Simplicity out of complexity: band structure for $W_{20}O_{58}$ superconductor

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Abstract: The band structure, density of states, and the Fermi surface of a recently discovered superconductor, oxygen-deficient tungsten oxide $WO_{2.9}$ that is equivalent to $W_{20}O_{58}$, studied within the density functional theory (DFT) in the generalized gradient approximation (GGA). Here we show that despite the extremely complicated structure containing 78 atoms in the unit cell, the low-energy band structure is quite feasible. Fermi level is crossed by no more than 10 bands per one spin projection (and even 9 bands per pseudospin projection when the spin-orbit coupling is considered) originating from the $d$-orbitals of tungsten atoms forming zigzag chains.

Keywords: Band structure; DFT; Superconductivity

1. Introduction

The discovery of a new type of superconductor is always exciting since it promotes a novel incite into the understanding of such a basic phenomenon. It is especially evident in the unconventional and high-$T_c$ superconductors like cuprates [1] and Fe-based materials [2]. Recent discovery of superconductivity in a tungsten oxide $WO_{2.9}$ is not an exception [3]. Structure and electrical properties of tungsten trioxide $WO_3$ and oxygen-deficient tungsten oxides $WO_{3-x}$ were thoroughly studied quite long ago [4,5]. Tungsten oxides are known for their thermoelectric applications [6] that makes them the distant relatives to the other superconductor, water-intercalated sodium cobaltate Na$_x$CoO$_2$·H$_2$O [7–10]. Another similarity with sodium cobaltates, cuprates, and iron-based materials arise from the partially filled $d$-orbitals of W involved in the conductivity. That is, the stoichiometric material $WO_3$ has an empty $d$-shell with tungsten $W^{6+}$ in 5$d^0$ configuration. Oxygen deficiency induces $W^{5+}$ ions with the 5$d^1$ configuration. Observation of superconductivity in twin-walls of $WO_{3-x}$ [11], thin films [12], and in $WO_3$ with the surface composition Na$_{4.05}$WO$_3$ [13] led to the proposal of the possible superconductivity in $WO_{3-x}$ [14] and a consequent discovery of it in $WO_{2.9}$ with $T_c = 80$K and with $T_c = 94$K after the lithium intercalation [3].

The main element of the crystal structure is $WO_6$ octahedron where the tungsten atom in the center is coordinated by the six oxygen atoms located in the vertices. Complexity of $WO_{2.9}$ arises from the oxygen deficiency. That is, the elementary unit cell contains 20 tungsten atoms and 58 oxygens making it the nano-object. Octahedra in the unit cell are stacked in two different ways, either as corner-shared, or as edge-shared. Later results in the stripe-like structures. Since the superconducting volume fraction is about 20%, the key role here may be played by these structures [3].

Here we make a first step toward the understanding of the $WO_{2.9}$ properties, namely, we explore its electronic band structure via density functional theory (DFT). The role of the spin-orbit coupling is also studied. The unit cell of $W_{20}O_{58}$ contains 78 ions and produces an extremely complicated band structure. Yet there are not so many bands crossing the Fermi level and, when the spin-orbit coupling is considered,
the Fermi surface consists of 18 sheets with 14 of them having a quasi-one-dimensional character and the rest having a two-dimensional character.

2. Calculation details and crystal structure

To calculate the band structure, density of states (DOS), and Fermi surface we use DFT with all-electron full-potential linearised augmented-plane wave (LAPW) implemented via the Elk code [15] together with the generalized gradient approximation (GGA) [16]. Below we present results with and without the spin-orbit coupling (SOC) that was included within the fully relativistic calculation scheme.

All calculations were converged self-consistently on a grid of $8 \times 8 \times 8$ k-points in the irreducible Brillouin zone. Due to the size of the system, the calculations are rather costly, so we firstly calculated only the band structure for several grid sizes and found that results for $6 \times 6 \times 6$ and $8 \times 8 \times 8$ grids are almost the same. Thus we can confidently use the $8 \times 8 \times 8$ k-points grid for all further calculations.

Figure 1. Crystal structure of the $W_{20}O_{58}$ supercell (left) and the structure contained in the layers of edge-shared octahedra with the labeled tungsten atoms (right).

Discussed compound $W_{20}O_{58}$ belongs to the family of the Magneli-type oxides with the general formula $W_nO_{3n−2}$ [4]. The space group is a $P2_1/m$ with the unique axis $b$. The lattice parameters are the following: $a = 12.1 \text{ Å}, b = 3.78 \text{ Å}, c = 23.39 \text{ Å}, \beta = 95°$. In Fig. 1, left panel, we show the $W_{20}O_{58}$ supercell ($2 \times 2 \times 2$). The entire structure may be described as consisting of two parts: blocks of the corner-sharing octahedra located between the zigzag stripes (white in the figure) and blocks of the edge-sharing octahedra.
located along the stripes. The WO$_6$ octahedra are distorted and irregular across all the (100) plane of the lattice. In the right panel of Fig. 1 one can see the tungsten atoms located along the zigzag stripe labeled as W15-W20; as we shall see below, these atoms gives the largest contribution to the band structure near the Fermi level.

3. Results and discussion

In Fig. 2(a) we show the Brillouin zone with the $\mathbf{k}$-path used in the band structure analysis. High-symmetry $\mathbf{k}$-points were selected according to the SeeK-path tool [17]. Fig. 3 shows the comparison of the DFT-calculated bands of W$_{20}$O$_{58}$ near the Fermi level with and without SOC. Evidently, the spin-orbital coupling leads to the disappearance of the electron pocket around the B point, the disappearance of two smaller electron pockets in the $\Gamma - A$ direction, and a total shift of the band structure to higher energies by about 0.2 eV.

![Figure 2](image)

Figure 2. (a) Brillouin zone for W$_{20}$O$_{58}$ with the $P2_1/m$ space group. Comparison of the DFT-calculated Fermi surface for W$_{20}$O$_{58}$ with SOC (b) and without SOC (c).

Fermi surfaces with and without SOC are shown in Fig. 2(b,c). Again, one can see the disappearance of the electron pocket around the B point and two small electron pockets in the $\Gamma - A$ direction once the SOC is switched on. Therefore, the SOC makes the band structure just a bit simpler.
Figure 3. Comparison of the DFT bands with (bold violet curves) and without SOC (green curves). The Fermi level corresponds to zero.

DOS and a band structure in a wide energy range for W\textsubscript{20}O\textsubscript{58} are shown in Fig. 4. Band structure clearly shows a small gap just above $-1$ eV. As is evident from DOS, the states under the gap originates mostly from oxygen while the states above the gap are mostly from tungsten. The tungsten atoms W\textsubscript{15}-W\textsubscript{20} located along the zigzag stripe in the crystal structure (see Fig. 1) give the largest contribution above the Fermi level whilst the other tungsten states are distributed fairly equally. SOC does not lead to any notable changes in DOS.

Figure 4. Left: DFT-calculated DOS for W\textsubscript{20}O\textsubscript{58} — total DOS with and without SOC (left section), DOS for tungsten atoms contained in the layers of the edge-shared octahedra (middle section), and DOS for oxygen atoms (right section). Right: DFT-calculated band structure in a wide energy range without SOC. The Fermi level corresponds to zero.

To demonstrate the importance of the tungsten atoms W\textsubscript{15}-W\textsubscript{20}, we plot their orbital character in Fig. 5. One can see that the dominating contribution near the Fermi level comes from these atoms. Again, SOC does not lead to any notable changes in the orbital characters.
Figure 5. DFT-calculated band structure with (top) and without SOC (bottom) where the orbital character of the tungsten atoms W15-W20 are shown by different colors. The width of the curves is proportional to the contribution of the corresponding orbitals. The Fermi level corresponds to zero.

4. Conclusions

We have studied the electronic structure of the non-stoichiometric material WO$_{2.9}$ that is equivalent to W$_{20}$O$_{58}$ via the state-of-art density functional theory in the generalized gradient approximation (GGA). The material has a sophisticated unit cell containing 78 ions thus producing an extremely complicated band structure. Bands crossing the Fermi level, however, originate mostly from the $d$-orbitals of the small number of tungsten atoms forming the zigzag stripe pattern in the crystal structure. It is the reason why the Fermi surface is quite simple. Indeed, it consists of five two-dimensional and several quasi-one-dimensional sheets. Thus we conclude that the electronic properties of WO$_{2.9}$ may be governed by the small number of $d$-bands. If the observed superconductivity involves electrons from these bands, it may explain the smallness of the experimentally estimated superconducting volume fraction.

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