

Quasi-two-dimensional Electronic Properties of the Sodium Molybdenum Bronze, $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$

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Four probe electrical resistivity measurements between 1.5 and 300 K were made on single crystals of the violet-red bronze $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ grown by a temperature gradient flux technique. The temperature variation of the resistivity shows metallic conductivity and highly anisotropic behavior similar to $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ and $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$. The room-temperature resistivity, measured in the direction parallel to the plate axis, is $3.0 \times 10^{-3} \Omega \text{ cm}$ and perpendicular to that axis it is $0.21 \Omega \text{ cm}$. A transition observed at $\sim 88 \text{ K}$ is possibly related to the onset of a charge density wave. The temperature variation of the susceptibility show Pauli paramagnetic behavior at high temperature, and highly anomalous behavior in the vicinity of the transition at low temperatures. © 1985 Academic Press, Inc.

Introduction

Ternary alkali metal molybdenum oxide bronzes with the general formula $M_x\text{Mo}_y\text{O}_z$ where $M = \text{Li}, \text{Na}, \text{K}, \text{Rb},$ and Cs have been intensively studied because of their interesting properties (1). In these materials the alkali metal usually donates its outer electron to the transition metal. These electrons can partially fill the π^* conduction band, formed by the overlap of molybdenum t_{2g} 4d orbitals and of oxygen p_π orbitals in the extended lattice (2) and the material

will exhibit metallic behavior. If the electrons donated by the alkali metals are in covalent bonds by pair formation, or form localized magnetic moments, the bronze $M_x\text{Mo}_y\text{O}_z$ will be semiconducting.

The metal-to-semiconductor transition observed at $\sim 180 \text{ K}$ in the blue $\text{K}_{0.3}\text{MoO}_3$ and $\text{Rb}_{0.3}\text{MoO}_3$ bronzes some years ago (3, 4) has recently been confirmed to be associated with a charge-density wave (CDW) driven structural phase transition (5, 6). The nonlinear behavior of the electric field dependence of the conductivity above a small threshold potential which has been attributed to a sliding CDW in the chalcogen-

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ides NbSe_3 (7) and TaS_3 (8) has now been observed in these oxide materials for the first time (9–13).

Electrical and magnetic properties of electrolytically grown single crystals of $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ have shown that the compound exhibits quasi-two-dimensional behavior (14). The temperature dependence of conductivity, the thermoelectric power, and magnetic susceptibility show an anomaly at approximately 120 K which has been attributed to the onset of a charge density wave (15).

A recent redetermination (16) of the crystal structure of this compound shown in Fig. 1 is in essential agreement with that reported by Gatehouse *et al.* several years ago (17). The ideal structure of hexagonal $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ (16) can be described in terms of slabs of Mo–O corner-sharing polyhedra. Each slab of Mo–O polyhedra consists of four layers of ReO_3 -like MoO_6 octahedra sharing corners which are terminated on either side by a layer of MoO_4 tetrahedra which share corners with adjacent MoO_6 octahedra. These slabs are perpendicular to the c axis and are held together by a layer of potassium ions in an icosahedral environment of oxygens. The MoO_4 tetrahedra in adjacent layers do not share corners, so that the Mo–O–Mo bonding, infinite in the a and b directions, is disrupted in the c direction. The effective Mo valences are +6 on the Mo in tetrahedral sites and approxi-

mately +5.1 and +5.8 on the two crystallographically nonequivalent Mo in octahedral sites. Thus the $4d$ electrons of molybdenum atoms are located in the two-dimensional slabs of octahedra and the structural properties should lead to a very anisotropic Fermi surface which is consistent with the observed quasi-two-dimensional conductivity (14).

We have recently reported results of four probe resistivity measurements between 0.3 and 300 K on single crystals of the violet–red bronze $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ grown by a temperature gradient flux technique (18, 19). The temperature variation of the resistivity shows metallic conductivity and highly anisotropic behavior similar to $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$. For the Li analog the room-temperature resistivity, measured in the direction parallel to the plate axis, is $9.5 \times 10^{-3} \Omega \text{ cm}$ and perpendicular to that axis it is $2.47 \Omega \text{ cm}$. A dramatic low-temperature upturn in resistivity beginning at $\sim 24 \text{ K}$ is cut off by superconductivity at $T_c \sim 1.9 \text{ K}$ in the lithium compound. Preliminary results of a neutron diffraction powder profile analysis of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ indicate that the gross features of the structure are the same as those observed in $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ (20). The oxygen coordination around the Li ions appears to be octahedral rather than icosahedral.

We have grown single crystals of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ by a temperature gradient flux technique (21). $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$, like $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$, is monoclinic, but in the case of the former the possible space groups are $C2/m$, $C2$, or Cm ($a = 9.565 \text{ \AA}$, $b = 5.525 \text{ \AA}$, $c = 12.978 \text{ \AA}$, $\beta = 90.09^\circ$), while for the lithium analog the cell is primitive ($P2/m$ or $P2$ or Pm). However, both the Li and Na analogs have a pseudohexagonal cell similar to that of $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ ($a_{\text{hex}} \approx b$, $c_{\text{hex}} \approx c$) (16, 17). In view of the interesting physical properties of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ and $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ it seemed worthwhile to undertake the study of the electronic properties of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$.

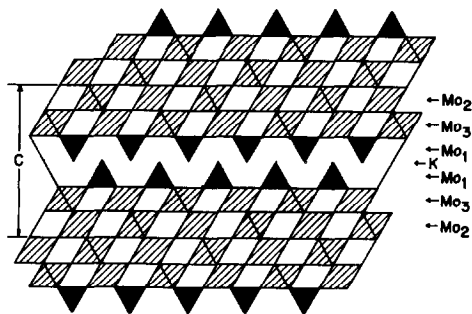


FIG. 1. Structure of $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$.

The results of electrical resistivity measurements between 1.5 and 300 K and magnetic susceptibility down to 4.2 K are reported.

Experimental

Single crystals of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ were grown by a temperature gradient flux technique as described elsewhere (21). The crystals are violet-red elongated platelets and those selected for study typically had dimensions in the range of $5 \times 3 \times 0.5 \text{ mm}^3$.

Samples were identified by X-ray diffraction techniques. Chemical analysis for sodium and molybdenum were performed by plasma emission spectroscopy.

The electrical resistivity has been measured between 1.5 and 300 K in a conventional liquid-helium cryostat by a standard four-probe configuration in which a dc current could be passed either parallel or perpendicular to the crystal plate axis, respectively. Low-resistance contacts to the crystals were made using Englehard No. 16 silver paint. The magnetic susceptibility was measured using the Faraday method as described previously (22).

Results

Figure 2 shows the temperature variation of resistivity between 1.5 and 300 K of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ both in the plane (ab) of the sample (I in Fig. 2) and along the c axis (II in Fig. 2). In the first case, the two current (I) contacts covered the ends of sample, such that (I) was parallel with the crystallographic b direction. In the second case they were attached to opposite faces of the crystal (I parallel with c). These measurements have been made on several different crystals and each exhibit similar behavior in the variation of resistivity with temperature. Figure 2 shows that the conductivity is metallic and highly anisotropic. The conductivity at room temperature is approximately 70 times greater in the direction parallel to

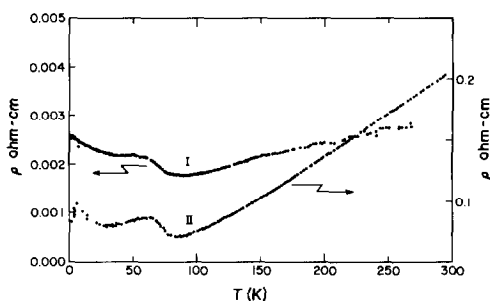


FIG. 2. Temperature variation of the resistivity of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ from 1.5 to 300 K. (I) Current in the plane of the platelet crystal. (II) Current perpendicular to plane of the platelet parallel with c .

the plate axis b , $3.3 \times 10^2 (\Omega \text{ cm})^{-1}$ as compared to the perpendicular direction along c , $4.76 (\Omega \text{ cm})^{-1}$. The resistivity decreases linearly with temperature from 300 to ~ 88 K. From 88 to 65 K the resistivity increases by about twofold in a "sigmoidal"-shaped curve reminiscent of a second-order phase transition, then it decreases for a short interval of decreasing temperature. Below ~ 30 K the resistivity increases again. Below 2 K several, but not all of the samples measured, show an abrupt falloff in the resistivity down to 1.5 K, the lower limit of our ^4He cryostat. In an attempt to clarify the nature of the transition below 2 K, the ac susceptibility of a small single crystal of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ was measured. Between 1 and 0.5 K a weak diamagnetic signal was observed, but the signal is too weak to confirm superconductivity. The resistivity measured perpendicular to the b axis in the plane of the crystal is about an order of magnitude larger than the resistivity observed along the b direction.

The magnetic susceptibility measured from 300 to 4.2 K parallel to the plate axis of a large single crystal is shown in Fig. 3. Similar results were obtained for a batch of randomly oriented small single crystals. Slightly temperature-dependent paramagnetic behavior is observed down to ~ 88 K, followed by a sharp increase. At ~ 30 K the

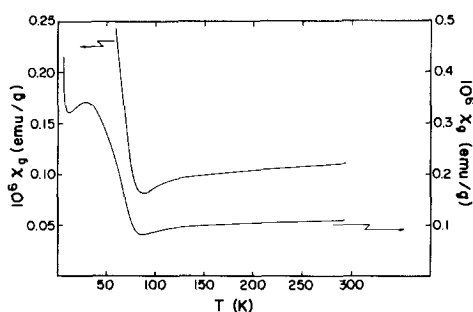


FIG. 3. Temperature variation of the magnetic susceptibility of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$.

susceptibility goes through a maximum. The Curie tail seen at low temperature is most likely due to paramagnetic impurities in the sample. The room-temperature susceptibility is $\chi = 8.9 \times 10^{-5}$ emu/mole.

Discussion

The crystal structure of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ in the twinned form was partially solved by Stephenson (23). Gatehouse *et al.* (17, 24) obtained a solution based on monoclinic symmetry. However, no atomic coordinates or bond distances have been published. It is essentially isostructural with $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ (16). Gatehouse (24) cites evidence that in small areas of the crystal some of the MoO_4 tetrahedra near the $z = \frac{1}{2}$ plane are replaced by MoO_6 octahedra (Fig. 1), thus extending the ReO_3 -type slabs and crosslinking the $z = \frac{1}{2}$ plane by corner-sharing octahedra. Nevertheless, the quasi-two-dimensional nature of the sodium analog appears to be maintained.

This is consistent with the observed temperature variation of the resistivity of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ (Fig. 2). While considerably different from that of $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ (19), $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ is more like $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ (14); it shows quasi-two-dimensional metallic behavior consistent with the network structure of molybdenum polyhedra in all three compounds.

The change in the sign of the temperature dependence of resistivity seen at ~ 88 K for $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ is similar to the anomaly observed in the resistivity of $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ at 120 K (14). It seems likely that this anomaly is due to a CDW, however, X-ray diffraction studies which would unambiguously confirm the CDW have not been attempted thus far.

The qualitative shape of the temperature variation of the resistivity below 88 K is similar to the metal-to-semiconductor transition associated with CDW formation in other quasi-two-dimensional molybdenum bronzes (6, 5, 14). The temperature variation of resistivity of $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ at the CDW transition is "sigmoidal;" below 120 K the resistivity increases as part of the Fermi surface is lost due to the CDW, but below ~ 80 K metallic behavior of the resistivity is observed again down to 2 K. In $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ the resistivity increases exponentially below 24 K down to T_c . The anomaly below ~ 88 K in the temperature variation of resistivity of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ is similar in shape to that observed for $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ at ~ 120 K, followed by an upturn in the resistivity at lower temperatures of the same form as seen in $\text{Li}_{0.9}\text{Mo}_6\text{O}_{17}$ (19).

The magnitude of the magnetic susceptibility of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ at room temperature ($\chi = 8.9 \times 10^{-5}$ emu/mole) is similar to values reported for other metallic molybdenum bronzes ($\chi(300 \text{ K}) \cong 5 \pm 5 \times 10^{-5}$ emu/mole for $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$ (15) and $\chi \cong 2 \times 10^{-5}$ emu/mole for $\text{K}_{0.3}\text{MoO}_3$ (3, 5)). This value of the susceptibility rules out extrinsic impurity levels as the prime source of conduction electrons. The decrease in the susceptibility below ~ 110 K (Fig. 3) may correspond to a transition (possibly the onset of a CDW). The sharp increase in the susceptibility at ~ 88 K clearly indicates a transition. There may be yet another transition at ~ 30 K indicated by a downturn in the susceptibility, which is similar to that observed in $\text{K}_{0.9}\text{Mo}_6\text{O}_{17}$, which has been

suggested to be due to a spin density wave (25).

The temperature variation of the resistivity of the blue bronzes $\text{K}_{0.3}\text{MoO}_3$ and $\text{Rb}_{0.3}\text{MoO}_3$ are very similar (5, 6). The alkali metal apparently has very little effect on the temperature of the CDW-driven metal-to-semiconductor phase transition as also confirmed recently by Schneemeyer *et al.* (26). Substitution of W for Mo in $\text{K}_{0.3}\text{MoO}_3$, on the other hand, significantly affects the resistivity results (26).

In view of the similarity of the basic Mo_6O_{17} polyhedra network structure of the three $\text{A}_{0.9}\text{Mo}_6\text{O}_{17}$, $\text{A} = \text{Li}, \text{Na}, \text{K}$ phases, similar electronic behavior might be expected, assuming that the basic band structure is primarily determined by the Mo-O polyhedra. However, large differences in the electronic and magnetic properties of these compounds are observed. Preliminary results of the temperature variation of resistivity on mixed alkali metal phases of the type $(\text{Li}_{1-x}\text{Na}_x)_{0.9}\text{Mo}_6\text{O}_{17}$, show very large changes as a function of the alkali metal content (27).

It is clear that the structural differences in the three parent compounds are due to slight variations in the alkali metal coordination, but the structural studies have not proceeded far enough to discern if there are differences in the molybdenum coordination or valency in the slabs. This in turn appears to have a large effect on the band structure.

The structure determination of $\text{Na}_{0.9}\text{Mo}_6\text{O}_{17}$ by neutron diffraction powder profile analysis (NDPPA) is in progress and will be reported elsewhere (28). Details of the structure are needed to clarify the electronic structure and the differences between the properties of the lithium, sodium, and potassium analogs.

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