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Deformation of the charge-density wave by electric fields in $K_{0.3}MoO_3$

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We report high-resolution x-ray-scattering experiments on the quasi-one-dimensional charge-density-wave material blue bronze. At low tempertures, a dc electric field applied along the chain direction causes the superlattice peaks to split in a direction perpendicular to the chain direction. The possible origin of this effect is discussed.

The incommensurate charge-density wave (CDW) ground state that forms in many linear-chain compounds has been associated with many unusual transport properties, including extremely large dielectric constants, non-Ohmic dc conductivity above a small threshold electric field E_T, and long-time relaxation phenomena associated with metastable configurations of the CDW's.[1] Several investigaors have taken advantage of the presence of the accompanying periodic lattice distortion to study the static and dynamic properties of the condensate using structural probes, such as elastic x-ray scattering[2,3] and neutron scattering.[4] Below the CDW transition temperature T_p, scattering experiments detect superlattice peaks with intensity proportional to the square of the distortion amplitude. The intrinsic width of the peaks provides a measure of the inverse of the CDW correlation length. In general, the amplitude distortions are gapped; however, there is an infrared active phase mode with linear dispersion near $\mathbf{q}=0$. Therefore, at low temperatures, the measured width corresponds to a phase-phase correlation length.

In this Rapid Communication we report the results of high-resolution x-ray-scattering experiments on the quasi-one-dimensional CDW material $K_{0.3}MoO_3$ (blue bronze) in the presence of applied electric fields. $K_{0.3}MoO_3$ has a monoclinic structure with space group $C2/m$.[5] The electrical conductivity is the highest along the b axis, corresponding to the direction of chains of MoO_6 octahedra. At room temperature, the material is a quasi-one-dimensional metal, but below $T_p=180$ K there is a transition to a semiconducting CDW state. This is accompanied by the appearance of the superlattice peaks at reciprocal space positions given by $\mathbf{Q}_{sl}=\mathbf{G}\pm n\tau$, where $\mathbf{G}$ is a reciprocal-lattice vector, n is an integer, and $\tau=(1,0.75-\varepsilon,-05.)$ is the CDW wave vector with incommensurability ε.

Previously, the satellite peaks have been observed to broaden in the presence of dc electric fields comparable to, or larger than, E_T.[6,7] Ordinarily, the dc fields cause the largest broadening along a direction normal to the incommensurate chain direction and, in some cases, a shift in the position of the peak along the same direction has accompanied the broadening.[8] The main result of the present work is that the application of the field leads to a splitting of the peak as opposed to a simple broadening. These experiments are carried out by applying the dc fields through contacts on the crystal surfaces, and because of the large anisotropy of the conductivity tensor, it is difficult to inject the current into the sample in a highly homogeneous manner. Tamegai *et al.*, attributed the asymmetry in the broadening they observed to this kind of inhomogeneity, reasoning that the nonuniform electric fields would distort the CDW's over macroscopic distances.[8] The question remains, however, whether the broadening itself is something that can be intrinsically associated with the response of pinned CDW's to an applied electric field, or whether it can be eliminated in the event that the macroscopic geometry of the sample is such that the current injection is completely uniform.

The single crystal of $K_{0.3}MoO_3$ used for most of the measurements in this experiment was rectangular shaped with dimensions $2.5\times2\times0.1$ mm^3 and a measured mosaic spread of 0.01° [full width at half maximum (FWHM)]. The longest direction was parallel to the crystalline b axis. Thin copper wires were affixed to the entire length of the short sides using silver paint. The sample was attached to a sapphire rod with varnish and mounted in a closed-cycle He refrigerator with Be windows. Transport measurements were carried out and showed the expected characteristic threshold behavior with a threshold field E_T of 190 mV/cm at 35 K.

The sample chamber was mounted in a rotating anode based four-circle x-ray diffractometer such that the horizontal scattering plane contained the (0,1,0) and (2,0,−1) directions. Measurements were made with Ge (111) monochromator and analyzer crystals and Cu $K\alpha^1$ x rays. Under these conditions, the half width at half maximum (HWHM) at 35 K of the superlattice peaks in the crystal was approximately 4×10^{-4} Å^{-1} along the chain direction and 2.2×10^{-3} Å^{-1} along the $(2a^*-c^*)$ direction. The experiment was conducted by first cooling the specimen in a zero field from room temperature to approximately 35 K. At 35 K the measured lattice constants are $b^*=0.8317$ Å^{-1} and $(2a^*-c^*)=0.7821$ Å^{-1}. Profiles of the superlattice peaks are symmetric, with widths essentially identical to those of the Bragg peaks. Examples of the zero-field scans are shown in Fig. 1 for the (13,−1.2557,−6.5) superlattice peak. Also shown in Fig. 1 are the same scans as observed after a dc electric field of 13.5 V/cm was applied along the chain direction and waiting for approximately 30 min before conducting the scan. Several important features are evident. The scan along the $2a^*-c^*$ direction with the electric field on is split into two peaks with intensity much lower than

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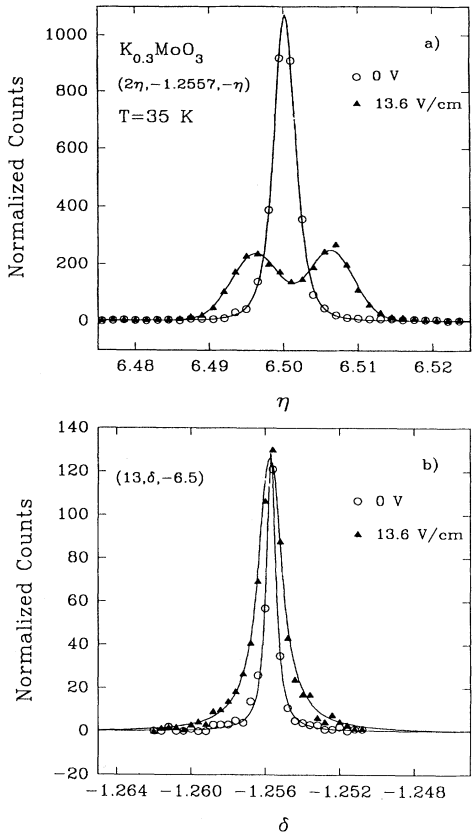

FIG. 1. Scan profiles of superlattice peak (13,−1.2557,−6.5) before and after the application of a dc electric field of 13.6 V/cm at 35 K. (a) shows the profiles along the $(2a^*-c^*)$ direction; the curves are a single Lorentzian squared fit for the zero-field data and a two-Gaussian fit for the data with the field on. (b) shows the profiles for the same peak along the b^* direction; the curves are single Lorentzian fits.

the zero-field peak. Each peak has a FWHM approximately 2.5 times as large as the zero-field peak. The center of mass of the scattering shifts slightly. The scan along the chain direction shows a broadening only. The sample geometry and relatively bad vertical resolution prohibited similar scans along the third direction perpendicular to the scattering plane. The line shapes of other superlattice peaks are similar given identical conditions and sample history.

It is worth noting that before the application of the electric field, the scan profiles can be fitted quite well by a Lorentzian along the chain direction and by a Lorentzian squared along the $2a^*-c^*$ direction. With the electric field on, a Lorentzian still fits the data very well in the chain direction; however, the line shape of the two peaks in the $2a^*-c^*$ direction can only be fitted well by a Gaussian. Generally, one expects a finite correlation length to lead to a Lorentzian line shape; whereas a Gaussian or Lorentzian squared line shape (the two are not always easy to distinguish experimentally) is a signature of a domain structure, with linewidth determined by the domain size. Therefore, the results suggest that the correlation length along the chain direction is shorter than the corresponding dimension of a domain, whereas perpendicular to the chain, the finite domain size dominates. This interpretation has been suggested previously[6,9] and the present results are consistent with this idea.

The relatively small broadening in the b^* direction is consistent with earlier experiments, as is the overall magnitude of the breadth of the scattering distribution along the $2a^*-c^*$ direction. The peak splitting, however, has not been reported in the literature. In order to establish what conditions are necessary to observe the splitting, the measurement was repeated with three separate crystals and several different sets of contacts. In some of these cases, the contacts were applied to freshly exposed sample surfaces. The double-peak feature was observed consistently. The relative intensity in each subpeak was seen to vary depending on the contacts and sample history. The crystal surfaces studied were generally smooth and shiny in appearance. One sample had a rough side, and studying the scattering obtained by reflection from the rough side gave a superposition of a split peak with extra scattering remaining in the zero-field position. We hypothesize that the remaining central component of the scattering arises from a portion of the sample that experiences a reduced field, possibly from "islands" sticking up above a smooth surface. With the variation in peak intensity and the possibility of scattering at the original position, the overall scattering distribution may appear as a very broad asymmetric peak. This may explain the line shape seen in other experiments.[7]

The scans shown in Fig. 3 were taken under the same condition as the grid scan in Fig. 2 except that they were collected during different thermal cycles. An asymmetric intensity distribution can arise from an inhomogeneous field distribution as shown by Tamegai *et al.*[8] We attempted to apply contacts to the sample in a manner that minimized any inhomogeneity. Nevertheless, some residual inhomogeneity is likely to be present. To ensure that residual inhomogeneity does not dominate the observed features of the line shape, deliberate attempts were made to change the geometry of the contact ends by mechanical means such as polishing or chipping. The two-peak structure is, however, still present. Figure 2 shows a contour plot of the (15,−0.7445,−7.5) peak after the application of a field of 6.8 V/cm. The peak splitting is clearly evident. The contacts were the same ones that had been attached for the run producing the data of Fig. 1, but were separated by many thermal cycles. The contact resistance had changed with cycling. The x-ray setup

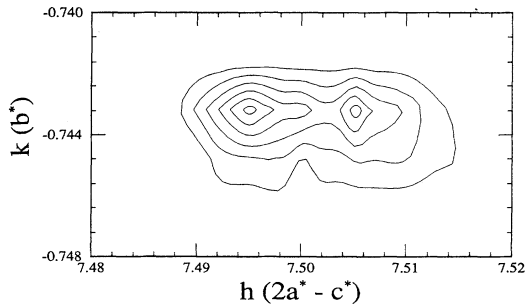

FIG. 2. A contour plot of superlattice peak (15,−0.7447,−6.5) taken with an electric field of 6.8 V/cm after waiting 25 min at approximately 35 K.

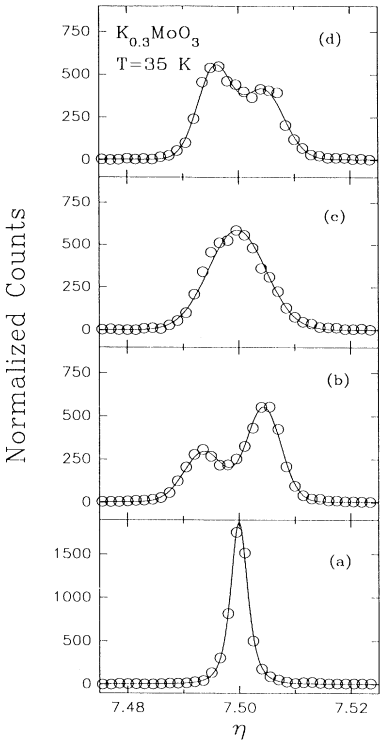

FIG. 3. Scan profiles of superlattice peak $(15,-0.7445,-7.5)$ along the $(2a^*-c^*)$ direction at approximately 35 K. (a) is the zero-field cool data and the curve is a single Lorentzian squared fit; (b) is the profile taken 30 min after a field of 6.8 V/cm was applied and the curve is a two-Gaussian fit; (c) is the profile taken 21 min after a field of -2.7 V/cm was applied after the field 6.8 V/cm was turned off for 2 h and the curve is a single-Gaussian fit; (d) is the profile taken 90 min after the field -2.7 V/cm was applied and the curve is a two-Gaussian fit.

also differed in the slitting and monochromator alignment. The scans shown in Fig. 3 are for the $(15,-0.7445,-7.5)$ peak. The zero-field scan is shown in Fig. 3(a). An initial dc field of 6.8 V/cm was applied, and the scan in the presence of this field is shown in Fig. 3(b). The peak splitting is obvious, but the intensity distribution is clearly asymmetric. It is worth noting that if the same scan is plotted for the $(15,0.7445,-7.5)$ peak, the asymmetry is apparently the mirror image of that for the $(15,-0.7445,-7.5)$ peak. More generally, the asymmetry in superlattice scans corresponding to $\mathbf{G}+\tau$ shows a mirror image relative to that in superlattice scans corresponding to $\mathbf{G}-\tau$, where $\mathbf{G}$ is some reciprocal-lattice vector and $\tau=(1,0.75-\varepsilon,-0.5)$ is the CDW wave vector. This is equivalent to two wave vectors τ_1 and τ_2, each independently leading to a superlattice peak with wave vectors $\mathbf{Q}_{1,2}=\mathbf{G}\pm\tau_{1,2}$. Different parts of the sample may be ordered with different CDW wave vectors corresponding to τ_1 and τ_2. The possibility of a domain structure has been raised previously.

The scattering distribution shows interesting effects when the polarity of the field is changed. After the scan represented in Fig. 3(b) was completed, the field was turned off for 2 h. With zero field, the asymmetric split peak line shape did not change over this time. Following

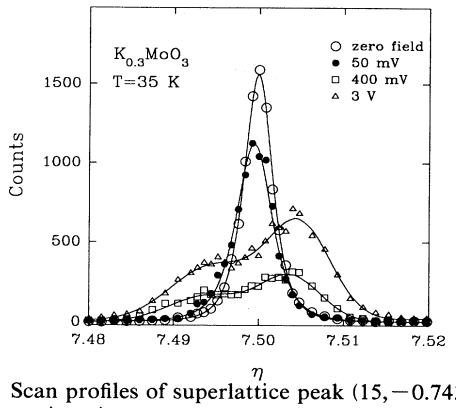

FIG. 4. Scan profiles of superlattice peak $(15,-0.7433,-7.5)$ along the $(2a^*-c^*)$ direction at approximately 35 K. The profiles have been normalized to counts/min except that of 3 V, which is counts/4 min. The curves are single Lorentzian squared fits for the zero field and the 50-mV data and two-Gaussian fits for the 400-mV and the 3-V data.

this, a field of 2.7 V/cm with opposite polarity was applied. The scan in Fig. 3(c) was collected starting 21 min after the application of the second field and that in Fig. 3(d) was taken after 90 min. The clear trend is towards a tradeoff intensity in the two peaks. This behavior was observed repeatedly. The time scale is faster for larger fields and for higher temperatures. A reversal of asymmetry upon field reversal was observed previously by Tamegai *et al.*[8] and probably arises from the same origin as that seen here. The indication is that the domains corresponding to τ_1 and τ_2 interchange upon reversal of the field.

Some preliminary investigations of the field dependence of the splitting were carried out. Figure 4 shows scans of the $(15,-0.7433,-7.5)$ superlattice peak carried out after cooling in zero field and gradually increasing the field, keeping the same polarity. This time, the contacts were completely new. The data must be interpreted somewhat cautiously. The ultimate line shape may be time dependent, with a long-time scale for small fields. For example, the line shape at 400 mV showed clear signs of changing over a 3-h period. Nevertheless, certain trends are apparent. For very small fields, the broadening is small and splitting is not apparent. As the field is increased, the overall broadening increases and the peak shape changes dramatically until the double-peak shape is apparent. However, the broadening or splitting saturates at a large field value (approximately 20 V/cm for the present data), possibly depending on the sample, contacts, and the temperature which puts an upper limit on the field because of Joule heating. The saturation field is of the order of the low-temperature upper threshold field $E_T^{(2)}$, above which a sudden increase in the electric current occurs and rigid sliding of the CDW is hypothesized to occur.[10] The relationship between the observed structure effects and $E_T^{(2)}$ remains to be investigated.

We note that Fleming and co-workers observed a broadening of the superlattice peak after applying an electric field along the chain direction, but they did not observe a splitting. This may be because the field they applied was much smaller and for their zero-field cooled

runs it was applied for only 1 s. Their data do not include scans along the symmetry directions. As mentioned earlier, a rough crystal surface can also smear out the double peaks.

We believe that the double-peak feature is an intrinsic effect and is related to the bulk properties of the sample. This structure cannot be related to a simple reduction of the transverse coherence length of the CDW in the presence of a field. The overall behavior suggests a domain structure. The open question is what might cause a domain structure that seems to correspond to two nearly degenerate states?

One possibility is that the pure system simply has a different ground state for $\mathbf{E}=\mathbf{0}$ and $\mathbf{E}\neq\mathbf{0}$ with the latter situation corresponding to a reduction in symmetry. We are not aware of a reason why this should occur. An alternative which we favor at present is that the double-peaked structure is a signature of the domains that form because the CDW is pinned by defects in a manner that causes the effective wave vector to shift. An idea of how this may work can be obtained as follows.

In the incommensurate CDW state characterized by wave vector $\mathbf{q}$, the positions of ions in the lattice are given as[11] (for simplicity, we assume a monatomic lattice without losing generality) $\mathbf{R}_i=\mathbf{R}_i^0+\mathbf{A}_0\sin[\mathbf{q}\cdot\mathbf{R}_i^0+\phi_0]$, where $\mathbf{R}_i^0$ is the position of the unit cell and $\mathbf{A}_0$ is the amplitude of lattice distortion. The total phase is given by $\phi_{\rm tot}=\mathbf{q}\cdot\mathbf{R}_i^0+\phi_0$ and $\mathbf{q}=\nabla\phi_{\rm tot}$. For $K_{0.3}MoO_3$ in zero electric field, $\mathbf{q}=\frac{1}{2}(2\mathbf{a}^*-\mathbf{c}^*)+(\frac{3}{4}-\varepsilon)\mathbf{b}^*$, where ε is a small irrational number and $\mathbf{b}^*$ is in the chain direction. An additional phase change that is linear in position will cause a shift of the CDW wave vector. If a defect on some chain pinned the CDW phase in a manner that relaxed linearly with distance, a splitting of the peak could result.

An applied field in the b^* direction couples to the phase of the CDW and thus causes the ions to shift slightly along the chains. Pinning of the CDW phase by defects induces the CDW to distort itself to best accommodate the potential. The magnitude of the variation is believed to reflect the elasticity of the density wave along a particular direction, which will depend of the electronic dispersion. It is normal for the broadest distribution in $\mathbf{q}$ to occur in the $2a^*-c^*$ direction, which has a very small electronic wave-function overlap.

With some simplifying assumptions, the Fukuyama-Lee-Rice phase Hamiltonian[12,13] can be used to estimate the distribution in $\mathbf{q}$ that would be expected. For small electric fields and Dirichlet boundary conditions, the phase change caused by the electric field can be written as[14] $\Delta\phi=\phi(E\neq0)-\phi(E=0)\approx(eE/\pi\bar{v}_F)\int_v G(\mathbf{r},\mathbf{x})d^3x$, where G is the Green's function and $\bar{v}_F=\hbar v_F/2\pi$ with v_F the Fermi velocity. Using the Lee-Rice coherence lengths as the domain size (which scale with relative stiffness) gives $\Delta Q_x=(85eE/\pi^4\bar{v}_F)(L_z^2/L_x)$, where L_z is the domain size in the b^* direction and L_x the size in the $2a^*-c^*$ direction. Estimating the domain sizes from the resolution-corrected peak widths leads to $\Delta Q_x\sim5\times10^{-3}$ Å^{-1} for a field of 7 V/cm. This is of the same order of magnitude as the observed peak shift of 4×10^{-3} Å^{-1}.

It is important to determine what elements are necessary to produce the splitting that we observe, rather than a simple broadening of the peak. Again, we adopt the starting point as the Fukuyama-Lee-Rice description for a single domain. Using the boundary condition that the phase is fixed on a domain boundary leads to a quadratic variation in one dimension, but higher-order terms are needed for higher dimensions. The result for one dimension leads to a gradient of the phase that is linear over the domain; hence $\mathbf{q}$ has equal weight for a distribution of values about the equilibrium value. Alternative distributions in $\mathbf{q}$ are possible in higher dimensions, but to achieve the peak splitting as we observed requires an elasticity that is anharmonic.

In summary, we carried out high-resolution x-ray-scattering measurements on $K_{0.3}MoO_3$ at low temperatures in applied dc electric fields. The CDW superlattice peaks are seen to split in the presence of electric fields, and do so in a manner indicative of a domain structure. Changing the polarity of the field causes interesting time-dependent effects. Our works suggests that broadening and splitting of the superlattice peaks may be an intrinsic property of the crystals while the asymmetry in the peak line shape may be closely related to the contact geometry. A simple model calculation suggests that the peak splitting could be a consequence of pinning, but more experimental and theoretical work must be done to clarify the situation.

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