Phys. Rev. Letters* **23**, 1384 (C) (1969).

³E. P. Warekoi, *J. Appl. Phys.* **31**, 346S (1960).

⁴R. M. Moon, *J. Appl. Phys.* **41**, 883 (1970).

⁵K. Kosuge, *J. Phys. Chem. Solids* **28**, 1613 (1967).

⁶E. D. Jones, *Phys. Rev.* **137**, A978 (1965).

⁷J. B. Goodenough, *Magnetism and the Chemical Bond* (Interscience, New York, 1963).

⁸J. Feinleib and W. Paul, *Phys. Rev.* **155**, 841 (1967).

⁹S. C. Abrahams, *Phys. Rev.* **130**, 2230 (1963).

¹⁰D. B. McWhan and J. P. Remeika, Paper I in this series, *Phys. Rev. B* **2**, 3734 (1970).

¹¹M. Zocchi, *Natl. Bur. Std. (US)*, 1966 (unpublished).

¹²R. C. Fulton, *Bell Telephone Laboratories*, 1968 (unpublished).

¹³B. J. Wuensch and C. T. Prewitt, *Z. Krist.* **122**, 24 (1965).

¹⁴E. T. Cromer and J. T. Waber, *Acta Cryst.* **18**, 104 (1965).

¹⁵E. T. Cromer, *Acta Cryst.* **18**, 17 (1965).

¹⁶W. R. Busing, K. O. Martin, and H. A. Levy, ORNL Report No. TM-305, 1962 (unpublished).

¹⁷W. R. Busing and H. A. Levy, ORNL Report No. 59-12-13, 1959 (unpublished).

¹⁸N. F. Mott, *Proc. Roy. Soc. (London)* **62**, 416 (1949).