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Electronic instabilities of the quasi-two-dimensional monophosphate tungsten bronze $P_4W_{12}O_{44}$

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We report results of electrical resistivity, Hall effects, and magnetic susceptibility measurements on oriented single crystals of $P_4W_{12}O_{44}$, which suggest that $P_4W_{12}O_{44}$ has two resistivity anomalies arising from charge-density-wave instabilities. Tight-binding electronic-band-structure calculations on the W_6O_{22} slab of $P_4W_{12}O_{44}$ support the above suggestion.

INTRODUCTION

Low-dimensional metals are interesting because of their physical properties associated with electronic instabilities such as charge-density waves (CDW) or spin-density waves. Several quasi-two-dimensional (2D) molybdenum bronzes, $Na_{0.9}Mo_6O_{17}$,[1] $K_{0.9}Mo_6O_{17}$,[1] and $TlMo_6O_{17}$,[2] as well as the Magneli phases γ- and η-Mo_4O_{11},[3,4] have been shown to exhibit CDW instabilities. $P_4W_{12}O_{44}$ (Ref. 5) is isostructural with γ-Mo_4O_{11}, and belongs to the family of the monophosphate tungsten bronzes with pentagonal tunnels ($MPTB_p$), $(PO_2)_4(WO_3)_{2m}$.[6] Although $P_4W_{12}O_{44}$ and γ-Mo_4O_{11} are isostructural, they are not isoelectronic. There are two electrons to fill the bottom three *d*-block bands of $P_4W_{12}O_{44}$, but four electrons to fill the corresponding band of γ-Mo_4O_{11}. As schematically shown in Fig. 1, $P_4W_{12}O_{44}$ contains ReO_3-type slabs of corner-sharing WO_6 octahedra (with the formula W_6O_{22}), which terminate with PO_4 tetrahedra. Empty pentagonal tunnels are created at the junction between the ReO_3-type slabs and the PO_4 tetrahedra. In the present paper, we report results of electrical resistivity, Hall effects, and magnetic susceptibility measurements on oriented single crystals of $P_4W_{12}O_{44}$, which suggest that $P_4W_{12}O_{44}$ has two resistivity anomalies arising from CDW instabilities. We interpret these experimental observations on the basis of the tight-binding electronic band structure calculated for a W_6O_{22} slab.

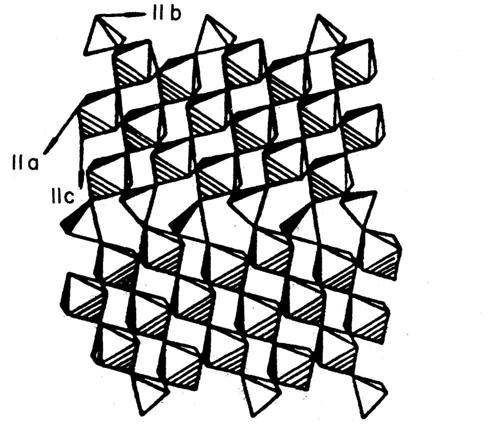

FIG. 1. Structure of the monophosphate tungsten bronze with pentagonal tunnels, $MPTB_p$ [$(PO_2)_4(WO_3)_{2m}$, $m=6$] projected along the *a* crystallographic direction.

EXPERIMENT

Polycrystalline $P_4W_{12}O_{44}$ was prepared according to a previously reported method.[5] A stoichiometric mixture of $(NH_4)_2HPO_4$ and WO_3 was first heated at 650 °C to decompose the ammonium hydrogen phosphate. Appropriate amounts of W metal was then added to the decomposed product and the mixture was pelletized and sealed in an evacuated quartz tube for reaction at ~1000 °C for at least four days. Single crystals of $P_4W_{12}O_{44}$ used in the characterization of electronic properties were obtained from an initial composition of $P_6W_{10}O_{44}$. The reaction for $P_6W_{10}O_{44}$ was carried out at 1150 °C for at least five days before annealing to room temperature. The cooling rate was increased from 0.6 °C/h to 2 °C/h as the temperature was lowered. $P_4W_{12}O_{44}$ crystals were separated from the matrix mechanically and washed in hot concentrated HF before attaching electrical contacts.

Low-temperature (2–300 K) resistivity was measured using a standard, four-probe technique with ultrasonically soldered indium contacts on single crystals. The largest error in the measurement is about 25%. Magnetic susceptibility was measured in a Quantum Design superconducting quantum interference device magnetometer from 3 to

270 K. A magnetic field of 1 T was employed to determine the susceptibility. The Hall-effect voltage was obtained from the difference of the transverse voltages for the two orientations.

Tight-binding electronic-band-structure calculations[7] were performed on the W_6O_{22} slab within the framework of the extended Hückel method.[8] The atomic parameters employed in our work were taken from the previous work.[9]

RESULTS

From the solid-state reaction of $P_6W_{10}O_{44}$, large ($\sim 3\times \sim 2\times \sim 0.7$ mm^3), platelike single crystals (see Fig. 2) were found in the hot zone of the silica ampoule. The crystals were subsequently identified by powder x-ray diffraction as $P_4W_{12}O_{44}$. The crystals are dark blue with red edges; grinding the crystals results in a red powder.

The anisotropic behavior of the electrical resistivity of $P_4W_{12}O_{44}$ was measured on a $P_4W_{12}O_{44}$ oriented single crystal. Room-temperature specific resistivities are $\rho_a = 1.2\times 10^{-4}$, $\rho_b = 2.0\times 10^{-4}$, and $\rho_c = 2.0\times 10^{-3}$ Ω cm, which show that $P_4W_{12}O_{44}$ is a quasi-2D metal. Figure 3 shows the ρ vs T plots in the *ab* plane and along the crystallographic *c* axis (the data of Fig. 3 and the room-temperature resistivities above were obtained on two different crystals). Above ~ 114 K, the resistivity decreases with temperature. From ~ 114 to 2 K, there occur two resistivity humps with the onset temperatures ~ 114 and ~ 60 K. The metal-to-metal transition at ~ 60 K is sharper than that at ~ 114 K. The two resistivity humps of $P_4W_{12}O_{44}$ are remarkably close in shape to those observed for $NbSe_3$.[10,11]

Magnetic susceptibility χ measured from 280 to 3 K on a batch of oriented single crystals of $P_4W_{12}O_{44}$ is shown in Fig. 4. The magnetic susceptibilities along the *c* axis and in the *ab* plane are similar, and are slightly temperature dependent above 125 K. Below 125 K the magnetic susceptibility shows downturns at ~ 120 and ~ 60 K and an upturn at ~ 30 K. These onset temperatures correspond closely to those seen from the ρ vs T plot. The susceptibility upturn at ~ 30 K observed for a batch of oriented single crystals is reduced to a small kink when measured for a batch of randomly oriented single crystals.

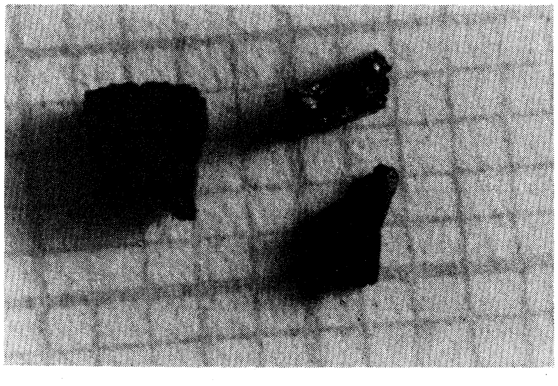

FIG. 2. Single crystals of $P_4W_{12}O_{44}$.

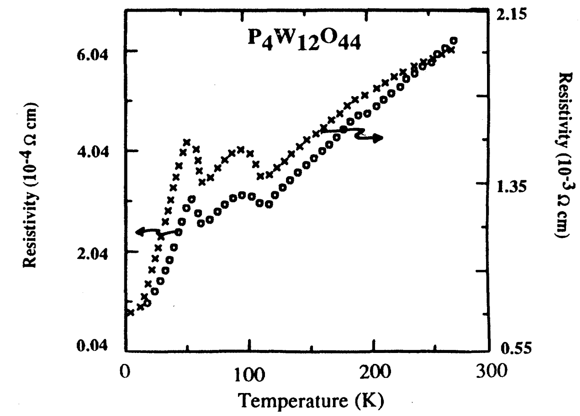

FIG. 3. Temperature dependence of the resistivity of a single crystal of $P_4W_{12}O_{44}$ for current along the *c* (hard) axis ($\times$) and in the *ab* (easy) plane (○).

The Hall voltage of $P_4W_{12}O_{44}$ varies linearly with currents from 1 to 10 mA, and is negative over the temperature range 5–125 K. Figure 5 shows the Hall coefficients measured with a current of 10 mA. Above 100 K, the Hall voltages become smaller than the limit of our experimental detection (~ 0.5 μV). However, qualitative Seebeck measurements at room temperature, and at ~ 100 K as well, show an *n*-type carrier for $P_4W_{12}O_{44}$. Thus, the predominant charge carriers in $P_4W_{12}O_{44}$ are electrons from room temperature to 5 K. An increase in the Hall coefficients is observed at ~ 60 K, while a plateaulike feature is seen at ~ 30 K. However, the ~ 114-K anomaly found in the ρ vs T and χ vs T plots cannot be detected by the Hall-effect measurements since the Hall voltages are very small above 100 K.

Figure 6(a) shows the bottom portion of the T_{2g}-block bands calculated for the W_6O_{22} slab, where the dashed line refers to the Fermi level. The orbital character of

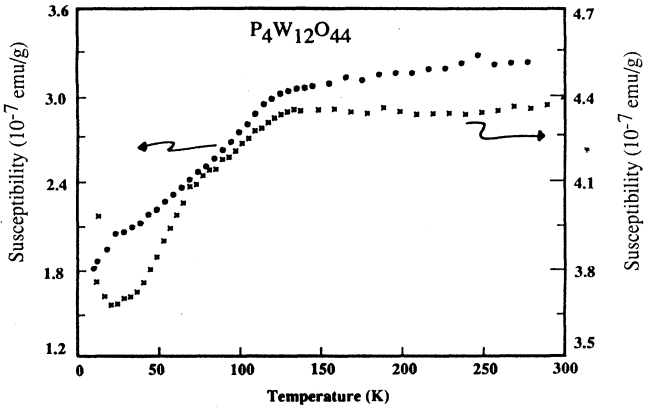

FIG. 4. Temperature variation of the magnetic susceptibility of a batch of oriented single crystals of $P_4W_{12}O_{44}$. The applied magnetic field ($H = 1$ T) is parallel with the *c* (hard) axis ($\times$) and in the *ab* (easy) plane (●).

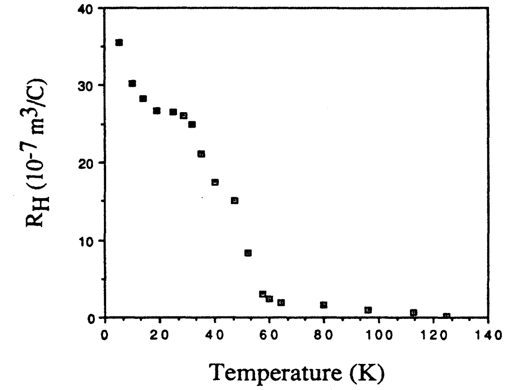

FIG. 5. Hall coefficient as a function of temperature for a single crystal of $P_4W_{12}O_{44}$.

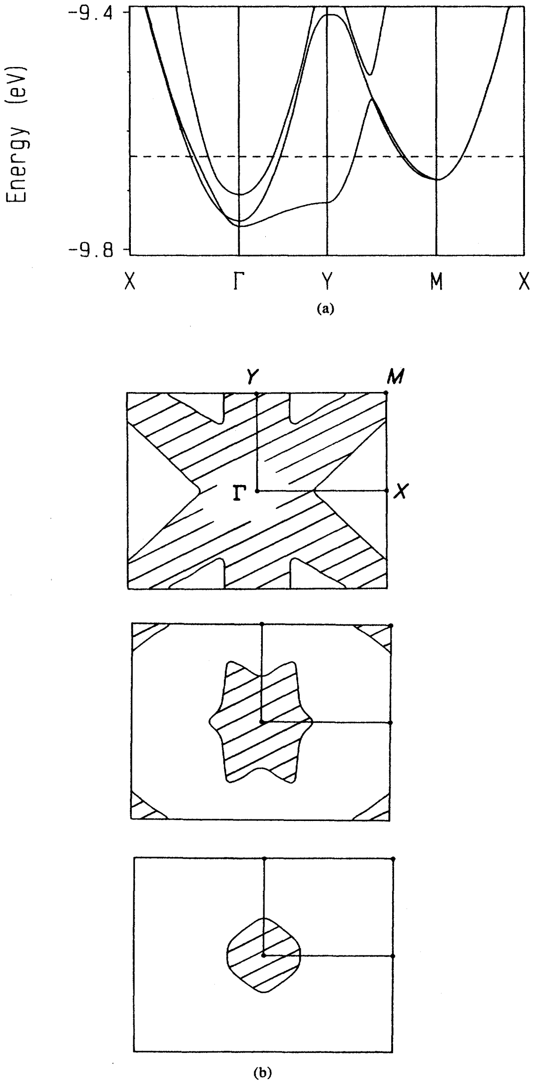

FIG. 6. (a) Dispersion relations of the bottom portion of the t_{2g}-block bands of the W_6O_{22} slab, where $\Gamma=(0,0)$, $X=(a^*/2,0)$, $Y=(0,b^*/2)$, and $M=(a^*/2,b^*/2)$. (b) The Fermi surfaces of the three partially filled bands.

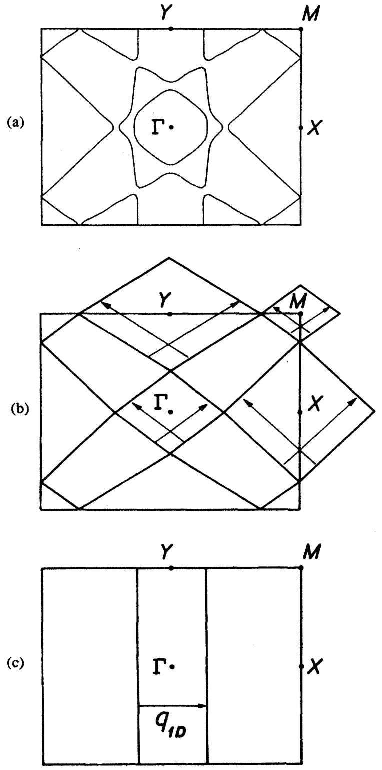

FIG. 7. The three Fermi surfaces of Fig. 6(b) are combined together in (a). The 2D and 1D components of the combined Fermi surfaces are separated in (b) and (c), respectively.

those bands are very similar in nature to that found for the t_{2g}-block bands of Mo_4O_{11}.[12] With two electrons to fill the d-block bands, the bottom three bands of Fig. 6(a) are cut by the Fermi level, and their Fermi surfaces are shown in Fig. 6(b), where the wave vectors of the shaded regions give rise to the filled band levels. To show the nesting among the three Fermi surfaces, they are combined together in Fig. 7(a). As will be described in detail elsewhere,[13] as far as the Fermi-surface nesting is concerned, the Fermi surfaces of Fig. 7(a) can be regarded as a combination of the 2D Fermi surfaces shown in Fig. 7(b) and the 1D Fermi surface shown in Fig. 7(c) (see Table I).

Given an extended zone representation, the 2D Fermi surfaces of Fig. 7(b) are made up of four corner-sharing rhombuses centered at Γ, X, Y, and M, which give rise to

TABLE I. Nesting vectors of the 2D and 1D Fermi surfaces shown in Figs. 7(b) and 7(c).

Vector	Vector components
q_Γ	$0.21a^* \pm 0.22b^*$
q_X	$0.29a^* \pm 0.36b^*$
q_Y	$0.35a^* \pm 0.28b^*$
q_M	$0.15a^* \pm 0.14b^*$
q_{1D}	$0.26a^*$

the important ones. Thus, CDW's associated with q_X and q_Y might be responsible for the occurrence of the two resistivity humps in $P_4W_{12}O_{44}$. The magnetic susceptibility downturns at ~ 120 and ~ 60 K, and the Hall coefficient increase at ~ 60 K as well, are consistent with the CDW formation at ~ 114 and ~ 60 K. If this is indeed the case, it will be interesting to examine whether or not the two CDW's are independent, as in $NbSe_3$.[10,11] Finally, it is of interest to study whether or not the ~ 30-K anomaly of $P_4W_{12}O_{44}$, seen as a magnetic susceptibility upturn and as a plateau of the Hall coefficient vs T plot, also originates from a nesting of the remaining Fermi surfaces (e.g., q_Γ, q_M, and q_{1D}).

ACKNOWLEDGMENTS

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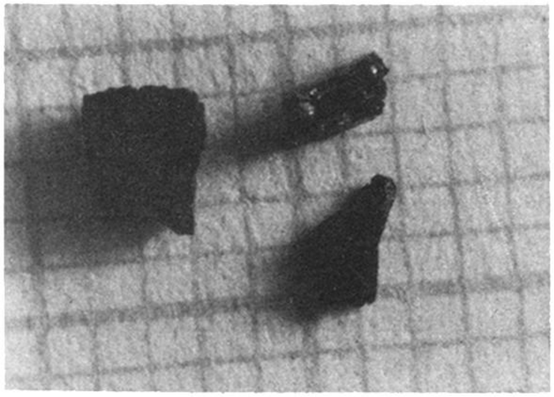

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