Brief Reports

Brief Reports are accounts of completed research which, while meeting the usual **Physical Review** *standards of scientific quality, do not warrant regular articles. A Brief Report may be no longer than four printed pages and must be accompanied by an abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Anomalous electrical and magnetic behavior in $(PO_2)_4(WO_3)_{2m}$ ($m=4$)

Z. S. Teweldemedhin, K. V. Ramanujachary, and M. Greenblatt*
Department of Chemistry, Rutgers, The State University of New Jersey, Piscataway, New Jersey 08855
(Received 17 June 1991; revised manuscript received 28 May 1992)

Single crystals of $P_4W_8O_{32}$ $\{(PO_2)_4(WO_3)_{2m}, m=4\}$ were prepared by chemical-vapor transport technique with KI as the transport agent. The temperature dependence of electrical resistivity in the range ~2–300 K shows metallic behavior with two anomalies at ~60 and ~85 K. The room-temperature resistivities along the long- and short-plate axis of a single crystal (*a* and *b* axes) are 3×10^{-4} and 2×10^{-4} Ω cm while that perpendicular to the crystal plate (*c* axis) is 7×10^{-3} Ω cm. The relatively higher conductivities in the crystallographic *a-b* plane confirm that the compound is a quasi-two-dimensional metal. Seebeck measurement indicates that at room temperature the primary charge carriers are electrons. The magnetic susceptibility is temperature independent down to ~92 K. At ~92 and ~56 K sharp decreases in the susceptibility are observed. The anomalous behavior in the magnetic susceptibility and electrical resistivity of $P_4W_8O_{32}$ at low temperatures is indicative of the onset of charge-density-wave states and is consistent with the proposed band electronic structure.

I. INTRODUCTION

Phosphate tungsten bronzes of the types $A_x(PO_2)_4(WO_3)_{2m}$ (Ref. 1) and $(PO_2)_4(WO_3)_{2m}$ (Refs. 2 and 3), known as monophosphate tungsten bronzes with hexagonal and pentagonal tunnels ($MPTB_h$ and $MPTB_p$), respectively, exhibit quasi-low-dimensional structural and electronic-transport properties similar to those observed in the molybdenum bronzes.[4] Diphosphate tungsten bronzes (DPTB) of the type $A_x(P_2O_4)_4(WO_3)_{4m}$ (Ref. 5) and $CsP_8W_8O_{40}$ (Refs. 6 and 7), have also been reported to display similar behavior at low temperatures. The structure of the phosphate tungsten bronzes is characterized by ReO_3-type slabs of WO_6 octahedra connected by PO_4 or P_2O_7 polyhedra.

Anomalies attributed to charge-density-wave (CDW) instabilities are also known in the quasi-two-dimensional (quasi-2D) metal Magneli phases, γ-Mo_4O_{11} and η-Mo_4O_{11} (Refs. 8–11). These compounds are structurally related to the MPTB in having ReO_3-type slabs formed from corner-sharing MoO_6 octahedra separated by MoO_4 tetrahedra.[12,13] Similar anomalies in the electrical resistivity and magnetic susceptibility arising from CDW instability are well established in the molybdenum bronzes and niobium chalcogenides. Among these compounds, the purple bronzes, $A_{0.9}Mo_6O_{17}$ (A=Na,K),[14,15] and $TlMo_6O_{17}$ (Ref. 16), which are quasi-2D metals, show a single resistivity hump at low temperatures, whereas $NbSe_3$ shows two humps.[17]

Recent theoretical studies on the electronic band structure of several members of $(PO_2)_4(WO_3)_{2m}$ series by Whangbo and co-workers concluded that these compounds have one- and two-dimensional metallic bands and similar electronic transport properties, regardless of the value of m (i.e., the width of the ReO_3-type slab) or local distortions within the WO_6 octahedra.[18] This theoretical prediction was one of the motivations for the experimental investigation of various members of the monophosphate tungsten bronze (MPTB) series. Recently, we reported on the temperature dependence of the electrical resistivity (ρ) and magnetic susceptibility (χ) of $P_4W_{12}O_{44}$, the $m=6$ member of $(PO_2)_4(WO_3)_{2m}$ ($MPTB_p$), which showed two anomalies at ~60 and 114 K. These results were consistent with band electronic structure calculations, which showed the presence of one- and two-dimensional conduction bands in this compound.[2] X-ray diffuse scattering investigations by Pouget and co-workers have confirmed the formation of two CDW's at 60 and 124 K, respectively, in $P_4W_{12}O_{44}$ (Ref. 19). More recently, our study of the $m=2$ member, PWO_5 has indicated semiconducting and quasi-1D electronic properties.[3,20] The structure of PWO_5 is built up from isolated chains of corner-sharing WO_6 octahedra; i.e., there are no ReO_3-type slabs.[21] Preliminary study of the $m=7$ member shows that $P_4W_{14}O_{50}$ is metallic with two CDW transitions, at $T_{c1}\sim183$ and $T_{c2}\sim47$ K (Ref. 19). Thus our results strongly suggest that the width of the ReO_3-type slabs ($m/2$) and the formal valence of tungsten ($6-2/m$) dramatically affect the electronic structure and properties of these phases. Here we report our experimental results of the electrical resistivity and magnetic susceptibility measurements between 2–300 K on oriented single crystals of $P_4W_8O_{32}$, the $m=4$ member of $(PO_2)_4(WO_3)_{2m}$.

II. EXPERIMENT

The platelike purple crystals (~ 1.5 mm $\times \sim 0.6$ mm $\times \sim 0.3$ mm) of $P_4W_8O_{32}$ were prepared by chemical-vapor transport technique with KI (Fisher) as the transporting agent. A mixture of $(NH_4)_2HPO_4$ (Fisher), WO_3 (SPEX), and Tl_2CO_3 (AESAR) in the molar ratio of 24:19:3 was first calcined in air at 300 °C for ~ 24 h to remove NH_3, CO_2, and H_2O. Appropriate amounts of W (Alfa products) and 5 mol % KI was then added to the resulting mixture to make about a 0.5-g sample in which the ratio of thallium, phosphorus, tungsten, and oxygen is 1:4:4:20. This mixture was then pelletized and sealed in an evacuated quartz tube (~ 15 cm long and 1.0 cm internal diameter). A temperature gradient of ~ 130 °C was maintained along the length of the quartz tube with the temperature at the sample end (i.e., the hot end of the quartz tube) of ~ 1070 °C. Normally the reaction was carried out under these conditions for about two weeks and then slowly cooled to room temperature. Attempts to grow single crystals of $P_4W_8O_{32}$ by chemical-vapor transport technique from stoichiometric mixtures of the reactants were not successful.

X-ray powder diffraction patterns of the products were recorded with a Scintag PAD V x-ray diffractometer using Cu $K\alpha$ radiation and a solid-state detector. Silicon was used as an internal standard to calibrate the observed d spacings.

The platelike purple crystals used in this study were first washed with 5% HF at ~ 70 °C for about a half hour. The orientation of the unit cell directions was determined by photographic techniques. Electrical resistivity measurements on selected crystals were made by a standard four-probe technique with a Displex cryostat (APD Cryogenics, DE-202) in the temperature range 20–298 K. A conventional liquid-helium cryostat was used for resistivity measurements down to ~ 4 K. Four copper leads were attached to the selected faces of the crystals under a microscope with silver paint. Alternately, indium contacts were first applied to the crystals using an ultrasonic solder, to which copper leads were then attached using silver paint. Contact resistances were typically $\leq 1\ \Omega$.

The magnetization of a batch of platelike crystals was measured with a superconducting quantum interference device magnetometer (Quantum Design) at several temperatures in the range 2–300 K. Typically, the sample was first cooled to 2 K and then a magnetic field of 5000 G was applied.

III. RESULTS AND DISCUSSION

In almost all experiments, the products obtained were two morphologically different crystals of $P_4W_8O_{32}$. The purple platelike crystals are formed in the region closer to the cold end of the quartz tube, which is always covered with a dark blue tint. Small (~ 0.4 mm along the longest dimension) multifaceted crystals of similar color are also obtained midway and toward the hot end of the quartz tube. The powder x-ray diffraction patterns of these two crystal forms were identical and could be indexed with an orthorhombic cell reported in the literature (space group: $P2_12_12_1$).[22] The electron microprobe analysis has also confirmed that these crystals do not contain detectable thallium or potassium as impurities. The cell parameters for the purple platelike crystals of the $P_4W_8O_{32}$ calculated by least-square refinement of the observed d spacings corrected for instrumental shifts are $a = 5.2857(4)$ Å, $b = 6.5805(7)$ Å, and $c = 17.377(1)$ Å.

The crystal structure of $P_4W_8O_{32}$ is built up of corner-sharing WO_6 octahedra and PO_4 tetrahedra (Fig. 1).[13,22,23] The WO_6 octahedra form ReO_3-type slabs; the width of these slabs is two WO_6 octahedra (i.e., $m/2$ octahedra). The slabs are separated by slices of PO_4 tetrahedra that share all their four corners with different WO_6 octahedra. The pentagonal tunnels along the a axis are formed from the corner sharing of three WO_6 octahedra and two PO_4 tetrahedra. Alternately, the structure can be described as zigzag chains of corner-sharing polyhedra of W_2O_{11} and PO_4 parallel to the c axis at $x \sim \frac{1}{4}$ and $\frac{3}{4}$. Such an arrangement leads to two crystallographically unique tungsten atoms with different oxidation states, that form octahedra distorted to different degrees.

Figure 2 shows the temperature-dependent electrical resistivities measured along the long-plate axis (a axis) in the a-b plane and perpendicular to this plane of a single crystal of $P_4W_8O_{32}$ in the range ~ 20–298 K. The resistivity shows two anomalous humps with onset temperatures ~ 85 K (T_{c1}) and ~ 60 K (T_{c2}). The metallic trend observed below the maximum of the low-temperature hump (~ 50 K) continues down to ~ 4 K. The room-temperature resistivities along the long and short plate axis of the crystal (a and b axes) are 3×10^{-4} and $2\times10^{-4}\ \Omega$ cm, respectively. The electrical resistivity perpendicular to the plate of the crystal (c axis), measured with a two-probe technique, at room temperature is $7\times10^{-3}\ \Omega$ cm (Fig. 2). Seebeck measurement shows that the primary charge carriers are electrons (n-type) at room temperature. The relatively higher conductivities in the a-b plane imply that $P_4W_8O_{32}$ is a quasi-2D conductor similar to $P_4W_{12}O_{44}$; the $m=6$ member of the $MPTB_p$ series.[2] Although the low temperature (T_{c2}) transitions remain similar for these two compounds,

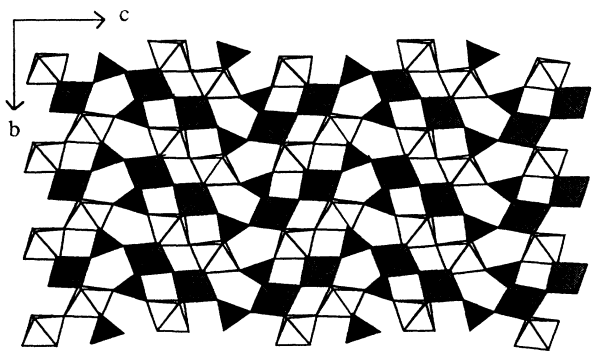

FIG. 1. Schematic of $P_4W_8O_{32}$ crystal structures in the b-c plane showing ReO_3-type slabs (different shadings of the WO_6 octahedra reflect the zigzag chains of polyhedra parallel to the c axis at different levels).

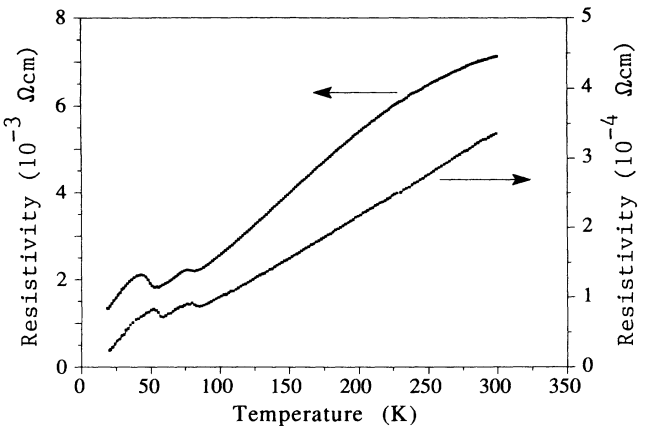

FIG. 2. Electrical resistivity as a function of temperature along the long-plate axis of a single crystal (*a* axis), in the *a-b* plane (right); and perpendicular to the plane (*c* axis) (left).

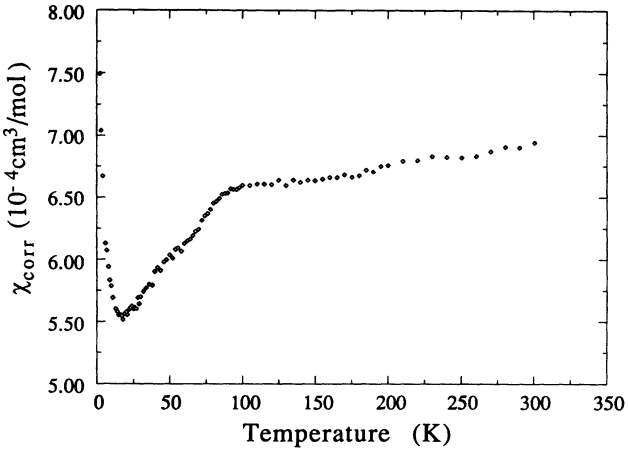

FIG. 3. Temperature dependence of magnetic susceptibility for a batch of $P_4W_8O_{32}$ crystals.

there is a significant difference in the high-temperature (T_{c1}) transitions: T_{c1} is 85 K for $P_4W_8O_{32}$, 114 K (124 K by x-ray diffuse scattering[19]) for $P_4W_{12}O_{44}$. Preliminary x-ray diffuse scattering data on $P_4W_8O_{32}$ indicates CDW phase transitions at 87 and 52 K, respectively.[24] Moreover, results of the transport properties[25] and x-ray diffuse scattering in $P_4W_{14}O_{50}$ (the $m=7$ member) show two anomalies at 183 K and 47 K associated with CDW transitions.[19] The variations in the high-temperature transitions among $MPTB_p$ phases can thus be correlated with differences in the thickness of the ReO_3-type slabs. Furthermore, the semiconducting and quasi-1D electronic transport properties[3,20] recently observed in PWO_5 ($m=2$) is another indication of the significance of the width of the ReO_3-type slabs. The structural framework of this compound is built from isolated chains of corner-sharing WO_6 octahedra and contains no ReO_3-type slabs.[21]

The magnetic susceptibility of the compound, corrected for the core diamagnetic contribution of the constituent ions, is nearly temperature independent down to ~92 K (Fig. 3). This behavior can be attributed to Pauli paramagnetism arising from the conduction electrons and is consistent with the metallic behavior observed in the electrical resistivity measurement. There is a sharp decrease in the susceptibility at ~92 K and χ decreases with temperature down to 18 K as shown in Fig. 3. The anomalous decrease in the temperature-dependent susceptibility, observed below ~92 K, is characteristic of quasi-low-dimensional metals that are known to exhibit charge-density wave (CDW) instability. Such a decrease in the susceptibility below the transition temperature (T_c) has been explained in terms of a partial opening of a gap at the Fermi surface.[10] A weak anomaly around ~56 K in the susceptibility (Fig. 3), which was always observed in several different measurements on different samples, is consistent with a similar anomaly in the electrical resistivity and x-ray scattering observed at about the same temperature. The sharp increase in the susceptibility below ~18 K is attributed to contributions from paramagnetic impurities. Thus the anomalous variations in both the magnetization and electrical resistivity are consistent with the partial opening of gaps at the Fermi surface induced by CDW instabilities. However the T_c in the magnetic and electrical resistivity data differ by ~7 K. This difference may not be unexpected considering that the magnetization study was carried out on a batch of randomly oriented crystals. Contributions to the total susceptibility at lower temperatures from sources other than paramagnetic impurities (e.g., Van Vleck orbital paramagnetism or Landau-Peierls diamagnetism of the conduction electrons),[10] which are neglected in our study, may become significant. The second anomaly observed in the electrical resistivity (T_{c2}) is manifested only as a weak feature in the magnetic susceptibility (~56 K); this could be attributed to the magnetic contributions of the conduction electrons mentioned above.[10]

In order to investigate the presence of possible nonlinear conductivity associated with the CDW state, the *I-V* characteristics of this compound were investigated at different temperatures. Experiments were performed on single crystals of $P_4W_8O_{32}$ at temperatures in the vicinity of the anomalies. However, no evidence of a nonlinear conduction was observed in the *I-V* plots at different temperatures for applied electric fields of up to 32 mV/cm. Similar results have been reported for the quasi-2D purple bronze $TlMo_6O_{17}$, which also exhibits an anomally in the resistivity and susceptibility.[16]

IV. CONCLUSION

Single crystals of $P_4W_8O_{32}$ or $(PO_2)_4(WO_3)_{2m}$ ($m=4$) have been prepared by a chemical-vapor transport technique and their electrical resistivity and magnetic susceptibility studied. The compound is a quasi-two-dimensional metal with room-temperature resistivity of 3×10^{-4} Ω cm along the *a* axis. $P_4W_8O_{32}$ exhibits metallic behavior with two anomalous humps in the electrical resistivity with onset temperatures at 85 K (T_{c1}) and 60 K (T_{c2}). The magnetization is nearly temperature independent down to 92 K. This is attributed to Pauli paramagnetism consistent with the metallic behavior ob-

served in the same temperature interval by electrical resistivity measurements. The drop in the susceptibility below 92 K and a weak anomaly at ~56 K are consistent with the electrical resistivity results and with the partial opening of gaps at the Fermi surface induced by CDW transitions.

Our results are also consistent with the band electronic structure calculations of $P_4W_8O_{32}$ which indicated the presence of one- and two-dimensional conduction bands in this compound. It appears that there are significant differences in the transition temperatures, particularly in the first transition temperature (T_{c1}), as a function of the width of the ReO_3-type slabs. Although for all three phases ($m=4,6,7$) two CDW's have been observed, there are differences in the electrical and magnetic properties (and even in the mechanism of successive CDW formation)[19] in $(PO_2)_4(WO_3)_{2m}$, as m increases from 4 to 7. The importance of the width of ReO_3-type slabs in $(PO_2)_4(WO_3)_{2m}$ is underscored by the properties of PWO_5, the $m=2$ member, which is semiconducting and shows antiferromagnetic ordering. Further experiments necessary to characterize and confirm unambiguously the presence of a CDW state in $P_4W_8O_{32}$ are currently underway.[24]

ACKNOWLEDGMENTS

We thank Dr. J. S. Delany for the electron microprobe analysis of the specimens and Professor W. H. McCarroll for his helpful comments and suggestions. Helpful discussions with Dr. E. Wang, Dr. Li Shu, and Dr. R. Fuller are greatly appreciated. This work was supported by the National Science Foundation–Solid State Chemistry Program Grants No. DMR-87-14072 and No. DMR-90-19301.

*To whom correspondence should be addressed.

[1]E. Wang, M. Greenblatt, I. E.-I. Rachidi, E. Canadell, and M.-H. Whangbo, J. Solid State Chem. **81**, 173 (1989).

[2]E. Wang, M. Greenblatt, I. E.-I. Rachidi, E. Canadell, and M.-H. Whangbo, and S. Vadlamannati, Phys. Rev. B **39**, 12 969 (1989); **40**, 11 964 (1989).

[3]Z. S. Teweldemedhin, K. V. Ramanujachary, and M. Greenblatt, J. Solid State Chem. **95**, 21 (1991).

[4]M. Greenblatt, Chem. Rev. **88**, 31 (1988).

[5]E. Wang, M. Greenblatt, I. E.-I. Rachidi, E. Canadell, and M.-H. Whangbo, J. Solid State Chem. **80**, 266 (1989).

[6]E. Wang and M. Greenblatt, J. Solid State Chem. **76**, 340 (1988).

[7]E. Wang, M. Greenblatt, I. E.-I. Rachidi, E. Canadell, and M.-H. Whangbo, Inorg. Chem. **28**, 2451 (1989).

[8](a) M. Sato, K. Nakao, and S. Hoshino, J. Phys. C **17**, L817 (1984); (b) H. Guyot, C. Schlenker, G. Fourcaudot, and K. Konaté, Solid State Commun. **54**, 909 (1985); (c) H. Guyot, C. E.-Filippini, G. Fourcaudot, K. Konaté, and C. Schlenker, J. Phys. C **16**, L1227 (1983).

[9]H. Guyot, C. Schlenker, J. P. Pouget, R. Ayroles, and C. Roucau, J. Phys. C **18**, 4427 (1985).

[10]C. Schlenker, S. S. P. Parkin, and H. Guyot, J. Magn. Magn. Mater. **54**, 1313 (1986).

[11]E. Canadell, M.-H. Whangbo, C. Schlenker, and C.-E. Filippini, Inorg. Chem. **28**, 1466 (1989).

[12]Ph. Labbe, M. Goreaud, and B. Raveau, J. Solid State Chem. **61**, 324 (1986).

[13]B. Domengés, F. Studer, and B. Raveau, Mat. Res. Bull. **18**, 669 (1983).

[14]M. Greenblatt, K. V. Ramanujachary, W. H. McCarroll, R. Neifeld, and J. V. Waszczak, J. Solid Chem. **59**, 149 (1985).

[15]R. Buder, J. Devenyi, J. Dumas, J. Marcus, J. Mercier, C. Schlenker, and H. Vincent, J. Phys. Lett. **43**, L59 (1982).

[16]K. V. Ramanujachary, B. T. Collins, M. Greenblatt, and J. V. Waszczak, Solid State Commun. **59**, 647 (1986).

[17]N. P. Ong and P. Monceau, Phys. Rev. B **16**, 3443 (1977).

[18](a) E. Canadell, M.-H. Whangbo, and I. E.-I. Rachidi, Inorg. Chem. **29**, 3871 (1990); (b) E. Canadell and M.-H. Whangbo, Phys. Rev. B **43**, 1894 (1991); Chem. Rev. **91**, 965 (1991).

[19]P. Foury, J. P. Pouget, E. Wang, and M. Greenblatt, Europhys. Lett. **16**, 485 (1991).

[20]E. Canadell and M.-H. Whangbo, J. Solid State Chem. **86**, 131 (1990).

[21]S. L. Wang, C. C. Wang, and K. H. Lii, J. Solid State Chem. **82**, 298 (1989).

[22]J. P. Giroult, M. Goreaud, Ph. Labbé, and B. Raveau, Acta Crystallogr. Sec. B **37**, 2139 (1981).

[23]B. Domengés, M. Hervieu, B. Raveau, and R. J. D. Tilley, J. Solid State Chem. **54**, 10 (1984).

[24]P. Foury, J. P. Pouget, E.Wang, Z. S. Teweldemedhin, and M. Greenblatt (unpublished).

[25]E. Wang (private communication).

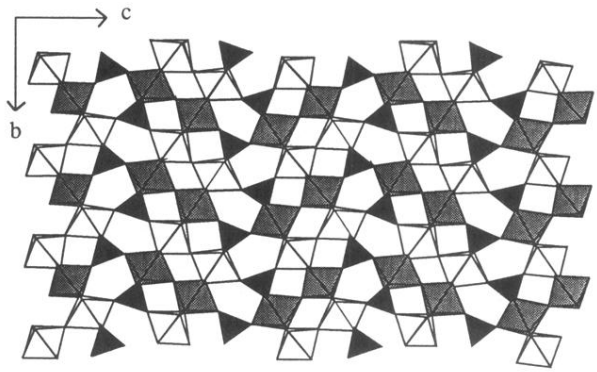

FIG. 1. Schematic of $P_4W_8O_{32}$ crystal structures in the *b*-*c* plane showing ReO_3-type slabs (different shadings of the WO_6 octahedra reflect the zigzag chains of polyhedra parallel to the *c* axis at different levels).