

Interpretation of $M_xV_2O_5-\beta$ and $M_xV_{2-y}T_yO_5-\beta$ Phases

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The Wadsley $Na_{0.33}V_2O_5-\beta$ structure is reexamined to demonstrate how the detailed atomic positions provide important information about the physical properties. After a review of the evidence for identifiable V^{4+} ions, it is shown how, from the bond distances, to distinguish triple, double and single V-O bonding with the d orbitals. From this analysis, it follows that the x electrons donated to the vanadium-oxygen array by M^+ ions are located in the d_{yz} orbitals at positions V_1 . Furthermore, consistency with the known properties of other vanadium oxides requires that the linear units $V_2-O_1-V_2$ form molecular d -state orbitals. It is noted that this changes the statistics entering the conventional formula for the small-polaron contribution to the Seebeck coefficient. Finally, the creation of a similar $V_3-O_7'-V_3$ d -state molecular unit is postulated for each M^+ ion that is introduced. It is argued that this analysis is supported by the following experimental results: (1) In the system $Na_xV_{2-x}Mo_xO_5-\beta$, the Mo atoms all go into V_2 positions if $x \leq 0.33$, but for $x > 0.33$ the V_2 positions contain $(1/2) Mo + (1/2) V$, presumably as $Mo^{6+}-O_1-V^{4+}$ units, and the excess $(x - 0.33)$ Mo atoms per formula unit occupy V_3 positions. (2) The Seebeck coefficient is accounted for without any adjustable parameter provided the linear units $V_2-O_1-V_2$ and one $V_3-O_7'-V_3$ per M^+ ion are counted as single available sites for small-polaron hopping. (3) Variation with x of the activation energy for electron hopping and of the magnetic susceptibility per small polaron extrapolate to collective-electron values for $x > 0.67$, which is consistent with a band of collective-electron orbitals of a V_3-O_7' array overlapping the energy of the d_{yz} orbitals at V_1 sites for larger values of x . (4) The V_1-V_1' separation is too large for a small activation energy for conduction within the V_1 sublattice, but the large anisotropy for conductivity would also be consistent with conduction via the V_3-O_7' array. (5) The structure of $Cu_{0.60}V_2O_5$, which has the lower symmetry Cm , has atomic separations consistent with half of the V_1 sites of the Wadsley phase (symmetry $C2/m$) donating electrons to half the Wadsley V_3-O_7' array. (6) The activation energy for conduction increases with y in the system $Na_{0.40}V_{2-y}Mo_yO_5-\beta$. (7) The magnetic data is reviewed and, although not quantitatively accounted for because the magnetic properties of the excited states are not known, is shown to be consistent with a V^{4+} ground state having its outer electron in the d_{yz} orbital of a V_1 site.

I. Introduction

As early as 1880, Hautefeuille (1) noted that upon slowly cooling molten acid vanadates of the lighter alkali metals through the freezing point, solidification was accompanied by a brisk oxygen evolution. He called the compounds "vanadyl vanadates" to signal the simultaneous presence of V^{4+} and V^{5+} ions. Subsequently, several distinct phases were observed (2), and an initial study (3) and (4) of the three-component phase diagrams of lithium, sodium, and silver oxide with V_2O_5 and V_2O_4 identified, besides V_2O_5 and the metavanadate

M^+VO_3 , the three additional phases $M_xV_2O_5-\alpha$, $M_xV_2O_5-\beta$, and $M_{1+y}V_3O_8$. Wadsley (5) determined the structures of both the β -phase and the $M_{1+y}V_3O_8$ phase. This structural determination provided not only further incentive to study the physical properties of these phases, but also the basis for the interpretation of their properties. However, until now too little attention has been given to the information available in the structural details originally provided by Wadsley, and this has made interpretation of the physical properties both speculative and, in some cases, inconsistent with physical ideas that have been established for other vanadium compounds having simpler structures. The purposes of this paper are (1) to call attention to the physical information contained in these details, (2) to show how the

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position of the V^{4+} ion—and the precise occupied d orbital—can be obtained from a knowledge of the structural details, (3) to show that molecular subunits can be identified within the structure, and (4) to indicate how the existence of molecular subunits must influence the Seebeck coefficient. Data on some mixed systems $M_x^+V_{2-y}T_yO_{5-\beta}$ (with $T = Mo, W$ and $M = Li, Na$) are shown to provide independent support for the site-preference energies of the V^{4+} ions and for the existence of molecular subunits. The magnetic susceptibility is also discussed from the point of view of this model.

II. Location of the V^{4+} Ions

A. Evidence for Small-Polaron Charge Carriers

The Wadsley $Na_{0.33}V_2O_5-\beta$ structure is shown in Fig. 1. Ozerov (6) was the first to report single-crystal resistivities of the β -phase oxides. His room-temperature resistivities for $Na_xV_2O_5-\beta$ parallel and perpendicular to the b axis were $\rho_b = 4.6 \times 10^{-2} \Omega \text{ cm}$ and $\rho_{ac} = 29 \Omega \text{ cm}$. Because of the large anisotropy favoring conductivity parallel to the tunnel axis, he assumed that the high conductivity was due to electrons in alkali-metal bands. However, it is chemically unsound to anticipate neutral sodium atoms in the presence of V^{5+} ions, and considerable evidence is now available (7) indicating that in such compounds the alkali-metal atoms donate their electrons to d -like orbitals of the covalent network of transition-metal atoms and oxygen atoms. In some systems, such as the tungsten bronzes Na_xWO_3 , these electrons partially fill a band of collective d -like states, the compounds exhibiting metallic properties

and a measurable Fermi surface. In others, they partially fill a set of localized d -like states. If the time it takes for an electron to transfer from one transition-metal atom to a like near neighbor at a like crystal site is long compared to the period of an optical-phonon vibration, the lattice has time to relax about the occupied site, thereby trapping the electron. Although the entire entity, electron plus entrapping atomic displacements, can move through the crystal, its mobility is small ($< 1 \text{ cm}^2/\text{V sec}$ at 300°K) and well described by diffusion theory. Such a "localized," yet mobile charge carrier is called a small polaron, and its mobility contains a finite activation energy ϵ_A .

Evidence for d -like small polarons in the $M_x^+V_2O_5-\beta$ phases comes from several directions. The absence of an nmr Knight shift on the Li atoms of $Li_xV_2O_5-\beta$ indicates that the Li^+ ions are completely ionized in this compound (8). Further, all the β -phase oxides have thermal activation energies for electrical conductivity (as measured on sintered bars) that fall within the range $0.03 < q < 0.09 \text{ eV}$, and these sintered-bar measurements compare well with single-crystal results for $Na_{0.33}V_2O_5-\beta$ (9), which give $\rho_b = 6 \times 10^{-3} \Omega \text{ cm}$ at room temperature and $q = 0.02\text{--}0.05 \text{ eV}$. This similarity indicates that the activation energy is independent of the alkali-metal atom inserted, which confirms the idea that these atoms are completely ionized, each donating an electron to the V_2O_5 array (10). Moreover, the dependence on x of the M-atom locations in the structure can be shown (14) to be readily rationalized from simple electrostatic arguments based on the donation of one electron per M atom to the V_2O_5

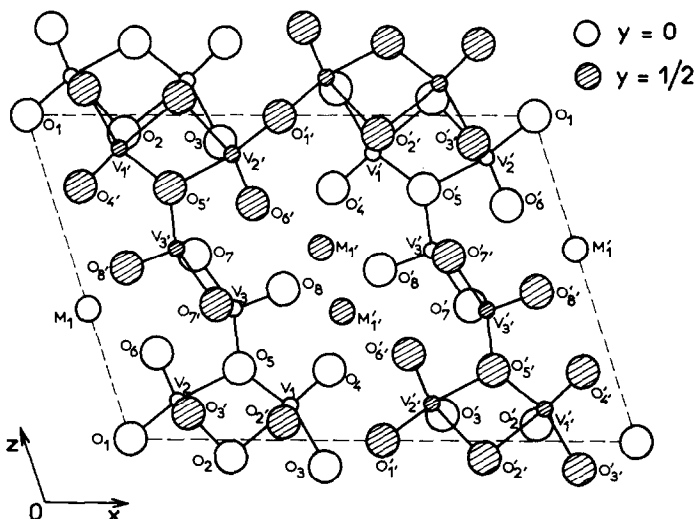


FIG. 1. Projection onto an (010) plane of the $Na_{0.33}V_2O_5-\beta$ phase, after Wadsley (5).

array. Direct evidence for identifiable V^{4+} ions, and hence small-polaron formation within the V_2O_5 array, comes from epr measurements (8) in $Li_xV_2O_5$ - β , which gave a single absorption line centered at $g = 1.96$. This is typical for V^{4+} -ion centers in other compounds. In addition, Hall measurements (11) on a single crystal of $Na_{0.33}V_2O_5$ indicate that, in the interval $100 < T < 300^\circ K$, the number of charge carriers is temperature-independent and equal to x . This means that the activation energy in the conductivity is due to an activated mobility ($\epsilon_A \approx 0.05$ eV), and the Hall mobility at room temperature is only $\mu_H \approx 0.2$ cm²/V sec. Finally, the Seebeck coefficients of β -phase compounds with $M^+ = Na^+, Ag^+$ as well as of $Cu_xV_2O_5$ were all temperature-independent above $150^\circ K$, which provides independent evidence that the activation energy in the conductivity above this temperature is due to an activated mobility (12) and (13).

Given the presence of d -like small polarons in the V_2O_5 array, it is meaningful to inquire how they are

distributed within this array. The fact that the variation of the Seebeck coefficient with x could not be interpreted with the conventional small-polaron formula and straightforward statistics (13) would indicate that this distribution is peculiar, since there is no reason to doubt the applicability of the small-polaron formula for the Seebeck coefficient. This seems to be well established, except in those rare compounds where the charge carriers are at the threshold of being converted into collective electrons.

B. Structural Evidence for a V_1 Site Preference

The V_2O_5 array of the $M_xV_2O_5$ - β and - β' structures is shown in Fig. 1, and the important interatomic spacings, given in Table I, are taken from (5) and (14). Figure 2 of this paper shows an idealized bipyramidal-site chain running parallel to the b axis of the Wadsley β -phase structure: it represents the V_3 subarray. Figure 3 shows an octahedral-site chain running parallel to the b axis: it represents the two interpenetrating V_2 and V_1 arrays. The cationic

TABLE I
BOND DISTANCES IN SEVERAL $M_xV_2O_5$ - β PHASES

	$Na_{0.33}V_2O_5$ (Wadsley)	$Li_{0.48}V_2O_5$	$Na_xV_{2-x}Mo_xO_5$ ($x = 0.40$)	$Cu_{0.60}V_2O_5$		
V_1-V_2	3.49	3.45	3.43	3.49	3.53	$V_5-V_6^a$
V_2-V_3	3.24	3.29	3.31	3.38	3.11	$V_4-V_6^a$
V_3-V_1	3.44	3.43	3.49	3.38	3.45	$V_4-V_5^a$
V_1-V_1'	3.36	3.31	3.33		3.34	$V_1-V_5^a$
V_1-V_2'	3.12	3.10	3.18		3.21	$V_1-V_6^a$
V_2-V_1'	3.12	3.10	3.18		3.19	$V_2-V_5^a$
V_3-V_3'	3.06	3.06	3.02		3.08	$V_3-V_4^a$
V_1-O_2	2.32	2.28	2.38	2.25	2.23	$V_5-O_{15}^a$
V_1-O_3	2.01	1.99	2.10	2.28	1.90	$V_5-O_{14}^a$
V_1-O_4	1.56	1.53	1.57	1.51	1.64	$V_5-O_{11}^a$
V_1-O_5	1.95	1.97	1.94	2.06	1.83	$V_5-O_{12}^a$
$V_1-O_{2'}, O_{15}^a$	1.89	1.88	1.89	1.92	1.91	$V_5-O_2^a$
V_2-O_1	1.80	1.80	1.82	1.89	1.69	$V_6-O_1^a$
V_2-O_2	2.34	2.32	2.34	2.40	2.35	$V_6-O_{15}^a$
V_2-O_5	2.16	2.12	2.19	2.31	2.12	$V_6-O_{12}^a$
V_2-O_6	1.58	1.62	1.69	1.55	1.51	$V_6-O_{13}^a$
$V_2-O_{3'}, O_{14}^a$	1.89	1.89	1.90	1.88	1.87	$V_6-O_3^a$
V_3-O_5	1.78	1.80	1.81	1.52	1.91	$V_4-O_{12}^a$
V_3-O_7	2.00	1.98	1.97	2.12	1.84	$V_4-O_9^a$
V_3-O_8	1.56	1.50	1.63	1.60	1.65	$V_4-O_{10}^a$
$V_3-O_{7'}, O_9^a$	1.91	1.91	1.91	1.96	1.87	$V_4-O_7^a$
V_3-O_6	2.68	2.78	2.67	3.12	2.69	$V_4-O_{13}^a$

^a Only in $Cu_xV_2O_5$ - β phase.

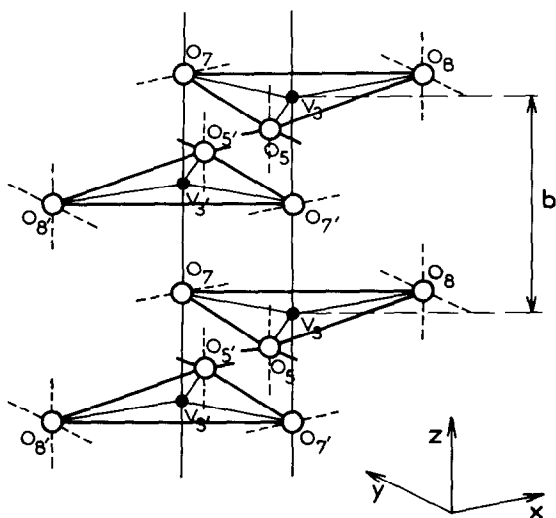


FIG. 2. Idealized bipyramidal-site chain parallel to the b axis. Dashed lines represent anion p_{π} orbitals available for bonding with vanadium d orbitals of t_{2g} symmetry in the absence of M^+ ions.

and anionic sites are labelled as in Fig. 1. The oxygen p orbitals not active in σ bonding are represented by the dashed lines in these two figures. These are necessarily active in π bonding with the vanadium ions. Perturbation of this π bonding by competitive interactions with the relatively electropositive M^+ ions is neglected in a zero-order approximation of the problem. However, M^+ -ion perturbations are important, and it will become necessary to introduce an explicit assumption about the influence of this

perturbation in order to account for the anomalous dependence on x of the Seebeck voltage. In $\text{Cu}_{0.60}\text{V}_2\text{O}_5$ there is a reduced symmetry, which may be characteristic of most if not all of the $\text{Cu}_x\text{V}_2\text{O}_5$ system in the range $0.26 \leq x \leq 0.64$. This reduced Cm symmetry, although introducing six distinguishable vanadium sites instead of three as noted in Table I, does not appear to influence appreciably the principal physical arguments presented in this paper, so the entire discussion is based on the more symmetric space group $\text{C}2/m$ of the Wadsley β phase shown in Fig. 1. However, it is pointed out at the end how this reduction in symmetry provides direct support for the explicit assumption that is introduced to give a quantitative theory for the Seebeck voltage. This assumption concerns the influence of the M^+ -ion perturbation on the character of the d -like orbitals of the V_2O_5 array.

Displacements of the vanadium ions from the center of symmetry of their respective octahedral sites is caused by two cooperative forces: electrostatic cation-cation repulsive forces and unequal cation-anion interactions as a result of different π -bond contributions from the different anions. The shortest cation-anion separations (see Table I) are $\text{V}_3\text{-O}_8 = \text{V}_1\text{-O}_4 = 1.56 \text{ \AA}$, where there are two π -bonding p orbitals on the anion. The $\text{V}_2\text{-O}_6 = 1.58 \text{ \AA}$ separation is almost as small. Here again the anion has two π -bonding p orbitals, but the relative strength of the bond appears to be slightly reduced because of competition from the $\text{V}_2\text{-O}_1$ bond. On the other hand, the $\text{V}_2\text{-O}_1 = 1.80 \text{ \AA}$ bond is not a triple bond, even though there are two π -bonding p

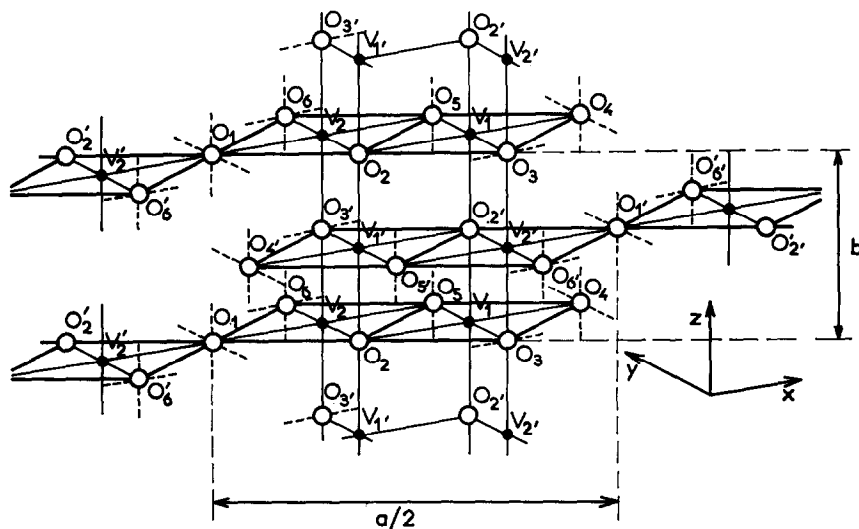


FIG. 3. Idealized octahedral-site chain parallel to the b axis. Dashed lines represent anion p_{π} orbitals available for bonding with vanadium d orbitals of t_{2g} symmetry in the absence of M^+ ions.

orbitals per O_1 ion, because the O_1 -ion π -bonding orbitals are shared by two V_2 atoms on opposite sides. However, it should be at least equivalent in strength to a double bond. These double bonds are stronger than the $V_3-O_7 \geq 1.91$ Å bonds not only because of the V_3-V_3' electrostatic repulsions, but also because the O_7 -ion π -bonding orbital is shared equally by three V_3 ions ($V_3 + 2V_3'$). The single-bond length $V_1-O_2' = 1.89$ Å is smaller than the $V_3-O_7' = 1.91$ Å separation because it must equal the V_2-O_3' separation, which contains some π -bond component. This reasoning leads to the following generalizations: in the vanadium oxides, bond lengths are a reliable indicator of the multiplicity of the cation anion bonding:

Triple d -orbital bonds have $V^{5+}-O^{2-} \leq 1.58$ Å

Double d -orbital bonds have $V^{5+}-O^{2-} \simeq 1.80$ Å

Single d -orbital bonds have $V^{5+}-O^{2-} \geq 1.89$ Å

An important conclusion of this discussion is that, since the $V_3-O_5 = 1.78$ Å separation is close to that for a double bond whereas the $V_1-O_5 = 1.95$ Å separation is larger than that for a single $V^{5+}-O^{2-}$ bond, the O_5 -ion π -bonding orbital bonds primarily with the V_3 ion.

In an oxide crystal, the primarily anionic- p orbitals are more stable than the d -like orbitals centered at the vanadium ions, which is why it is possible to use meaningfully the formal valence state of the ions to represent the number of d -electrons present per cation. Therefore the d orbitals are anti-bonding with respect to the anions, and cation-anion covalent mixing stabilizes the occupied p -like states while simultaneously destabilizing the d -like states under the constraint of a total conservation of energy. If the d -like states are empty, covalent mixing stabilizes the system, which is why cations with empty d orbitals tend to bond strongly with the near-neighbor anions. Where the cations are small relative to their anion interstice, as is the case for V^{5+} ions in an oxygen octahedral interstice, they tend to be displaced from the center of site symmetry so as to form double or triple cation-anion bonds (15). This bonding destabilizes the corresponding d -like orbitals, so it is possible to conclude that where discrete π -bond formation occurs, the corresponding d -like orbitals are empty.

It is possible to use this idea to demonstrate that the detailed atomic positions provided by Wadsley already require that the V^{4+} ions are localized at the V_1 positions in the structure, a conclusion that was also inferred from the $Na_xV_{2-x}Mo_xO_5$ experiments discussed in (14). In an octahedral interstice, the

atomic fivefold-degenerate d orbitals are split into two unstable orbitals that participate in σ -bonding with the six near-neighbor anions and three more stable orbitals: d_{xy} , d_{yz} , d_{zx} , which may participate in π bonding with the anion p_π orbitals. The σ -bonding vanadium orbitals are always empty, and in the β -phase vanadium oxides those d orbitals active in the formation of isolated cation-anion π bonds must also be empty. Of the three more stable d orbitals per cation, the following are active in the formation of isolated cation-anion π bonds within the three identified triple bonds V_1-O_4 , V_3-O_8 , V_2-O_6 :

V_1 -ion d_{zx} , d_{xy}

V_2 -ion d_{zy} , d_{xy}

V_3 -ion d_{zx} , d_{zy} , d_{xy} ,

where z is parallel to the crystallographic b -axis and x is parallel to the $V_2-O_1-V_2'$ axis for ideal octahedral sites. The remaining two d orbitals that are available for electron occupancy are the V_1 -ion d_{zy} and the V_2 -ion d_{zx} orbitals. It is at once apparent from the interatomic separations listed in Table I that, of these, there is more π -bond covalent mixing in the V_2 -ion d_{zx} orbitals. Therefore, we are led to the unambiguous conclusion that in the Wadsley β -phase structures, the mobile electrons are localized to the V_1 -ion d_{zy} orbitals. This explains why the V_1-O_5 and V_1-O_3 separations are larger than single-bond $V^{5+}-O^{2-}$ separations.

Another important fact is that $180^\circ V^{5+}-O^{2-}-V^{5+}$ interactions are known (7) to be strong enough to form collective d -like orbitals wherever two π -bonding p orbitals are available at the intermediary anion. This means that the $V_2-O_1-V_2'$ configurations should be considered as single molecular units characterized by molecular rather than atomic orbitals. One important consequence is that the small polaron at a V_1 site will jump to a pair of V_2 sites, which reduces the number of countable sites for electron hopping. This idea will be shown to be important for an interpretation of the Seebeck coefficients. Further, the idea of a $V_2-O_1-V_2'$ molecular unit explains why only half of the V_2 sites could be substituted by molybdenum ions (14). Substitution of Mo^{6+} for one of the V^{5+} ions polarizes the O_1 -ion p_π orbitals toward the Mo^{6+} ion. Thus, there is little π -bond covalent mixing with the paired-vanadium d orbitals, so that its d -like π -bonding states are relative stable, and the extra electron donated by the molybdenum ion becomes "trapped" at the paired site. Therefore, $Mo^{6+}-O_1-V^{4+}$ molecules are formed, the occupied molecular orbital representing a fairly deep donor level.

III. Physical Properties

A. Electron Localization

Given the evidence for small-polaron formation discussed above, it is important to ask whether this result is compatible with the known properties of other vanadium oxides. There are two mechanisms by which the *d*-like orbitals may become collective in an oxide crystal: cation–cation or cation–anion–cation interactions (16). A semiempirical formula for the critical cation–cation separation R_c for localized versus collective electrons has been given (17):

$$R_c = [3.20 - 0.05m - 0.03(Z - Z_{Ti}) - 0.04S_i(S_i + 1)] \text{ \AA}$$

for oxides containing first-row transition-metal ions with formal valence state $m+$, a nuclear charge $(Z - Z_{Ti})$ units greater than that of Ti and a localized-electron net ionic spin S_i . For V^{4+} ions, this gives $R_c(V^{4+}) = 2.94 \text{ \AA}$. Since the shortest V–V separation $V_3 - V_3' = 3.06 \text{ \AA}$ is larger than R_c , there should be no electron delocalization as a result of cation–cation interactions. In addition, there is no cation–anion–cation interaction that couples the V_1 -ion d_{zy} orbitals to each other, so there can be no electron delocalization within the V_1 -ion subarray via this mechanism. Coupling to the crystallographically inequivalent V_2 and V_3 sites is via the O_5 -ion p_z orbital, which bonds preferentially with the V_3 ions. Therefore, the existence of small polarons in the $M_xV_2O_5$ - β phases is consistent with the known properties of other oxides even though VO_2 has collective *d* electrons in the rutile phase and the perovskites $CaVO_3$ and $SrVO_3$ are reported to exist and to exhibit metallic conductivity and Pauli paramagnetism.

B. Transport Properties

1. *Hopping Mechanism.* Given a localization of the mobile electrons in the V_1 -ion d_{zy} orbitals, electron transport must take place via an electron hopping from one d_{zy} orbital to another within the V_1 array. Direct V_1 – V_1' hopping along an octahedral-site chain would account nicely for the large anisotropy in the resistivity, which is about three orders of magnitude smaller parallel to the *b* axis at room temperature. However, the relatively large V_1 – $V_1' = 3.36 \text{ \AA}$ separation does not seem compatible with the relatively small activation energy $\epsilon_A \simeq 0.05 \text{ eV}$ for an electron hop. Therefore, it is necessary to consider the possibility of hopping via an intermediary V_2 or V_3 site.

Since all V_1 – V_2 or V_1 – V_3 separations exceed 3.12 \AA , the V–V coupling of interest is via an intermediary anion. It has already been emphasized

above that this coupling is generally strong enough between V^{5+} and/or V^{4+} ions in vanadium oxides to create collective-electron orbitals, as in the molecular unit V_2 – O_1 – V_2' . Therefore, relatively small activation energies for hopping via an intermediary anion may be anticipated where small-polaron formation is due to preferential π bonding on one side of an anion. In the β and β' phases $M_xV_2O_5$, the V_2 and V_3 sites are each coupled to the occupied d_{zy} orbital of a neighboring V_1 ion via the O_5 -ion p_z orbital. Since each V_2 -ion d_{zx} orbital is strongly coupled to the V_2 -ion d_{zx} orbital on the opposite side of the O_1 anion, forming a V_2 – O_1 – V_2' molecular orbital, displacement of an O_5 ion towards a V_1 ion would not make the V_2 -ion d_{zx} orbital more available, whereas it would reduce the V_3 -ion π bonding to make a V_3 -ion *d* orbital more available. In addition, the strong coupling between V_2 ions on opposite sides of an O_1 ion means that hopping via a V_2 -ion intermediary permits transfer perpendicular to the *b* axis, which experiment shows to be a much less probable event. Thus, we are led to the conclusion that hopping via an intermediary cation goes through the V_3 subarray. Electron transfer within this array would be parallel to the *b* axis via the π -bonding *p* orbitals on the O_7 ions. (However, in order that there be no energy for transfer within the V_3 subarray, collective orbitals must be formed via mixing with O_7 p_π orbitals.) With such an electron-transfer process, any mobile electron would be confined to a single tunnel, and a large anisotropy in the electrical resistivity would result. Therefore, the existence of a much smaller resistivity parallel than perpendicular to the *c* axis cannot, of itself, distinguish between V_1 to V_1' hopping within an octahedral-site chain and V_1 to V_3 to V_1 or V_1' hopping within a tunnel. However, the relatively low-activation energy ϵ_A seems to argue against direct V_1 – V_1' transfer, therefore favoring transfer via the V_3 -subarray intermediary—provided collective-electron orbitals are available within this array.

2. *Seebeck Coefficient.* Seebeck coefficients for the $Na_xV_2O_5$, $Ag_xV_2O_5$ and $Cu_xV_2O_5$ systems (13) are shown in Fig. 4 as a function of x . The Seebeck coefficient for a small-polaron semiconductor is given by the expression (18):

$$\alpha = A - 198 \log [(N - x)/x], \quad (1)$$

where A is a transport term of order unity and N is the total number of sites per formula unit available to the small polarons. Superficially, it would appear that $N = 2$, but it has already been pointed out (13) that this gives an inadequate interpretation of the

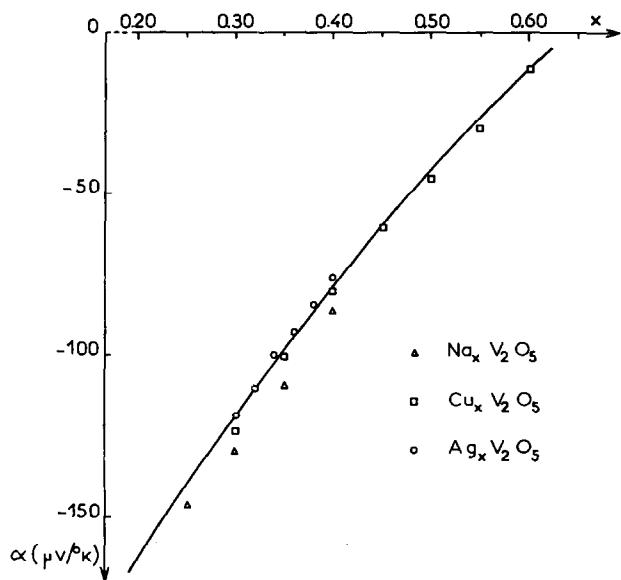


FIG. 4. Room-temperature Seebeck coefficient versus alkali-metal concentration x . Experimental points after (13), theoretical curve from Eq. (3).

data of Fig. 4. However, if account is taken of the fact that a $V_2-O_1-V_2'$ pair is a molecular unit that can only count as *one* available site, this reduces N to $5/3$. Nevertheless the small-polaron expression for α is still inadequate to account for the data of Fig. 4, and it becomes necessary to ask whether introduction of the M^+ ions perturbs the lattice so as to create other "molecular-unit" pairs (or simply collective versus localized orbitals) that can only be counted as one available site. The simplest possible assumption is that each M^+ ion eliminates one countable site by creating a molecular orbital (at a pair or cluster). With this assumption:

$$N = \frac{2}{3}(n_1 + n_2 + n_3) = \frac{5}{3} - \frac{2}{3}x, \quad (2)$$

where the n_i are the numbers of available sites per formula unit on sublattices V_1 , V_2 , and V_3 . Since A can generally be neglected for small-polaron oxides, this gives from Eq. (1):

$$\alpha = 198 \log [5/3](1-x)/x]. \quad (3)$$

This expression, which contains no adjustable parameter, is shown as the full curve in Fig. 4. The exceptionally good agreement with experiment suggests that our assumption is fundamentally correct, and it becomes meaningful to reinvestigate the structures of the β and β' phases for an identification of possible molecular units to be created by the introduction of M^+ ions.

Although it is tempting to think that $V_1-O_5-V_3$ units may be transformed into molecular pairs, since

a displacement of the oxygen O_5 ion toward V_1 could be all that was required, examination of Table I together with the X-ray results on the Mo distribution in $Na_xV_{2-x}Mo_xO_5$ (14) have led us to the conclusion that the small polaron is located in the d_{xy} orbital of a V_1 ion and not in a $V_1-O_5-V_3$ molecular orbital. Examination of Fig. 2, on the other hand, shows the availability of $O_7 p_\pi$ orbitals for the creation of $V_3-O_7-V_3'$ molecular orbitals. What prevents the formation of π^* -band states (via covalent mixing of the $O_7 p_\pi$ orbitals into V_3 -ion d orbitals) is the competitive triple-bond formation with O_8 and double-bond formation with O_5 . Without any M^+ ions, this competitive π bonding creates relatively unstable V_3-O_8 and V_3-O_5 antibonding, molecular orbitals instead of the π^* -band orbitals via O_7 anions. However, introduction of M^+ ions must strongly perturb the O_8 -anion p_π orbitals [see Fig. 5 of (14)] whether the M^+ ions enter M_1 , M_2 or M_3 positions. The M^+ ion σ bonds with its near-neighbor anions, and although covalent mixing is relatively weak for an electropositive cation, it should be competitive enough to reduce the V_3-O_8 bond from a triple to a double bond, especially as the electrostatic force from the M^+ ion would displace the V_3 ion toward an O_7 ion with its p_π orbital available for π bonding. The influence of the M^+ ion need be only strong enough to invert the bonding preference from V_3-O_8 "triple" bonds and little V_3-O_7 bonding to V_3-O_8 "double" bonding and $V_3-O_7-V_3'$ molecular-orbital formation. Unfortunately, it is difficult to confirm such an hypothesis by direct methods. Therefore, it is necessary to look for indirect evidence, other than the Seebeck coefficient, for the creation of molecular orbitals—and these within the V_3 subarray—as a result of M^+ -ion insertion.

3. $Cu_xV_2O_5$. The system $Cu_xV_2O_5$ is particularly interesting to study because of its large single-phase field. From the Seebeck coefficients of Fig. 4, the hypothesis of molecular-orbital formation within the V_3 array seems to be independent of the location of the M^+ ions in M_1 , M_2 or M_3 positions.

Casalot and Hagenmuller (13) have argued that, with increasing x , there is a transition from small-polaron toward collective-electron properties, the actual transition to Pauli paramagnetism and metallic conductivity extrapolating to values of $x > 0.67$, which are just beyond the single-phase boundary $x_f = 0.64$. Figure 5 shows a plot versus x of the activation energies for electrical conduction, and Fig. 6 a plot versus x of the magnetic susceptibility per charge carrier (χ_p/x) for different temperatures. The activation energies and the temperature

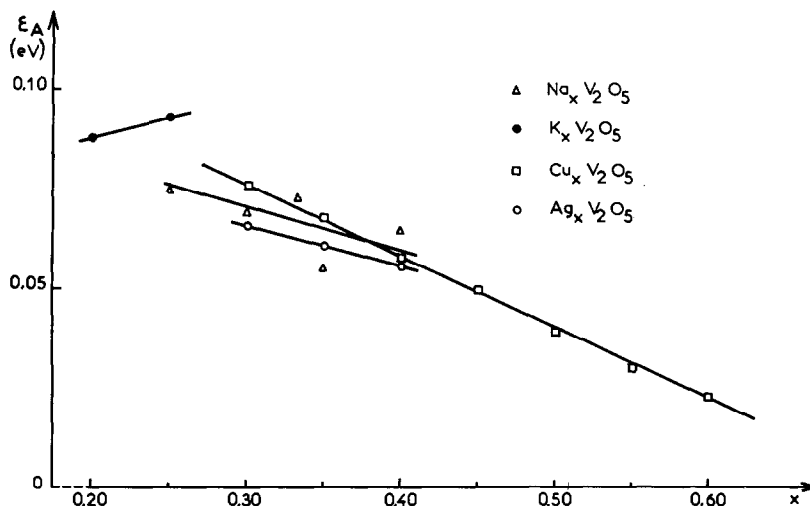


FIG. 5. Activation energy for conductivity versus alkali-metal concentration x after (12) and (13).

dependence of the magnetic susceptibility are each shown to extrapolate to zero for $x > 0.67$. Since there is no marked change in the cation-cation separations, this argues strongly against conduction via V_1-V_1' hopping along the b -axis chains.

These and other experimental data led to a phenomenological model for this small-polaron \rightleftharpoons collective-electron transition (13). It was proposed that the insertion of Cu^+ ions creates small domains within which the electrons occupy molecular orbitals and that the volume of these domains increases with x , the separate domains eventually coalescing to form one large domain for the entire crystal. It may now be asked whether there is a plausible microscopic model to correspond with this suggestion.

Thus far in this paper we have come to the following conclusions: (1) The charge carriers in the $M_x V_2 O_5-\beta$ or β' phases are small polarons located, in their ground state, at V_1 positions in crystalline (including covalent mixing) d_{xy} orbitals. (2) There are two possible conduction paths compatible with the observed electrical anisotropy: direct V_1-V_1' hopping with octahedral-site chains parallel to the b axis or hopping via a V_3 -subarray intermediary. (3) Since the V_1-V_1' separation is large and does not change appreciably with x while access to the V_3 subarray only requires a small displacement of an O_5 ion toward a V_1 ion, electron transfer via a V_3 -subarray intermediary is much more compatible with an activation energy $\epsilon_A \leq 0.05$ eV, provided no energy is required for electron transfer within the V_3 subarray. (4) The Seebeck coefficients can be quantitatively accounted for if it is assumed that one molecular orbital is created for each M^+ ion inserted. (5) From a crystallographic viewpoint, the most plausible location for these molecular orbitals, which are introduced by insertion of M^+ ions, is within the V_3 subarray.

It now requires no new assumption to make the final conclusion for contact with the phenomenological model: (6) If insertion of the M^+ ions indeed create molecular orbitals within the V_3 subarray, this not only accounts for the Seebeck voltage, but also provides for electron transfer within the V_3 subarray without any activation energy, thus satisfying the condition for a small ϵ_A ; and it requires that as x increases, the volume of the V_3 -subarray molecular-orbital domains increase until they coalesce to form π^* -band orbitals running parallel to the tunnels. Further,

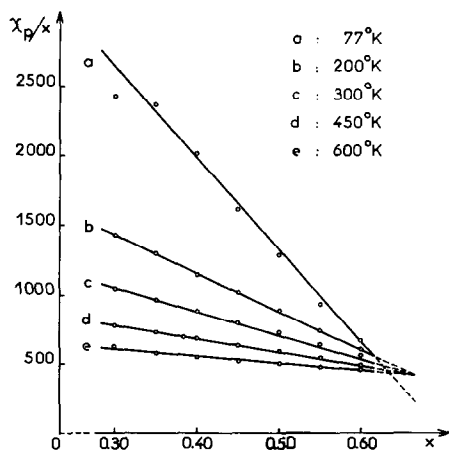


FIG. 6. Magnetic susceptibility per charge carrier in $Cu_x V_2 O_5$ versus compositional parameter x for different temperatures, after (13).

since the covalent mixing into π^* -band orbitals is smaller than that into the individual cation-anion bond orbitals of the double or triple bonds, the multiple- V_3 -center, molecular antibonding d orbitals are the more stable d orbitals in the V_3 subarray. Finally, formation of multiple- V_3 -center orbitals, which is accompanied by a weakening of the individual cation-anion bonding, must decrease the energy required to induce an O_5 -ion displacement towards a V_1 ion—and hence the activation energy ϵ_A . Thus the microscopic model would modify the macroscopic, phenomenological model in only one aspect: whereas introduction of M^+ ions does indeed introduce molecular-orbital domains that increase in size with x , a small polaron has access to these levels only via a vibrational displacement of an O_5 ion, a displacement that becomes energetically more accessible with increasing x .

Crystallographic evidence for this model is found in the $Cu_{0.60}V_2O_5$ structure given in (14). From Table I, V_4 - O_9 - V_4 molecular units together with a nearly equal sharing of an O_{12} ion by a V_4 and a V_5 ion indicate an electron transfer from V_5 to a multiple- V_4 subarray. (Here V_3 and V_4 correspond to V_1' and V_3' , O_9 and O_{12} to O_7 and O_5' of Fig. 1.)

4. $Na_{0.40}V_{2-y}Mo_yO_5$ - β . Darriet and Casalot (19) have also shown that the high-temperature (HT) with $T > 250^\circ K$ and low-temperature (LT) activation energies (determined from electrical conductivity versus temperature of sintered bars) for the system $Na_{0.40}V_{2-y}Mo_yO_5$ - β increase linearly with y : $de_A^{HT}/dy = 0.58$ and $de_A^{LT}/dy = 0.13$. If the molybdenum atoms substitute as Mo^{6+} ions and the small-polaron \rightleftharpoons collective-electron transition were only a function of the number of mobile electrons, then the activation energies should decrease with y , not increase as observed. However, the microscopic model developed here calls for V^{4+} - O_1 - Mo^{6+} deep-donor pairs, so that addition of molybdenum atoms does not, at low temperatures, contribute electrons to the V_1 - V_3 subarray, which is presumed primarily responsible for electron transport. Further, the formation and stabilization of collective orbitals within the V_3 subarray is apparently dependent upon the M^+ -ion concentration, which in this system is kept constant. Finally, interaction of the V_1 ions with the Mo^{6+} ions at V_2 positions can only increase the stability of a d_{xy} orbital at position V_1 , thereby increasing the activation energy ϵ_A for access to the collective-electron orbitals of the V_3 subarray. Thus, an increase in ϵ_A with y , though perhaps surprising from a superficial viewpoint, is completely consistent with the microscopic model developed here.

C. Magnetic Properties

A plot of the measured reciprocal molar susceptibility $1/\chi_m$ against temperature T does not give a straight line after a diamagnetic correction has been introduced (12), (13) and (9). Perlstein and Sienko (11) assumed this indicates a temperature-dependent magnetic moment, but they used an incorrect method of analysis to interpret the data. Defining an effective atomic moment as $\mu_{eff} = (3kT\chi_m/N)^{1/2}$, they argued that the V^{4+} ions must have a singlet ground state since their μ_{eff} approaches zero as T goes to zero. Such a singlet ground state would require an orbital, azimuthal angular-momentum quantum number $m_l = \pm 1$, which is in contradiction with the assignment in this paper of the ground-state V^{4+} d electrons in the d_{yz} orbitals at V_1 sites. (An $m_l = \pm 1$ requires occupancy of a $(d_{yz} \pm id_{zx})$ orbital, for example.) However, the fact that $1/\chi_m$ bends towards the temperature axis with decreasing T shows that χ_m is not zero at lowest temperatures, as would be required of a singlet ground state. These authors also indicated a semiquantitative fit for the activation energies for electron transport given their magnetic-data analysis plus the additional assumption that the three vanadium positions are equivalent. Since the magnetic analysis is incorrect, there is also no experimental support for this latter assumption.

An alternative analysis of the magnetic data has been suggested by Pouchard (12). It is based on the following two observations: (1) After correction for a diamagnetic contribution $N\alpha_d = -64 \times 10^{-6}$ emu/mole to the measured susceptibility, the nominal compound V_2O_5 exhibits a temperature-independent paramagnetism $N\alpha \approx 120 \times 10^{-6}$ emu/mole. (2) A plot of $1/(\chi_m - N\alpha - N\alpha_d)$ against temperature gives an apparent straight line for $T > 300^\circ K$ for all the vanadium oxides $M_xV_2O_5$, $M_{1+y}V_3O_8$. Although the origin of the term $N\alpha$ is not clear, its consistent appearance in all the vanadium oxides, which contain different crystalline fields at the vanadium sites, suggests that it is a definite contribution common to these vanadium oxides. If this is correct, the temperature-independent terms must be separated from the temperature-dependent component of the susceptibility before a meaningful analysis can be made. The values of the effective moment per V^{4+} ion μ_{eff} plotted against x in Fig. 3 of (14) were obtained from the relation,

$$\begin{aligned}\mu_{eff} &= 2.83[(\chi_m - N\alpha - N\alpha_d)(T - \theta_p)]^{1/2}\mu_B \\ &= 2.83[\chi_p(T - \theta_p)]^{1/2}\mu_B,\end{aligned}$$

where χ_m is the molar susceptibility, θ_p is the paramagnetic Curie temperature, and only high-temperature ($T > 300^\circ K$) data were used. (Below

300°K, the χ_p^{-1} vs T curves for the $M_x^+V_2O_5$ - β phases, except $M = K$, exhibit various anomalies (12) and (13) suggestive of magnetic or atomic order-disorder transitions.) This gives a μ_{eff} in the range $1.9 < \mu_{\text{eff}} < 2.2 \mu_B/V^{4+}$ ion. This range of values is to be compared with a spin-only effective magnetic moment per V^{4+} ion of $1.73 \mu_B$. Although the data are consistent with a spin-only ground state, as required of d_{yz} orbitals at V_1 sites, the discrepancy indicates a temperature-dependent magnetic moment. However an adequate analysis requires a knowledge of the moments of the excited states. The existence of a large $|\theta_p|$ in the absence of identifiable magnetic ordering, especially for $Cu_xV_2O_5$ - β at larger values of x , is consistent with the presence of collective-electron excited states inferred from the transport data. Since at least some of the excited states thus appear to be collective, a precise knowledge of their moments is not available, and a quantitative analysis is not possible at present without the introduction of additional assumptions. Therefore, no attempt is made to analyze the data further in this paper.

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References

1. P. HAUTEFUILLE, *Compt. Rend. (Paris)* **90**, 744 (1880).
2. W. PRANDTL, *Berichte* **38**, 657 (1905); W. PRANDTL AND H. MURSCHAUSER, *Z. Anorg. Chem.* **56**, 173 (1907); **60**, 441 (1908).
3. H. FLOOD AND H. SØRUM, *Tidsskr. Kjemi Bergvesen Met.* **5**, 55 (1943).
4. H. FLOOD, TH. KROG, AND H. SØRUM, *Tidsskr. Kjemi Bergvesen Met.* **3**, 36 (1946); **5**, 59 (1946).
5. A. D. WADSLEY, *Acta Cryst.* **8**, 695 (1955); **10**, 261 (1957).
6. R. P. OZEROV, *Sov. Phys. Cryst.* **2**, 219 (1957); **4**, 181 (1959); *Russian J. Inorg. Chem.* **4**, 476 (1959).
7. J. B. GOODENOUGH, "Metallic Oxides" in "Progress in Solid State Chemistry," (H. Reiss, Ed.), Vol. V, Pergamon Press, Inc., New York, in press.
8. J. GENDELL, R. COTTS, AND M. J. SIENKO, *J. Chem. Phys.* **37**, 220 (1962).
9. J. B. SOHN, Thesis, Cornell Univ., 1965; M. J. SIENKO AND J. B. SOHN, *J. Chem. Phys.* **44**, 1369 (1966).
10. P. HAGENMULLER, J. GALY, M. POUCHARD, AND A. CASALOT, *Mat. Res. Bull.* **1**, 45 (1966).
11. J. H. PERLSTEIN, Thesis, Cornell Univ., 1967; J. H. PERLSTEIN AND M. J. SIENKO, *J. Chem. Phys.* **48**, 174 (1968).
12. M. POUCHARD, Thesis, Bordeaux Univ., 1967; M. POUCHARD, A. CASALOT, G. VILLENEUVE, AND P. HAGENMULLER, *Mat. Res. Bull.* **2**, 877 (1967).
13. A. CASALOT, Thesis, Bordeaux Univ., 1967; A. CASALOT, H. CAZEMAJOR, P. HAGENMULLER, M. POUCHARD, AND J. ROCH, *Bull. Soc. Chim. France* **1**, 85 (1968); A. CASALOT AND P. HAGENMULLER, *J. Phys. Chem. Solids* **30**, 1341 (1969).
14. J. GALY, J. DARRIET, A. CASALOT, AND J. B. GOODENOUGH companion paper.
15. J. B. GOODENOUGH AND J. M. LONGO, "Crystallographic and Magnetic Properties of Perovskite and Perovskite-Related Compounds," p. 126, Landolt-Bornstein Tabellen Neue Serie III/4a, Springer-Verlag, Berlin, 1970.
16. J. B. GOODENOUGH, *Bull. Soc. Chim. France* **4**, 1200 (1965).
17. J. B. GOODENOUGH, *Czech. J. Phys.* **B17**, 304 (1967).
18. R. R. HEIKES AND W. D. JOHNSTON, *J. Chem. Phys.* **26**, 582 (1957).
19. J. DARRIET AND A. CASALOT, private communication.