Commensurate-incommensurate transition in the charge-density-wave state of $K_{0.30}MoO_3$

R. M. Fleming and L. F. Schneemeyer
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

D. E. Moncton
Brookhaven National Laboratories, Upton, New York 11973
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The "blue bronze" $K_{0.30}MoO_3$ has a charge-density wave (CDW) which forms at $T=181$ K. At temperatures below 181 K, nonlinear conductivity due to charge transport by the CDW has been observed. We have performed x-ray and elastic-neutron-scattering experiments which show that at onset the CDW is incommensurate with a reduced wave vector of $\vec{q}=(0,0.263,0.5)$. The b^* component of $\vec{q}$ is temperature dependent and the incommensurability $\delta=q-b^*/4$ decreases to zero near $T=100$ K. Measurements of the threshold electric field for nonlinear charge transport show a broad decrease as the temperature is lowered beginning near 100 K. No increase of the threshold field in the commensurate CDW phase is inconsistent with the depinning of a rigid CDW, but may be explained by the transport of CDW phase solitons or dislocations.

The "blue bronze" $K_{0.30}MoO_3$ has a charge-density wave (CDW) which forms at a metal-semiconductor phase transition at $T=181$ K.[1,2] In $K_{0.30}MoO_3$, as well as in some transition-metal chalcogenides such as $NbSe_3$, TaS_3, and $(TaSe_4)_2I$, nonlinear electron transport properties are observed at temperatures below the CDW phase transition.[3,4] The nonlinear electrical response, thought to be the results of charge transport by the CDW, results in unusual behavior in a variety of electrical properties. First, the dc conductivity increases when the electric field exceeds a threshold field[5] (E_T) which can be as low as 30 mV/cm for $K_{0.30}MoO_3$. Second, the ac conductivity[6,7] exhibits a response characteristic of a low-frequency dielectric relaxation (≈ 50 kHz for $K_{0.30}MoO_3$). Finally, the transient electrical response shows a very long decay[8] (on the order of milliseconds). The nonlinear transport properties have been explained using models in which the CDW is pinned at low electric fields but is depinned and carries charge for electric fields in excess of threshold.[9–14] Theories[9] and phenomenological models[10] have described a rigid CDW which is pinned by the random impurity potential in the incommensurate phase and by the periodic lattice potential in the commensurate phase. Since pinning by the lattice is expected to be very large, incommensurability is a prerequisite for charge transport by a *rigid* CDW. Early experiments with $NbSe_3$ were consistent with the assumption that an incommensurate CDW is required. $NbSe_3$ has two CDW's with periodicities which are incommensurate with the host lattice and temperature independent.[15,16] A nonlinear dc current-voltage (I-V) response is seen with electric fields as low as 5 mV/cm, which suggests very weak pinning.[5] Recently, however, TaS_3 has been reported to have a commensurate-incommensurate (C-I) transition at 180 K,[17] and E_T remains finite below the $T_{C\text{-}I}$.[18]

In this work we have made x-ray and neutron scattering measurements of the CDW in $K_{0.30}MoO_3$. We find that the CDW wave vector is incommensurate at onset ($T_c=181$ K) with a reduced wave vector of $\vec{q}=(0,0.263,0.5)$. In contrast with the earlier neutron scattering results,[19] we find the CDW undergoes a C-I transition at about 100 K. Earlier measurements of the dc threshold electric field,[1] which is a measure of the CDW pinning strength, show a maximum in the depinning field at about 100 K, very close to the C-I transition. Measurements of the depinning field of our samples show a broad decrease of the depinning field as the temperature is decreased instead of a maximum. In any case, the depinning field does not increase in the commensurate phase, as might be expected from a single-particle model of impurity pinning. This result suggests that models in which charge is transported via depinned phase solitons[20,21] or dislocations[9] may apply to $K_{0.30}MoO_3$.

For x-ray scattering, cleaved $K_{0.30}MoO_3$ specimens about 10—50 μm thick were mounted on quartz fibers in an atmosphere of He gas. Temperature control was maintained with a closed-cycle helium refrigerator capable of stable operation between 10—300 K. The He refrigerator was mounted in an offset phi circle of a Huber model 424/511 four-circle goniometer capable of full access to the reciprocal lattice. Focused copper $K\alpha$ radiation from 15-kW rotating-anode x-ray generator was employed. For measurements of the temperature dependence of the CDW superlattice intensity, a low-q-resolution configuration consisting of a singly bent pyrolytic graphite monochromator and a flat graphite analyzer was used. This configuration resulted in a longitudinal q resolution with a half width at half maximum (HWHM) of 0.02 Å^{-1}. For higher resolution measurements of the CDW commensurability at 10 K, a singly bent LiF monochromator and a flat Ge analyzer were used, giving a longitudinal resolution with a HWHM of 0.0015 Å^{-1}.

Measurements of the magnitude of the CDW wave vector as a function of temperature were made by elastic neutron scattering on a triple-axis spectrometer at the Brookhaven High-Flux Beam Reactor. Collimation from

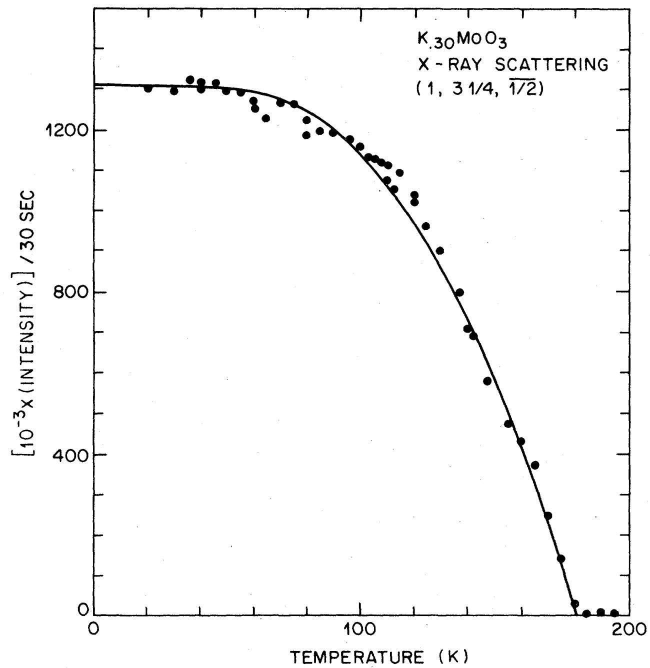

FIG. 1. The integrated intensity of the (1,3.25,−0.5) superlattice peak of $K_{0.30}MoO_3$ as a function of temperature. The solid line is the square of the BCS energy gap.

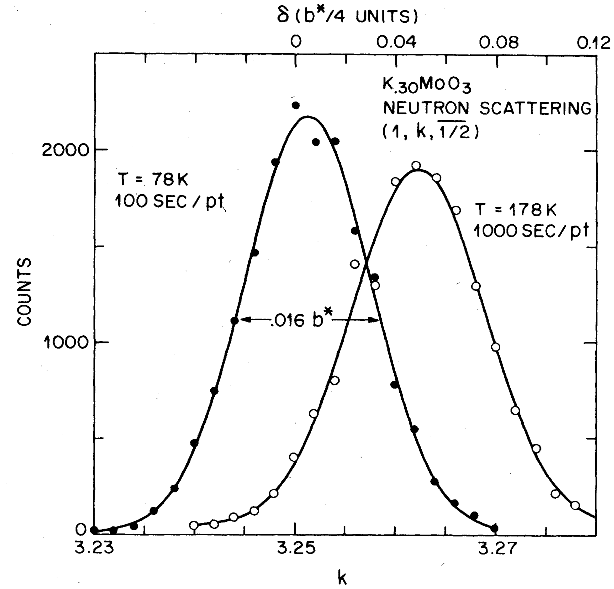

FIG. 2. Elastic neutron scattering scans along $(0,k,0)$ through the (1,3.25,−0.5) superlattice at 178 and 78 K.

the beam port was 20′-10′-10′-20′ with an incident-beam energy of 14.5 meV. A sample with an approximate volume of 0.05 cm^3 gave a count rate of 8000/sec in the (040) peak and a longitudinal q resolution of 0.007 $Å^{-1}$ HWHM.

A measurement of the temperature dependence of the CDW order parameter is shown in Fig. 1. The integrated x-ray intensity of the (1,3.25,−0.5) superlattice reflection obtained with graphite resolution (0.02 $Å^{-1}$ HWHM) is plotted as a function of temperature. It is interesting to note that the square of the BCS order parameter (the solid line) describes the data well over the entire temperature range.

At the onset of 181 K, the CDW in $K_{0.30}MoO_3$ is incommensurate along b^* with a reduced wave vector of $\vec{q}=(0,0.263,0.5)$. The magnitude of the b^* component of the CDW wave vector is temperature dependent; at about 100 K, a commensurate-incommensurate transition occurs and the CDW wave vector becomes $\vec{q}=(0,0.25,0.5)$. Scans along b^* at temperatures of 178 and 78 K are shown in Fig. 2. The data in Fig. 2 were taken by elastic neutron scattering with a q resolution of 0.007 $Å^{-1}$. The solid lines in Fig. 2 are Gaussian fits to the data. Near the onset temperature of 181 K, the b^* component of the CDW wave vectors differs from $b^*/4$ by about 5%. A plot of the b^* component of the superlattice peak position as a function of temperature is shown in Fig. 3, where the solid line is a guide to the eye. The error bar in Fig. 3 reflects an uncertainty of $\pm 0.002b^*$, about 25% of the HWHM of the scans shown in Fig. 2. Within the resolution of the experiment, the CDW is commensurate at temperatures below 100 K. The shape of the temperature dependence of the incommensurability $\delta = q - b^*/4$ is unusual in that δ approaches zero with a finite slope rather than infinite slope as predicted theoretically.[20]

Other workers have reported that the CDW does not quite lock in to a commensurate value at low temperatures, but rather retains a residual incommensurability of $\delta = 0.008b^*/4$ at low temperatures.[19] The uncertainty in our neutron scattering data overlap both the commensurate position and the reported residual incommensurability. To resolve this question we have also performed a

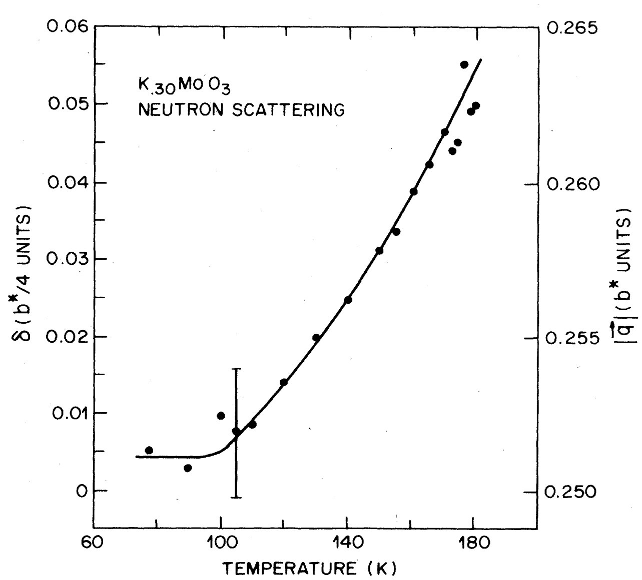

FIG. 3. The temperature dependence of the CDW incommensurability of $K_{0.30}MoO_3$ taken from neutron scattering data. For temperatures below 100 K, the CDW is commensurate within the resolution of the experiment.

higher resolution x-ray scattering experiment to examine the commensurability of the CDW at 10 K. A LiF monochromator and a Ge analyzer resulted in a q resolution of 0.0015 $Å^{-1}$. Since the CDW in $K_{0.30}MoO_3$ has components along both b^* and c^*, questions of commensurability cannot easily be answered by a single, radial scan as would be the case if the CDW had only one nonzero component. For example, in 2H-$TaSe_2$ where the CDW has only a component along a^*, a single scan which varies only the magnitude of $\vec{q}$ can measure the momentum transfer of both the plus and the minus CDW satellites as well as the Bragg peak of the host lattice.[16] To collect the same data in $K_{0.30}MoO_3$, one must do scans which vary both the magnitude *and* the direction of $\vec{q}$. Since the resolution is broad normal to the diffraction plane, giving rise to uncertainties in the sample orientation, and since the lattice parameters at 10 K are not known accurately, systematic errors in the b^* component of $\vec{q}$ can easily be the same size as the claimed incommensurability at 10 K. Rather than measure the b^* component of $\vec{q}$ by a nonradial scan, we have measured the incommensurability by a different method. First, we measured the magnitude of $\vec{q}$ for 25 reflections of the host $K_{0.30}MoO_3$ lattice. For each peak the signal was maximized by varying the polar scattering angles ϕ and χ. θ-2θ scans were then performed and the observed 2θ was obtained from a Gaussian fit to the data. This procedure had the effect of reproducing a powder pattern for $K_{0.30}MoO_3$ at 10 K, except that the signal-to-noise ratio is that of a single crystal and there was no ambiguity in indexing the peaks. We then obtained accurate lattice parameters at 10 K from a standard powder refinement. The results are shown in Table I. The same data collection procedure was then followed for thirteen superlattice reflections. Given the lattice parameters obtained at 10 K, the incommensurability parameter δ could then be obtained from a one-parameter fit. The results are shown in Table II. The error reported is the standard deviation of the observed 2θ values from the calculated position with $\delta=0.0028b^*/4$ ($q=0.2507b^*$). This value of δ is slightly less than the residual incommensurability shown in Fig. 2 and about a factor of 3 less than the low-temperature results of Sato

TABLE I. (a) $K_{0.30}MoO_3$ main lattice peaks, $T=12$ K and (b) lattice parameters.

(a) Main lattice peaks

h	k	l	2θ(obs)	2θ(calc)	Difference
3	3	−1	38.792	38.794	−0.003
3	3	−2	40.898	40.903	−0.005
8	0	−4	45.106	45.108	−0.003
6	2	−4	46.480	46.484	−0.005
8	2	−3	47.942	47.944	−0.002
0	4	0	48.138	48.136	0.001
2	4	−1	49.536	49.536	0.000
4	4	−1	52.436	52.438	−0.002
6	2	−5	53.520	53.522	−0.002
4	4	−2	53.572	53.573	−0.001
10	2	−4	58.668	58.663	0.005
1	5	−1	62.104	62.107	−0.004
10	2	−5	62.801	62.800	0.001
6	4	−4	63.954	63.955	−0.002
3	5	−2	64.966	64.964	0.001
8	4	−3	65.141	65.141	0.000
11	1	−6	67.925	67.927	−0.002
8	4	−4	68.092	68.091	0.000
10	2	−6	68.727	68.723	0.004
12	0	−6	70.244	70.246	−0.003
10	0	−7	71.306	71.303	0.003
10	4	−4	74.301	74.300	0.000
0	6	0	75.434	75.430	0.004
0	6	−1	76.352	76.353	−0.001
2	6	−1	76.518	76.516	0.002
Average absolute difference:					0.0022

(b) Lattice parameters

$T=12$ K[a]	$T=300$ K[b]
$a=18.133(2)$	18.249(10) Å
$b=7.5548(1)$	7.560(5) Å
$c=9.810(1)$	9.855(6) Å
$\beta=117.34(2)$	117.53(8)

[a]This work.
[b]From Ref. 26.

TABLE II. $K_{0.30}MoO_3$ CDW superlattice peaks, $T=12$ K.

h	k	l	2θ(obs)	$\delta=0.0028$ 2θ(calc)	$\delta=0.0028$ Difference	$\delta=0.0$ 2θ(calc)	$\delta=0.0$ Difference
1	2.75	−0.50	33.041	33.043	−0.002	33.052	−0.011
−1	2.75	0.50	33.044	33.043	0.001	33.052	−0.008
3	2.75	−1.50	36.724	36.728	−0.004	36.736	−0.012
−1	3.25	0.50	39.124	39.130	−0.006	39.122	0.002
1	3.25	−0.50	39.128	39.130	−0.002	39.122	0.006
0	3.75	−0.50	45.262	45.264	−0.002	45.273	−0.011
−2	3.75	0.50	46.104	46.107	−0.003	46.116	−0.012
2	3.75	−0.50	46.105	46.107	−0.002	46.116	−0.011
0	4.25	−0.50	51.658	61.651	−0.003	51.642	0.006
2	4.25	−0.50	52.414	52.416	−0.002	52.407	0.007
1	4.75	−0.50	58.234	58.233	0.001	58.242	−0.008
6	3.75	−3.50	59.014	59.019	−0.005	59.026	−0.012
1	5.25	−0.50	65.021	65.025	−0.004	65.015	0.006
Average absolute difference:					0.003		0.009
Best fit, $q=(0.2507\pm0.003)b^*$, $\delta=0.0028b^*/4$							

et al.[19] Since δ only differs from zero by two standard deviations, the data support the existence of a *C-I* transition near 100 K.

It is interesting to consider the behavior of the threshold electric field E_T through the *C-I* transition near 100 K. Earlier measurements indicated that E_T has a maximum value near the *C-I* transition.[1] Measurements of the temperature dependence of the threshold field in our laboratory gave somewhat different results. Figure 4 shows E_T as a function of temperature for a $K_{0.30}MoO_3$ specimen in the range 54—140 K. The data in Fig. 4 are from differential measurements of dV/dI as a function of dc electric field for a sample with four indium contacts applied with an ultrasonic soldering iron. The data are limited to the temperature interval 54—140 K because at low temperatures the relative conductivity increase as the field is increased through E_T becomes very small and at high temperatures the resistivity of the sample becomes too low for E_T to be reached without excessive heating. We found that E_T varied from sample to sample but usually fell into the range 30—200 mV/cm. The principal difference between our results and those of Dumas *et al.*[1] is that the average value of E_T is about a factor of 3 smaller in our sample and we see no decrease of E_T for temperatures above 100 K. Both measurements show a broad decrease of E_T beginning approximately at the *C-I* transition.

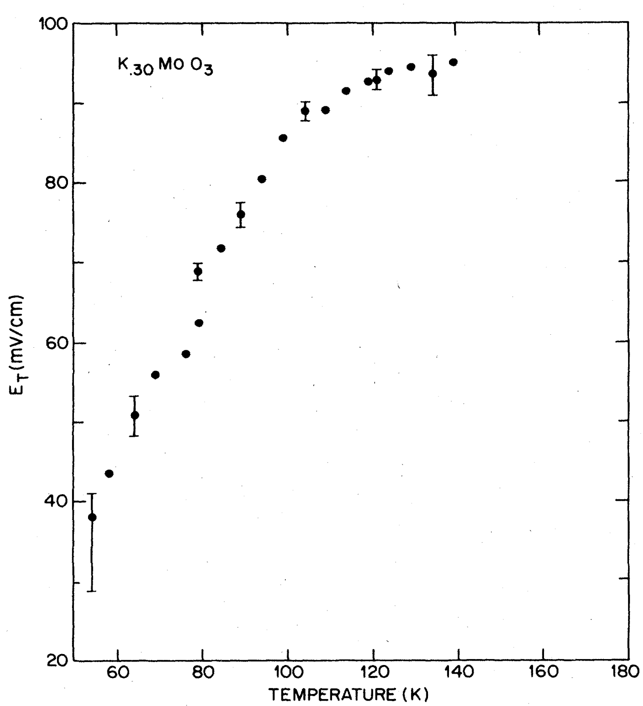

FIG. 4. The temperature dependence of the threshold electric field for nonlinear conductivity. A broad decrease in the depinning field occurs below the commensurate-incommensurate transition at 100 K.

The single-particle model predicts that a commensurate CDW will have a large depinning field because of pinning by the periodic lattice potential. However, as shown in Fig. 4, the depinning field does not increase at commensurability. Two possible explanations exist. First, it is possible, as discussed above, that the CDW is not commensurate. Second, the relevant physics may go beyond the single-particle picture of CDW pinning. If internal degrees of freedom are allowed, charge transport can occur without moving the CDW as a rigid object. Charge transport via either phase-solitons (discommensuration)[20,21] or dislocations[9] has been proposed. Both of these transport mechanisms will be subject to impurity pinning, but will not be strongly affected by lattice pinning. In $K_{0.30}MoO_3$ a low-threshold field at low temperatures is consistent with increased Coulomb interactions along the CDW as thermally excited carriers are frozen out. The resulting "stiffer" CDW pins less readily.[22]

The temperature dependence of the CDW wave vector in $K_{0.30}MoO_3$ may also be affected by impurity pinning.

In the absence of pinning, the CDW incommensurability δ is expected to decrease to zero with infinite slope near $T_{C\text{-}I}$,[20] contrary to the behavior shown in Fig. 3. If pinning is important unusual behavior of δ versus temperature can be observed, such as that seen in Cr.[23,24] The q vector of the spin-density wave in Cr shows hysteretic behavior which depends on the temperature and pressure history of the sample. Instead of moving monotonically toward commensurability, the q vector in Cr can remain in a metastable state. One might speculate that similar effects occur in $K_{0.30}MoO_3$. The CDW q vector moves toward commensurability as the temperature is decreased, but it retains a small residual incommensurability at low temperatures which may be impurity dependent. This remains, however, a speculation. Our measurements of the q vector in $K_{0.30}Mo_{1-x}W_xO_3$ ($x=0.01$) give results identical with those of the pure material. In addition, Raman scattering measurements[25] on samples grown in our laboratory show a dramatic narrowing of the amplitude mode of the CDW on cooling through 100 K. These observations along with the diffraction data reported here, indicate that a commensurate-incommensurate phase transition occurs near 100 K.

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