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ELASTIC ANOMALIES IN THE CHARGE DENSITY WAVE CONDUCTOR $K_{0.3}MoO_3$

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We have measured Young's modulus Y of the charge density wave (CDW) conductor $K_{0.3}MoO_3$, both parallel ($Y_{\parallel}$) and perpendicular ($Y_{\perp}$) to the highly conducting (b) axis. The elastic constants are anisotropic, and both $Y_{\parallel}$ and $Y_{\perp}$ show sharp anomalies at the Peierls transition temperature at T=180K. The anomaly in $Y_{\perp}$ is dramatic and similar to that observed in TaS_3. No change in $Y_{\parallel}$ or in internal friction is observed upon CDW depinning. We compare the detailed form of $Y_{\perp}$ near the transition temperature to predictions of a recent theoretical model which considers coupling between electrons and the soft phonon.

INTRODUCTION

Of the few low dimensional materials which have been observed to display sliding charge density wave (CDW) transport, the blue bronzes $A_{0.3}MoO_3$ (A=K, Rb) form a particularly interesting class [1]. Unlike the transition metal trichalcogenides $NbSe_3$ and TaS_3, for example, $K_{0.3}MoO_3$ is, despite its quasi one dimensional electronic structure, a very cohesive three dimensional crystal. Below the Peierls transition temperature T_p=180K, $K_{0.3}MoO_3$ displays a host of unusual electronic properties, including nonlinear dc conductivity [2] and enormous low-frequency polarization effects [3,4]. These properties are attributed to excitations of the collective CDW mode.

Studies of layered 2-D and quasi 1-D linear chain CDW systems have demonstrated that CDW formation is often associated with anomalies in the elastic properties (namely Young's modulus Y and internal friction δ) of the host crystal [5-7]. More recent experiments have revealed a sensitivity of the elastic properties to the dynamic state of the CDW condensate, for example dc depinning, ac excitation, or electronic mode locking (induced by combined ac and dc electric fields) [8-10].

In this Communication, we report on measurements of the elastic properties (primarily Young's modulus) of $K_{0.3}MoO_3$. We have measured Y both parallel to the highly conducting (b) axis (denoted $Y_{\parallel}$), and perpendicular to this axis, parallel to (102) (denoted $Y_{\perp}$). At room temperature the elastic constants are anisotropic, and we find well defined, non hysteretic anomalies in $Y_{\perp}$ and $Y_{\parallel}$ at T_p=180K. Somewhat surprisingly, no changes are observed in $Y_{\parallel}$ or δ upon CDW depinning.

EXPERIMENTS AND RESULTS

Single crystals of $K_{0.3}MoO_3$ were grown by electrolytic reduction of a K_2MoO_4-MoO_3 melt. The crystals were cleaved into thin plates of typical dimension 1mm x 0.3mm x .05mm, with the long dimension corresponding to the direction for which the elastic properties were measured. Our experimental technique was based on the Barmatz vibrating reed method [5], where the (preferably long and thin) sample is clamped at one end and mechanically driven to resonance by a capacitively coupled ac electric field. In our experiments resonance was detected by a 600 MHz rf carrier and a phase locked loop circuit was employed to continuously monitor the resonance frequency f_r and resonance amplitude A_r. Our system was originally designed to study elastic properties of $NbSe_3$ and TaS_3 crystals with typical resonance frequencies in the kHz frequency range. In order to excite a similar low frequency resonance in $K_{0.3}MoO_3$, a concentrated mass M (small globule of silver paint) was added to the free end of the cantilevered crystal, effectively rescaling the resonance frequency to a lower, detectable level. The sample was clamped by first evaporating indium pads to the ends, followed by silver paint mounting. On occasion, a very fine (weakly perturbing) gold wire was attached to the free end of the crystal (in addition to the mass M) to facilitate simultaneous dc and nonlinear conductivity measurements.

In the configuration of clamped sample with mass M attached, the Young's modulus Y is given by [11]

$$Y = \frac{4L^3M}{t^3s}(2\pi f_r)^2 \qquad (1)$$

where L is the distance from the clamped sample end to the center of the mass M, t is the sample thickness in the direction of flexture, and s is the sample width.

At room temperature, Young's modulus for $K_{0.3}MoO_3$ was determined to be $Y_{\parallel}=(0.8\text{-}2.0)\times10^{12}$ dyne cm^{-2} and $Y_{\perp}=(0.4\text{-}0.8)\times10^{12}$ dyne cm^{-2}. The variations reflect differences between samples, due primarily to difficulties in determining effective sample geometry (at the clamp, for example). On the average, $Y_{\parallel}/Y_{\perp}\approx2$ at room temperature.

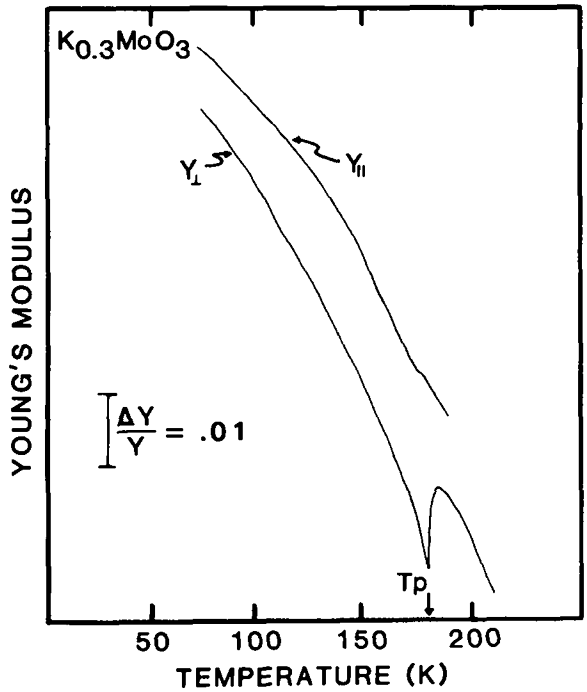

Fig. 1 Young's modulus Y measured both parallel and perpendicular to the b axis in $K_{0.3}MoO_3$. The data have been normalized to room temperature values. The vertical arrow identifies the Peierls transition temperature.

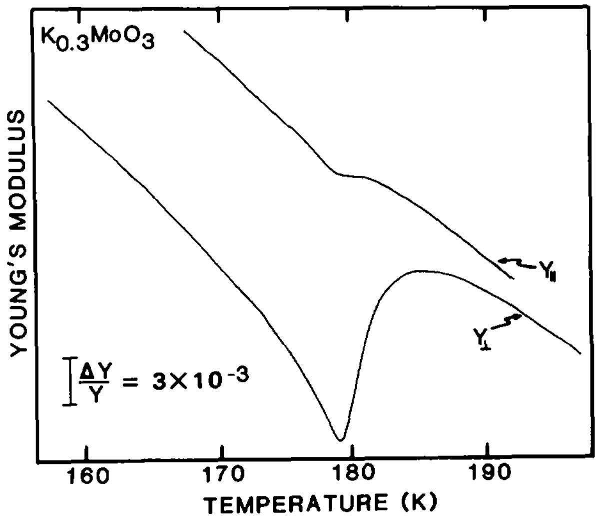

Fig. 2 Detail of Young's modulus near the Peierls transition temperature T_P=180K in $K_{0.3}MoO_3$.

Figure 1 shows $Y_{\parallel}$ and $Y_{\perp}$ for $K_{0.3}MoO_3$ as functions of temperature. The two curves have been arbitrarily displaced vertically. For both $Y_{\parallel}$ and $Y_{\perp}$, well defined anomalies are apparent at T=180K, corresponding to the Peierls transition temperature as determined by resistivity measurements on the same crystal. Measurements on several other $K_{0.3}MoO_3$ crystals yielded identical results; one crystal from a high impurity concentration growth batch, with a transition temperature of 174K, showed similar modulus anomalies at T=174K. Subtracting in Fig. 1 the strictly thermal changes in Y, we find, due to the transition, relative changes in elasticity of $\Delta Y_{\parallel}/Y_{\parallel}$=1.6x10^{-3} and $\Delta Y_{\perp}/Y_{\perp}$=1.7x10^{-2}. Hence the anomaly in $Y_{\perp}$ is nearly an order of magnitude stronger than that associated with $Y_{\parallel}$. The strong anomaly in $Y_{\perp}$ is very similar to that previously observed in the CDW material TaS_3 [7,8]. The weaker anomaly in $Y_{\parallel}$ is nearly identical in form (though larger in magnitude to $Y_{\parallel}$ found in $(TaSe_4)_2I$ at Tp [12]. Between room temperature and 77K, only one anomaly was found in $Y_{\parallel}$ and $Y_{\perp}$, and, in carefully cycling temperature through Tp several times, no significant hysteresis was observed in the elastic anomalies. The detailed behavior of $Y_{\parallel}$ and $Y_{\perp}$ near T_P is shown in Fig. 2.

In the related CDW conductors $NbSe_3$ (upper CDW state), TaS_3, and $(TaSe_4)_2I$, applied dc electric fields E exceeding the threshold field E_T for the onset of nonlinear conduction have dramatic effects on the elastic properties of the crystal: for $E > E_T$, Y smoothly decreases (and eventually saturates) and δ strongly increases and quickly saturates [7-10]. We have searched for similar electric field dependences of $Y_{\parallel}$ and δ in $K_{0.3}MoO_3$. For two separate crystals, the CDW was depinned at several temperatures in the range 50-85K; Fig. 3 shows a typical graph of the differential resistance dV/dI and elastic constants as functions of dc bias. Despite strong nonlinear conductivity behavior with a well defined threshold, no associated anomalies are observed in the elastic constants $Y_{\parallel}$ or δ. Careful measurements using signal averaging at 77K and 57K placed limits on the fractional change of the elastic constants of 5x10^{-5} for $Y_{\parallel}$ and 2x10^{-3} for δ. Of interest would be the behavior of $Y_{\perp}$ during CDW depinning; such an experiment was not performed.

DISCUSSION

The single non-hysteretic anomaly in Y observed at Tp in Fig. 1 is consistent with a single second order phase transition in $K_{0.3}MoO_3$. The width of the transition, most apparent from Fig. 2, is consistent with X-ray and neutron diffraction studies which show superlattice structure above Tp [1,13]. There has been some speculation as to the existence of an incommensurate-commensurate (IC-C) phase transition in $K_{0.3}MoO_3$ near 100K [14]. In the layered CDW compound 2H-$TaSe_2$, the IC-C transition is associated with a giant (hysteretic) elasticity anomaly, presumably due to the formation and movement of boundaries between IC and C domains [5]. We find no similar behavior in $K_{0.3}MoO_3$, suggesting the absence of an IC-C transition, consistent with structural neutron studies [13].

For a second order phase transition, anomalies in Young's modulus may be thermodynamically related to other measurable parameters [15],

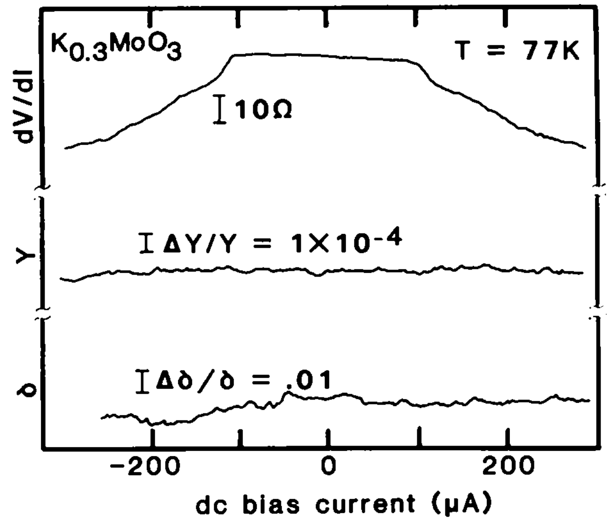

Fig. 3 Differential electrical resistance dv/dI, Young's modulus $Y_{||}$ and internal friction δ in $K_{0.3}MoO_3$, as functions of dc bias current. CDW depinning has no effect on $Y_{||}$ or δ.

for example

$$\frac{\partial T_c}{\partial \sigma_i} = \left[\left(\frac{-\Delta Y}{Y}\right) \frac{T_c}{Y(\Delta C_p)}\right]^{1/2} \qquad (2)$$

$$\Delta\alpha_i = \frac{\Delta Y}{Y} \cdot \frac{1}{Y\frac{\partial T_c}{\partial \sigma_i}} \qquad (3)$$

where σ_i and α_i are respectively the i^{th} components of stress and thermal expansivity, and Cp is the specific heat. Schlenker and Dumas [1] report an entropy change of 150 mJ/mole K at the transition in $K_{0.3}MoO_3$, corresponding to a specific heat anomaly $\Delta Cp = 4.12\times10^4$ dyne/cm^{2}K. With $(\Delta Y_\perp/Y_\perp) = 1.7\times10^{-2}$ and $(\Delta Y_{||}/Y_{||}) = 1.6\times10^{-3}$, Eq (2) gives a stress dependence $\partial Tp/\partial\sigma_\perp = 1.05\times10^{-8}$ K/dyne cm^{-2} and $\partial Tp/\partial\sigma_{||} = 2.3\times10^{-9}$ K/dyne cm^{-2}. From Eq (3), the expansivity coefficients are $\alpha_\perp = -2.6\times10^{-6}$ K^{-1} and $\alpha_{||} = -5.4\times10^{-7}$ K^{-1}. Assuming a small interlayer interaction between planes ($\bar{2}01$) in $K_{0.3}MoO_3$, we estimate the pressure dependence of the transition temperature to be $dTp/dP \approx 1.3\times10^{-8}$ K/dyne cm^{-2}= 13 K/kbar. We note that this predicted pressure dependence is somewhat larger than that observed in $NbSe_3$ (dTp/dP=4 K/kbar) or TaS_3 (dTp/dP=1.3 K/kbar) [16,17].

The Peierls distortion in $K_{0.3}MoO_3$ is associated with a complete destruction of the Fermi surface, leading to a metal-insulator transition. One might expect the loss of normal electrons below Tp to decrease electron screening, thereby stiffening the mode and increasing the sound velocity. Such an effect is apparently observed at the density wave transitions of TTF-TCNQ [6], 2H-$TaSe_2$ [5], and $(TMTSF)_2PF_6$ [18]. On the other hand, at Tp the softening of the lattice results in a decrease of Y, as observed in TaS_3 [7], $(TaSe_4)_2I$ [12], 2H-$NbSe_2$ [5], and the upper CDW transition of $NbSe_3$ [7]. In 2H-$TaSe_2$, the competition between lattice stiffening and softening near Tp is readily observed: there the modulus of elasticity first slightly decreases just above Tp before strongly increasing below Tp [5].

The data of Figs. 1 and 2 suggests that, despite the complete loss of Fermi surface in $K_{0.3}MoO_3$, lattice softening dominates the behavior of Y near Tp in this system. In a recent theoretical investigation of elastic anomalies in CDW systems, Nakane [19] has discussed the dip in Young's modulus at the Peierls transition in terms of coupling between the electrons and the soft phonon. The theory predicts a scaling relation for the elasticity behavior above and below the transition temperature,

$$\frac{\Delta Y}{Y} = C\tau^{1/2} \quad , (T > Tp) \qquad (4)$$

$$\frac{\Delta Y}{Y} = 2C(2\tau)^{1/2} \quad , (T < Tp) \qquad (5)$$

valid for small τ, where $\tau = |(T-Tp)/Tp|$ and C is proportional to T^2. At larger values of τ, where T moves away from Tp, there is a dimensionality crossover of the critical fluctuations from three to one dimensions. In this "crossover" temperature regime, the scaling relations Eqns. (4) and (5) still hold, but the critical exponent becomes 3/2 rather than 1/2.

We have searched for scaling behavior in the Young's modulus of $K_{0.3}MoO_3$, for T close to Tp. Figure 4 shows the large anomaly in $Y_\perp$ of Fig. 2 replotted as a function of log(τ), where a linear term has been subtracted from $\Delta Y_\perp/Y_\perp$ to account for conventional thermal expansion. In the range 1.0-10 degrees K from the transition temperature, there is no well-defined critical

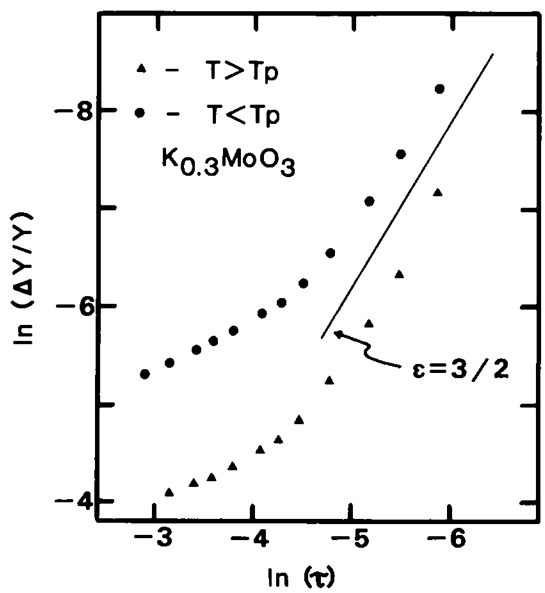

Fig. 4 Scaling behavior of Y_{11} near the Peierls transition temperature. The right-hand-most data points are 0.5 k from the transition temperature; the left-hand-most data points are 10 k from the transition. The sloping line is for a critical exponent of 3/2.

exponent; closer to T_P, however, the slope approaches 3/2. Thus, if there is a dimensionality crossover to the lower exponent 1/2, the crossover temperature must necessarily be very close to T_P. We also note that the anomaly in Y is somewhat larger above T_P than it is below T_P, in contradiction to the predicted behavior of Nakane's model where the scaling relation $f(\tau)$ above T_P transforms into $2f(2\tau)$ below T_P. Our data suggests a rough correspondence $\Delta Y/Y(T>T_P) \approx 4\Delta Y/Y(T<T_P)$, although we do not attach much importance to this relation.

In summary, we have observed anisotropic elasticity anomalies at the CDW transition of $K_{0.3}MoO_3$, with no evidence for an additional lock-in transition at 100K. The anomalies at T_P predict stress and expansivity coefficients that are experimentally accessible. For T close to T_P, Y approximately scales with a critical exponent 3/2.

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