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Field-induced disorder in the charge-density-wave state of $K_{0.30}MoO_3$

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The application of an electric field along the b axis of $K_{0.30}MoO_3$ in the charge-density-wave (CDW) state causes a metastable loss of transverse order as measured by x-ray diffraction. In contrast, scans parallel to the CDW modulation wave vector are resolution limited with no field-induced change of position or width. These results provide structural evidence for metastable CDW states previously seen in transport measurements.

Some anisotropic materials with charge-density-wave (CDW) phase transitions show a remarkable range of unusual, nonlinear behavior associated with electric-field-induced motion of the CDW.[1] A key experiment used to support the model of a current-carrying CDW is an x-ray diffraction experiment which established that the amplitude of the CDW is independent of electric field.[2] This early experiment showed that the CDW can provide charge transport but it failed to detect finite-range order of the CDW. Finite-range order is a feature of all models of CDW transport with a threshold field (E_T) determined by random pinning. More recent transport measurements suggest that metastable states of the CDW also exist which are structurally different from the ground state.[3-5] Metastable states may be populated by applying an electric field or by changing the temperature in the presence of a field. In particular, it has been shown that a macroscopic polarization of the CDW may be induced by cooling in a dc electric field.[6] Thus far, structural evidence for finite-range order or metastable states in the CDW has proven elusive, and experiments sensitive to the CDW coherence, wave vector, and defect structure have failed to detect consequences of charge-density-wave motion.[7-9] A recent study of $K_{0.30}MoO_3$, however, has reported a field-induced rotation of the CDW wave vector with hysteresis.[10]

$K_{0.30}MoO_3$ has a CDW onset temperature of 180 K and an initial CDW wave that is incommensurate along b^*, $\mathbf{q}=(0,0.263,0.5)$.[11] The CDW wave vector becomes more commensurate as the temperature is lowered, and by 100 K no incommensurability can be measured.[12] In this experiment high $\mathbf{q}$-resolution x-ray-diffraction measurements were made on a $K_{0.30}MoO_3$ sample that was connected to a dc current source. As in $NbSe_3$, we observe no change in the magnitude of the CDW wave vector or longitudinal CDW coherence as a function of the electric field; however, we find two surprising results in studies of the transverse CDW coherence as a function of temperature and electric field. First, in zero electric field we see disorder in a direction transverse to $\mathbf{q}$ in the temperature interval 180 K (CDW onset) to 90 K. Second, if an electric field is applied to the specimen below 90 K, a dramatic transverse broadening of the superlattice peak occurs. This broadening is metastable; it remains after the field is reduced to zero. The intrinsic peak width is only regained after warming the sample and cooling again in zero field. Large transverse disorder can be "frozen" into the sample by cooling in a dc electric field. Once cold, the field can be removed and the transverse peak width only relaxes to its intrinsic value as the sample is warmed.

A cleaved sample of $K_{0.30}MoO_3$ of dimensions $1.8\times0.8\times0.06$ mm^3 was mounted on a quartz post in a sealed, He-filled cell and cooled with a closed-cycle refrigerator. A two-lead measurement of the sample resistance was made by silver painting fine gold wires to indium contacts that were previously applied to the sample with an ultrasonic soldering iron. The electrical properties of the sample were similar to those described previously.[4,13] The sample had a threshold electric field of 340 mV/cm at 77 K and small-scale "switching" could be observed near threshold.[14] Data were acquired in both dc fields and 25-Hz pulsed fields. The pulsed method minimizes the temperature difference between field on and field off since 25 Hz is faster than the thermal relaxation time of the sample. The pulsed method also eliminates possible errors resulting from differences in the mechanical alignment of the x-ray goniometer on two separate scans. Studies of metastable properties of the CDW, however, require the application of dc electric fields.

X-ray measurements were made with copper $K\alpha_1$ x rays from a 15-kW rotating anode generator. Single, flat crystals of Ge(111) were used as the monochromator and the analyzer. Vertical scatter slits were used to eliminate background radiation, but did not define the beam divergence. A resolution of 7×10^{-4} Å^{-1} full width at half maximum (FWHM) was achieved with a counting rate at $T=14$ K of 10^4/sec in the (040) Bragg peak as compared with 15/sec in the (1, 3.25, −0.5) superlattice peak. The resolution achieved in this experiment was equal to our earlier experiment on $NbSe_3$ with synchrotron radiation;[7] however, the intrinsic peak shapes were more Lorentzian in the present experiment. The sample was mounted so that the diffraction zone containing (010) and (201) was in the horizontal scattering plane. All high-resolution studies of the effect of an electric field were made on the (1, 3.25, −0.5) superlattice peak.

A radial scan through the (1, 3.25, −0.5) superlattice peak is shown in Fig. 1. The smaller peak at high q results from residual $K\alpha_2$ radiation in the incident beam. Data were obtained at each reciprocal lattice point by pulsing the field on and off at 25 Hz and gating the counter synchronously. No field-induced change in either the position of the superlattice peak or the peak width can be seen. The longitudinal width is instrumentally narrow implying that the charge-density wave is ordered on a length scale exceeding 6000–7000 Å. These data, along with previous results on $NbSe_3$,[7] place upper bounds on the variation of the b^* component of $\mathbf{q}$ over the area of the x-ray beam, which was ~0.5 mm^2. For $K_{0.30}MoO_3$ $\Delta q/q < 1/1500$ and for $NbSe_3$ $\Delta q/q < 1/2800$. This long-range coherence rules out simple

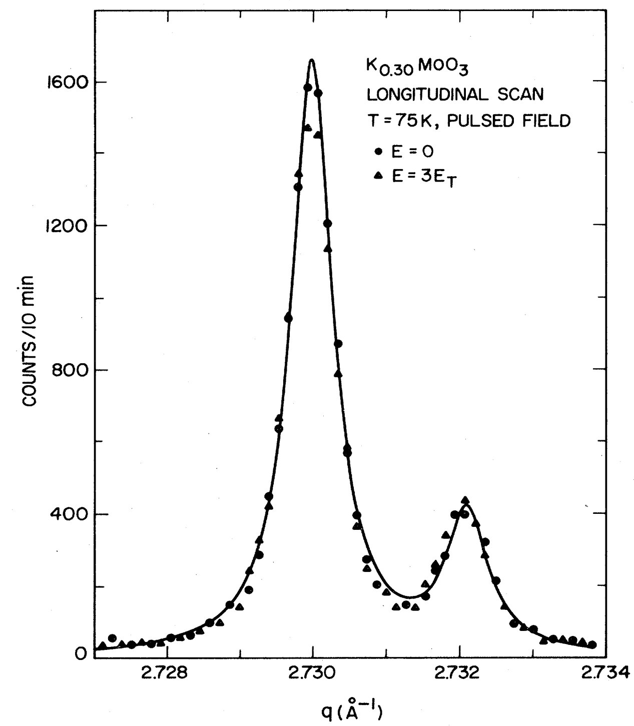

FIG. 1. A radial scan through the (1, 3.25, −0.5) superlattice peak of $K_{0.30}MoO_3$ at a temperature of 75 K. At each point data were collected for field on ($E = 3E_T$) and field off with a duty cycle of 25 Hz. The peak is resolution limited (7×10^{-4} Å^{-1} FWHM) for both field off and field on.

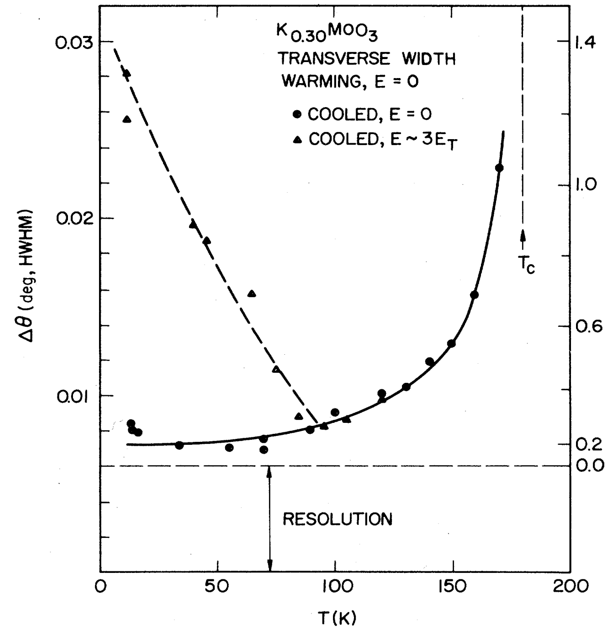

FIG. 2. The transverse width of the (1, 3.25, −0.5) superlattice peak of $K_{0.30}MoO_3$ measured as a function of increasing temperature. The circles are data obtained after cooling the sample at $E = 0$. The triangles are data obtained at $E = 0$ after cooling in a field approximately three times threshold. The transverse resolution of the instrument is shown by the horizontal dashed line. The right-hand axis is the excess half-width obtained by subtracting the resolution width in quadrature.

models of CDW polarization, such as one suggested recently,[15] which invokes a macroscopic spatial variation in the magnitude of **q** to produce a polarization.

$K_{0.30}MoO_3$ samples can have mosaic spreads which are smaller than instrumental resolution in contrast to the fibrous samples of $NbSe_3$ and other trichalcogenides. Consequently, in $K_{0.30}MoO_3$, the transverse CDW choerence is easily examined on long length scales. Two interesting features of the CDW structure can be seen in high-resolution transverse scans. First, in zero electric field, disorder in the transverse direction occurs between 90 and 180 K (CDW onset). Near 90 K, transverse scans through the superlattice peaks are nearly resolution limited. At 178 K they have transverse widths almost four times resolution. Second, there is a metastable, field-induced disorder in the transverse direction on the application of an electric field. After the field is reduced to zero, the superlattice peak widths remain broad until the sample is warmed and recooled.

The transverse width of the (1, 3.25, −0.5) superlattice peak in zero electric field is shown as a function of temperature in Fig. 2. The instrumental resolution, shown by the horizontal dashed line, is about 0.008° half-width at half maximum (HWHM). The transverse width at CDW onset exceeds 0.022° HWHM. If we subtract the resolution in quadrature, we obtain an excess half-width Γ of about 10^{-3} Å^{-1} at CDW onset. As the temperature is lowered, the transverse coherence increases, and Γ becomes nearly zero by 90 K. Perhaps coincidentally, this is near the temperature where the CDW becomes commensurate (100 K). Figure 3 shows data taken at 68 K where the transverse width is nearly resolution limited. The circles are initial data taken after cooling in zero field. The triangles are subsequent data taken after turning a field on for about one second ($E = 3E_T$) and then off. The application of an electric field along b^* induces a dramatic broadening of the superlattice peak. The loss of order is metastable and can only be regained by heating the sample and cooling in zero field. This is the structural signature of the metastable states of the CDW first reported by Gill.[3] In addition, our measurements show that the loss of order begins to occur as soon as the dc field is applied; it does not occur suddenly at threshold. Therefore, the metastable states are populated in electric fields below threshold.

Cava *et al.* have shown that one can "freeze" a polarization of the CDW by cooling the sample in a dc electric field.[6] Similarly, we show that one can "freeze" transverse disorder of the CDW by cooling a sample in a field. The triangles in Fig. 2 show data taken on warming in zero electric field following cooling in a dc field. After field cooling Γ is initially 1.3×10^{-3} Å^{-1} at 14 K. The superlattice peaks get more narrow as the sample is warmed, and the zero-field curve is reached near 100 K. Each point in Fig. 2 represents a scan taking about on hour, so the transverse widths are quasistatic and a measure of the metastable "equilibrium" configuration of the CDW. One can explain the CDW polarization in terms of local displacements of the CDW. If we assume that the pinning varies spatially, local regions of the CDW may move before the entire CDW is depinned. This leads to a loss in the transverse phase coherence and also to a macroscopic dipole moment since there is a local displacement of charge. Since the CDW is commensurate below 100 K, local movement may corre-

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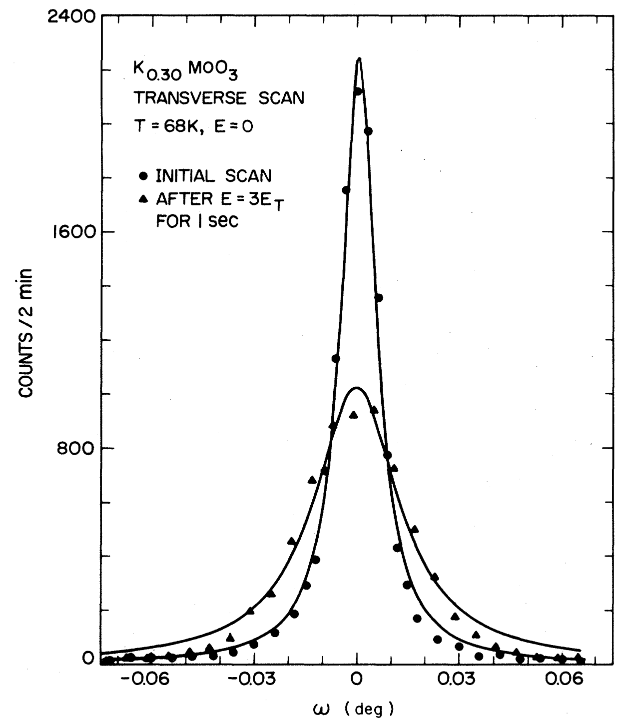

FIG. 3. Transverse scans through the (1, 3.25, −0.5) superlattice peak of $K_{0.30}MoO_3$ at a temperature of 68 K. The circles are data obtained after cooling the sample in zero electric field. The triangles are zero-field data obtained after turning the field on for 1 sec ($E = 3E_T$).

spond to a bowing of widely spaced phase soliton (discommensuration) sheets oriented perpendicular to b^*.[16] The distortion produced by local movement of the CDW is metastable; local regions do not relax when the field is removed. Hence, the number of metastable states available is probably closely related to the number of impurity pinning sites.

The microscopic nature of the disorder in $K_{0.30}MoO_3$ is not completely determined by the present data and several models are possible. The field-induced broadening results from either (a) an inhomogeneous field or pinning resulting in a continuous variation of the CDW phase across the sample, or (b) from finite-range order. The peak width in the inhomogeneous case would be a function of the sample and the beam size and not a measure of the CDW correlation length. Inhomogeneous effects have been observed in selected samples of $K_{0.30}MoO_3$ in the form of a field-induced transverse displacement of the superlattice spot by about 38×10^{-4} Å^{-1} at 77 K.[10] The broadening we have observed at 77 K is symmetric with an excess width of about 4×10^{-4} Å^{-1}, which is considerably smaller than the transverse displacement previously noted. Moreover, our peak is symmetric with no observed field-induced transverse displacement. It is therefore likely that our observed broadening results from finite-range order of the CDW in the transverse direction.

For the case of finite-range order the real-space CDW coherence can be derived from the excess width of the superlattice peak, Γ. The actual number is a model-dependent quantity which depends on the type of disorder, which in turn determines the line shape of the diffraction satellite. For example, if the disorder can be described by a two-dimensional order-disorder model with correlations that fall off as $e^{-r/\xi}/r^{1/2}$, the line shape of the peak is expected to be Lorentzian and the real-space correlation length is $1/\Gamma$. If, on the other hand, the disorder can be described by microdomains with a Gaussian or a random distribution of domain sizes, the line shape will be Gaussian or a Lorentzian squared, respectively. Other models of disorder are possible, and all models give correlation lengths which are equal to $1/\Gamma$ within numerical factors of 2–3. The line shapes obtained in the present experiment at 14 K are shown in Fig. 4. For the zero-field data, the line shape is determined by the instrumental resolution which is nearly Lorentzian. For the field-cooled case the linewidth is over four times larger than resolution and the shape is more nearly Gaussian (solid line) than Lorentzian (dashed line). One could also fit the data equally well with a Lorentzian-squared function. Although the exact distribution of domain sizes is not resolved by the present data, the line shape suggests that the disorder is more appropriately described by microdomains rather than short-range order. For the field-cooled data, $1/\Gamma$ is about 770 Å. The CDW domain size is therefore about 2000 Å transverse to b^* and over 7000 Å parallel to b^*.

In summary, we have shown that like $NbSe_3$ the application of an electric field along b^* in $K_{0.30}MoO_3$ does not

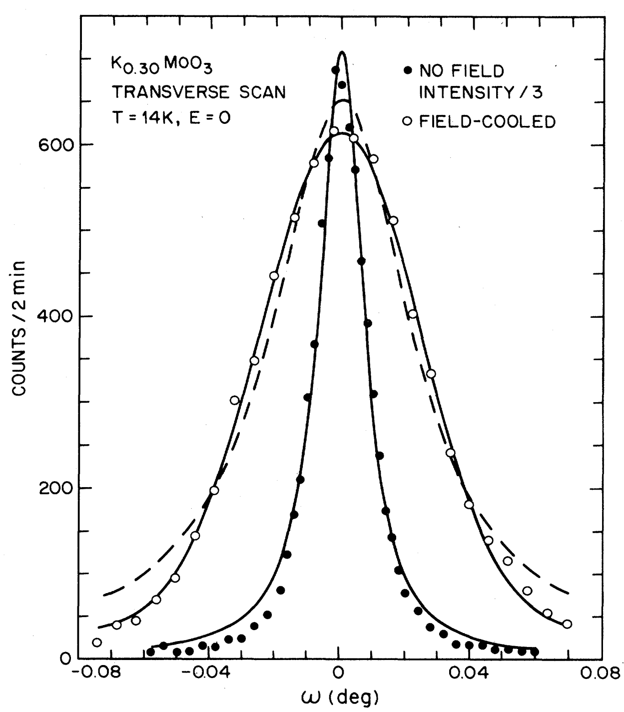

FIG. 4. Transverse scans through the (1, 3.25, −0.5) superlattice peak of $K_{0.30}MoO_3$ at a temperature of 14 K. The intensity of the zero-field data (solid circles) has been divided by 3. The zero-field data are resolution limited and are approximately fit by a Lorentzian. The open circles are a scan taken at $E = 0$ after cooling in a field $E \approx 3E_T$. A comparison between a Gaussian fit (solid line) and a Lorentzian fit (dashed line) is shown.

result in a change in the CDW wave vector or a broadening of the CDW superlattice in the longitudinal direction. Disorder in the transverse direction can be introduced by either raising the temperature to above 90 K, or by the application of an electric field. The metastable, field-induced disorder begins to occur as soon as the field is applied and can only be removed by warming and recooling the sample. The disorder is likely due to microdomains with domain walls parallel to b^*, but inhomogeneous effects may play a role.

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