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On the Possible Electronic Instability of the Monophosphate Tungsten Bronze $(WO_3)_4(PO_2)_4$

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The electronic structure of the monophosphate tungsten bronze $(WO_3)_4(PO_2)_4$ was examined by performing tight-binding band calculations. Our study suggests that the W_2O_{10} chains of $(WO_3)_4(PO_2)_4$ have both localized and delocalized electrons, and the latter may cause an electronic instability such as a charge density wave. © 1990 Academic Press, Inc.

The monophosphate tungsten bronze (MPTB) series (*1*) $(WO_3)_{2m}(PO_2)_4$ with $m > 2$ contain perovskite-type layers of WO_6 octahedra, and these layers are interlinked by PO_4 tetrahedra. Band electronic structure studies (*2*) on the MPTB phases show that these oxides have both one-dimensional (1D) and two-dimensional (2D) metallic bands, and that the Fermi surfaces of the 2D metallic bands are nested. Consequently, these MPTB phases are expected to exhibit electronic instabilities. In fact the fourth ($m = 4$) and sixth ($m = 6$) members of the MPTB series show anomalies in their electrical resistivities (*2*). Recently, the second ($m = 2$) member of the MPTB series, i.e., $(WO_3)_4(PO_2)_4$ (or WPO_5 in short) has been reported (*3*). Unlike the higher members of the MPTB series, the second member does not contain perovskite-type layers but zigzag W_2O_{10} chains made up of corner-sharing WO_6 octahedra. Consequently, the electronic properties of $(WO_3)_4(PO_2)_4$ are anticipated to differ from those of other MPTB phases. The present note reports some essential aspects of the electronic structure of $(WO_3)_4(PO_2)_4$, which we obtain by performing tight-binding band calculations (*4*) based upon the extended Hückel method (*5*). The atomic parameters employed in the present study were taken from our previous work (*6*).

In discussing the electronic structure of $(WO_3)_4(PO_2)_4$, it is necessary to describe its crystal structure. A perspective view of an ideal WO_6 octahedron is shown in scheme **1a.** If a projection view of scheme **1a** along the axial W–O bond is represented by

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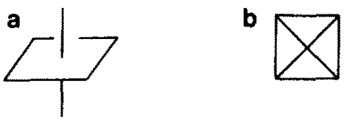
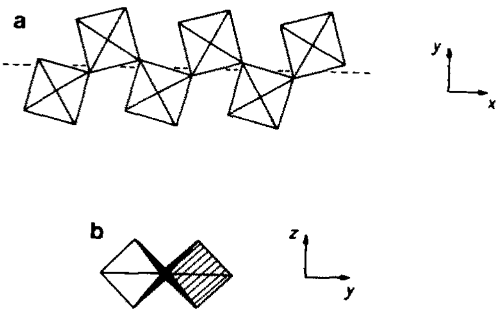


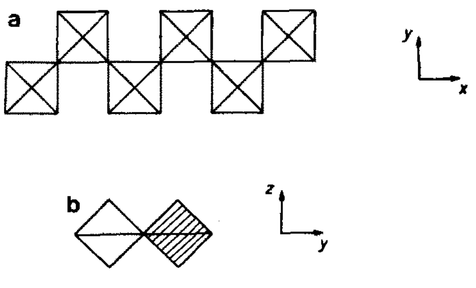
SCHEME 1

scheme **1b**, a zigzag W_2O_{10} chain made up of corner-sharing WO_6 octahedra can be shown as scheme **2a**. Representation of scheme **2a** is further simplified by its projection view along the chain direction (scheme **2b**). In $(WO_3)_4(PO_2)_4$, the W_2O_{10} chains are distorted as depicted by scheme **3a**, so that its projection view along the chain may be given by scheme **3b**. As shown in scheme **4**, these distorted W_2O_{10} chains are linked by PO_4 tetrahedra (shown by solid triangles) in $(WO_3)_4(PO_2)_4$. Every PO_4 tetrahedron shares all its four oxygen atoms with the W_2O_{10} chains, and the latter are isolated from one another so that the electronic properties of $(WO_3)_4(PO_2)_4$ are expected to be 1D.

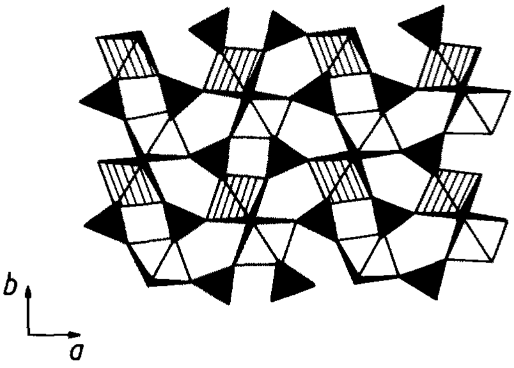
Figure 1 shows the dispersion relations of the t_{2g}-block bands calculated for a single W_2O_{10} chain found in $(WO_3)_4(PO_2)_4$. This band structure is essentially identical with that of the zigzag Mo_2O_{10} chain studied in connection with the electronic structure of lithium molybdenum purple bronze $Li_{0.9}Mo_6O_{17}$ (*7*). The dispersive bands *a*, *b* are mainly constructed from the δ-orbital (i.e., $x^2 - y^2$ orbital in scheme **5**) of each WO_6 octahedron, and the flat bands *c*–*f* from the π-orbitals (i.e., *xz* and *yz* orbitals of scheme **5**). A detailed orbital interaction analysis has shown (*7*) that the flat bands *c*, *d* should lie in the middle of the dispersive band *a*. Likewise, the flat bands *e*, *f* should lie in the middle of the dispersive band *b*. With the oxidation states of O^{2-} and P^{5+}, the *d*-electron count on W is d^1 in $(WO_3)_4(PO_2)_4$. Namely, there are two electrons to fill the t_{2g}-block bans of Fig. 1 (two W atoms per unit cell in the W_2O_{10} chain). Therefore the dispersive band *a* is nearly half-filled, and the nearly degenerate bands *c*, *d* are quarter-filled as a whole. In simple chemical terms, this implies that two δ-orbitals of a unit cell accommodate one electron, and so do four π-orbitals of a unit cell.



SCHEME 3



SCHEME 2



SCHEME 4

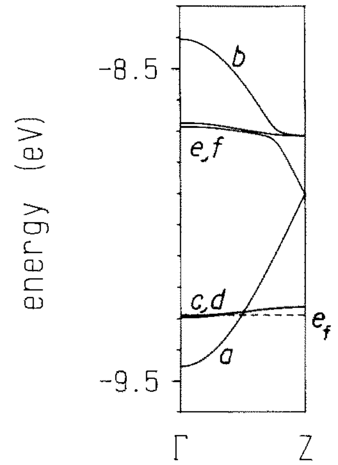


FIG. 1. Dispersion relations of the t_{2g}-block bands calculated for W_2O_{10} chain of $(WO_3)_4(PO_2)_4$, where the dashed line refers to the Fermi level. $\Gamma = 0$; $Z = c^*/2$.

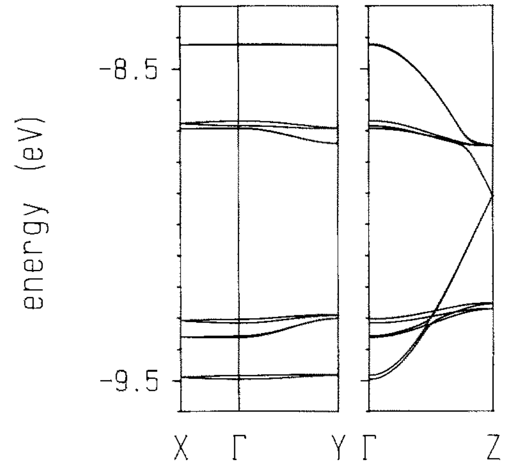
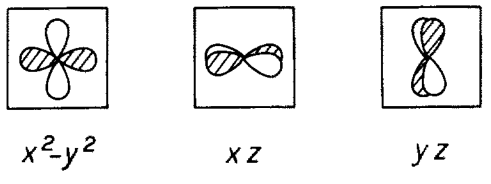


FIG. 2. Dispersion relations of the t_{2g}-block bands calculated for the three-dimensional lattice of $(WO_3)_4(PO_2)_4$. $\Gamma = (0, 0, 0)$; $X = (a^*/2, 0, 0)$; $Y = (0, b^*/2, 0)$; $Z = (0, 0, c^*/2)$.

Since bands *c*, *d* are extremely narrow, electrons in these bands are most likely to be localized (*8*). On the other hand, band *a* is quite dispersive so that electrons in this band are expected to be delocalized. Thus the W_2O_{10} chain would have both localized and delocalized electrons. This observation remains valid for the three-dimensional lattice of $(WO_3)_4(PO_2)_4$. Figure 2 shows the dispersion relations of the t_{2g}-block bands calculated for $(WO_3)_4(PO_2)_4$. Except for the doubling of each band level, which reflects the fact that the 3D lattice of $(WO_3)_4(PO_2)_4$ has two W_2O_{10} chains per unit cell, the band electronic structure of $(WO_3)_4(PO_2)_4$ is essentially identical with that of the W_2O_{10} chain. As a result, $(WO_3)_4(PO_2)_4$ is expected to be metallic and possess magnetic properties associated with localized electrons. In addition, the 1D metallic band (i.e., band *a*) may lead to an electronic instability such as a charge density wave (*9*). Therefore, it would be of interest to measure the physical properties of $(WO_3)_4(PO_2)_4$.



SCHEME 5

Acknowledgment

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