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Concerning the Possibility of Hidden One-Dimensional Fermi Surfaces for the $K_{0.25}WO_3$ Hexagonal Bronze

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On the basis of first-principles density functional theory calculations, it is shown that, in contrast with a recent suggestion, $K_{0.25}WO_3$ does not exhibit hidden one-dimensional Fermi surfaces. A charge-density-wave instability should not be at the origin of the resistivity anomaly of this bronze, which most likely results from potassium vacancy ordering.

Low-dimensional molybdenum and tungsten oxides and bronzes have been the focus of much attention because of the charge-density-wave (CDW) instabilities that they exhibit.[1] The CDWs are incommensurate with the lattice in the blue bronzes or the η- and γ-Mo_4O_{11} Magnéli phases but commensurate in the sodium and potassium purple bronzes. Another widely studied family of these compounds is that of the monophosphate tungsten bronzes, which exhibit successive CDWs with modulations varying considerably for the different members of the family.[1b,2] Condensation of these CDWs is usually driven by instabilities of the Fermi surface (FS).[3] In some cases, the FS clearly exhibits nesting features that are at the origin of the CDW instability. However, in other cases, the FSs are apparently non-nested, and it is difficult to understand the origin of the CDWs. The development of the so-called *hidden nesting* concept[4] provided a simple way for analyzing apparently non-nested FSs in terms of a superposition of nested ones.

Recently, Raj et al.[5] reported angle-resolved photoemission spectroscopy (ARPES) and density functional theory (DFT) results concerning the FS of the hexagonal potassium tungsten bronze, $K_{0.25}WO_3$ (see Figure 1a).[6] On the basis of these results, they suggested that the well-known high-temperature resistivity anomaly of this metal originates from a possible CDW instability as a result of the existence of hidden pseudo-one-dimensional (1D) bands in the hexagonal a^*b^* planes. This is quite puzzling because metallic hexagonal tungsten bronzes usually exhibit partially filled bands with quite large energy dispersion in the perpendicular c direction,[7] something that makes the previous suggestion surprising. Here we report DFT calculations and an orbital interaction analysis of the results showing that $K_{0.25}WO_3$ *does not possess pseudo-1D partially filled bands* and that it is a three-dimensional (3D) metal. An insufficient exploration of the Brillouin zone (BZ) is at the origin of the above-mentioned suggestion by Raj et al.[5]

The present calculations were carried out using a numerical atomic orbital DFT[8] approach implemented in the SIESTA code.[9] We have used the generalized gradient approximation to DFT and, in particular, the functional of Wu and Cohen.[10] Only the valence electrons are considered in the calculations, with the core being replaced by norm-conserving scalar relativistic pseudopotentials[11] factorized in the Kleinman−Bylander form.[12] We have used a split-valence double-ζ basis set including polarization orbitals for all atoms, as obtained with an energy shift of 0.02 Ry.[13] The energy cutoff of the real-space integration mesh was 300 Ry, and the BZ was sampled using a grid of 12 × 12 × 12 k points.[14] The existence of partially empty potassium sites was treated via the virtual crystal approximation.

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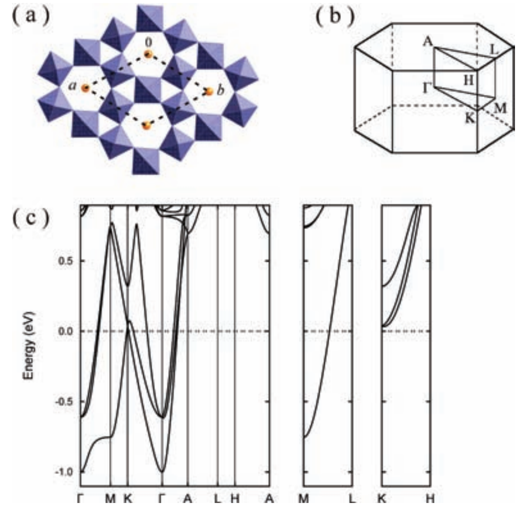

Figure 1. (a) Crystal structure, (b) hexagonal BZ, and (c) calculated band structure for $K_{0.25}WO_3$. The dashed line refers to the Fermi level.

The essence of the reasoning by Raj et al.[5] is that both the calculated and ARPES (a^*b^*) sections of the FS result from weak hybridization of pairs of parallel lines, perpendicular to the $a^* + b^*$ direction and those equivalent by 120° rotations. From this observation, they conclude that "the FS is the consequence of hidden 1D bands". This means that these bands should have a nil dispersion along the c^* direction. The calculated band structure for $K_{0.25}WO_3$ in the region around the Fermi level is shown in Figure 1c. It is immediately clear that the three partially filled bands exhibit a very large dispersion along c^* (i.e., along $\Gamma \rightarrow A$, $M \rightarrow L$, and $K \rightarrow H$). Consequently, there are no partially filled 1D bands along the direction $a^* + b^*$ and those equivalent by 120° rotations. Because the three partially filled bands are already slightly above the Fermi level at the K point, this means that their dispersion in the $c^* = 0.0$ section is also large and, consequently, the partially filled bands of $K_{0.25}WO_3$ should be 2D or 3D.

The calculated FS for $K_{0.25}WO_3$ is reported in Figure 2 as different sections perpendicular to the c^* direction. The FS for the plane with $c^* = 0.0$ is practically identical with the theoretical and experimental sections reported by Raj et al.[5] (the very slight differences are due to the different ways in which the potassium doping has been treated in the calculations: via a rigid band approach using hexagonal WO_3 by Raj et al.[5] or through the explicit consideration of K cations via the virtual crystal approximation here). This section may indeed be seen as resulting from the interaction of three pairs of parallel lines. However, it is also clear that when one departs from the plane at $c^* = 0.0$, the shape of the FS section seriously changes. At the plane with $c^* = 0.25$, any trace of the apparent hidden 1D bands is already lost and none of the sections with $c^* \geq 0.3$ contribute to the FS. Thus, the three components of the FS are 3D, as is expected from the calculated band structure. In fact, this conclusion could have been reached by Raj et al.[5] because they noted that there is no band crossing the Fermi level in the AHL plane. Alternatively, simple electron-counting arguments also lead to the same conclusion. The repeat unit of $K_{0.25}WO_3$ contains six formula units and, thus, there are 1.5 electrons to fill the three t_{2g}-type bands of Figure 1c. Consequently, if three bands were 1D, they should be one-quarter-filled and the nesting vectors cannot be those proposed by Raj et al.,[5] which would be appropriate for half-filled 1D bands.

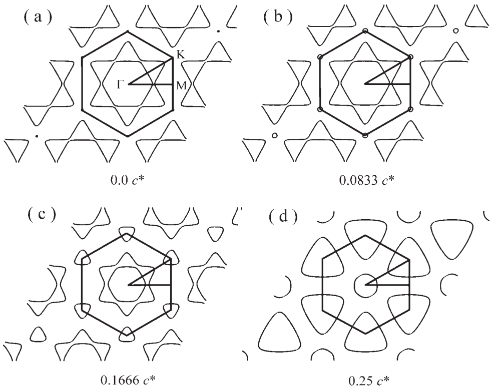

Figure 2. Calculated FS for $K_{0.25}WO_3$ shown as different sections perpendicular to the $\Gamma \rightarrow A$ direction of the BZ (i.e., the c^* direction): (a) $0.0c^*$, (b) $0.0833c^*$, (c) $0.1666c^*$, and $0.25c^*$.

With these observations in mind, we believe that there is no compelling reason to assume that the superlattice spots and weak resistivity anomaly around 350 K[15] result from the condensation of CDWs. Several experimental observations support this conclusion: (i) when the transition occurs, there is an *increase* of the conductivity instead of the usual decrease found in typical CDW materials; (ii) the FS determined by photoemission in the a^*b^* reciprocal plane[5] at 20 K *does not reveal the formation of large partial gaps* expected from the stabilization of a CDW; (iii) structural work by Schulz et al.[6] showed that the W atoms are not implicated in the superstructure, as it should be if a CDW based on the t_{2g} bands of Figure 2 were at work.

Coming back to the FS of Figure 2, it is intriguing that both the experimental and theoretical sections for $0.0c^*$ are made of sets of weakly interacting pairs of parallel lines, as if they were originating from partially filled 1D bands. This feature is, however, easy to understand after analysis of the band structure.[3] The three partially filled bands are essentially built from the tungsten xz and yz orbitals, which mix with the oxygen p orbitals in an antibonding way. In an *ideal* hexagonal structure, the tungsten xz and yz orbitals are antisymetric with respect to the basal planes of the octahedra. For wave functions corresponding to a $0.0c^*$ component of the k vector, the $p_{x,y}$ orbitals of the apical oxygen atoms cannot mix by symmetry into the wave function. Consequently, there is no interaction between the tungsten xz/yz orbitals of different hexagonal planes *for this specific section of the BZ*. In that particular case, the band dispersion can only arise from interactions within an hexagonal plane. The pseudo-1D nature of the bands for this section is easy to understand when it is realized that (a) as shown in Figure 3a one hexagonal octahedral plane can be seen as resulting from the intersection of octahedral chains along the a, b, and $a + b$ directions, in such a way that every octahedron belongs simultaneously to two different types of chains and (b) every octahedron possesses one pair of xz/yz orbitals, which can mix and rotate, leading to two new orbitals and avoiding as much as possible the antibonding mixing with the basal oxygen p_z orbitals, thus leading to the lowest energy t_{2g}-based crystal orbitals. In other words, every octahedron can

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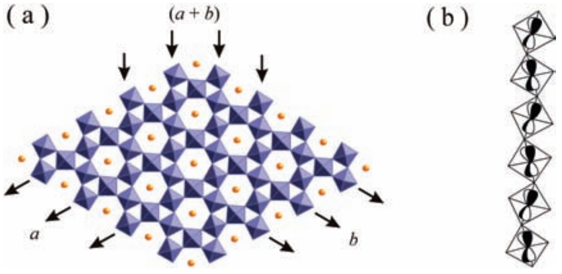

Figure 3. (a) Schematic diagram showing that an hexagonal octahedral plane like those found in $K_{0.25}WO_3$ can be seen as resulting from the intersection of octahedral chains along the *a*-, *b*- and (*a* + *b*)-directions. (b) Top view of an orbital chain along the (a + b)-direction (see text).

use independently the *two* appropriate xz/yz combinations to make extended interactions along the *two* chains common to every octahedron. This leads to chains of orbital interactions like that schematically shown in Figure 3b (top view), which runs along the $a + b$ direction. These chains of orbitals do not interact with those of parallel chains because the tungsten xz/yz combination cannot overlap with the p_z orbital of the oxygen atoms of the basal site perpendicular to the chain direction as a result of the local symmetry (see Figure 3b). The absence of such oxygen contributions isolates the different parallel chains. In addition, the fact that two types of chains intersect at each octahedron does not lead to a sizable interaction because of the local orthogonality of the two combinations of xz/yz orbitals. The actual distortions of the lattice with respect to the ideal one do not alter significantly this description. As a matter of fact, the crystal orbitals at Γ are essentially made of sets of parallel chains of orbitals like that of Figure 3b (or those equivalent along the *a* and *b* directions), which practically do not communicate. When the component of the *k* vector changes along the direction of the chain, the p_z orbitals of the oxygen shared along the chain can mix into the crystal orbital because of the associated phase changes and the band acquires dispersion. However, when the *k*-vector component changes along the interchain direction, the chains practically do not communicate because of the local symmetry argument pointed out above. Thus, for this particular section of the BZ, the system can be considered to result from the very weak hybridization brought about by the octahedral distortions of three 1D chains running along the *a*, *b*, and $a + b$ directions. However, as soon as the c^* component of the *k* vector departs from zero, the interoctahedral plane interactions are switched on and any trace of the pseudo-1D behavior is lost.

At this point, one may wonder if the previously proposed pseudo-1D behavior could occur in some hexagonal tungsten bronze with similar t_{2g} band filling. To cut the energy dispersion along the c^* direction, a strong bond-length alternation of the octahedral apical bonds is needed.[3] However, if this occurs, the xz/yz orbitals (which are those responsible for the pseudo-1D behavior) are strongly destabilized,[3] and hence the bottom of the t_{2g}-block bands would originate from the xy orbitals. Consequently, it is reasonable to conclude that *the proposed pseudo-1D behavior cannot occur in these bronzes.*

If a CDW originating from the partially filled t_{2g} bands of Figure 2 is not at the origin of the superlattice spots and the weak resistivity cusp at 350 K,[16] it is then legitimate to assume that the potassium vacancy ordering actually controls the phenomena, as originally proposed by Krause et al.[15] In fact, the situation here is reminiscent of the stabilization of long period stacking orders in metallic alloys (as described, for instance, in the so-called Hume−Rothery rules).[16] There it has been shown that long period orderings occur if the modulation induces a new BZ with boundaries to which non-negligible portions of the FS are tangential because gap openings stabilizing the electronic energy then occur. This would be the situation here for modulations with wave vectors $^1/_2a^*$, $^1/_2b^*$, and $^1/_2a^* - {}^1/_2b^*$. Thus, an ordering of the vacancies with those wave vectors may induce a gain in the electronic energy through this mechanism even if the coupling between the conducting electrons and the potential brought about by the vacancies is weak. The slight increase in the conductivity results from a competition of two factors: (i) a decrease due to the slight reduction of carriers (which is likely also related to the decrease of T_c for superconductivity around $x = 0.25$ because the density of states at the Fermi level decreases) and (ii) an increase due to the gain in the electronic mobility resulting from the ordering of the potential due to the vacancies, which apparently dominates.

In summary, we find that $K_{0.25}WO_3$ does not exhibit 1D partially filled bands and that the suggested vacancy ordering mechanism, in which the peculiar shape of the FS around the $0.0c^*$ section plays, however, an important role, provides adequate ground to understand the origin of the superlattice spots and resistivity anomaly of this bronze around 350 K.

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