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High-resolution angle-resolved photoemission investigation of potassium and phosphate tungsten bronzes

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ABSTRACT

We have performed high-resolution angle-resolved photoemission spectroscopy (ARPES) and density functional *ab initio* theoretical calculation to study the electronic structure of potassium ($K_{0.25}WO_3$) and phosphate ($P_4W_{12}O_{44}$) tungsten bronzes. We have experimentally determined the band dispersions and Fermi surface topology of these bronzes and compared with our theoretical calculations and a fair agreement has been seen between them. Our experimental as well as theoretical investigation elucidates the origin of transport anomalies in these bronzes. The Fermi surfaces of these bronzes consist of flat patches, which can be connected with each other by a constant nesting wave vector, q. The scattering wave vectors found from diffraction measurements match with these nesting vectors and the anomalies in the transport properties of these bronzes can be well explained by the evolution of charge-density wave with a partial nesting between the flat segments of the Fermi surfaces.

1. Introduction

The electronic structure of the various transition metal bronzes has provided much food for thought, questioning the various fundamental issues of physics over the past century due to their exotic physical properties. Out of all bronzes, systems like tungsten and molybdenum bronzes have been the subject of numerous experimental and theoretical studies for the last five decades. Tungsten bronzes are well-defined non-stoichiometric compounds of general formula A_xWO_3, where A is an alkali metal and x varies from zero to unity [1]. These alkali tungsten-oxide (WO_3) based compounds have created tremendous interest among material physicists because of their large technological implications [2,3]. When sodium (Na) is doped as an alkali metal to WO_3, then sodium tungsten bronze (Na_xWO_3) is formed and Na_xWO_3 exhibits one of the most interesting properties like metal–insulator transition (MIT) with the variation of Na doping (x). It has been found that Na_xWO_3 is insulating for lower concentrations of $x < 0.25$ [4]. MIT in these types of materials has always been a topic of intense discussion among condensed matter physicists since decades. However, there are other bronzes where the MIT-like phenomena take place with the variation of temperature and these transitions are generally associated with transport anomalies. When alkali metal potassium (K) is doped in WO_3 lattice, then it forms K_xWO_3 with hexagonal crystal structure. The corner-sharing WO_6 octahedra form six-membered rings leading to the formation of a channel with the K atom sitting at the center as shown in Fig. 1(a). K_xWO_3 for $0.18 < x < 0.32$ exhibits anomalies in their electrical resistivity measurements and the characteristic anomaly temperature T_c, which is a strong function of x, is maximum for the concentration $x = 0.25$ at 350 K. This result is also corroborated by the Hall voltage and Seebeck coefficient measurements [5]. Another class of tungsten bronze material, which shows similar anomalies in transport measurements, is the family of monophosphate tungsten bronzes with pentagonal tunnels ($MPTB_p$). These tungsten bronzes are mostly low dimensional systems with strong structural and electronic anisotropy [6]. Their transport properties show uncommon features such as anomalous magnetic properties, metal–insulator and metal–metal transitions, periodic lattice distortions, and charge-density wave (CDW) phase transitions [7]. The $MPTB_p$ family has the general formula $(PO_2)_4(WO_3)_{2m}$, where m is an integer (2, 4–16) [8]. The electronic structure of this family is interesting since the electronic and the magnetic properties of the members of this family strongly vary with m. $P_4W_{12}O_{44}$ is a member of the $MPTB_p$ family and has an orthorhombic crystal structure. It consists of infinite ReO_3-type slabs of corner sharing WO_6 octahedra connected by PO_4 tetrahedra forming layers in the ab plane as shown in Fig. 1(b) and are thus referred as quasi-two-dimensional systems [9]. The structure leads to anisotropic physical properties as reflected in their electrical resistivity as well as the magnetic susceptibility measurements, which show two anomalies at $T_{c1} = 120$ K and $T_{c2} = 60$ K temperatures [10]. Anomalies found

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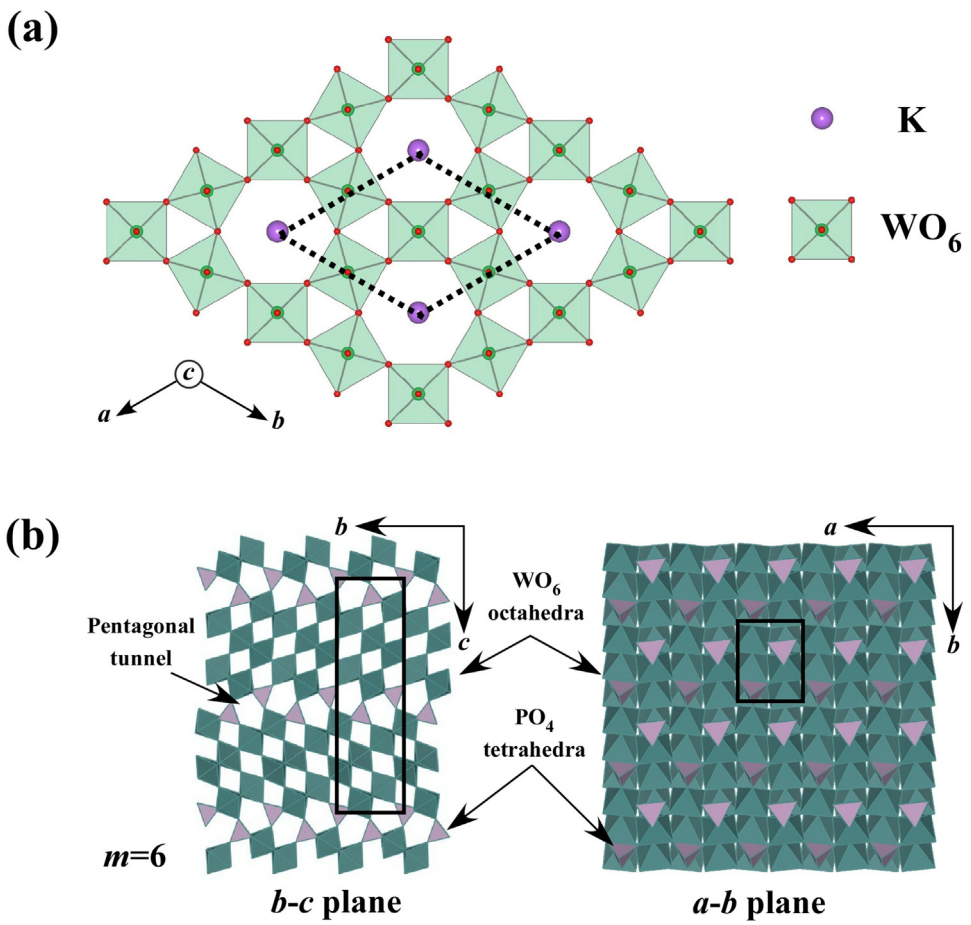

Fig. 1. (a) Crystal structure of K_xWO_3 projected in the *ab*-plane. The structure consists of corner-shared WO_6 octahedra with six-membered rings forming a channel with K atom at its center. The dotted rhombus represents the unit cell. (b) Orthorhombic crystal structure of $P_4W_{12}O_{44}$ with pentagonal tunnels projected along the *bc* and *ab* plane. The framework is built with ReO_3-type slabs of corner sharing WO_6 octahedra, interconnected through slices of PO_4 tetrahedra forming layers in the *ab* plane. A single unit cell is indexed with a rectangular box.

in the transport properties of potassium and phosphate tungsten bronzes have been explained by CDW transitions where the CDW states are driven by nesting topology of the Fermi surface [11,12]. Therefore, it is expected that the observed anomalies in these bronzes arise from the CDW instabilities. Hence, a detailed study on the electronic structure of these bronze systems is absolutely necessary.

In this review, we have investigated the electronic structure of $K_{0.25}WO_3$ and $P_4W_{12}O_{44}$ by high-resolution angle-resolved photoemission spectroscopy (ARPES). We have derived the band structure and Fermi surface (FS) of these bronze systems both theoretically and experimentally. Our experimental Fermi surface shows considerable flat portions, which satisfy the nesting condition and thus shows the possibility of favoring CDW formation, which explains the origin of anomalous physical properties.

2. Crystal growth and experimental techniques

High quality single crystals of $K_{0.25}WO_3$ and $P_4W_{12}O_{44}$ were used for our ARPES studies. The hexagonal single crystals of $K_{0.25}WO_3$ were synthesized by fused salt electrolysis of K_2WO_4 and WO_3. The Laue diffraction measurements performed on the crystals of $K_{0.25}WO_3$ show a single hexagonal phase. Similarly the single crystals of $P_4W_{12}O_{44}$ were grown via solid state reaction from stoichiometric mixture of $(NH_4)_2HPO_4$ and WO_3 with W added in appropriate proportion in an evacuated quartz tube [10]. ARPES is one of the most direct method by which one can study the electronic structure of the solids by measuring the kinetic energy and angle of emitted photoelectrons with respect to the surface normal. ARPES measurements of $K_{0.25}WO_3$ were carried out with a VG-SCIENTA R4000 electron analyzer with 22 eV photons at the undulator 4m-NIM beam line at the Synchrotron Radiation Center in Wisconsin, USA. The energy and angular resolutions were set at 15 meV and 0.7°, respectively. The wide-angle (38°) mode of the analyzer was used for the ARPES measurements of $K_{0.25}WO_3$. High-resolution ARPES experiments on $P_4W_{12}O_{44}$ were performed with a VG-SCIENTA SES 2002 spectrometer at the beamline BL 28A, Photon Factory, KEK, Japan. Photon energy of 50 eV was used to excite the photoelectrons. The energy and the angular resolution were set at 20–40 meV and 0.2°, respectively. For both the experiments a clean surface of the sample was obtained by in situ cleaving along the (0 0 1) surface.

3. Theoretical calculations

We have performed extensive *ab initio* electronic structure calculations of $K_{0.25}WO_3$ and $P_4W_{12}O_{44}$ within the framework of density functional theory (DFT). For band structure calculations of $K_{0.25}WO_3$, we have performed the calculation of hexagonal WO_3 with lattice parameter $a = 7.38$, $c = 7.513$ Å and space group P6/mmm [13] using all-electron full-potential linearized augmented plane wave method (FP-LAPW) [14]. The effect of K doping