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High-pressure studies of some lithium vanadium bronzes and the related oxide $V_6O_{13.27}$

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High-pressure resistivity studies clearly distinguish two different types of conductors: (1) basically electronic semiconductors with negligible ionic conductivity, such as lithium β bronze and γ-$Li_{1+x}V_3O_8$, and (2) proper mixed conductors like γ-LiV_2O_5 and $V_6O_{13.27}$ wherein, due to the low electronic conductivity, the ionic contribution makes its presence felt. A first-order semiconductor-metal transition in the quasi-one-dimensional anomalous conductor $Li_{0.4}V_2O_5$ (β bronze) and a second-order semiconductor-metal transition in γ-$Li_{1+x}V_3O_8$ have been observed. However, in the mixed conductors, no such phase transition occurred. Instead, in γ-LiV_2O_5 and $V_6O_{13.27}$, the logarithms of the resistivity plotted versus pressure indicate a maximum, which has been explained as arising from the ionic conductivity, as observed in Lisicon, an ionic conductor.

The vanadium bronzes $M_xV_2O_5$, especially the quasi-one dimensional conductor $Na_{0.4}V_2O_5$ (β bronze), have been extensively investigated from different aspects, viz. structural,[1] electronic,[2] magnetic, transport,[3,4] NMR,[5-8] and electron paramagnetic resonance (EPR),[9,10] etc. Other systems such as Li, K, Cu[1,8,11] Ag,[12] Rb, Cs,[13] and Pb (Ref. 14) bronzes have also been studied. The $M_xV_2O_5$ intercalates are very interesting tailor-made mixed-valence systems, but unlike many fluctuating valence systems do not exhibit the metal-insulator (*M-I*) or metal-semiconductor (*M-S*) transitions with variation in temperature. $M_xV_2O_5$ systems are semiconductors, and in spite of the single-crystal sodium β bronze exhibiting an anomalously high anisotropic conductivity (6 $\Omega^{-1}\,cm^{-1}$ along the *b* direction and two orders lower in the perpendicular direction),[15] it is not metallic. Thus $M_xV_2O_5$ systems have localized electrons and belong to the class of thermally activated hopping semiconductors. However, to explain the anomalously high conductivity (in spite of the low mobility), the importance of polarons was invoked by Chakraverty and Sienko,[16] who proposed the formation of intersite bipolarons to explain the low-temperature magnetic susceptibility, specific heat, and electronic conductivity. Nagasawa and collaborators corroborated the formation of bipolarons on the basis of NMR (Refs. 5-7) and EPR (Refs. 9 and 10) experiments. Finally, x-ray satellite reflections[17] from sodium and lithium β bronzes not only confirmed bipolaron formation, but also long-range bipolaron ordering (the so-called Wigner crystallization in real space) with structural rearrangement (small ionic displacement) below 200 K. The period of the superstructure is twice that of the lattice constant along the *b* axis. The anomalous high anisotropic conductivity was explained as arising from correlated bipolaron hopping, along with excited-state-produced single polarons along the *b* axis. More recently, silver[12] and lead[14] bronzes have been shown to be bipolaronic semiconductors. It may, however, be pointed out that both sodium and lithium vanadium bronzes are also fast-ionic conductors,[18,19] due to motion of Na and Li ions.

Lithium intercalation in V_2O_5 produces three principal phases, viz. α, β, and γ. All these phases are formed from VO_6 octahedra and VO_5 distorted bipyramids, with distinct ordering.[20,21] α-$Li_xV_2O_5$ is very similar to V_2O_5 and has a layered orthorhombic structure with identical vanadium sites. The monoclinic β bronze (Fig. 1) has three different vanadium sites V(1), V(2), and V(3) forming a three-dimensional tunnel structure, within which the Li ion resides in octahedral sites. The oxygen-rich γ-$Li_{1+x}V_3O_8$, though monoclinic, has two different vanadium coordination sites.[22] Thus V(2) and V(3) are in the distorted octahedral coordination (in which V atoms are displaced from the octahedral center), while V(1) is at the center of a distorted trigonal bipyramid (Fig. 2). This gives rise to a two-dimensional layered lattice, with Li^+ residing in octahedral or tetrahedral sites between the layers. The normal γ-LiV_2O_5 has a layered orthorhombic structure (Fig. 3), with two inequivalent vanadium sites.[23] However, the layers are highly distorted due to the strong polarization from the large number of Li^+ ions. Finally, the mixed-valence monoclinic V_6O_{13} system, nominally ($V_4^{4+}V_2^{5+}$), has three inequivalent sites, in

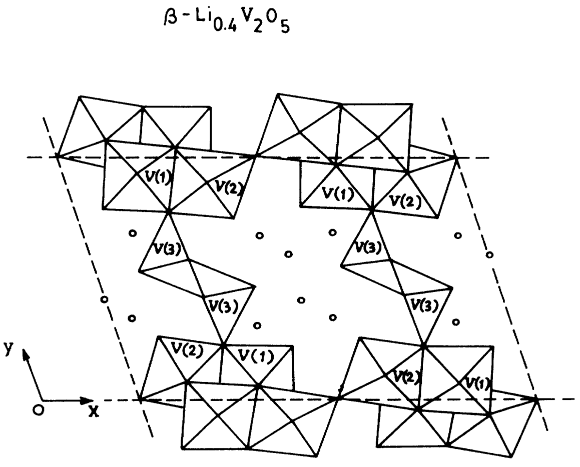

FIG. 1. Crystal structure of lithium β bronze.

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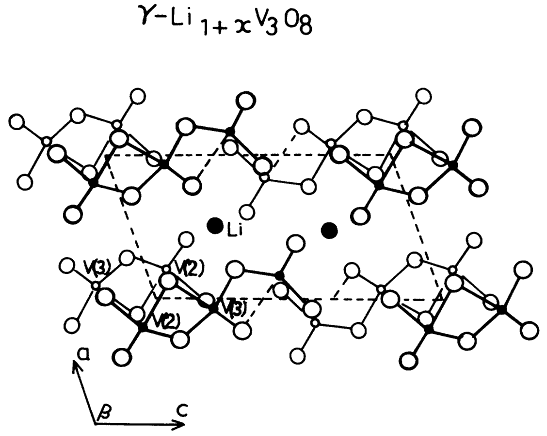

FIG. 2. Crystal structure of γ-$Li_{1+x}V_3O_8$.

which V^{5+} at the V(2) site is sandwiched between V^{4+} ions in V(1) and V(3) sites (Fig. 4). This oxide has for quite some time been erroneously[24] considered a metal (thought to undergo an *M-I* transition at 150 K from a cusp in the χ-T plot), though Kachi, Takada, and Kosuge[25] had reported as early as 1963 that at 150 K, it undergoes a semiconductor-to-semiconductor transition with a break in $\sigma \sim 10-10^2$. X-ray studies have indicated a structural distortion at this temperature,[26] when the symmetry of $C2/m$ at room temperature changed to $C2$, with a redistribution of charges over the three inequivalent vanadium sites. However, none of these V_2O_5-based systems exhibit the *M-I* or *M-S* transitions with temperature, as observed in V_2O_3 and VO_2. To date, there has been no report on the effect of pressure on these bronzes or V_6O_{13}. As is well known, pressure has a pronounced effect on electronic structure, leading to an *M-I* transition in V_2O_3.

Here results of our high-pressure conductivity studies on $Li_{0.4}V_2O_5$ (β bronze), γ-$Li_{1+x}V_3O_8$, γ-LiV_2O_5, and the oxygen-rich $V_6O_{13.27}$ are reported. The compounds β- and γ-$Li_xV_2O_5$, as well as $V_6O_{13.27}$,[24] were prepared as reported previously.[8] γ-$Li_{1+x}V_3O_8$ was prepared by melting the appropriate mixtures of Li_2CO_3 and V_2O_5 in argon or air. High-pressure resistivity measurements were made at room temperature with a four-point probe technique in a tungsten carbide anvil apparatus.

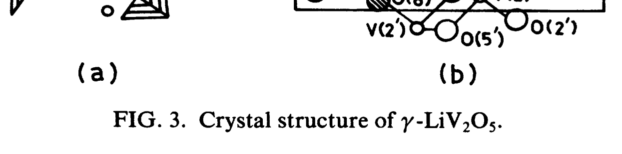

FIG. 3. Crystal structure of γ-LiV_2O_5.

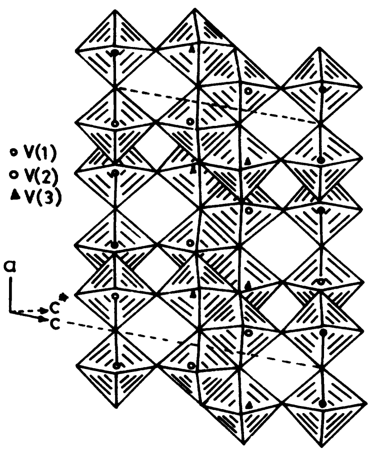

FIG. 4. Crystal structure of V_6O_{13}.

(i) $Li_{0.4}V_2O_5$ (β bronze). On increasing pressure, resistivity (R) decreases continuously up to 4 GPa [Fig. 5(a)], then drops sharply, indicating a first-order semiconductor-metal (*S-M*) transition, after which R remains unchanged with increase of pressure. The three-dimensional (3D) lattice appears not to be amenable to further compression. This is the first report of an *S-M* transition at high pressure and room temperature in the $M_xV_2O_5$ system (bronzes). As σ is already high for the semiconducting β bronze, the change in R during the *S-M* transition is just above an order of magnitude. Whether any structural rearrangement is responsible for the *S-M* transition can only be answered by high-pressure x-ray studies. However, for $Na_{0.4}V_2O_5$, Perlstein and Sienko[3] had commented that the V-V spacing is just short of the critical distance predicted by Goodenough[2] for electron delocalization via *d*-orbital overlap. The same situation is also valid for the Li bronze. As pressure is expected to reduce all V-V and V-O distances, it may so happen that Goodenough's critical distance for electron delocalization is reached, leading to the metallic state.

In this connection, it may be pointed out that Kaputskin, Volkov, and Fotiev[27] had reported a semiconductor-metal transition in single crystals of lithium and sodium β bronzes along ⟨010⟩ in the region 340 K. They interpreted this *S-M* transition as being due to a vanishing of the activation energy of carrier mobility due to shift of the V atoms in the plane perpendicular to the *b* axis.

(ii) γ-$Li_{1+x}V_3O_8$ has a conductivity at room temperature that is lower than of the Li β bronze $\sim 10^{-2}$ $\Omega^{-1}\,cm^{-1}$ but much higher than that of V_2O_5 [Fig. 5(b)]. With increasing pressure, R decreases slowly up to 4 GPa, but between 4 and 6 GPa, $\log_{10}R$ changes by three orders of magnitude. However, unlike the β bronze, the change is not sharp and possibly corresponds to a second-order *S-M* transition. Interestingly, R further decreases with increasing pressure from 6 to 9 GPa due to easy compressibility of the layered structure.

(iii) γ-LiV_2O_5. With increasing pressure, R first falls sharply (not large in magnitude) but registers a maximum around 1 GPa, after which it falls on further increase of pressure and then tends to become constant [Fig. 5(c)].

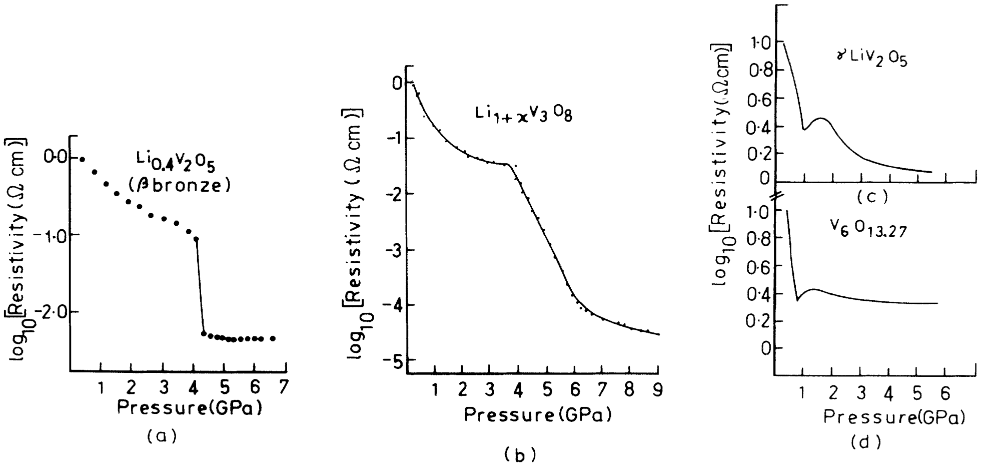

FIG. 5. Plot of $\log_{10}$ [resistivity (Ω cm)] vs pressure.

In γ bronze, in spite of the highest Li content and the consequent highest ratio $[V^{4+}]/[V^{5+}] \sim 1$, conductivity is rather low, even lower than that of α-$Li_xV_2O_5$. γ-LiV_2O_5 is a random spin system and V^{4+} and V^{5+} are not alternately placed in the chain. Thus, the possibility of finding V^{4+}-V^{4+} pairs arises. In γ-LiV_2O_5 there are two types of vanadium sites, V(1) and V(2) in the V_2O_5 chain with V(1)-V(1) distances $\sim$2.98 Å, almost at Mott's critical distance R_c, whereas the V(1)-V(2) distance $\sim$3.30 Å. Thus, due to *d-d* pairing, the conduction path is disrupted, and σ is of the same order as oxygen-deficient V_2O_5. As the electronic conductivity (EC) in γ-LiV_2O_5 is low, ionic conductivity (IC) from Li^+ ions can no longer be neglected. Thus, it behaves as a proper mixed conductor. In EC, pressure generally has the effect of increasing σ by closing the band gap, decreasing the hopping distance, etc. However, in the case of IC, due to increasing ionic repulsion, decreasing the number of interstitials, etc., the effect of pressure may be the opposite. Thus, not only the entropy changes, but the activation volume may change from positive to negative at a critical pressure, as in Lisicon,[28] when one gets a maximum in the *R*-versus-pressure plot. Thus in γ-LiV_2O_5 the initial sharp decrease is from an increase in EC, after which the maximum appears from the IC contribution. However, as γ-LiV_2O_5 has a 2D layered structure, *R* further decreases with increasing pressure.

(iv) $V_6O_{13.27}$. The room-temperature σ is a little less than 1 $\Omega^{-1}cm^{-1}$, whereas stoichiometric V_6O_{13} has a $\sigma \sim 10^{-3}$ $\Omega^{-1}cm^{-1}$. Further, in $V_6O_{13.27}$ the break in the χ-T plot, as seen in V_6O_{13}, vanishes. Interestingly, the pressure effect is very similar to that of γ bronze [Fig. 5(d)]. The excess oxygen creates disorder in the mixed valence V_6O_{13}, which has been shown to be a bipolaronic conductor.[24] Part of the excess oxygen is possibly present in the lattice as an O^- anion, responsible for the weak maximum. As the compound has a 3D network structure, *R* remains unaltered with a further increase in pressure, unlike that of the layered γ-LiV_2O_5. However, in spite of the lattice disorder, bipolaron ordering at 150 K is not affected, as shown by NMR.[24]

Pressure thus makes a clear distinction between these two classes of semiconductors: one in which the contribution of IC to the total conductivity can be neglected, viz. Li β bronze and γ-$Li_{1+x}V_3O_8$ (basically electronic conductors); the other in which IC is not negligible and may be classed as proper mixed conductors, viz. γ-LiV_2O_5 and the oxygen-rich $V_6O_{13.27}$.

A comparison of the *S-M* transitions in the present case with that in VO_2 and V_2O_3 may be of some interest. Though investigated over four decades, the mechanism of *M-I* or *M-S* transitions in VO_2 and V_2O_3 brought about by temperature and pressure has been highly controversial.[15,29] Moreover, a comparison of the two reveals striking differences. Recent vacuum ultraviolet reflectance and photoemission studies of VO_2, V_2O_3, and V_6O_{13} (Ref. 30) investigate the 3*d* band structures and electron correlation effects. In VO_2, drastic changes in the 3*d* (π^* and d_{11}) band structures are found in both spectra through the *M-I* transition. On the other hand, no drastic change is found in the 3*d* band structure of V_2O_3 and V_6O_{13}, except for slight changes in bandwidths. The density of states at the Fermi level is rather low, even in the metallic phase. Shin *et al.*[30] muster these facts in support of electron correlation effects. However, Abbate *et al.*[31] from soft-x-ray absorption studies of VO_2 (wherein O 1*s* spectrum maps mainly V 3*d* band character) have shown a clear splitting of the unoccupied d_{11} band. This he cites in support of the theories, which explain the transition in terms of localized pairing interactions, within the *V-V* dimer.

In this background, it is apparent that further sophisticated studies are needed to elucidate the mechanism of the high-pressure *S-M* transitions in the more complex lithium vanadium bronzes.

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