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# Structure of the $M_xV_2O_5$-β and $M_xV_{2-y}T_yO_5$-β Phases

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In the Wadsley $Na_{0.33}V_2O_5$-β phase, the $M^+$ ions occupy randomly $M_1$, $M_1'$ positions within tunnels. The $M_1$–$M_1'$ separation in an *a–c* plane is only ca. 1.95 Å, which prohibits simultaneous occupancy of these sites, so that the maximum value of $x$ for the $M_xV_2O_5$-β phase should be $x = 0.33$. Nevertheless, several $M_x^+V_2O_5$ systems have been reported to have the β phase extending to $x > 0.33$. The system $Li_xV_2O_5$ has been shown from powder data to consist of two phases, the Wadsley β phase in the range $0.22 \leqslant x \leqslant 0.37$ and a β′ phase in the range $0.44 \leqslant x \leqslant 0.49$. This paper reports a single-crystal study of the β′ phase: the vanadium–oxygen array is essentially the same as in the β phase, but the $Li^+$ ions occupy tetrahedral sites $M_3$ within the tunnels rather than the $M_1$ sites. In addition, partial substitution of Mo or W for V suppresses the two-phase region, indicating that in the presence of $Mo^{6+}$ or $W^{6+}$ ions the $Li^+$ ions may occupy $M_3$ sites in preference to $M_1$ sites even if $x < 0.33$. It is further shown that the $M_3$ positions are preferred over the $M_1$ positions in $Cu_{0.60}V_2O_5$, and it is argued that this preference is probably maintained over the entire range $0.26 \leqslant x \leqslant 0.64$ in the system $Cu_xV_2O_5$. For the larger cations $M^+ = Na^+$ and $Ag^+$, the maximum $x$ is $x_f = 0.40$ and 0.41, and a single-crystal study of $Na_{0.4}V_{1.6}Mo_{0.4}O_5$ indicates that the excess $Na^+$ ions occupy interstitial $M_2$ positions within the tunnels. Finally, it is found that in the system $Na_xV_{2-x}Mo_xO_5$-β, the Mo atoms all go into $V_2$ positions at $x \leqslant 0.33$, but for $x > 0.33$ the $V_2$ positions contain $\frac{1}{2}Mo + \frac{1}{2}V$, presumably as $Mo^{6+}$–$O_1$–$V^{4+}$ units, and the excess $(x - 0.33)$ Mo atoms per formula unit occupy $V_3$ positions.

## I. Introduction

The structure and the interatomic spacings originally given by Wadsley (*1*) for $Na_{0.33}V_2O_5$-β are shown in Fig. 1 and Table I. In this tunnel structure, the sites labeled $M_1$ and $M_1'$ are assumed randomly occupied by $Na^+$ ions. However, within a tunnel the $M_1$–$M_1'$ separation in an *a–c* plane is only ca. 1.95 Å, and it is clear that, if the atoms are ionized, electrostatic forces must force a short-range order: the $M_1$ and $M_1'$ positions within the same tunnel and *a–c* plane cannot be occupied simultaneously. Since the ionization of the M atoms has been satisfactorily established by physical studies (*2*), this reasoning shows that the "available" tunnel sites $M_1$, $M_1'$ are completely occupied at $x = 0.33$. Nevertheless, although systems with larger M cations such as $K^+$ or with bivalent cations $M^{2+}$ are only stable for $x < 0.33$, the systems having the smaller cations $M^+ = Cu^+$, $Li^+$, $Ag^+$, $Na^+$ have apparent single-phase regions up to $x_f = 0.64$, 0.49, 0.41, 0.40, respectively (*3*)–(*6*). This had already suggested to Wadsley that there must be alternate sites within the tunnels that may receive a smaller $M^+$ cation. Further, from powder-pattern X-ray analysis Darriet (*6*) was able to identify a two-phase region within the "β-phase" field of $Li_xV_2O_5$ (see Fig. 2); in the phases $Na_xV_2O_5$-β, discontinuities in the effective paramagnetic moment $\mu_{eff}$ versus composition $x$ were observed by Pouchard (*4*) and by Casalot (*5*) (see Fig. 3). These findings indicate the possibility of cooperative displacements of the $M^+$ ions into alternate tunnel sites at higher values of $x$. Since previous X-ray studies on compounds having $x > 0.33$ were done on powders, a reinvestigation of the structures of the $M_x^+V_2O_5$-β phases having $x > 0.33$ was undertaken with single-crystal data.

The distributions of $Mo^{6+}$ ions within the β-phase structures of $Na_xV_{2-x}Mo_xO_5$ were also studied for evidence of a $V^{4+}$-ion site preference. A peculiar inequivalence of the three distinguishable vanadium sites was observed, but it proves to be

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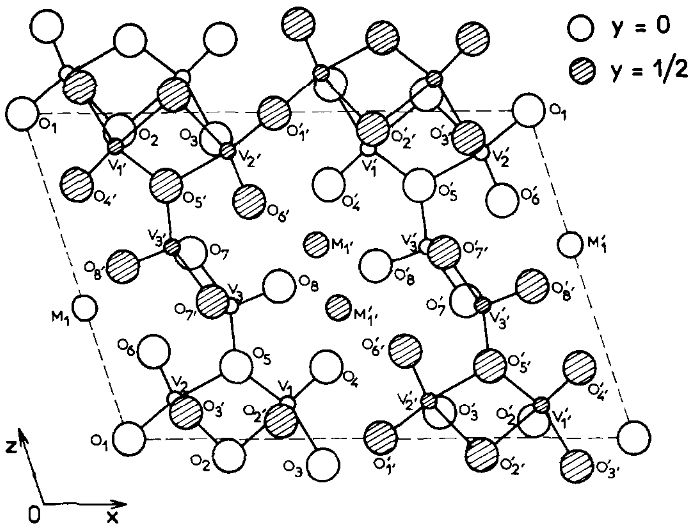

FIG. 1. The Wadsley $Na_{0.33}V_2O_5$-$\beta$ phase projected onto an $a$–$c$ plane. Sites $M_1$, $M_1'$, $M_{1'}$, $M_{1'}'$ are "randomly" occupied by $Na^+$ ions, although two neighboring sites in the same tunnel and $a$–$c$ plane cannot be occupied simultaneously. (Adapted from Ref. 1.)

TABLE I

BOND DISTANCES IN SEVERAL $M_xV_2O_5$-$\beta$ 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 $Cu_xV_2O_5$-$\beta$ phase.

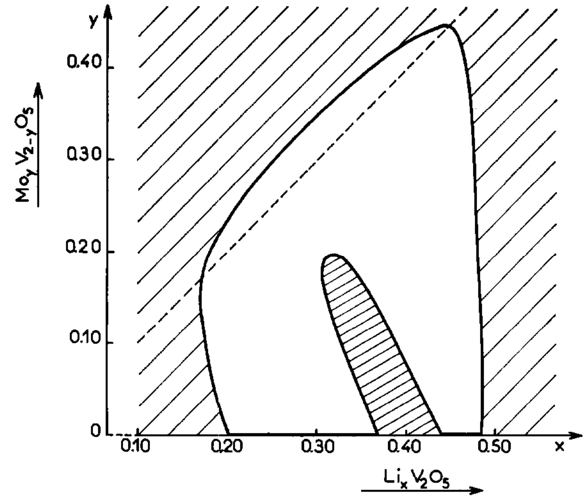

FIG. 2. The $\beta$-phase region for the system $Li_xMo_yV_{2-y}O_5$. The shaded finger centered at $x = 0.4$ for $y = 0$ is a two-phase ($\beta + \beta'$) region. As $y$ increases, the distinction between $\beta$ and $\beta'$ phases disappears (J. Darriet, Thesis, University of Bordeaux, 1967).

consistent with the molecular-subunit model proposed (*2*) to account for the Seebeck voltage of the $M_xV_2O_5$-$\beta$ phases.

## II. Compounds with $x > 0.33$

### A. Alternative $M^+$-Ion Positions

The structure of Fig. 1 contains three alternate tunnel sites that are geometrically feasible: an eight-coordinated site $M_2$, a tetrahedral site $M_3$, and an octahedral site $M_4$. These positions are indicated in Fig. 4. The tetrahedral and octahedral sites $M_3$ and $M_4$, which represent two possible positions within the same anionic cage, are shifted $\pm b/2$ with respect to their neighboring $M_1$ position. The $M_2$ position, on the other hand, is in the same *a–c* plane as its neighboring $M_1$ position. By inspection, it is apparent that electrostatic repulsive forces from the near-neighbor vanadium ions would force an $M^+$ ion from the $M_4$ position into the tetrahedral position $M_3$, and perhaps even into a triangular face of this tetrahedral position. Therefore the position $M_4$ does not appear to be a competitive alternative. The anion coordinations of the sites $M_1$, $M_2$, and $M_3$ are shown in Fig. 5.

Two factors influence the site-preference energy of the $M^+$ cations: the repulsive cation–cation interactions and the attractive cation–anion interactions. Since the $M_3$ tetrahedral sites share only common corners with neighboring $VO_6$ octahedra, the repulsive interactions are not too much greater at $M_3$ than at $M_1$. Further, the smaller cations $Li^+$ and $Cu^+$ have a greater cation-anion attractive interaction in fourfold coordination. This effect is particularly true for the more acidic $Cu^+$ ion, so that in $Cu_xV_2O_5$, which shows no discontinuity in $\mu_{\text{eff}}$ vs $x$ (see Fig. 3), the $M_3$ position may be competitive with the $M_1$ position. Finally, the separation between $M_3$ positions within the same tunnel and *a–c* plane is relatively large, so that occupation of the $M_3$ positions need not reach saturation until $x = 0.67$. The fact that $x_f = 0.64$ is largest for $Cu_xV_2O_5$ is, therefore, suggestive that the tetrahedral site $M_3$ is the alternative site for $Cu^+$ and $Li^+$. However, in the case of the larger cations $Ag^+$ and $Na^+$, which would not be stabilized by fourfold coordination, the $M_2$ position seems to be the more plausible alternative.

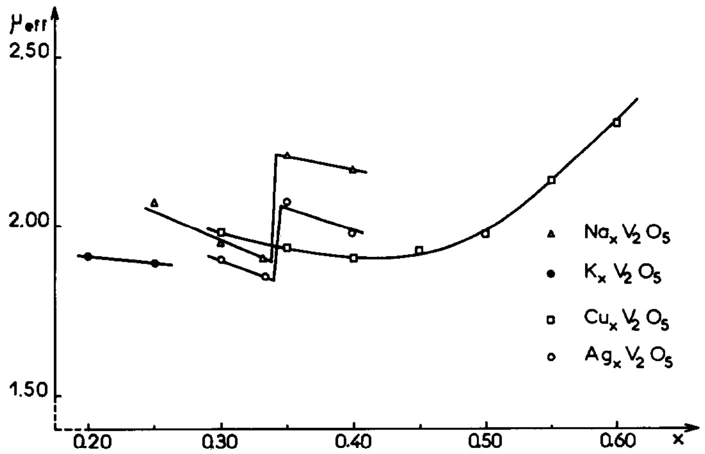

FIG. 3. Effective moment per $V^{4+}$ ion $\mu_{\text{eff}} = 2.83\,[\chi_p(T - \theta_p)]^{1/2}\,\mu_B$ as a function of the alkali-metal concentration $x$ [after (*4*) and (*5*)]. Here $\chi_p$ is the measured molar susceptibility corrected for a diamagnetic contribution $-64 \times 10^{-6}$ emu/mole and a temperature-independent paramagnetic contribution $120 \times 10^{-6}$ emu/mole.

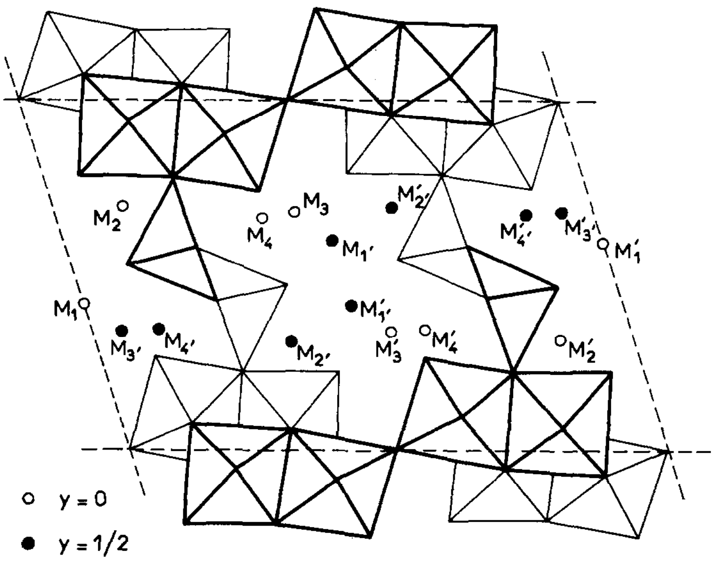

FIG. 4. Definitions of possible tunnel sites for the $M^+$ ions.

B. $Li_xV_2O_5$

From powder data, it was possible to determine that the $\beta$ phase is stable only to $x_f = 0.37$. In the range $0.44 < x < 0.49$ there appears to be a closely related $\beta'$ phase, and $0.37 < x < 0.44$ is a $(\beta + \beta')$ two-phase region (*6*), as shown in Fig. 2. A plot of the variation in lattice parameters with $x$ is shown in Fig. 6. Therefore, single crystals having compositions in the range $0.44 < x < 0.49$ were prepared for careful X-ray analysis. Appendix I gives the results of such an analysis for a crystal of composition

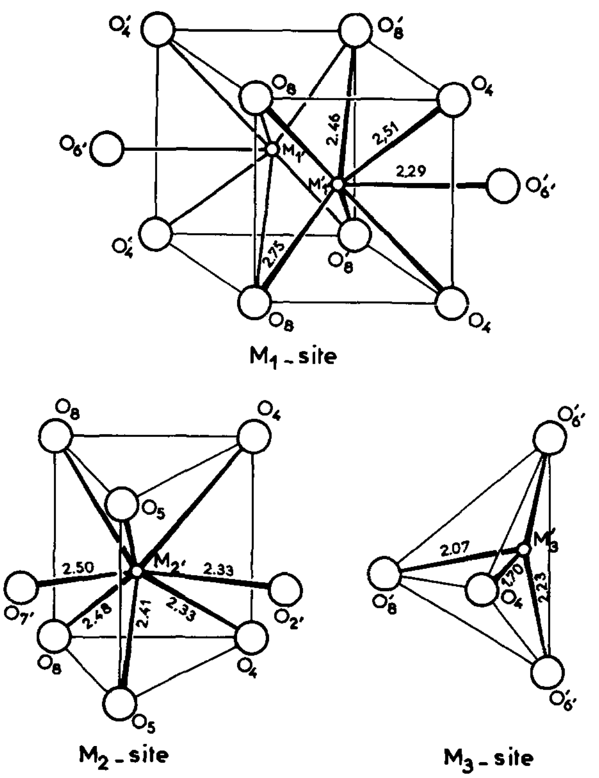

FIG. 5. Anion coordinations of various tunnel sites for the $M^+$ ions.

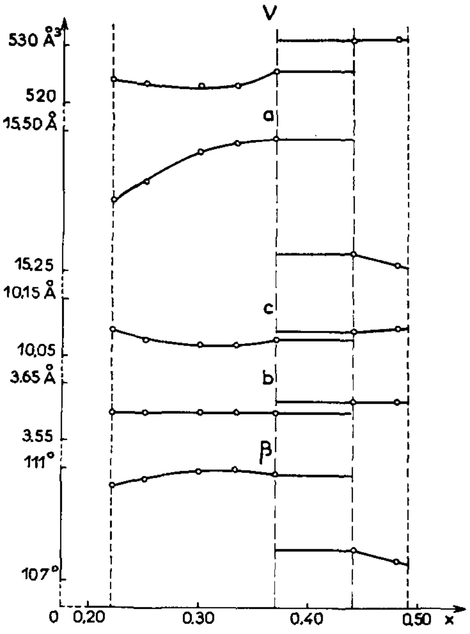

FIG. 6. Lattice parameters versus $x$ for the system $Li_xV_2O_5$ showing the $\beta$ and $\beta'$ phases separated by the $(\beta + \beta')$ two-phase region $0.37 < x < 0.44$ (J. Darriet, Thesis, University of Bordeaux, 1967).

$Li_{0.48}V_2O_5$. These results provide definite evidence, despite the weak scattering power of the $Li^+$ ions, that in the $\beta'$ phase all of the $Li^+$ ions are located in the tetrahedral sites $M_3$. Previous single-crystal work on $Li_{0.30}V_2O_5$ has verified that the $Li^+$ ions are in the $M_1$ positions in the $\beta$ phase (*7*). From this finding, it follows that the Wadsley $\beta$ phase, which is stable to $x_f = 0.37$, is capable of tolerating a small excess of $M^+$ ions in "interstitial" positions. These excess cations could be accommodated, for example, by a displacement of pairs of $M^+$ cations in the same tunnel and *a–c* plane into $M_2$, $M_2'$ positions, all other $M^+$ cations remaining in the $M_1$ positions. Since this excess is $(x_f - 0.33) \leqslant 0.08$ for all three systems $Li_xV_2O_5$-$\beta$, $Na_xV_2O_5$-$\beta$, and $Ag_xV_2O_5$-$\beta$, it appears that the $M^+$ ions are not particularly stable in this "interstitial" site, which is presumably $M_2$. However, the existence of a $\beta'$ phase, which has a theoretical $x_f = 0.67$, shows that a relocation of all the $M^+$ ions from the $M_1$ to the tetrahedral $M_3$ positions may be a competitive alternative to a $\beta$ phase having an excess of $M^+$ cations. In fact, it introduces the possibility that for the more acidic $Cu^+$ ion, which has a larger tetrahedral-site preference energy, the $\beta'$ phase may be more stable than the $\beta$ phase for all values of $x$.

### C. $Li_xV_{2-x}T_xO_5$, T = Mo or W

It is possible to replace $V^{5+}$ ions by $Mo^{6+}$ or $W^{6+}$ ions while retaining the $\beta$ phase (*6*) and (*8*). This offers the possibility to study compositions $Li_xV_{2-y}T_yO_5$, $T = Mo$ or W, over broad phase fields, as indicated in Fig. 2. Initial investigations have concentrated on the case $y = x$, and Fig. 7 shows the variations with $x$ of the lattice parameters for the two systems $Li_xV_{2-x}Mo_xO_5$-$\beta$ and $Li_xV_{2-x}W_xO_5$-$\beta$. In sharp contrast to the system $Li_xV_2O_5$ (compare with Fig. 6), these systems show no abrupt change in lattice parameters across a two-phase region, although the variations with $x$ in the $c$ and $\beta$ parameters of $Li_xV_{2-x}W_xO_5$ are somewhat more rapid in the region $0.22 < x < 0.33$. From such studies it is possible to delineate the boundaries of the two-phase ($\beta + \beta'$) field, as shown in Fig. 2.

In contrast to the system $Li_xV_2O_5$, $M_3$-site $Li^+$ ions are evidently already present at $x < 0.33$ in $Li_xV_{2-x}T_xO_5$-$\beta$, T = Mo and W. As noted above, the relative site-preference energies for $M_1$ and $M_3$ positions depend upon the relative magnitudes of the cation-anion interactions, which favor tetrahedral-site coordination for a small $Li^+$ ion, and the cation–cation electrostatic interactions, which stabilize $Li^+$ in the $M_1$ sites in $Li_xV_2O_5$-$\beta$. Therefore, the conclusion inferred from Figs. 2 and 7 requires that the replacement of $V^{5+}$ ions by $Mo^{6+}$ or $W^{6+}$ ions is able to reduce sufficiently the positive component of the crystalline field at near-neighbor $M_3$ positions that the site-preference energies become inverted. Although such a requirement is possible, it must be somewhat fortuitous since the energy

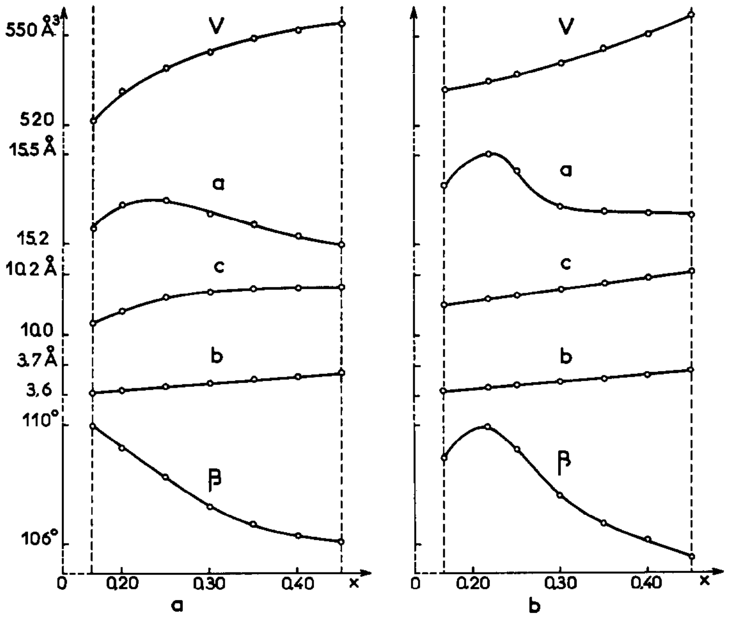

FIG. 7. Lattice parameters versus $x$ for the systems $Li_xV_{2-x}T_xO_5$-$\beta$, where (a) T = Mo and (b) T = W (J. Darriet, Thesis, University of Bordeaux, 1967).

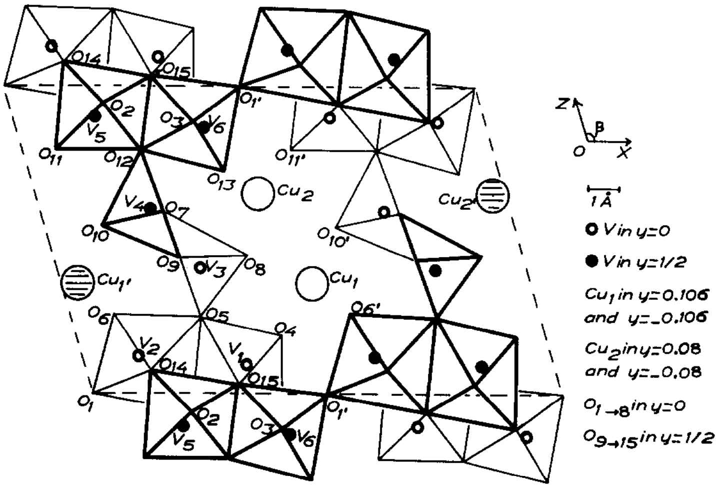

FIG. 8. Projection of the $Cu_{0.60}V_2O_5$ structure onto an (010) plane. The space group is Cm and the lattice parameters are $a = 15.25$ Å, $b = 3.624$ Å, $c = 10.205$ Å, $\beta = 106°\ 9'$.

changes would appear to be quite small—too small for reliable calculation. However, if such a fortuitous circumstance exists, then substitution of $Li^+$ ions by the more acidic $Cu^+$ ions should also invert the site-preference energies, and in $Cu_xV_2O_5$ the $Cu^+$ ions must preferentially occupy the tetrahedral $M_3$ positions rather than the $M_1$ positions. It is possible to determine experimentally whether the phase previously designated $Cu_xV_2O_5$-$\beta$ does indeed have the $\beta'$ structure for all values of $x$.

## D. $Cu_xV_2O_5$

Previous studies (*5*) of the system $Cu_xV_2O_5$ have noted that, in addition to the large extension of the single-phase field ($0.26 \leqslant x \leqslant 0.64$), none of the physical properties examined showed any apparent discontinuity as a function of $x$. This contrast with the systems having $M^+ = Li^+$, $Ag^+$, and $Na^+$, in all of which one or more physical properties exhibit abrupt changes near $x = 0.33$, is well illustrated by Fig. 3. It is consistent with a $\beta'$ phase for all $x$ and independently recommends a reexamination of the structure of $Cu_xV_2O_5$, single-crystal data replacing the previous powder data.

The structure determination for $x = 0.60$ is summarized in Appendix II and Fig. 8. At these large values of $x$, $Cu^+$ ions are all in the tetrahedral-site $M_3$ positions, as anticipated for this system, but they are displaced from the center of the tetrahedron toward its triangular faces above and below the mirror plane. Thus, each $M_3$-site position is slightly split in two: although only one $Cu^+$ ion can occupy an $M_3$ site, it has two possible positions within this site. In addition, the symmetry is reduced from the space group C2/m of the Wadsley structure to the space group Cm. This reduced symmetry requires the identification of six independent vanadium ions and two independent $M_3$ positions per unit cell, as shown in Figs. 8 and 9.

The lack of any known physical discontinuities (see for example Fig. 3) over the entire range $0.26 \leqslant x \leqslant 0.64$ would imply that the $Cu^+$ ions are exclusively in tetrahedral sites over the entire phase field. However, Fig. 2 indicates the simultaneous presence

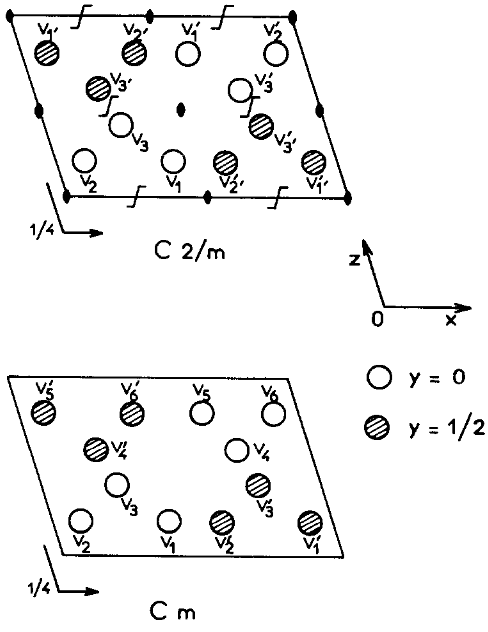

FIG. 9. Comparison of the C2/m symmetry of the Wadsley $\beta$ phase with the Cm symmetry of $Cu_{0.60}V_2O_5$.

of $M_1$-site and $M_3$-site $Li^+$ ions in $Li_xV_{2-x}Mo_xO_5$-$\beta$, the $Li^+$ ions being preferentially in $M_1$ sites for smaller $x$ and in $M_3$ sites for larger $x$. Similar changes with $x$ in $Cu^+$-ion distribution could occur in the system $Cu_xV_2O_5$, $0.26 \leqslant x \leqslant 0.64$, without introducing physical discontinuities.

### E. $Na_xV_{2-x}Mo_xO_5$

Figure 10 shows a plot of the lattice parameters as a function of $x$ for the mixed system $Na_xV_{2-x}Mo_xO_5$. There is a pronounced anomaly near $x = 0.33$. This is consistent with the observed discontinuity in $\mu_{eff}$ vs $x$ first found in $Na_xV_2O_5$-$\beta$ by Pouchard (*4*) and shown in Fig. 3. Nevertheless a structural analysis, summarized in Appendix III, of a single crystal of $Na_{0.4}V_{1.6}Mo_{0.4}O_5$ shows that the $M_1$ sites are occupied by $Na^+$ ions, thus confirming the Wadsley $\beta$-phase structure. Although the number ($x - 0.33 = 0.07$) of excess $Na^+$ ions per molecule is insufficient to locate unambiguously the "interstitial" position, size considerations would favor $M_2$, and the analysis of Appendix III provides definite evidence for this. Since the composition $x = 0.40$ is on the Na-rich side of the discontinuity found in Fig. 3 and of the lattice-parameter anomaly, this raises a fundamental question: What is the difference between the two $\beta$ phases, one on each side of the discontinuity? The existence of a discontinuity in susceptibility versus $x$ signals some cooperative phenomenon, but it is clearly quite subtle. It may reflect, for example, a long-range ordering of occupied $M_1$ positions within the tunnels. For $x > 0.33$, occupancy of "interstitial" positions is required, and long-range ordering among occupied $M_1$ sites is probably destroyed. Without long-range ordering between the tunnels, such an ordering would be extremely difficult to detect by X-rays. However, $\mu_{eff}$ would be sensitive to ordering within the tunnels even without ordering between tunnels, and the lattice parameters would be sensitive to the presence of "interstitial" atoms.

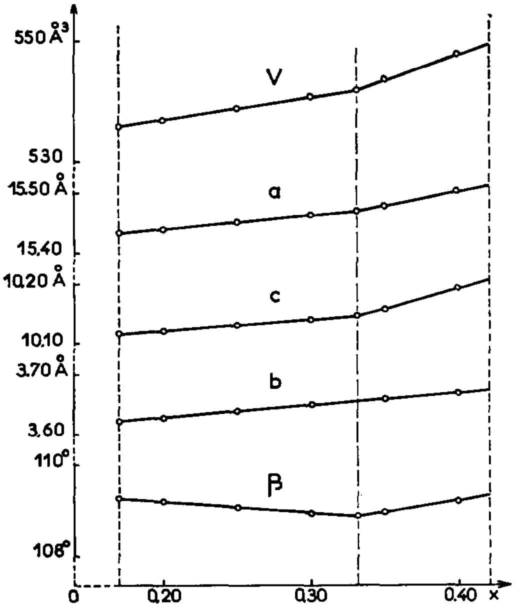

FIG. 10. Lattice parameters versus $x$ for the system $Na_xV_{2-x}Mo_xO_5$-$\beta$.

## III. $V^{4+}$-Ion Site Preference

A variety of physical measurements have demonstrated that the electrons donated by $M^+$ ions to the $V_2O_5$ array are captured by single vanadium-ion sites for times long compared to the periods of optical-mode vibrations (*2*). It is, therefore, meaningful to inquire whether these small polarons are preferentially distributed over the three distinguishable vanadium sites of the $\beta$-phase structure.

Since it is not possible to distinguish $V^{4+}$-ion from $V^{5+}$-ion sites directly from X-ray analysis, it is necessary to resort to indirect techniques. For this purpose, it is preferable to introduce few and noncontroversial assumptions into the analysis. The system $Na_xV_{2-x}Mo_xO_5$ is appropriate, since $Mo^{6+}$ ions should be stable in the presence of $V^{4+}$ ions. The essential assumption is then the following: *$Mo^{6+}$ ions substitute preferentially into a sublattice containing only $V^{5+}$ ions.*

From X-ray analysis of single crystals in the system $Na_xV_{2-x}Mo_xO_5$, it is found that for $x < 0.33$ the Mo atoms substitute exclusively into the $V_2$ positions of Fig. 1. For $x > 0.33$ the evidence favors $V_2$ positions containing ($\frac{1}{2}$ Mo + $\frac{1}{2}$ V) and ($x - 0.33$) excess Mo atoms per formula unit substituted exclusively into the $V_3$ positions (see Appendix III).

From these results, it is immediately apparent that the three crystallographically distinguishable sites $V_1$, $V_2$, $V_3$ are not equivalent chemically and that any analysis of the physical properties must take this fact into account. Further, with the assumption that the Mo atoms enter the structure as $Mo^{6+}$ ions substituting for $V^{5+}$ ions, it would seem to follow that for $x < 0.33$ the $V_2$ positions contain $V^{5+}$ ions and the $V^{4+}$ ions are located preferentially at the $V_1$ and/or $V_3$ positions. However, the atomic distributions for $x > 0.33$ suggest that the $Mo^{6+}$ ions are introduced into the $V_2$ array as $Mo^{6+}$–$V^{4+}$ pairs. Examination of Fig. 1 shows that every $V_2$ site is paired to another $V_2$ site via a common octahedral-site corner, and it is reasonable to assume [as argued in (*2*)] that substitution of molybdenum into these $V_2$–$O_1$–$V_2'$ pairs would form 180° $Mo^{6+}$–$O_1$–$V^{4+}$ pairs within the $V_2$ array. With this modification of the original assumption about Mo-atom substitution, it follows that at $x = 0.33$ the $V_2$ array is saturated with $Mo^{6+}$–$O_1$–$V^{4+}$ pairs. However, in accordance with the original assumption, the $x$ $V^{4+}$ ions introduced by the $M^+$ ions should be located in the $V_1$ and/or $V_3$ positions. Further, the fact that for $x > 0.33$ the $(x - 0.33)$ excess Mo atoms per formula unit enter the $V_3$ positions indicates that the $V^{4+}$ ions occupy preferentially the $V_1$ array. In addition, either a $V_3$–$O_7'$–$V_3$ or a $V_3$–$O_5$–$V_1$ unit could become a $Mo^{6+}$–O–$V^{4+}$ unit. These experiments thus give indirect evidence for a $V^{4+}$-ion preference for the $V_1$ array and a $V^{5+}$-ion preference for the $V_2$ array in the $M_x{}^+V_2O_5$-$\beta$ phases.

## APPENDIX I: Structure of $Li_xV_2O_5$-$\beta'$

The system $Li_xV_2O_5$, which was studied (*7*) here at Bordeaux a few years ago, has been entirely reexamined both chemically and crystallographically.

Whereas the previous preparation was accomplished by direct interaction between the oxides $Li_2O$, $VO_2$ and $V_2O_5$ under a stream of nitrogen according to the reaction equation

$$x\mathrm{Li_2O} + 2x\mathrm{VO_2} + (2 - x)\mathrm{V_2O_5} \rightarrow 2\mathrm{Li}_x\mathrm{V_2O_5},$$

the present syntheses were accomplished at 680°C in sealed gold tubes starting from intimate mixtures of $LiV_2O_5$ and $V_2O_5$:

$$x\mathrm{LiV_2O_5} + (1 - x)\mathrm{V_2O_5} \rightarrow \mathrm{Li}_x\mathrm{V_2O_5}.$$

$LiV_2O_5$ was prepared by interacting $VO_2$ with the metavanadate $LiVO_3$.

X-ray diffraction analysis has shown (*6*) that under these conditions the phase $Li_xV_2O_5$-$\beta$ previously reported for the compositional range $0.22 \leqslant x \leqslant 0.62$ is in fact decomposed into two phases, $\beta$ and $\beta'$, having respective compositional ranges

$0.22 \leqslant x \leqslant 0.37$ for $Li_xV_2O_5$-$\beta$,
$0.44 \leqslant x \leqslant 0.49$ for $Li_xV_2O_5$-$\beta'$.

The $\beta$ and $\beta'$ phases have *very* similar X-ray diffraction patterns.

The $\beta$-phase structure has been determined (*7*) for $x = 0.30$.

Prolonged (4 days) heating of a mixture of (0.48) $LiV_2O_5$ + (0.52) $V_2O_5$ in a sealed gold tube permitted us to isolate from the polycrystalline charge a deeply colored single crystal in the shape of a thin needle. From data collected with the Weissenberg technique (CuK$\alpha$ radiation) the structure of $Li_{0.48}V_2O_5$-$\beta'$ has been studied. The vanadium and oxygen positions are practically identical with those of the $\beta$ phase.

Least-squares refinements were made with an IBM 1130. After the positions of all the vanadium and oxygen atoms had been fixed, an electron-density difference function $F_0$–$F_{c(V+O)}$ was calculated. A negative electron density at position $M_1$, $M_1'$ (Fig. 4) of the difference map shows that these positions, which are occupied by lithium atoms in the $\beta$ phase, are empty in the $\beta'$ phase. Three alternate positions can be considered for the lithium atoms: $M_2$, $M_3$ or $M_4$ of Fig. 4. On the electron-density difference map for $F_0$–$F_{c(V+O)}$, one of these positions, $M_3$, is marked by a small, positive charge density. In addition, refinement gives the following reliability factors $R$:

| (V + O) | (V + O) + Li in $M_2$ |
|---|---|
| $R = 6.84\%$ | $R = 7.16\%$ |

(V + O) + Li in $M_3$
$R = 6.60\%$

If the lithium atoms are placed in $M_4$, they go to $M_3$ after three or four refinement cycles.

These results make us believe that in the $\beta'$ phase the lithium ions are located in the tetrahedral sites $M_3$.

## APPENDIX II: Structure of $Cu_{0.60}V_2O_5$

Well-formed, thin needles of the $Cu_{0.60}V_2O_5$ bronze were prepared by melting the corresponding composition in sealed gold tubes at 800°C. X-ray diffraction analysis before and after the melting did not show any differences.

Intensity data were obtained from a crystal measuring 0.02 × 0.2 × 0.02 mm by the integrated Weissenberg technique using filtered copper radiation. The structure of $Cu_xV_2O_5$-$\beta$ was assumed to be closely related to the $Li_xV_2O_5$-$\beta'$ structure. It was solved by the Patterson technique and refined by the least square method on an IBM 7090 (Stewart's X-ray program 63). Wilson's test indicates that the structure is probably noncentric, and this fact was confirmed by the inability of the program to refine the structure with the space group C2/m. Space group C2 was not considered because of its centric projection. With the space group Cm the structure refined to a reliability index of 10.5%. It is illustrated in Fig. 8, and the interatomic distances are given in Table I.

Although the $V_2O_5$ network of $Cu_{0.60}V_2O_5$ contains six (instead of three) independent vanadium atoms and fifteen (instead of eight) independent oxygen atoms, it is similar to the $V_2O_5$ network of the $\beta$ and $\beta'$ phases. Furthermore, the $Cu^+$ ions are located in the same tetrahedral site as the $Li^+$ ions of the $Li_xV_2O_5$-$\beta'$ phase. However, unlike the $Li^+$ ions, the $Cu^+$ ions are not in the mirror plane passing through the center of the tetrahedron; the stable cation position is split in two, being shifted slightly above and below the mirror plane. The splitting within the two independent copper tetrahedra is a little different: $Cu_I$ is in $y = \pm 0.108$ and $Cu_2$ in $y = \pm 0.08$. Since there can be only one $Cu^+$ ion per tetrahedral site, even though there are two possible locations within a site, it is obvious that the upper compositional limit for the $Cu_xV_2O_5$-$\beta'$ phase is $Cu_{2/3}V_2O_5$.

## APPENDIX III: Structure of the Mixed Bronzes $Na_xV_{2-x}Mo_xO_5$

### 1. Preparation

The mixed bronzes $Na_xV_{2-y}Mo_yO_5$ have been prepared by synthesis in a sealed gold tube according to the reaction scheme

$$2xNaVO_3 + 2(x+y)VO_2 + 2yMoO_3 + 2(1-x-y)V_2O_5 \rightarrow 2Na_xV_{2-y}Mo_yO_5.$$

After two 24-h treatments at 650°C separated by a grinding, the products were quenched.

X-ray analysis has shown that there is a considerable single-phase region for the phase $Na_xV_{2-y}Mo_yO_5$-$\beta$. In the special case where $y = x$, the phase $Na_xV_{2-x}Mo_xO_5$-$\beta$ exists throughout the range $0.17 \leqslant x \leqslant 0.42$.

Single crystals of composition $x = 0.22$, 0.30, and 0.40 have been prepared by melting, followed by slow cooling, of the corresponding powders.

### 2. Crystal Structure if $x \leqslant 0.33$

If $x \leqslant 0.33$, refinement of the structures by Fourier projection and by the method of least squares shows that the sodium ions occupy exclusively and randomly the $M_I$ positions in the structure, and also that the molybdenum atoms substitute for the vanadium atoms in the $V_2$ sites.

For $x = 0.30$, as an illustrative example, the following reliability factors are found for the different possibilities:

| | |
|---|---|
| Mo distributed randomly in $V_1 + V_2 + V_3$ | $R = 8.35\%$ |
| Mo distributed randomly in $V_1 + V_2$ | $R = 8.67\%$ |
| Mo distributed randomly in $V_1 + V_3$ | $R = 10.20\%$ |
| Mo distributed randomly in $V_2 + V_3$ | $R = 7.20\%$ |
| Mo distributed randomly in $V_1$ | $R = 12.76\%$ |
| Mo distributed randomly in $V_2$ | $R = 5.72\%$ |
| Mo distributed randomly in $V_3$ | $R = 11.65\%$. |

### 3. Crystal Structure if $x > 0.33$

(a) *Molybdenum-Occupied Sites.* For $x > 0.33$, refinement of the structure of $Na_{0.4}V_{1.6}Mo_{0.4}O_5$ was made by combining the Fourier projections with the method of least squares, the latter applying also to the concentration of molybdenum atoms substituting into a given vanadium position. (Globally this concentration corresponds to a 60% occupancy of a given vanadium site $V_1$, $V_2$ or $V_3$.)

The Fourier projection shows a positive electron-density maximum for $V_2$ that is much greater than that for $V_3$, the $V_3$ maximum being, in turn, larger than the $V_1$ maximum.

Initial refinement shows that the best results are obtained when the molybdenum concentration in the $V_2$ sites is about 50%. It is then necessary to distribute the remaining 10% molybdenum atoms. The following results indicate that the excess molybdenum atoms go into the $V_3$ sites:

| | |
|---|---|
| 50% Mo in $V_2$ + 10% Mo in $V_1$ → | $R = 8.22\%$ |
| 60% Mo in $V_2$ → | $R = 8.10\%$ |
| 50% Mo in $V_2$ + 10% Mo in $V_3$ → | $R = 7.53\%$. |

Refinement on the IBM 1130 for the molybdenum concentration at the three vanadium sites gives the following final results:

| Site | $V_1$ | $V_2$ | $V_3$ |
|---|---|---|---|
| Mo concentration, refinement | 0.2% | 49.7% | 9.6% |
| Mo concentration, conclusion | 0% | 50% | 10% |

(b) *Sodium-Occupied Sites.* Initial calculations confirmed that the $M_I$ sites were preferentially occupied by sodium, as in the structures having $x \leqslant 0.33$, and that these sites were about half-filled. Location of the small ($\approx 10\%$) sodium excess is the remaining problem.

The following table gives for each of the possible sodium distributions the $R$ factors and the sodium thermal-vibration factors $B_{Na}$, which must be of the order of 2 Å$^2$:

| Na Distribution | $B_{Na}$[Å$^2$] | $R$[%] |
|---|---|---|
| 60% in $M_1$ | 3.9 | 7.57 |
| 50% in $M_1$ | 2.4 | 7.53 |
| 10% in $M_2$ | 1.8 | |
| 50% in $M_1$ | 2.4 | 7.55 |
| 10% in $M_3$ | 8.0 | |
| 50% in $M_1$ | 2.3 | 7.53 |
| 10% in $M_4$ | 8.0 | |

The increase in the thermal-vibration factor that occurs if a small (10%) concentration of Na atoms is located in positions $M_3$ or $M_4$ shows the absence of electron density in these regions of the lattice.

Although these results must not be taken literally, given the very weak contribution from $M_2$-site occupation to the total calculation of the structure, nevertheless it seems reasonable to assume that when $x > 0.33$, either the $(x - 0.33)$ excess sodium atoms go into the $M_2$ sites or for each excess sodium atom a pair of sodium atoms go into the $M_2$ sites.

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