Band Structure and Lattice Distortion in V_2O_3

I. Nebenzahl and M. Weger
The Hebrew University, Jerusalem, Israel

(Received 6 January 1969)

A model for the band structure of a hexagonal (beehive) lattice in the tight-binding approximation is examined. The stability of the structure against distortions and the effects of distortions in splitting bands are investigated. The relationship of this model to the theory of Adler and Brooks for the metal-insulator transition of V_2O_3 is discussed. It is shown that this model can account for a transition from a distorted, insulating state to an undistorted, semimetallic one, for certain values of the d-d interaction integrals. The distortion does not double the size of the unit cell; therefore, the gap appears at the point $\mathbf{k}=0$, rather than half way to the zone boundary.

I. INTRODUCTION

The compound V_2O_3 undergoes a phase transition from metal to semiconductor when cooled below 150°K.[1] At the same time, there occurs a lattice distortion from the corundum structure to monoclinic (see Fig. 1). It was suggested in Ref. 1 that the metal-to-semiconductor transition may be a result of the lattice distortion. This may be seen in analogy with the case of a linear chain of equally spaced hydrogen atoms. Such a chain would normally constitute a metal, for each unit cell contains only one electron but two permitted states (up and down spin), so that there is a half-filled s band. But if the lattice is distorted in the manner shown in Fig. 2, the unit cell will contain two atoms; as a result two bands will be formed, with an energy gap between them, and the substance will become insulating. Now the analogy to the case of V_2O_3 is not complete, since in that case each unit cell contains four vanadium atoms both in the corundum and in the monoclinic states. It can be questioned whether in the case of V_2O_3 lattice distortion produces an energy gap at all. It is the purpose of the present paper to find the conditions under which this is so, and also to discuss the plausibility of such an explanation of the phase transition.

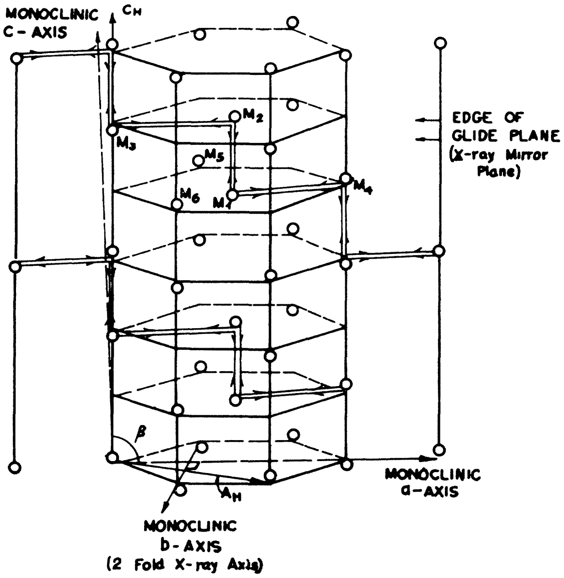


FIG. 1. Structure of V_2O_3 (only V ions are shown). Arrows indicate the lattice distortion occurring at the phase transition. (Figure taken from Ref. 1).

II. BAND STRUCTURE FOR THE UNDISTORTED LATTICE

The arrangement of the vanadium ions in each basal plane, together with the surrounding oxygens, is shown in Fig. 3. The small noncoplanarity which can be seen in Fig. 1 is neglected in the present paragraph (its importance will be made clear in the following). Each V^{+3} ion is assumed to be located at the middle of an octahedron of oxygens (see also Fig. 4).

Two assumptions will now be made, which seem to be quite generally accepted when dealing with oxides of transition metals,[2] namely, that the conductivity of the compound is due to the two d electrons localized on each V^{+3} ion, and that the ligand-field splitting is much larger than any interaction between the metallic ions.[3] Thus, it will be assumed in the following that the two d electrons may occupy only the orbitals d_{xy}, d_{xz}, and d_{yz} (Fig. 4), but not d_{z^2} and d_{x^2},d_{y^2}, and the bands of interest for us will only be formed out of these orbitals.

FIG. 2. Linear chain of atoms and the directions giving a possible lattice distortion.

---

[1] D. Adler and H. Brooks, Phys. Rev. **155**, 826 (1967); J. Feinleib and W. Paul, *ibid.* **155**, 841 (1967); D. Adler, J. Feinleib, H. Brooks, and W. Paul, *ibid.* **155**, 851 (1967). These papers include a comprehensive review of previous experimental work on V_2O_3. See also D. Adler, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic Press, Inc., New York, 1968), Vol. 21, p. 1.

[2] J. Goodenough, *Magnetism and the Chemical Bond* (Interscience Publishers, Inc., New York, 1963).

[3] The interaction between the vanadium ions may be direct, due to d-d overlap, or indirect, due to overlap with the oxygen orbitals; but it is assumed that the oxygen $2s$ and $2p$ bands are sufficiently low and do not overlap the vanadium d band. This last point is critically discussed by J. Friedel, Bull. Soc. Chim. Fran. **4**, 1186 (1965). Without making this assumption, it will be more difficult to explain the effect of lattice distortion on the conductor-insulator transition.

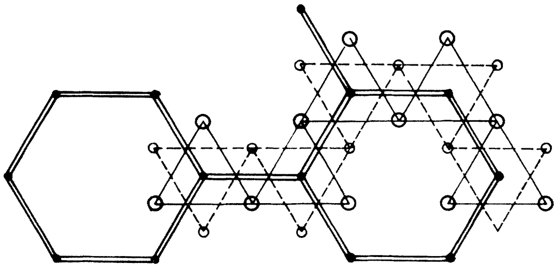


FIG. 3. Arrangement of vanadium ions (full circles) in the basal planes of V_2O_3, together with surrounding oxygens above (large open circles) and below (small open circles) the plane. Each V^{+3} ion is very near the middle of an octahedron of O^{-2} ions; neighboring octahedra share a common edge.

Let us make the following transformation:

$$\begin{aligned}f_1&=(1/\sqrt{2})(d_{xy}-d_{yz})=(\sqrt{\tfrac{2}{3}})d_{\xi\eta}+(\sqrt{\tfrac{1}{3}})d_{\xi\zeta},\\ f_2&=(\sqrt{\tfrac{2}{3}})[d_{xz}-\tfrac{1}{2}(d_{xy}+d_{yz})]=(\sqrt{\tfrac{2}{3}})d_{\eta^2-\xi^2}-(\sqrt{\tfrac{1}{3}})d_{\eta\zeta}, \quad (1)\\ f_3&=(1/\sqrt{3})(d_{xy}+d_{xz}+d_{yz})=d_{\zeta^2}.\end{aligned}$$

A further assumption will now be made. As the distance between vanadium ions is shorter in the c direction than in the basal plane (2.70 and 2.88 Å, respectively), the functions f_3 will form their own bands, corresponding to bonding and antibonding states of pairs of electrons localized on c-axis neighboring sites. This reflects, in our view, Goodenough's theory[2] of noncooperative c-axis bonding, in which one electron per V ion takes part. In the following, therefore, only the other electron on the V ion will be dealt with; it will be allowed to occupy the states f_1 and f_2 only.

Let us now define the following integrals between the wave functions (see Fig. 5):

$$\begin{aligned}\alpha&=-\int f_1(a_0)Vf_1(b_0)d^3x,\\ \beta&=\int f_2(a_0)Vf_2(b_0)d^3x,\\ \gamma&=\int f_1(a_0)Vf_1(b_1)\,d^3x, \quad (2)\\ \delta&=-\int f_2(a_0)Vf_2(b_1)d^3x,\\ \epsilon&=-\int f_1(a_0)Vf_2(b_1)d^3x,\end{aligned}$$

where V is the one-electron potential of each of the ions. Overlap between functions on different ions will be neglected, except for its role in giving rise to exchange interaction.[4]

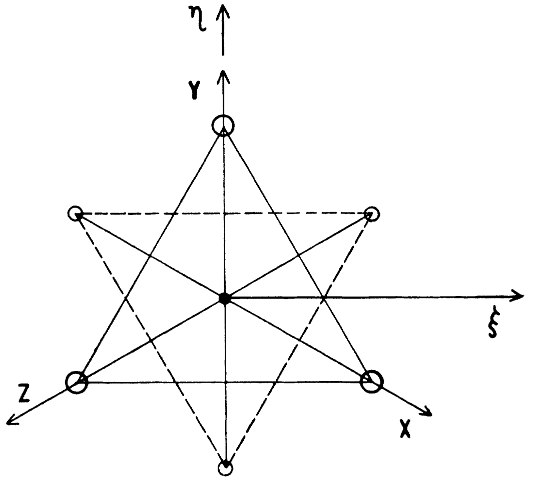


FIG. 4. Coordinates used to specify atomic wave functions. X, Y, Z connect the V^{+3} at the center of the octahedron with three oxygens, while ξ, η lie in the plane of the drawing. ζ is perpendicular to that plane.

Because of the threefold symmetry of the honeycomb lattice of Fig. 5, connections can be found between the integrals.[2] This is done by defining functions rotated by 120° :

$$f_1'=-\tfrac{1}{2}f_1-\tfrac{1}{2}\sqrt{3}f_2, \quad f_2'=\tfrac{1}{2}\sqrt{3}f_1-\tfrac{1}{2}f_2,$$

so that

$$\gamma=\int f_1(a_0)Vf_1(b_1)d^3x=\int[-\tfrac{1}{2}f_1'(a_0)+\tfrac{1}{2}\sqrt{3}f_2'(a_0)]$$
$$\times V[-\tfrac{1}{2}f_1'(b_1)+\tfrac{1}{2}\sqrt{3}f_2'(b_1)]d^3x=-\tfrac{1}{4}\alpha+\tfrac{3}{4}\beta, \quad (3a)$$

and, similarly,

$$\delta=\tfrac{3}{4}\alpha-\tfrac{1}{4}\beta, \quad (3b)$$

$$\epsilon=\tfrac{1}{4}\sqrt{3}(\alpha+\beta). \quad (3c)$$

Thus, there are only two free parameters, α and β.

The plane honeycomb structure of Fig. 5 contains two vanadium ions per unit cell, which we shall take to be a_0 and b_0, a_1 and b_1, etc. (The unit cell of the full three-dimensional corundum structure contains four

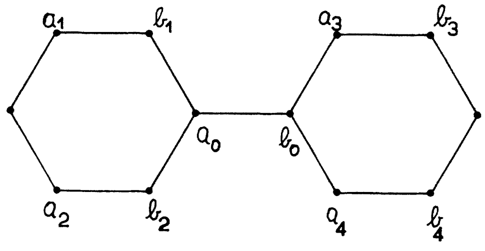


FIG. 5. Unit cell containing V ions a_0b_0, together with the four neighboring unit cells connected to a_0, b_0 by nonvanishing transfer integrals.

---

[4] The interaction integrals may be due to indirect coupling via the oxygen ions; however; this does not change the considerations based on the symmetry of the lattice.

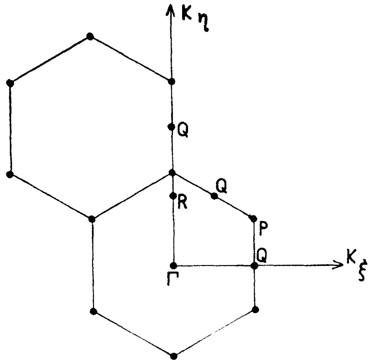


FIG. 6. Momentum plane and the boundaries of the Brillouin zone. Along k_ξ, the boundary is at $X=\frac{3}{2}ak_\xi=\pi$, and along k_η at $Y=\frac{1}{2}\sqrt{3}ak_\eta=\frac{2}{3}\pi$.

vanadium ions.) In each cell there are four atomic functions which will be denoted by

$$\phi_1=f_1(a_0)\,,\quad \phi_2=f_1(b_0)\,,$$
$$\phi_3=f_2(a_0)\,,\quad \phi_4=f_2(b_0)\,.$$

In the tight-binding approximation, Bloch wave functions are formed as

$$\Psi_n(\mathbf{k})=\frac{1}{\sqrt{N}}\sum_{j=0}^{N}\phi_n(\mathbf{a}_j)e^{i\mathbf{k}\cdot\mathbf{a}_j},\quad n=1,\cdots,4. \tag{4}$$

With the aid of the integrals (2), the 4×4 matrix of the interaction between the $\Psi_n(\mathbf{k})$ can immediately be written

$$V=(\langle\Psi_i|V|\Psi_j\rangle)=\begin{bmatrix} 0 & -\alpha+2\gamma e^{iX}\cos Y & 0 & 2i\epsilon e^{iX}\sin Y \\ -\alpha+2\gamma e^{-iX}\cos Y & 0 & -2i\epsilon e^{-iX}\sin Y & 0 \\ 0 & 2i\epsilon e^{iX}\sin Y & 0 & \beta-2\delta e^{iX}\cos Y \\ -2i\epsilon e^{-iX}\sin Y & 0 & \beta-2\delta e^{-iX}\cos Y & 0 \end{bmatrix}, \tag{5}$$

where $X=\frac{3}{2}ak_\xi$, $Y=\frac{1}{2}\sqrt{3}ak_\eta$, and a is the interionic distance.

The Brillouin zone in the XY plane is shown in Fig. 6. The point P may be given as $X=\pi$, $Y=\frac{1}{3}\pi$ or, alternatively, as $X=0$, $Y=\frac{2}{3}\pi$. Similarly, Q is given by $X=\pi$, $Y=0$, or by $X=Y=\frac{1}{2}\pi$, or by $X=0$, $Y=\pi$. We also define the point R by $X=0$, $Y=\frac{1}{2}\pi$.

The characteristic equation of the matrix (5) is

$$\lambda^4-\lambda^2(|a|^2+|b|^2+2|c|^2)+|c|^4+ab\bar{c}^2+\bar{a}\bar{b}c^2+|ab|^2=0, \tag{6}$$

where

$$a=\alpha-2\gamma e^{iX}\cos Y,\quad b=\beta-2\delta e^{iX}\cos Y,$$
$$c=2i\epsilon e^{iX}\sin Y. \tag{7}$$

Solutions of Eq. (6) were calculated for $\mathbf{k}$ lying on special symmetry lines—the X axis, the Y axis, and also the line $Y=\frac{1}{2}\pi$ connecting R and Q. Results are shown in Fig. 7. α and β were varied only over a restricted zone in the $\alpha\beta$ plane (Fig. 8), since other zones may be reached by the transformations $\alpha\rightarrow\beta$, $\beta\rightarrow\alpha$ or $\alpha\rightarrow-\alpha$, $\beta\rightarrow-\beta$, which do not change the form of the energy bands. The values of γ, δ, and ϵ are fixed by Eqs. (3a)-(3c).

Each of the four bands has space for two electrons per unit cell (with spin up or down). As there are two electrons per unit cell to be put into the bands, only one band is filled and three remain empty. The material will then be metallic in the cases corresponding to Figs. 7(a), 7(e), and 7(f), and semimetallic in 7(b), 7(c), and 7(d). Clearly a necessary, but not sufficient, condition for the material to transform from conducting to insulating under *infinitesimal* lattice distortion is that it be in a semimetallic state when undistorted. This conclusion is a result of the fact that the distortions here discussed do not change the number of atoms per unit cell, and therefore do not split the bands but possibly separate them near $\mathbf{k}=0$.

The values of α and β that give rise to a semimetallic state can be shown to be determined by the conditions

$$\operatorname{sgn}\alpha=\operatorname{sgn}\beta, \tag{8a}$$

$$\text{either }|\alpha|\geq3|\beta|\quad\text{or}\quad|\alpha|\leqslant\tfrac{1}{3}|\beta|\,. \tag{8b}$$

[Cf. the shaded areas in Fig. 8. It must be remarked, however, that the necessary conditions (8a) and (8b) were checked to be sufficient to ensure the formation of a semimetal only along the symmetry lines.]

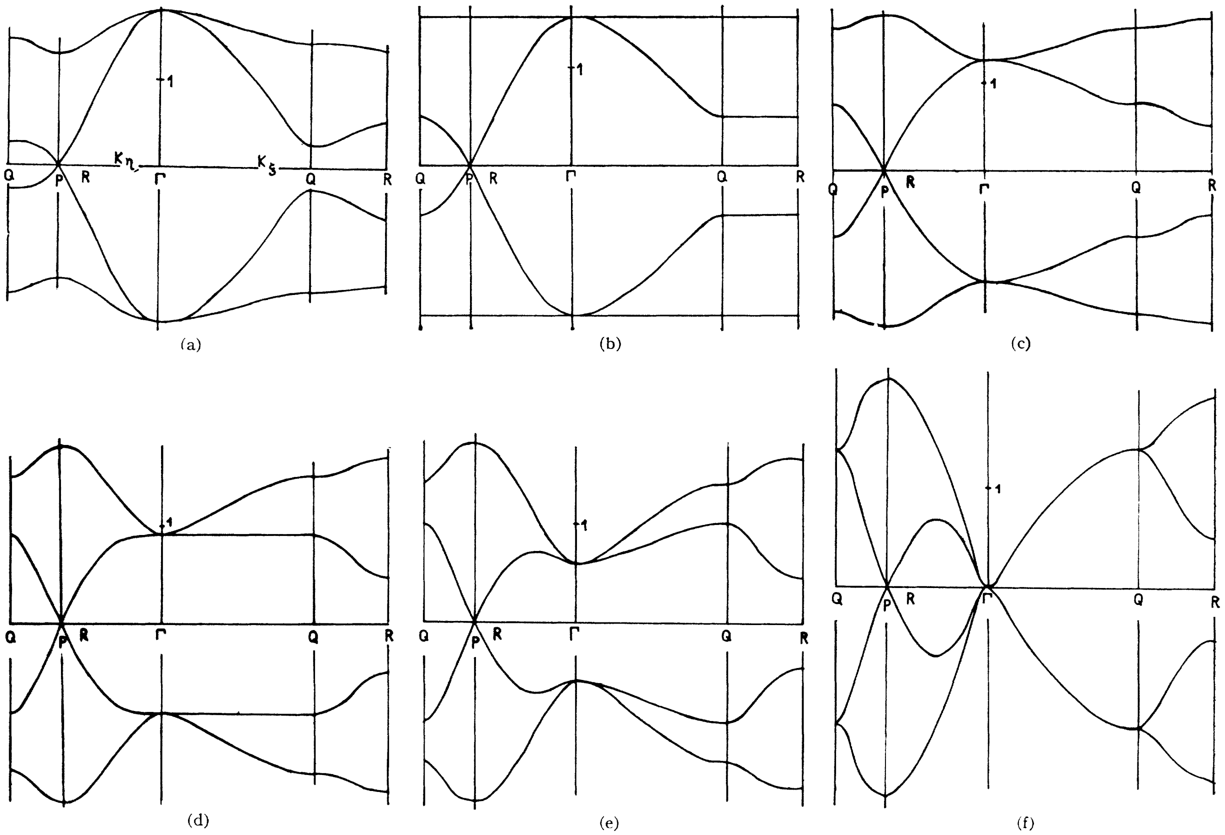
The condition stated above for the formation of an insulator corresponds only to an infinitesimal distortion (a finite one may change the whole pattern of band structure). Whether the distortion occurring in V_2O_3 at the transition (of about 2% of the interionic distance) may be termed infinitesimal or not is, of course, a question we cannot answer. This raises the more difficult question whether or not such a small distortion can be expected to produce an energy gap of the same order of magnitude (0.1 eV) as the bandwidth itself, as is suggested by Adler and Brooks.[1]

III. LATTICE DISTORTIONS

Two types of lattice distortions take place in V_2O_3:

(a) The distances a_0-b_0, a_1-b_1, etc. (Fig. 5) get shorter than a_0-b_1, a_0-b_2, etc. This is the distortion occurring at the phase transition.

(b) The atoms a_0, a_1, a_2, etc. are somewhat above the plane of the drawing (Fig. 5), atoms b_0, b_1, b_2, etc., somewhat below. This distortion is present both below and above the transition temperature.



(a) (b) (c) (d) (e) (f)

FIG. 7. Band structure for various α and β; (a) $\alpha=-0.15$, $\beta=0.9$; (b) $\alpha=0$, $\beta=1$; (c) $\alpha=0.15$, $\beta=0.9$; (d) $\alpha=0.3$, $\beta=0.9$; (e) $\alpha=0.4$, $\beta=0.8$; and (f) $\alpha=0.7$, $\beta=0.7$.

As a result of the distortion (a) the matrix (5) remains unchanged in its form, but the relations (3) connecting γ, δ, and ϵ to α and β are violated.

Figures 9(a)–9(c) give the band structure for a distorted lattice. They were calculated from the characteristic equation (6), with and without use of the relations (3). This represents the effect of a slight distortion on the case given in Fig. 7(c). As is seen from Figs. 9(b) and 9(c), there occurs a splitting at the point Γ, but the bands are not separated. Instead, a point of conical singularity is formed.

More generally, it can be shown that the characteristic equation (6) has a degenerate root (concial singularity) either along the X direction or along the Y direction. The roots of Eq. (6) are given by

$$\lambda^2=\tfrac{1}{2}(|a|^2+|b|^2)+|c|^2 \pm[(\tfrac{1}{2}(|a|^2-|b|^2))^2+|a\bar{c}-\bar{b}c|^2]^{1/2}, \quad (9)$$

so that there occurs a degeneracy if

$$|a|=|b| \quad \text{and} \quad a\bar{c}=\bar{b}c. \quad (10)$$

The condition (10) is satisfied for a point along the X axis such that

$$\cos X=\frac{\alpha^2-\beta^2+4\gamma^2-4\delta^2}{4\alpha\gamma-4\beta\delta} \quad (11a)$$

and a point along the Y axis such that

$$\cos Y=(\alpha+\beta)/2(\gamma+\delta). \quad (11b)$$

Condition (10) cannot be satisfied for a point that is neither on the X axis nor on the Y axis (for an infinitesimal distortion). To see this, note that $\mathrm{Re}(a\bar{c}-\bar{b}c) =2(\beta-\alpha)\epsilon\sin X\sin Y\neq 0$.

When the distortion occurs, let us assume that γ and δ remain unchanged, but α and β change; thus Eqs. (3a) and (3b) are violated. Then it can easily be shown that if α and β [or even the one of them much larger than the other, according to Eq. (8b)] get larger in absolute value, the right-hand side of Eq. (11a) is smaller than unity, so that there is a degenerate point along the X axis. Similarly, if α and β get smaller in

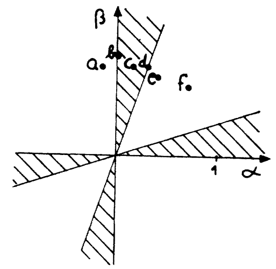


FIG. 8. α-β plane. Dots correspond to values for which the band structure is given in Figs. 7. The shaded areas indicate values of α, β for which the metrial is semimetallic.

absolute value, then the right-hand side of Eq. (11b) is smaller than unity and the degenerate point lies on the Y axis [cf. Fig. 9(b) and 9(c)].

In both cases the distortion does not give way to the formation of an energy gap, but merely to a change from one type of a semimetal (bands touching at a point where $dE/d\mathbf{k}=0$) to another (bands touching at a conical singularity). This conclusion is changed, however, in the presence of a distortion of type (b). This has the effect that the integral

$$\chi=\int f_1(a_0)Vf_2(b_0)d^3x\neq 0\,, \qquad (12)$$

and also that the integrals γ, δ, and ϵ defined in Eq. (2), have different values for the pair of neighbors a_0, b_1 than for the pair a_0, b_2.

Let us therefore define

$$\gamma=\tfrac{1}{2}\int f_1(a_0)Vf_1(b_1)d^3x+\tfrac{1}{2}\int f_1(a_0)Vf_1(b_2)d^3x\,,$$

$$g=\tfrac{1}{2}\int f_1(a_0)Vf_1(b_1)d^3x-\tfrac{1}{2}\int f_1(a_0)Vf_1(b_2)d^3x\,,$$

$$\delta=-\tfrac{1}{2}\int f_2(a_0)Vf_2(b_1)d^3x-\tfrac{1}{2}\int f_2(a_0)Vf_2(b_2)d^3x\,,$$

$$t=-\tfrac{1}{2}\int f_2(a_0)Vf_2(b_1)d^3x+\tfrac{1}{2}\int f_2(a_0)Vf_2(b_2)d^3x\,,$$

$$\epsilon=-\tfrac{1}{2}\int f_1(a_0)Vf_2(b_1)d^3x+\tfrac{1}{2}\int f_1(a_0)Vf_2(b_2)d^3x\,,$$

$$h=-\tfrac{1}{2}\int f_1(a_0)Vf_2(b_1)d^3x-\tfrac{1}{2}\int f_1(a_0)Vf_2(b_2)d^3x\,.$$

In a procedure similar to that leading to Eqs. (3a)–(3c), it can then be shown that, in the absence of distortion (a) (i.e., threefold symmetry conserved),

$$\begin{aligned} \gamma&=-\tfrac{1}{4}\alpha+\tfrac{3}{4}\beta\,, & g&=-\tfrac{1}{2}\sqrt{3}\chi\,,\\ \delta&=\tfrac{3}{4}\alpha-\tfrac{1}{4}\beta\,, & t&=-\tfrac{1}{2}\sqrt{3}\chi\,,\\ \epsilon&=\tfrac{1}{4}\sqrt{3}(\alpha+\beta)\,, & h&=\tfrac{1}{2}\chi\,, \end{aligned} \qquad (13a)$$

where χ is defined in Eq. (12), so that there is only one new parameter. If now distortion (a) is introduced as well as distortion (b), then Eqs. (13) are violated, but the parameters are still connected by

$$\epsilon=\tfrac{1}{2}\sqrt{3}(\gamma+\delta)\,, \quad g=t\,, \quad h=-g/\sqrt{3}\,. \qquad (13b)$$

The matrix (5) now takes the form

$$V=(\langle\Psi_i|V|\Psi_j\rangle)$$
$$=\begin{pmatrix} 0 & -\alpha+2\gamma e^{iX}\cos Y-2ige^{iX}\sin Y & 0 & 2i\epsilon e^{iX}\sin Y+\chi-2he^{iX}\cos Y\\ -\alpha+2\gamma e^{-iX}\cos Y+2ige^{-iX}\sin Y & 0 & -2i\epsilon e^{-iX}\sin Y+\chi-2he^{-iX}\cos Y & 0\\ 0 & 2i\epsilon e^{iX}\sin Y+\chi-2he^{iX}\cos Y & 0 & \beta-2\delta e^{iX}\cos Y+2ite^{iX}\sin Y\\ -2i\epsilon e^{-iX}\sin Y+\chi-2he^{-iX}\cos Y & 0 & \beta-2\delta e^{-iX}\cos Y-2ite^{-iX}\sin Y & 0 \end{pmatrix}. \qquad (14)$$

The characteristic equation (6) and its solution (9) retain their forms, but, instead of (7), one has now

$$\begin{aligned} a&=\alpha-2\gamma e^{iX}\cos Y+2ige^{iX}\sin Y\,,\\ b&=\beta-2\delta e^{iX}\cos Y+2ite^{iX}\sin Y\,,\\ c&=2i\epsilon e^{iX}\sin Y+\chi-2he^{iX}\cos Y\,. \end{aligned} \qquad (15)$$

It can now be shown that in the presence of both distortions (a) and (b) an energy gap is formed. In order to prove this, one has to show that the two conditions for degeneracy, Eq. (10), cannot hold simultaneously. The equality $a\bar{c}=\bar{b}c$ holds at two points [at the intersections of the curves $\mathrm{Re}(a\bar{c}-\bar{b}c)=0$ and $\mathrm{Im}(a\bar{c}-\bar{b}c)=0$], and the location of these points depends on the value of χ, whereas the curve on which $|a|=|b|$ is independent of χ; thus, in the general case, the points do not lie on the curve $|a|=|b|$ unless there is an accidental connection between the values of the parameters for a certain value of the distortion. Unless this happens, at the point where $a\bar{c}-\bar{b}c=0$ one has $|a|\neq|b|$. Therefore, at these points $c=0$ (this can also be shown directly), but there is no degeneracy. [For a numerical example, see Figs. 9(e) and 9(f). Note that there is a certain symmetry between Figs. 9(e) and 9(f), so that the model does not explain why the distortion is such that the distance to one neighbor gets shorter than the distance to the other two—Fig. 9(e)—and not larger—Fig. 9(f).]

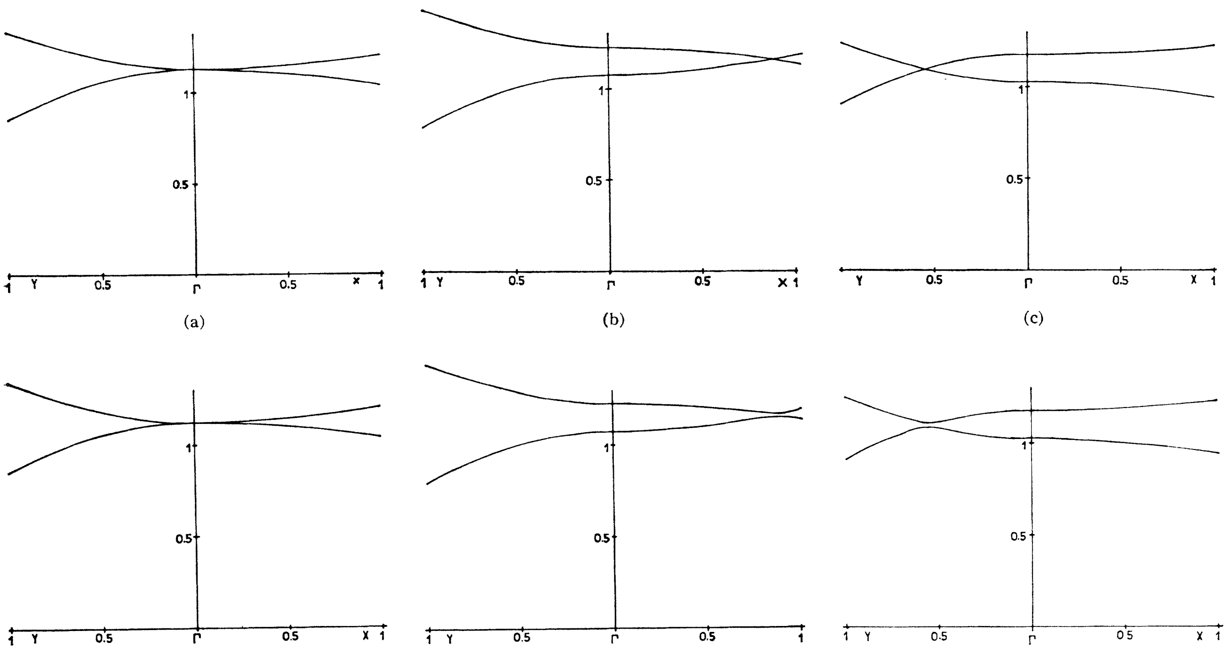
IV. CONCLUSION

For a lattice distortion not involving a change in the number of atoms per unit cell, a necessary condition was found for its causing a conductor to insulator transition, namely, that the conducting state be semimetallic. This does not apply to the case of VO_2, for instance, where the distorted unit cell is twice as large as the undistorted one.[5]

The necessary condition is not a sufficient one, and it was found that only the combined effect of two sorts of lattice distortions can explain the conductivity transition of V_2O_3. The complexity of the explanation gives

---

[5] T. Kawakubo, J. Phys. Soc. Japan **20**, 4, 516 (1965).



(a) (b) (c)

(d) (e) (f)

FIG. 9. Effect of lattice distortion on the semimetal of Fig. 7(c) (a detail of the band structure, near the point Γ); (a) $\alpha=0.15$, $\beta=0.9$, $\gamma=0.6357$, $\delta=-0.1125$, $\epsilon=0.455$, $\chi=0$, $g=0$, $h=0$ [no distortion; same as Fig. 7(c)]; (b) $\alpha=0.2$, $\beta=1$, $\gamma=0.6375$, $\delta=-0.1125$, $\epsilon=0.455$, $\chi=0$, $g=0$, $h=0$ [distortion (a)]; (c) $\alpha=0.1$, $\beta=0.8$, $\gamma=0.6375$, $\delta=-0.1125$, $\epsilon=0.455$, $\chi=0$, $g=0$, $h=0$ [distortion (a), reversed sense]; (d) $\alpha=0.15$, $\beta=0.9$, $\gamma=0.6375$, $\delta=-0.1125$, $\epsilon=0.455$, $\chi=0.1$, $g=-0.0867$, $h=0.05$ [distortion (b) alone]; (e) $\alpha=0.2$, $\beta=1$, $\gamma=0.6375$, $\delta=-0.\ 1125$, $\epsilon=0.455$, $\chi=0.12$, $g=-0.0867$, $h=0.05$, [both distortions (a) and (b)]; and (f) $\alpha=0.1$, $\beta=0.8$, $\gamma=0.6375$, $\delta=-0.1125$, $\epsilon=0.455$, $\chi=0.08$, $g=-0.0867$, $h=0.05$ [both distortions; (a) reversed].

rise to questions concerning the set of assumptions used from the outset. In particular, the itinerant electron picture may be doubtful for dealing with oxides of transition metals. This leads one naturally to seek the explanation of the phase transformation in the concept of Mott transition,[6] which amounts to breakdown of the itinerant electron picture and establishment of localized electron states. In this connection it is interesting to note that a transition similar to that of V_2O_3 occurs also in materials such as Ti_3O_5, where the number of *d* electrons per cation is not integral,[7] so the Mott explanation cannot be applicable to these materials—at least in its simplest form.

Another theory often mentioned in connection with transition-metal oxides is that due to Goodenough[2] (see also Asbrink and Magneli[8]). It is assumed that at low temperature the *d* electrons are occupied in some sort of "cation-cation bond." This is, in fact, not an explanation but an approach towards a set of possible explanations. One of these, in terms of itinerant electrons, is described in the present work (see also Ref. 5). Another one, aimed at understanding the nature of the insulating phase in terms of localized states, was developed in a previous work.[9] Both attempts lead to very complicated explanations, which shows how far we still are from comprehending the phase transition.

ACKNOWLEDGMENT

The authors thank Professor J. Friedel, Professor S. Alexander, and Professor W. Paul for most stimulating discussions.

---

[6] N. F. Mott, Phil. Mag. **6**, 287 (1961).

[7] L. K. Keys and L. N. Mulay, Appl. Phys. Letters **9**, 248 (1966).

[8] S. Asbrink and A. Magneli, Acta Cryst. **12**, 575 (1959).

[9] I. Nebenzahl, Phys. Rev. **177**, 1001 (1969).