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Quasi-One-Dimensionality in the New Bronze-like Compound $La_2Mo_2O_7$

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Directional, four-probe electrical resistivity and magnetic susceptibility measurements were carried out on the bronze-like, purple compound, $La_2Mo_2O_7$, between room temperature and 1.5 and 4.2 K, respectively. The resistivity is anisotropic with $\rho(300\ K) = 6.4 \times 10^{-2}$, 5.9×10^{-2}, and 4.0×10^{-3} (Ω cm) along the *a*, *b*, and *c* directions of the orthorhombic unit cell, respectively. There is an increase in the resistivity near 125 K, and a drop in the susceptibility seen with *H* parallel to the *c* axis but not perpendicular to it. These observations are indicative of a charge-density-wave (CDW) transition.

Introduction

One of us has recently reported the preparation of single crystals of numerous rare earth molybdenum oxides, $Ln_xMo_yO_z$, where Ln = Y, La, Nd (*1*). Subsequently, the crystal structure and transport properties were reported on one of these compounds, $La_2Mo_2O_7$ (*2*). The structure of $La_2Mo_2O_7$ consists of infinite sheets of MoO_6 octahedra which are made up of Mo_2O_{10} clusters formed by two edge-sharing MoO_6 units. The clusters which have a Mo–Mo distance of only 2.478 Å corner-share along the *a* and *c* crystallographic directions (Fig. 1). The molybdenum oxygen sheets in the *ac* plane are joined by lanthanum ions along *b*. Earlier results of electrical resistivity measurements on single crystals of $La_2Mo_2O_7$ along *c*, and magnetic susceptibility on nonoriented crystalline agglomerates, indicated a phase transition at 125 K which was suggested to be due to the formation of a charge-density-wave (CDW) (*2*). Very recently, tight-binding band calculations (*3*) indicated that $La_2Mo_2O_7$ is a pseudo-one-dimensional metal and that the transition observed at 125 K is driven by a CDW in-

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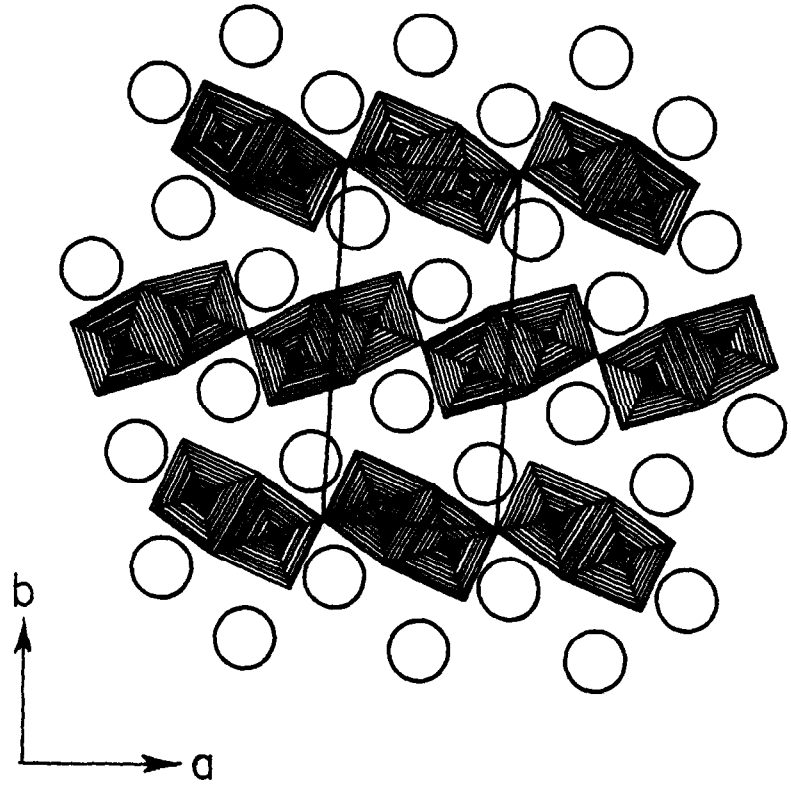
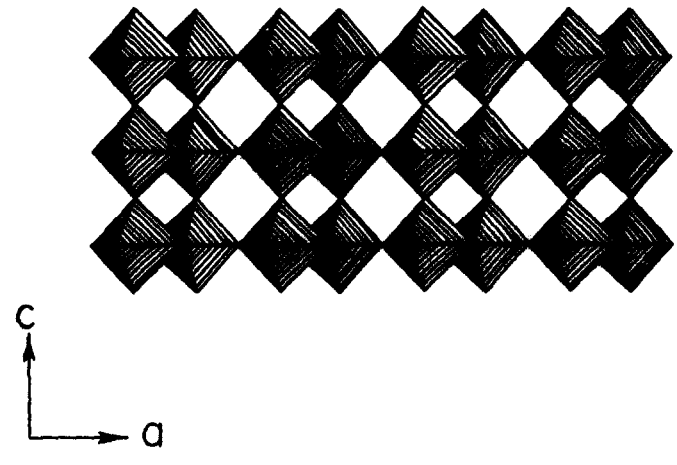


(a)



(b)

FIG. 1. (a) Corner-sharing regimen of the Mo_2O_{10} clusters in $La_2Mo_2O_7$ (open circles are La). Projection down the *c* axis. (b) A section of the $La_2Mo_2O_7$ structure showing the corner sharing of the Mo_2O_7 layers in the crystallographic *ac* plane.

stability whose wave vectors are $q_1 \simeq (0.5a^*, 0.73c^*)$ and $q_2 \simeq (0, 0.27c^*)$.

Since these previous studies indicated that $La_2Mo_2O_7$ has transport properties similar to the well-established molybdenum oxide bronzes with quasi-low-dimensional properties (*4–9*), we have undertaken further measurements of the directional electronic and magnetic properties to more completely characterize this compound. In addition, we have explored the possibility of the existence of a sliding CDW in this material. Sliding CDW's, which have been reported in, e.g., $K_{0.3}MoO_3$ (*10*), are responsible for a variety of interesting phenomena. These results on $La_2Mo_2O_7$ are reported below.

Experimental

Crystals of $La_2Mo_2O_7$ were prepared by molten salt electrolysis, as previously reported (*1*). Electrical resistivity was measured between 1.5 and 300 K in a conventional liquid-helium cryostat by a standard four-probe configuration employing ultrasonically applied indium contacts. All contact resistances were between 0.5 and 5 Ω at room temperature. Crystal orientation was determined by X-ray diffraction oscillation photography. The single crystal magnetic susceptibility was measured with a SHE SQUID magnetometer. Current-voltage characteristics were evaluated with the sample cooled in an Air Products Displex internally-cycled refrigeration system.

Results

Close examination of a batch of needle-like crystals of $La_2Mo_2O_7$ under the microscope revealed two different crystal morphologies. Approximately 95% of the sample was in the form of prismatic needles with a width of less than 1 mm; some of these crystals were used to measure resistivity along c. The remaining 5% of $La_2Mo_2O_7$ crystals exist as thin platelets with c as the long direction; these crystals were employed to measure resistivity along both a and b.

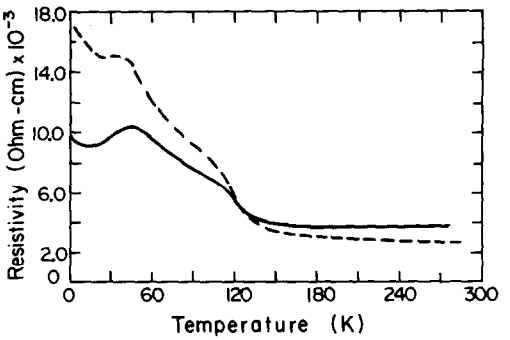


FIG. 2. Resistivity vs temperature for current passed along c showing sample-dependent low-temperature behavior for $La_2Mo_2O_7$.

It was previously reported (*2*) that the room temperature resistivity of $La_2Mo_2O_7$ was 3×10^{-4} Ω cm for current parallel to c. However, we have measured the resistivity of two crystals along c and have obtained values of 4.0×10^{-3} and 4.7×10^{-3} Ω cm, respectively. As shown in Fig. 2, we find that the resistivity is sample dependent below ~40 K. Similar sample-dependent behavior at low temperatures has been observed in $Na_{0.9}Mo_6O_{17}$ (*8*). For $La_2Mo_2O_7$, we observe metallic behavior down to 200 K. Below 200 K, the resistivity increases until ~40 K where there is a downturn. Below 15 K, ρ increases again. The numerical derivative of the resistivity versus temperature is shown in Fig. 3. The sharp negative peak at 125 K is used to define the transition temperature in $La_2Mo_2O_7$. For our samples, the derivative of the resistivity drops to a much lower value at 125 K than that found by Moini *et al.* (*2*). This behavior is indicative of fewer defects and/or impurities in the samples we have measured. This may explain the absence of downturn in ρ at 40 K in the data reported previously (*2*).

The temperature variation of resistivity for current passed parallel to b is shown in

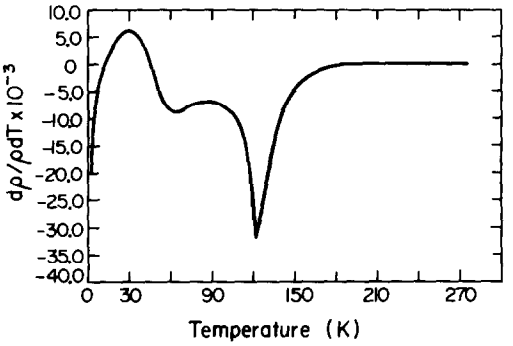


FIG. 3. $d\rho/\rho dT$ vs temperature for current parallel to c for $La_2Mo_2O_7$.

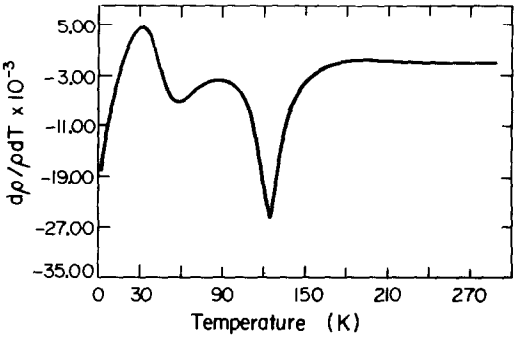


FIG. 5. $d\rho/\rho dT$ vs temperature for current parallel to b for $La_2Mo_2O_7$.

Fig. 4. The room temperature value is 5.9×10^{-2} Ω cm. The derivative plot shown in Fig. 5 again indicates the transition at 125 K. We have also measured resistivity at room temperature for current parallel with a, obtaining a value of 6.4×10^{-2} Ω cm.

The magnetic susceptibility was measured on approximately 10 mg of single crystals aligned parallel with the c axis. The crystal morphology precluded our ability to distinguish between a and b for all the crystals. Therefore, an external magnetic field of 5 kG was applied both parallel and perpendicular to the c axis. For field along c we observe a drop in χ at around 125 K (Fig. 6), as was previously reported for nonoriented, single-crystal agglomerates (*2*). The drop in χ at ~125 K is not observed for field perpendicular to c. For both directions, $La_2Mo_2O_7$ remains weakly paramagnetic throughout the entire temperature range, 300 to 4.2 K (Fig. 6).

The electronic and magnetic transport properties of $La_2Mo_2O_7$ are indicative of a CDW transition at 125 K; since tight-binding band calculations (*3*) predict $La_2Mo_2O_7$ to be a pseudo-one-dimensional metal, we measured the current-voltage (I-V) profile of $La_2Mo_2O_7$ in search of a sliding CDW. The I-V curves become nonohmic in the sliding state due to extra current supplied by the moving CDW. However, we have found linear current-voltage behavior at 77

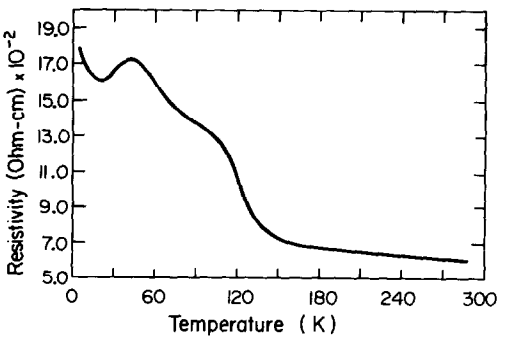


FIG. 4. Resistivity vs temperature for $La_2Mo_2O_7$ with current along b.

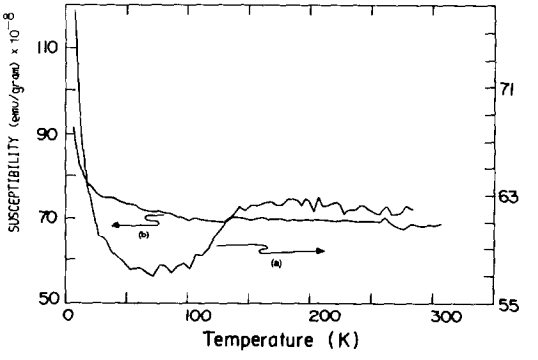


FIG. 6. Single crystal magnetic susceptibility vs temperature for $La_2Mo_2O_7$ with (a) H parallel and (b) perpendicular to c.

and 40 K for fields as high as 700, 1000, and 800 mV/cm for the *a*, *b*, and *c* directions, respectively.

Discussion

In many ways the structure and transport properties of $La_2Mo_2O_7$ resemble those of the molybdenum oxide bronzes. In the molybdenum blue bronzes, $A_{0.3}MoO_3$, where A = K, Tl, and Rb, the structure consists of infinite sheets of distorted MoO_6 octahedra held together by the A cations. The MoO_3 layers are built up from clusters of 10 edge-sharing octahedra linked by corners in the [101] and [102] directions. Subsequently, there are infinite chains of MoO_6 units sharing corners along the unique monoclinic *b* axis (*11, 12*). The $A_{0.3}MoO_3$ compounds are quasi-one-dimensional metals at room temperature (*13*) which undergo a CDW-driven phase transition below 180 K (*14*).

The molybdenum purple bronzes, $A_{0.9}Mo_6O_{17}$, with A = Na, K, and $TlMo_6O_{17}$ are pseudo-two-dimensional metals. The structure consists of four layers of ReO_3-like MoO_6 octahedra terminated on each side by MoO_4 tetrahedra which share corners with adjacent MoO_6. These slabs are perpendicular to the *c* axis and are separated by a layer of A ions (*6, 15*). These materials undergo a CDW-driven metal-to-metal transition at 88, 113, and 120 K for the sodium, potassium, and thallium analogs, respectively (*6, 8, 9*).

Although $La_2Mo_2O_7$ is a new structural type, there are some aspects of the atomic arrangement which are similar to both the blue and purple molybdenum bronzes. Similarities to the blue bronzes are evident in the infinite Mo–O–Mo overlap along the *c* axis. Furthermore, sheets of molybdenum and oxygen are separated by lanthanum ions, reminiscent of both the blue and purple bronzes.

Tight-binding band calculations by Whangbo and Canadell (*3*) predict that $La_2Mo_2O_7$ should be a pseudo-one-dimensional metal at room temperature. The metal-to-metal transition occurring at 125 K can be explained in terms of only partial nesting of the Fermi surface by the CDW wave vector. The incomplete nesting accounts for the metallic character present below the transition temperature. The calculations suggest that the transition in $La_2Mo_2O_7$ is due to CDW's of wave vectors $q_1 \simeq (0.5a^*, 0.73c^*)$ and $q_2 \simeq (0, 0.27c^*)$. Accordingly, the *c* direction should be the most conducting in $La_2Mo_2O_7$. Experimentally, we find the room temperature resistivity for current passed along *c*, 4.0×10^{-3} Ω cm, is an order of magnitude lower than for current parallel to *a* and *b*, 6.4×10^{-2} Ω cm and 5.9×10^{-2} Ω cm, respectively.

Upon closer examination of the structure of $La_2Mo_2O_7$, one notices that along *c*, i.e., the direction of infinite MoO_6 octahedra corner-sharing, the molybdenum oxygen bond distance of 1.951 Å is sufficiently short for good Mo–O $p\pi$ overlap. The high conductivity would appear to arise from electron delocalization due to this overlap as predicted by the calculations of Whangbo and Canadell (*3*). A similar behavior has been predicted for other transition metal oxides (*16*) and also confirmed in the related Mo bronzes (*17*). The lower conductivity along *b* is expected since the Mo–O overlap is disrupted by the lanthanum ions joining the molybdenum oxygen sheets.

Chains of Mo_2O_{10} clusters are formed by corner-sharing oxygens which run parallel to the *a* axis (Fig. 1). The short Mo–Mo distance within the cluster is 2.478 Å and is less than the distance of 2.51 Å found in MoO_2 (*18*). It is also noteworthy that a Mo–Mo distance of 2.496 Å has been found recently in $Y_5Mo_2O_{12}$ (*19*). Since Mo–Mo interactions are confined to the clusters one might expect that the extent of electron delocalization will depend on the strength of the Mo–O π orbital overlap. This is ex-

pected to be poor along the *a* direction because of the zigzag nature of the chain formed by the Mo_2O_{10} units and the longer Mo–O distance of 2.008 Å for the corner-sharing oxygens as compared to that found along the *c* direction. The fact that the observed values of conductivity along *a* and *b* are nearly equal is most likely an artifact of the experimental conditions.

ρ_b and ρ_a can be much lower than the actual values if a small contribution of the conductivity arises due to partial contact along the *c* direction. On the basis of the structure (Fig. 1) we would expect $\rho_c < \rho_a \ll \rho_b$; we observe $\rho_c < \rho_a \sim \rho_b$. We believe that the low value of ρ_b is the result of parasitic current leakage along *c*, partly due to the small size and erratic cleavage of the crystals, which made contact applications difficult.

The oriented crystal magnetic susceptibility data, shown in Fig. 6, is consistent with a CDW transition at 125 K for field parallel to *c*. The drop in the susceptibility is due to loss of Fermi surface below the CDW transition temperature. For field parallel to *c*, χ is similar to that found for $K_{0.3}MoO_3$ (*20*). When the field is applied perpendicular to *c*, i.e., parallel to both *a* and *b*, no drop in χ is observed. For both field orientations, $La_2Mo_2O_7$ remains slightly paramagnetic down to 4.2 K.

Due to the low dimensionality of $La_2Mo_2O_7$, we have measured the I-V behavior below the transition temperature of 125 K. If a CDW begins to slide at some applied threshold field, E_T (expressed in mV/cm), the I-V curve will be nonlinear. As noted earlier, at both 77 and 40 K, we observe linear (ohmic) behavior for fields as high as 700, 1000, and 800 mV/cm for current along *a*, *b*, and *c*, respectively. One might expect nonlinear conduction along *c* if $La_2Mo_2O_7$ is a quasi-one-dimensional metal. Nonlinear conduction has been observed in the blue bronzes (*5, 10*). However, we do not see any evidence of a sliding CDW in $La_2Mo_2O_7$. Only linear I-V characteristics have been observed in the quasi-2-D purple $A_{0.9}Mo_6O_{17}$-type bronzes (*9, 21*). Although electronically $La_2Mo_2O_7$ appears to be a 1-D metal, the metal-to-metal transition, caused by partial nesting of the Fermi surface, resembles that seen for the purple bronzes. It is apparent that a low-temperature X-ray diffraction measurement is necessary to unambiguously determine that the transition at 125 K for $La_2Mo_2O_7$ is due to a charge-density-wave.

In summary, we confirm the anisotopic behavior of the resistivity and magnetic susceptibility of $La_2Mo_2O_7$ as expected by the structure and band calculations. However, we were not able to unambiguously resolve whether $La_2Mo_2O_7$ is a quasi-two-dimensional metal as suggested by the metal-to-metal transition at 125 K, or a quasi-one-dimensional metal as predicted by the tight-binding band structure calculations.

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