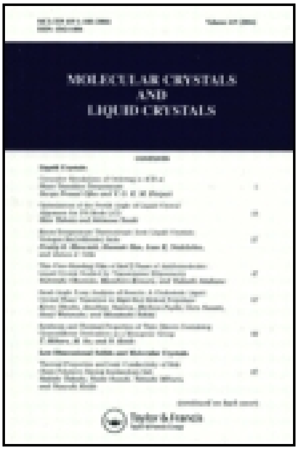

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L. F. Schneemeyer [a] , S. E. Spengler [a] , F. J. Disalvo [a] & J. V. Waszczak [a]
[a] At & T Bell Laboratories, Murray Hill, New Jersey, 07974

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NONLINEAR TRANSPORT PHENOMENA IN MOLYBDENUM OXIDE BRONZES

L. F. SCHNEEMEYER, S. E. SPENGLER, F. J. DiSALVO, AND J. V. WASZCZAK AT&T Bell Laboratories, Murray Hill, New Jersey 07974

Abstract $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$ exhibit effects associated with sliding charge density wave transport and studies of this material should provide insights into the role played by structure and chemical composition. The alloy systems, $K_{0.30}Mo_{1-x}W_xO_3$ and $K_{0.30-x}Rb_xMoO_3$, have been examined. The effects of tungsten substitution are quite large, larger than such doping effects in other CDW systems, whereas alkali substitution produces only small effects.

INTRODUCTION

A variety of unusual phenomena have been associated with electrical conduction via a moving ("sliding") charge density wave (CDW), a CDW which is depinned from the lattice and moves in a dc electric field.[1] A CDW, a periodic distortion of both the conduction electron electron density and the underlying lattice[2] is a charged object. Since current is moving charge, a moving CDW represents a new mechanism for charge transport. To date, only a handful of materials are reported to show sliding CDW conductivity. Initial studies focussed of $NbSe_3$, the first material in which sliding CDW conductivity was identified.[3] The other known sliding CDW conductors are orthorhombic and monoclinic TaS_3,[4] $(TaSe_4)_2I$ and $(NbSe_4)_{3.33}I$,[5] and $K_{0.30}MoO_3$ and $Rb_{0.30}MoO_3$.[6]

The factors that distinguish materials such as $NbSe_3$ or $K_{0.30}MoO_3$, in which the CDW can be depinned from the lattice by an electric field remain unclear. All are anisotropic with a single high conductivity axis, and thus are quasi-one-dimensional with respect to normal conductivities. Oddly, similar effects have not been observed so far in quasi-two-dimensional systems. However, designating materials like $NbSe_3$ or $K_{0.30}MoO_3$ as one-dimensional is misleading as close examination of the structures of all of the sliding CDW conductors show considerable two and three dimensional bonding interactions. Our work has focussed on studies of CDW transport in $K_{0.30}MoO_3$, often referred to as the "blue bronze". In this paper, we describe the use of dopants to probe chemically the response of the CDW.

SAMPLE PREPARATION

Crystals were grown electrochemically as described elsewhere.[7] 99.9% K_2MoO_4, Rb_2MoO_4, MoO_3, and WO_3 (Cerac) were dried before use. Alkali concentrations were controlled by the rubidium to potassium ratios in the melt with concentrations in the crystals verified by atomic absorption analysis. The molybdenum to tungsten ratio in the melt controlled the tungsten concentration in the samples. Chemical analysis of selected samples (by Schwartzkopf Analytical Laboratories) showed that tungsten concentration in the crystals, which was constant within a given batch of crystals, was a factor a four greater than the tungsten concentration in the melt. The mass of crystals grown from each melt was a small fraction of the initial mass to ensure compositional uniformity in the crystals. Powder x-ray diffraction confirmed that the monoclinic $K_{0.30}MoO_3$ structure was maintained in all of the samples studied here.

ELECTRICAL MEASUREMENTS

Electrical resistivity parallel to the monoclinic *b* axis was measured in four probe configuration on cleaved samples with ultrasonically-soldered indium contacts. Low resistance contacts, essential to the studies described here, were difficult to make to $K_{0.30}MoO_3$ especially with other methods of making contacts. Typically, ρ vs temperature was obtained by cooling from room temperature to 4.2K at 1K/min (slowed to ~0.5K/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.

Phenomena Observed in Sliding CDW Conductors

1. Nonlinear dc conductivity– In these materials, current is proportional to voltage (Ohmic response) below a threshold field, E_T, which is of the order of 10's of mV/cm (a very small electric field). In the Ohmic regime, the phase of the CDW is pinned to the lattice either by impurities or by commensurability. Above E_T, the CDW breaks free from the impurities (is "depinned") and provides an additional contribution to the electrical conductivity resulting in a nonlinear (non-Ohmic) current-voltage response (fig. 1a).

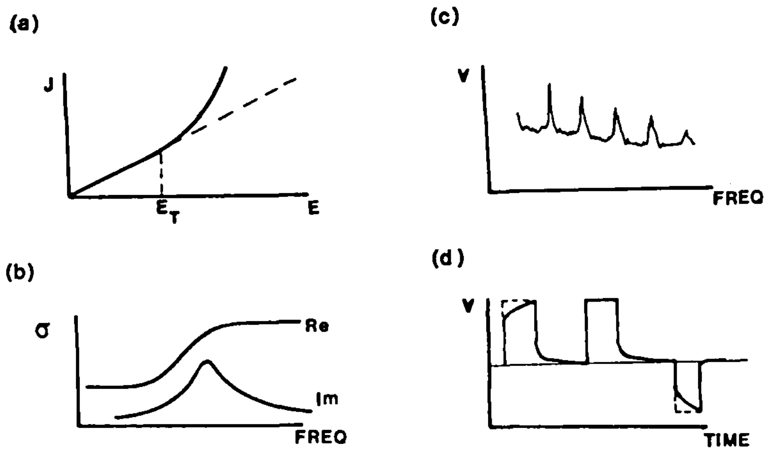

FIGURE 1. Phenomena observed in sliding CDW conductors: a. Nonlinear dc conductivity b. Enhanced ac conductivity c. ac response to a dc bias d. Hysteresis and memory effects.

2. Enhanced ac conductivity– Sliding CDW conductors exhibit an enhanced ac conductivity and a peak in the dielectric response at frequencies on the order of 10 MHz or lower which is determined by the pinning energy (fig. 1b).[8–9] Recent work by Cava et al., has shown that the pinning can be described by a distribution of Debye oscillators.[10]

3. ac response to a dc bias– Evidence for CDW motion is obtained from the time dependent voltage response to a dc current. For applied dc electric fields which exceed threshold, both a broad band response and a discrete frequency

response (narrow band noise) are observed (fig 1c). While the exact nature of the narrow band noise has not yet been resolved,[11–15] the basis for the effect is the interaction of the CDW phase distribution with the impurity potential, or washboard, arising from the distribution of defects and/or impurities in the sample.

4. Hysteresis and memory effects– Sliding CDW conductors exhibit a variety of field and temperature dependent metastable phenomena.[16–17] For example, the response time of the voltage to a series of current pulses depends on the electrical history of the specimen. If a bias pulse has the same polarity as the preceding pulse, the voltage response is fast, while if the bias pulse has the opposite polarity as the preceding pulse, the voltage response is sluggish (fig. 1d). We have shown analogies between the transient electrical response in $K_{0.30}MoO_3$ and the magnetic response of a spin glass,[18] suggesting that the CDW state of materials with moving CDW's involves coupled domains which are rearranged over macroscopic time intervals.

RESULTS AND DISCUSSION

The effects of the isoelectronic dopants, W and Rb, on the solid state properties of $K_{0.30}MoO_3$ have been described elsewhere.[19] Briefly, though, while alkali substitution produces only small effects, the effects of tungsten substitution are the largest seen in any CDW system. Upon incorporation of only 1% tungsten, peaks in the derivatives of resistivity and susceptibility with temperature, $\frac{dx}{dT}$ and $\frac{1}{\rho}\frac{d\rho}{dT}$, which were used to define a crossover temperature, were essentially lost, suggesting that the CDW coherence length becomes very short at low tungsten concentrations.

We previously showed that the resistance data for nominally pure $K_{0.30}MoO_3$ can be fit to a log ρ vs 1/T form at low temperatures yielding an activation energy of 350K and a BCS-like gap, $2\Delta/T_o \sim 3.9$. Our value is somewhat below that obtained from an analysis of magnetic susceptibility data using a one-dimensional fluctuation model.[20] Fig 2 shows plots of log ρ/ρ_o vs 1/T for samples in the series $K_{0.30}Mo_{1-x}W_xO_3$. Two features of the plot are of interest. First, examination of the high temperature region shows that the

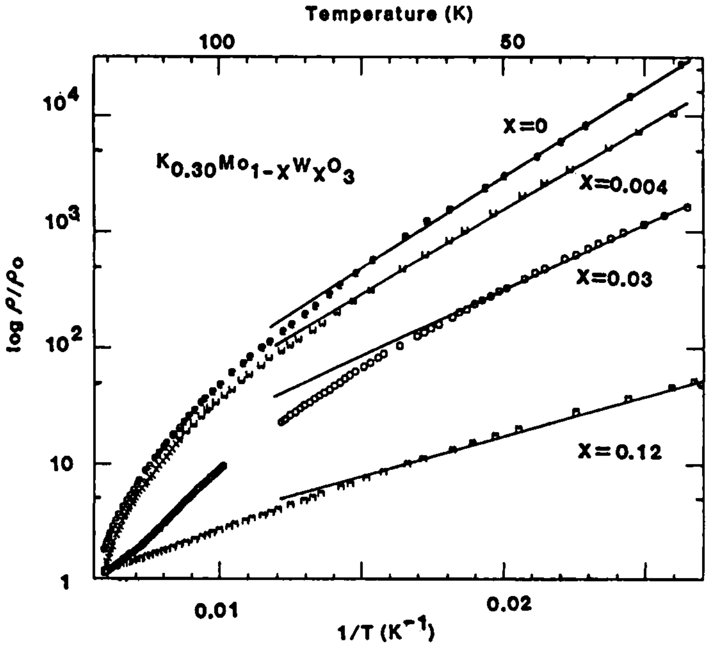

FIGURE 2. Log ρ/ρ_o vs inverse temperature for $K_{0.30}Mo_{1-x}W_xO_3$ samples.

resistivity anomaly is washed out with increasing impurity concentration. Also, the low temperature data can be fit to a log ρ vs 1/T form for these doped samples as for the nominally-pure $K_{0.30}MoO_3$. The slope decreases with increasing tungsten concentration indicating that the activation energy is decreasing. Effects of the impurity may be complex, possibly introducing impurity levels within the gap as well as shifting the band edges. Fig. 3 shows that the apparent activation energy varies as the square root of the impurity concentration. Additional data is necessary to confirm the functional dependence of activation energy on impurity concentration.

Among the most interesting phenomenon observed in $K_{0.30}MoO_3$ is nonlinear current-voltage behavior below the CDW driven phase transition at 180K. Lee and Rice[2] have considered the effects of two classes impurities on the CDW condensate. These are distinguished by the functional dependence of the dc

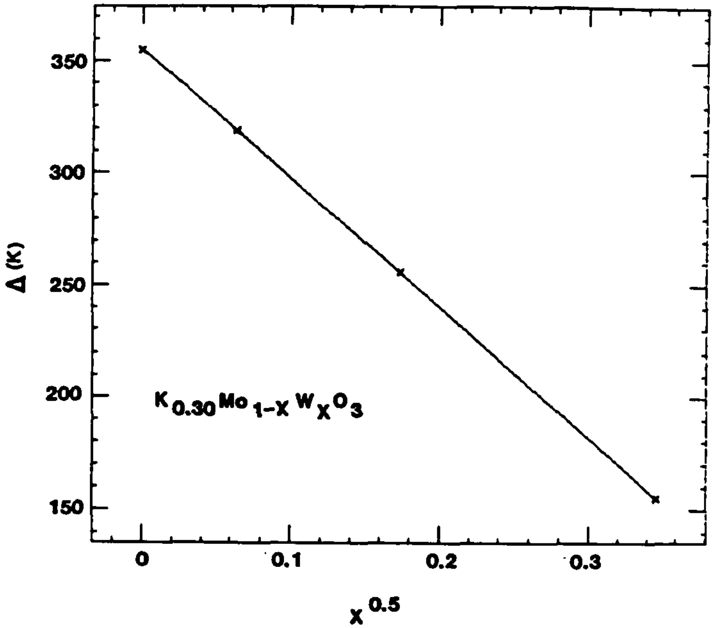

FIGURE 3. Activation energies (obtained from fig. 2) vs tungsten concentration for $K_{0.30}Mo_{1-x}W_xO_3$ samples.

threshold field on impurity concentration. For strong pinning impurities, a single impurity determines the CDW phase. In the case of weak pinning impurities, the CDW phase is determined by an average over a number of impurity sites. Fig. 4 shows the variation of threshold field with impurity concentration for a., $K_{0.30}Mo_{1-x}W_xO_3$, and b., $K_{0.30-x}Rb_xMoO_3$. The linear variation of E_T with tungsten concentration suggests that tungsten acts as a strong pinning impurity in $K_{0.30}MoO_3$, while the quadratic variation of E_T with rubidium concentration suggests that rubidium acts as a weak pinning impurity. We have shown elsewhere that tungsten impurities produce interesting and surprising effects on the transient electrical response of $K_{0.30}MoO_3$.[21]

The conduction band in $K_{0.30}MoO_3$ is based on a combination of Mo t_{2g} and oxygen $p\pi$ orbitals. In the alloy system, $K_{0.30}Mo_{1-x}W_xO_3$, the number of overlapping Mo d_{xz} orbitals is disrupted near the W impurity site. Thus the W impurity is expected to act as a strongly perturbing influence, and, indeed, large effects on the CDW onset temperature and on the threshold field are observed. By contrast, the alkali is only indirectly involved, and alkali substitution produces small effects on the CDW onset and threshold field for depinning.

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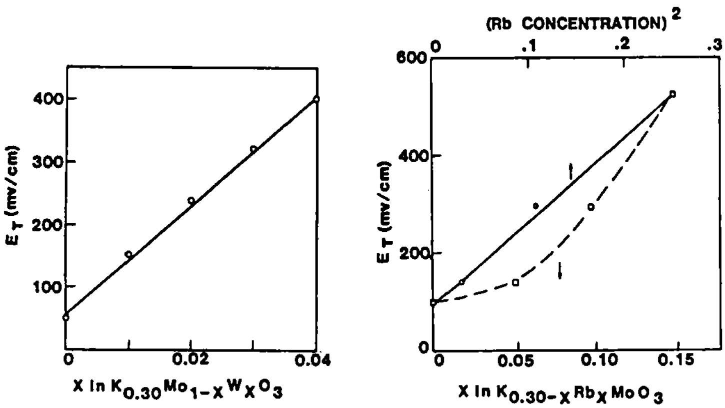

FIGURE 4. Variation of the dc threshold field with a. tungsten concentration in $K_{0.30}Mo_{1-x}W_xO_3$ b. rubidium concentration in $K_{0.30-x}Rb_xMoO_3$

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