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Anisotropic Electronic Properties of the Bronze, $CsP_8W_8O_{40}$

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Cesium tungsten phosphate oxide, $CsP_8W_8O_{40}$, bronze single crystals were grown by chemical vapor transport with KBr as the transporting agent. Electrical resistivity measurements on oriented crystals with ρ_a (RT) = 5.9×10^{-2} Ω cm, ρ_b (RT) = 4.5×10^{-2} Ω cm, and ρ_c (RT) = 5.7×10^{-3} Ω cm indicate quasi-one-dimensional behavior. A broad transition observed at ~160 K may be attributed to order–disorder transition associated with the Cs^+ ions, or a change of the type of conductivity from hopping type (activated) to band type (nonactivated). Qualitative Seebeck measurements of $CsP_8W_8O_{40}$ indicate *p*-type behavior at room temperature and *n*-type behavior at liquid N_2 temperature. A sharp transition seen at ~24 K might be due to a charge-density wave instability inherent in a quasi-one-dimensional metal. Magnetic susceptibility data indicate Pauli paramagnetic behavior. The anomalies observed in the resistivity do not show up in the magnetic susceptibility.

Introduction

Raveau and co-workers reported a series of monophosphate tungsten bronzes, $(PO_2)_4(WO_3)_{2m}$ (m = 4–11) (*1*) and diphosphate tungsten bronzes, $A_x(P_2O_4)_2(WO_3)_{2m}$ (A = K with m = 5–11 (*2*a); Rb with m = 4–11 (*2*a); Tl with m = 8(*2*b); Ba with m = 6–10(*2*c)). The structure of these mixed-valent oxides can be described as ReO_3-type slabs of corner-sharing WO_6 octahedra which are connected by either monophosphate (PO_4) or diphosphate (P_2O_7) groups to form three-dimensional network structures with pentagonal and hexagonal tunnels, respectively. The tunnels may be empty, as in the monophosphate tungsten bronze $P_4W_8O_{32}$ (m = 4) (*3*), or may be occupied by K^+, Rb^+, or Tl^+ as in the diphosphate tungsten bronzes. The larger Cs^+ ion forms an entirely new structural type in the P–W–O system—$CsP_8W_8O_{40}$ (*4*). The framework of this compound can be described as ReO_3-type columns of 2 × 2 WO_6 octahedra extending infinitely along the [001] direction of the orthorhombic unit cell. The columns are linked together by P_2O_7 groups in such a way that large, interconnected octagonal tunnels are created along [001]. Cs^+ ions are distributed randomly, off-center in the tunnels (Fig. 1). The columns of WO_6 octahedra are linked together only through P_2O_7 groups so that these columns are isolated. Thus $CsP_8W_8O_{40}$ is expected to have highly anisotropic, potentially quasi-one-dimensional electronic properties.

In this paper we report results of our investigations of the electronic transport and magnetic properties on oriented single crystals of $CsP_8W_8O_{40}$.

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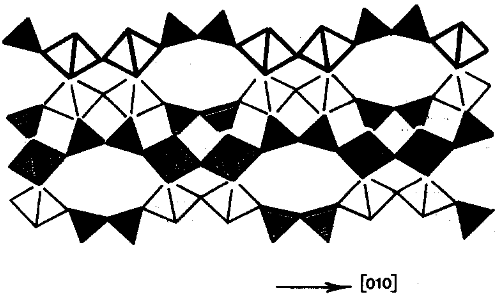

FIG. 1. Structure of the $CsP_8W_8O_{40}$ bronze. Note the 2 × 2 columns of corner-sharing WO_6 octahedra and the partially occupied octagonal tunnels.

Experimental

Single crystals of $CsP_8W_8O_{40}$ were grown by first heating a mixture of Cs_2CO_3, $(NH_4)_2HPO_4$, and WO_3 in air at 923 K to decompose the phosphate and the carbonate. Appropriate amounts of W metal and 5 mole% KBr powder were then added to the resultant decomposition products before final heating in an evacuated silica tube at 1223 K for 2 weeks (*4*); the furnace temperature was then programmed to cool slowly to room temperature at a rate of ~3° /hr.

Electrical resistivity as a function of temperature was measured along the three principal orthorhombic axes from 2 to 760 K by a standard four-probe technique. Ultrasonically soldered indium contacts were used for the low-temperature (2–300 K) measurement, and painted graphite Electrodag (Acheson Colloids Co., Michigan) was used for the high-temperature (300–760 K) measurement. Crystals were oriented by single-crystal X-ray diffraction methods. Magnetic susceptibility was measured on both a single crystal and powdered specimens using the Faraday method described previously (*5*).

Results and Discussion

Without the addition of KBr to the reaction mixture, only small ($\ll$1 mm) crystals form. However, when ~5 mole% KBr is added to the charge in the evacuated quartz tube, large (1.5 × 2 × 3 mm^3), well-formed, golden, highly faceted, elongated, chunky crystals of $CsP_8W_8O_{40}$ (Fig. 2) were obtained. KBr as a transporting agent has been used in a similar way to grow single crystals of K_xWO_3 (*7*). Single crystals of the red phosphate tungsten bronze $P_8W_{12}O_{52}$ were always found to grow along with the $CsP_8W_8O_{40}$ crystals. The structural properties of these two phases are closely related which is the likely reason for their intergrowth (*4*). Most crystals were found to grow at the cooler, empty part of the quartz tube. Therefore, it is assumed that KBr served as a transporting agent and the crystals grew by a chemical vapor phase transport mechanism. Chemical analysis by X-ray fluorescence and plasma emission spectroscopy revealed only trace amounts of K^+ (~0.005 mole) in these crystals.

The electronic transport properties are highly anisotropic: $\rho_c = 5.7 \times 10^{-3}\ \Omega$ cm, $\rho_b = 4.5 \times 10^{-2}\ \Omega$ cm, $\rho_a = 5.9 \times 10^{-2}\ \Omega$ cm at room temperature. These results suggest that $CsP_8W_8O_{40}$ indeed behaves as a quasi-one-dimensional (1D) conductor.

The temperature dependence of resistivity along the *c* crystallographic (easy axis) and along a direction in the *ab* plane (hard axis) confirms the anisotropy observed at room temperature (Fig. 3). The resistivity behavior along both the easy and hard axis is identical, but the resistivity is about an order of magnitude smaller along *c* (the easy axis); the temperature dependence of resistivity in the *ab* plane is isotropic. From 760 to about 160 K, the temperature coefficient of resistivity shows semiconducting behavior (see inset of Fig. 3) with the magnitude of resistivity ($\sim 10^{-3}$–10^{-2}) being borderline between that of a metal and that of a semiconductor.

A broad anomaly at ~160 K accompanied by a drop in the resistivity by a factor of ~2 is seen along both directions

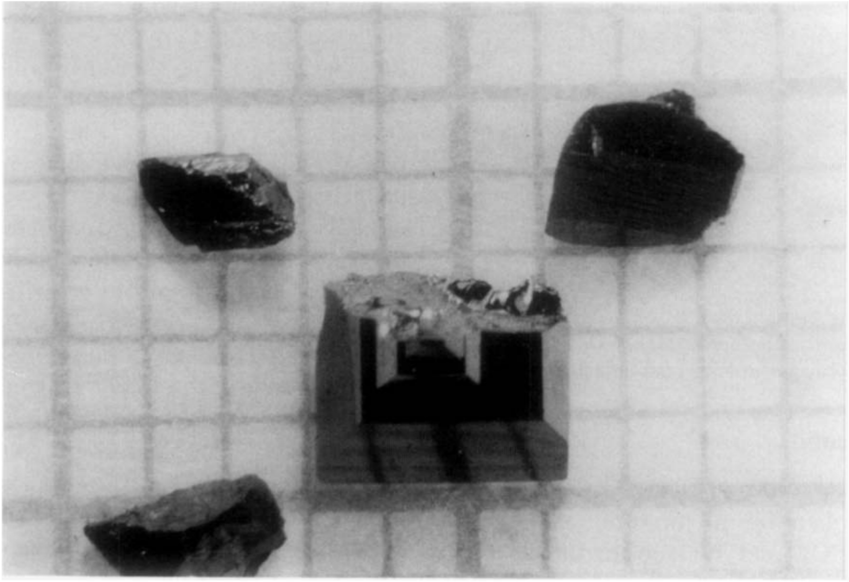

FIG. 2. Highly faceted, chunky, golden crystals of $CsP_8W_8O_{40}$.

(Fig. 3). In addition, a metal-to-semiconductor transition at 24 K and another small upturn in the resistivity at 6 K are observed. The anomaly at 6 K is sample dependent and might be due to impurities or defects.

Several possible explanations for the broad transition at ~160 K are suggested. It may be attributed to a CDW instability due to the quasi-one-dimensional electronic structure of $CsP_8W_8O_{40}$. The broadness of the transition might be ascribed to defects in the lattice, which represent a distribution of pinning energies for CDW formation, leading to a gradual opening of the gap, and the observed width of the transition. If this transition is indeed CDW driven, there might be a metal-to-semiconductor transition at temperatures higher than 760 K, which is the limit of our high-temperature resistivity capability at present.

A more plausible explanation for the ~160 K anomaly seen in the resistivity of $CsP_8W_8O_{40}$ is an order–disorder phase transition associated with the ordering of the Cs^+ ions within the octagonal tunnels. Goreaud *et al.* (*4*) reported that Cs^+ ions randomly occupy one out of four cages in

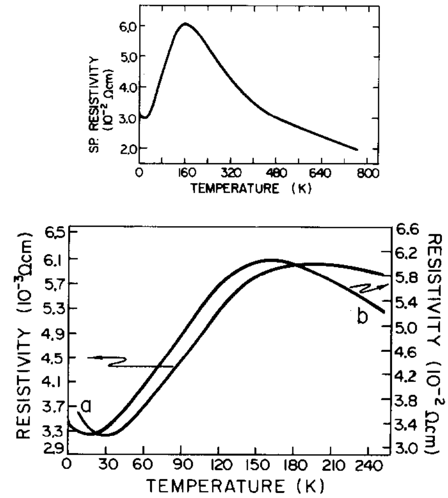

FIG. 3. Temperature-dependent resistivity of $CsP_8W_8O_{40}$ (lower graph) with (a) current along the *c*-axis (easy axis) and (b) current along a direction in the *ab* plane (hard axis). ρ vs T between 760 and 4.2 K with current in the *ab* plane (hard axis) (upper graph).

the chain of cavities which form the octagonal tunnels. As the temperature and the thermal energy of the system is lowered, the Cs^+ ions might order. Similar order–disorder transitions have been reported in the closely related Rb_xWO_3 (*8*, *9*), K_xWO_3 (*7*), and $Na_x(PO_2)_4(WO_3)_{2m}$ (*10*) bronzes where it has been shown that the transition in these compounds is dependent on the concentration of the ordering cations within the cavities. This is not surprising, since any perturbation in the alkali metal content will alter the ordering pattern. Preliminary results in our laboratory on cesium-deficient samples of $Cs_{1-x}P_8W_8O_{40}$ and other cation-substituted samples of $Cs_{1-x}A_xP_8W_8O_{40}$ (A = Rb, Sn, Ag) show that the transition at ~160 K is dramatically affected by the Cs^+ content.

The activation energies (E_a) in the semiconducting region (160–760 K) are found to be temperature dependent ranging from ~0.07 to 0.02 eV (Fig. 4). The temperature-dependent behavior of the resistivity might be ascribed to modifications of the W–O band structure due to changes in the W–O bond distances affected by variations in the temperature and/or changes in the polarization of the lattice by the ordering Cs^+ ions. Qualitative Seebeck measurements show a definite transition from room temperature p-type to n-type conductivity at liquid nitrogen temperature. Moreover, preliminary Hall effect measurements on a Cs-deficient $Cs_xP_8W_8O_{40}$ crystal (to be discussed in more detail in a subsequent paper (*11*)) also indicate a change in the sign of charge carriers below 160 K. This is consistent with the semiconductor–metal transition at ~160 K, the temperature-dependent resistivity in the high-temperature region, and supports the notion that the band structure might be changing with decreasing temperature.

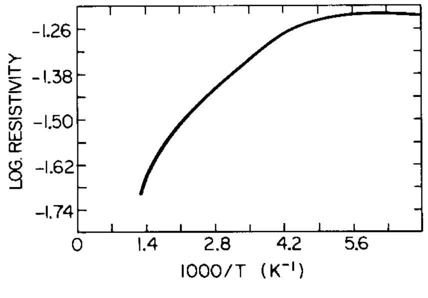

FIG. 4. Log ρ vs $1/T$ for $CsP_8W_8O_{40}$.

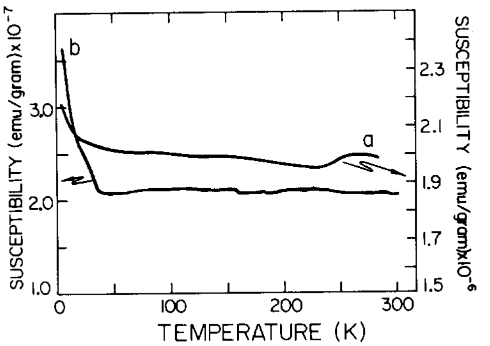

FIG. 5. Magnetic susceptibility as a function of temperature for a single crystal of $CsP_8W_8O_{40}$. (a) The applied magnetic field (H) is along the c direction (easy direction of conductivity); (b) H is in the ab plane.

Recent band structure calculations by Canadell and Whangbo (*12*) show that the 160 K transition may be attributed to a change of conduction mechanism which is dominated in the high-temperature region by hopping type (activated) to a band-type (nonactivated) electron transport at low temperature. This is consistent with the observed change from p- to n-type conductivity. Once the metallic regime is reached, the instability inherent in a 1D metal leads to the CDW transition. Thus the transition seen at 24 K might be due to a CDW instability. Alternatively the 24 K transition might be due to localization.

The magnetic susceptibility data (Fig. 5) confirm that $CsP_8W_8O_{40}$ is anisotropic: $\chi_c \sim 10^{-6}$ and $\chi_{ab} \sim 10^{-7}$ (emu/g) along the easy and hard axis, respectively. The very low value of the susceptibility ($\chi \sim 10^{-7}$ emu/g) between 300 and 4.2 K indicates a low concentration of free electrons. These χ values are typical for Pauli paramagnetic materials. No anomalies corresponding to those seen in the resistivity data are observed in the susceptibility data. However, the absence of correlation between ρ and χ data does not necessarily exclude the possibility of CDW formation. Similar behavior has been observed in the case of $Li_{0.9}Mo_6O_{17}$ (*13*) and $NbSe_3$ (*14*). As in $NbSe_3$, the anisotropy of the transport properties ($\rho_{\|}/\rho_{\perp}$) in $CsP_8W_8O_{40}$ is only one order of magnitude; thus, upon formation of a CDW, the amount of Fermi surface lost might be too small to effect any observable change in the magnetic susceptibility at the transition. A low-temperature single-crystal X-ray diffraction study is needed to determine whether CDW formation is responsible for the metal–semiconductor transition in this compound.

Conclusions

Transport properties of oriented crystals of the $CsP_8W_8O_{40}$ bronze have been found to be anisotropic, which is consistent with the quasi-one-dimensional structural properties of this compound. Anomalies observed in the temperature dependence of resistivity at 160 K may be attributed to a possible order–disorder phase transition associated with the Cs^+ ions. An alternative explanation for the 160 K transition is a change from hopping type of conductivity which predominates at high temperature to a band type of electronic transport predominating at low temperature. The transition at 24 K is possibly due to a CDW instability inherent in a quasi-one-dimensional metal. Experiments are now in progress to study this possibility.

Acknowledgments

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