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Sliding Charge-Density Wave Conductivity in Potassium Molybdenum Bronze*

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The monoclinic blue-bronze, $K_{0.30}MoO_3$, is an anisotropic metal that undergoes a charge density wave (CDW)-driven phase transition at 180 K, below which nonlinear current–voltage characteristics are observed. In this paper, we examine the anisotropy of the electric and magnetic properties of $K_{0.30}MoO_3$ and their relationship to observed CDW phenomena. We show that the conductivity is highest along the monoclinic *b* axis and 10 and 100 times lower in two directions perpendicular to *b* (in the $(\bar{2}\ 0\ 1)$ plane and perpendicular to these planes, respectively). In the CDW state, the conductivity along the *b* axis is nonlinear when the applied electric field exceeds a small threshold on the order of 50 mV/cm, but is field-independent in perpendicular directions. A periodic response to a dc bias was observed in one small $K_{0.30}MoO_3$ sample, however, the observation of an $NbSe_3$-like response in $K_{0.30}MoO_3$ may depend on sample size or the quality of the electrical contacts to the sample.

Introduction

Nonlinear electrical properties are observed in the charge density wave (CDW) state of the transition metal oxide bronze, $K_{0.30}MoO_3$, when the applied electric field exceeds a small threshold on the order of 50 mV/cm (*1*). This dc nonlinear conductivity is believed to be due to charge transport via a moving ("sliding") CDW (*2*), a CDW which is depinned from the lattice and moves in a dc field. Previous studies of CDW conductivity have concentrated on the transition metal trichalcogenides (*3*) and structurally related compounds such as the transition metal tetrachalcogenide halides (e.g., $(TaSe_4)_2I$) (*4*). $K_{0.30}MoO_3$ is the first material of a completely different structural type which exhibits effects associated with sliding CDW transport and studies of this material should provide insights into the role played by structure and chemical composition. While the nonlinear effects observed in all of these materials are qualitatively similar to those observed in $NbSe_3$, examination of the detailed behavior in the nonohmic regime in $K_{0.30}MoO_3$ suggests that the quantitative behavior in this oxide is much different than that of the chalcogenides (*5*).

The first alkali molybdenum oxide bronzes were prepared by Wold *et al.* (*6*), by electrolytic reduction of molybdenum trioxide-alkali molybdate melts. Bouchard *et al.* (*7*) measured the temperature dependence of the electrical resistivity, magnetic susceptibility, Hall voltage, and thermoelectric power of one of these, $K_{0.30}MoO_3$, as part of a general program to study the electric and magnetic properties of nonstoi-

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chiometric transition metal compounds. Measurements indicated a semiconductor–metal transition at ~180 K, and the possibility that the observed behavior was associated with structural changes was noted, but the nature of the transition remained elusive. Further studies of $K_{0.30}MoO_3$ by Fogle and Perlstein revealed nonohmic behavior above a critical voltage at low temperature (*8*) although that source of that behavior was not then recognized.

Electron transport via a moving CDW was postulated as early as 1954 (*9*) but among the majority of materials found to undergo CDW-driven phase transitions, the phase of the CDW is pinned to the lattice either by impurities or by commensurability. In $NbSe_3$, however, the CDW is pinned to the lattice at zero field, but upon application of small electric fields, the CDW is depinned and provides an additional contribution to the electrical conductivity (*10*). We now recognize a collection of interesting phenomena exhibited by all of the materials showing increased conductivity via a sliding CDW. First, the current–voltage characteristics are linear below a small threshold field, E_T, and nonlinear above E_T. Second, these materials show an ac response to an applied dc field ($>E_T$). Both a broad band response and a discrete frequency response (narrow band noise) are observed, however, the exact origin of the narrow band noise has not yet been resolved (*10–14*). Third, these materials show an enhanced ac conductivity and a peak in the dielectric response at frequencies on the order of 10 MHz or lower (*15–17*). Finally, hysteresis effects, so called "memory effects," are observed (*18–22*). If a current pulse drives the voltage through the threshold electric field for CDW depinning, an extremely slow voltage response is observed. We have shown that this transient electrical response in $K_{0.30}MoO_3$ is similar to the magnetic response of a spin glass (*23*), suggesting that the CDW state of materials with moving CDW's may be described by large, weakly coupled domains.

In this paper, we examine the solid state properties of $K_{0.30}MoO_3$ in relation to its CDW-driven phase transition. Magnetic susceptibility of oriented single-crystal samples and resistivity as a function of crystal orientation are reported. Current–voltage characteristics as function of crystal orientation are also discussed. These results will be discussed in relation to current models for CDW conductivity.

Experimental

Crystals were grown electrochemically from 99.9% K_2MoO_4 and MoO_3 (Cerac) as described elsewhere (*6*). Powder X-ray diffraction confirmed the preparation of monoclinic $K_{0.30}MoO_3$. Electrical resistivities were measured in four-probe configurations on cleaved samples with ultrasonically soldered indium contacts. For one sample, Montgomery's method (*24*) was used to measure both the resistivity parallel to the *b* axis as well as perpendicular to that axis in the $(\bar{2}\ 0\ 1)$ plane. Typically, ρ vs temperature was obtained by cooling from room temperature to 4.2 K at 1 K/min (slowed to about 0.5 K/min near the transition). Uncertainties in the absolute accuracy of the resistivity as large as 20% are due to uncertainties in measurements of sample size and to the finite size of the voltage contacts.

In measurements of current–voltage behavior, we controlled current and observed the voltage response. We have previously verified that the phase relationship is the same for both current and voltage biasing (*23*). Noise measurements were made using a Textronix 7000 series scope equipped with a 7L5 spectrum analyzer plug-in.

Magnetic susceptibility was measured on oriented single-crystal samples from 4.2 to 300 K using the Faraday technique. Details of this experiment including a discussion of

measurements of susceptibility anisotropy are described elsewhere (*25*). Relative changes in χ_g vs temperature of 5×10^{-10} emu/g could be detected, but, relative to several standards, the absolute accuracy of the susceptibility is ±2%. In a monoclinic crystal, one diagonal element of the susceptibility tensor lies along the *b* axis. By mounting the sample along that axis and rotating the magnetic field about that axis, we could obtain the other principal values. These values measured at 298 K are given in Table I.

Results

Figure 1 shows the temperature dependence of the resistance measured parallel to the monoclinic *b* axis on a cleaved $K_{0.30}MoO_3$ sample mounted in four-probe configuration. Above 180 K, the behavior is metallic. Below 180 K, the resistivity rises steeply and the material becomes semiconducting. The detailed behavior near the 180 K transition is shown in the inset. The transition is second-order, evidenced by a lack of hysteresis on warming and cooling. The transition is slightly rounded, which could be due to extrinsic effects such as broadening due to impurities or defects or alternatively could be intrinsic, arising from fluctuations. We have previously shown that the data can be fit to a log ρ vs $1/T$ form below about 67 K or to a log ρ vs $1/T^{0.5}$ form below about 150 K (*26*). However, our inability to measure the resistivity below ~30 K where the material becomes highly resistive prevents us from differentiating between these two fits to the data.

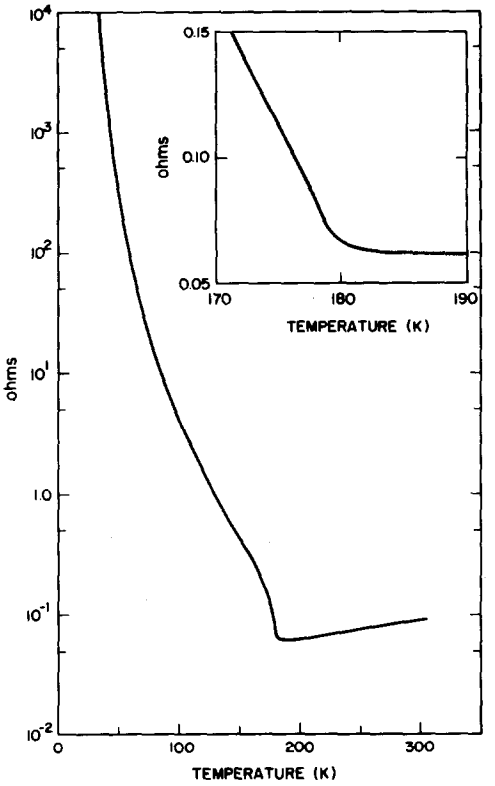

FIG. 1. Log resistance parallel to the monoclinic *b* axis vs temperature for $K_{0.30}MoO_3$. Inset shows the region of the phase transition in detail.

TABLE I

SUSCEPTIBILITY AS A FUNCTION OF $K_{0.30}MoO_3$ CRYSTAL ORIENTATION AT 298 K

Orientation	Susceptibility (emu/g)
$\chi(H \parallel b)$	$+0.107 \times 10^{-6}$
$\chi(H \perp$ layers)	$+0.042 \times 10^{-6}$
$\chi(H \parallel$ layers $\perp b)$	$+0.118 \times 10^{-6}$

$K_{0.30}MoO_3$ is an anisotropic material and the resistivity behavior as a function of crystallographic orientation is of interest. The temperature dependence of the resistivity perpendicular to the $(\bar{2}\ 0\ 1)$ cleavage plane (I, $V \perp b$) is shown in Fig. 2. Again, metallic behavior is observed at high temperature, above ~240 K in this orientation. The resistivity then flattens from ~240 to ~210 K. The resistivity anomaly shows greater rounding relative to samples measured with I, $V \parallel b$. Since all samples examined in this study have similar impurity

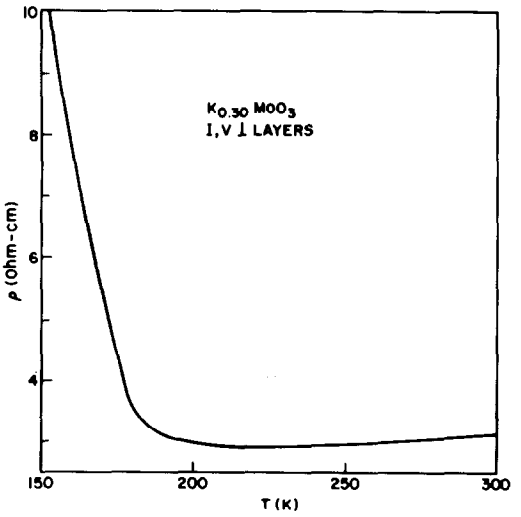

FIG. 2. Resistivity perpendicular to the $(\bar{2}\ 0\ 1)$ layers in $K_{0.30}MoO_3$.

concentrations, the greater broadening observed in this orientation is, most likely, an intrinsic effect. Finally, at low temperature the resistivity rises sharply and the sample becomes semiconducting.

In order to obtain an estimate of the conductivity anisotropy in the plane of the layers, we measured the resistance of a rectangular sample with the long edge parallel to *b* (see inset Fig. 3). The cleavage plane is parallel to the $(\bar{2}\ 0\ 1)$ plane of the reciprocal lattice. However, the in-plane direction perpendicular to *b* may be a general rather than a principal resistivity direction (*27*). We thus report a resistance ratio rather than the resistivity ratio along principal directions. The temperature dependence of this resistance ratio is shown in Fig. 3. The resistance ratio rises smoothly from ~90 near 300 K to a maximum of ~170 K near the CDW-driven phase transition at 180 K. It then falls sharply, reaching a constant value near the room temperature value below ~150 K.

The temperature dependence of the susceptibility in the three principle orientations is illustrated in Fig. 4. From the data given in Table I, we find that the susceptibility anisotropy is approximately a factor of 1.1 in the $(\bar{2}\ 0\ 1)$ plane, and a factor of 2.5 between these planes. The susceptibility anomaly is similar in shape and amplitude in all crystal orientations. Above ~200 K, the susceptibility is paramagnetic with a small temperature dependence. Below this temperature, the susceptibility drops steeply, becoming diamagnetic at low temperature. A small anomaly of unknown origin is noted near 40 K.

Among the most interesting phenomena observed in $K_{0.30}MoO_3$ is nonlinear current–voltage behavior below the CDW-driven phase transition at 180 K. Upon the application of a small dc field, the CDW is depinned from the lattice and moves in that field, thus providing an additional contribution to the conductivity. The orientation of the applied dc field determines whether the

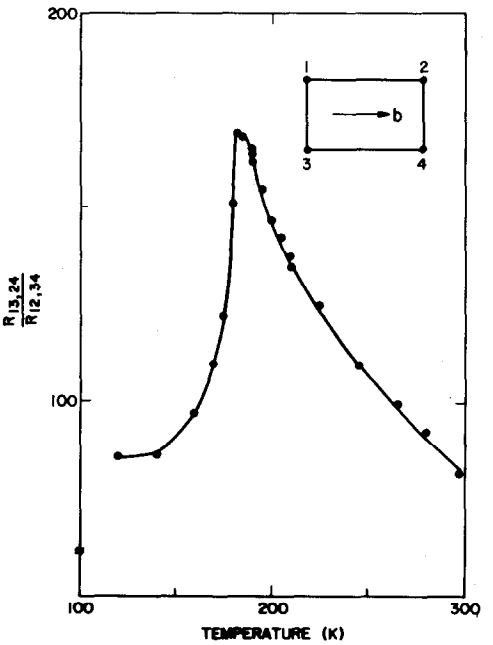

FIG. 3. Resistance ratio, $R_{\perp b}/R_{\parallel b}$, in the $(\bar{2}\ 0\ 1)$ layer.

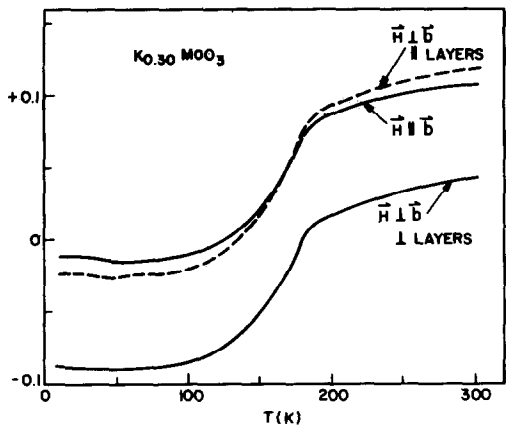

FIG. 4. Temperature dependence of the susceptibility for three $K_{0.30}MoO_3$ orientations.

response is nonlinear. In $NbSe_3$, nonohmic behavior is observed only along the chain axis while the conductivity perpendicular to the chains remains ohmic for fields up to two orders of magnitude higher than E_T. A rectangular platelet of $K_{0.30}MoO_3$ was prepared with ultrasonically soldered indium contacts at four corners as for Montgomery's method (see inset in Fig. 3). This lead configuration results in electric fields in the sample which are nonuniform both in magnitude and direction. As soon as the threshold field is exceeded in any part of the sample, the response becomes nonohmic. When the current flows from contact 1 to contact 2 (inset Fig. 3), the electric fields along that edge of the sample are parallel to b and larger than between the voltage contacts (3 and 4). The first part of the sample in which the threshold field is exceeded will thus be near the current contacts. The threshold field seen across the voltage contacts is consequently underestimated by this method, (Fig. 5), yielding values much less than 35–50 mV/cm seen in $K_{0.30}MoO_3$ when the current and field are parallel to b. With the large resistance anisotropy observed in these samples (as in Fig. 3), the nonlinear threshold for a dc field applied perpendicular to b would be only slightly underestimated. However, when the current is applied perpendicular to b (Fig. 5), a linear current–voltage curve is observed for fields below the maximum applied, 300 mV/cm. This shows that no nonlinear behavior is seen perpendicular to b for fields less than this value, or up to about 10 times the threshold field along b.

The origin of a quasiperiodic ac response, or "noise," to an applied dc field in these materials is the subject of recent controversy. Two competing models suggest that the noise arises either from distortions in the fields internal to the crystal arising from the placement of leads (*28*), or is a finite size effect (*29*). We have not observed a periodic response from any large sample (typically $1 \times 0.5 \times 4$ mm^3). One small sample, however, did show a periodic response ("noise") to a dc bias at 77 K as shown in Fig. 6. The noise consists of discrete frequencies superimposed on a broad band background. The spectrum apparently shows the amplitude of the second harmonic, f_2, to be greater than that of the first, f_1 and contains an additional unrelated fre-

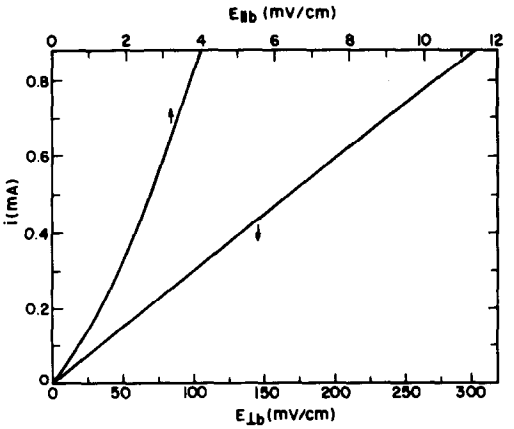

FIG. 5. DC current as a function of the average electric field (voltage between contacts divided by contact separation) measured parallel and perpendicular to b in the $(\bar{2}\ 0\ 1)$ plane in the same configuration as shown in Fig. 3.

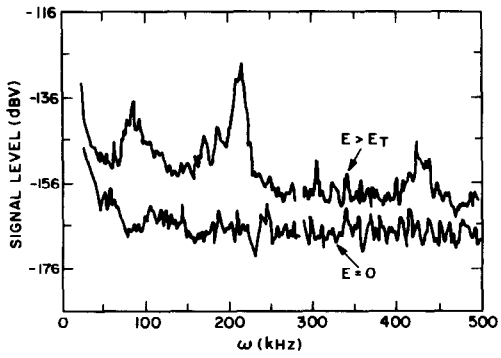

FIG. 6. Noise spectrum of $K_{0.30}MoO_3$ at 77 K for applied dc fields, $E = 0$ and $E > E_T$.

quency. The frequencies shift with applied bias, behavior similar to that observed in $NbSe_3$ (*10, 11*). Other small samples with evaporated gold leads show no change in the noise with applied field. Our results clearly indicate that an $NbSe_3$-like response can be seen in $K_{0.30}MoO_3$ under appropriate conditions. We have not presently established whether the type of leads or the size of the sample is responsible for the ac response shown in Fig. 6.

Discussion

The nonlinear conductivity observed in $K_{0.30}MoO_3$ results from electron transport via a moving CDW. This conclusion is supported by the observation of nonlinear conductivity at very small electric fields, by the abrupt onset of nonohmic behavior at the threshold field, and by the occurrence of quasiperiodic noise. While $K_{0.30}MoO_3$ has been described as "quasi-one-dimensional" based on optical reflectivity data interpreted as showing a Drude edge as typical of metals only when the electric field is polarized along the *b* axis (*30*), higher dimensional interactions are clearly of importance in this material as they are in other materials with moving CDW's. $K_{0.30}MoO_3$ has a layered structure consisting of sheets of MoO_3 separated by potassium ions which leads to anisotropy in various properties. For example, the room temperature resistivity is a factor of 10 and 100 times higher along two direction perpendicular to the highly conducting *b* axis (in the $(\bar{2}\,0\,1)$ plane and perpendicular to it, respectively). The nonlinear properties are observed only along the highly conducting axis, again suggesting quasi-one-dimensional behavior.

The CDW that is observed below 180 K, however, has full three-dimensional order (*31*), presumably due to interchain coupling. Rod-shaped diffuse scattering reported above the phase transition suggests quasi-two-dimensional correlations (*32*). The factors which distinguish a few of the many materials known to undergo CDW-driven phase transitions, those such as $NbSe_3$ or $K_{0.30}MoO_3$ in which the CDW is depinned and moves in an applied electric field, remain unclear. To date, all materials in which sliding CDW's are observed are anisotropic with a single high conductivity axis. However, our understanding of these interesting nonlinear phenomena remains incomplete.

Acknowledgments

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