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Grazing-incidence x-ray study of the charge-density-wave phase transition in $K_{0.3}MoO_3$

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The charge-density-wave (CDW) phase transition has been studied for a range of depth of 20–1000 Å below the $(20\bar{1})$ surface of $K_{0.3}MoO_3$ by use of grazing-incidence x-ray diffraction. It is found that the CDW wave vector is the same as in the bulk. The transition temperature as well as the temperature dependence of the order parameter (down to 125 K) appear to be independent of the depth probed by the x-ray beam. The fact that the surface does not appear to modify the characteristics of the CDW in this particular case is probably related to the weak coupling between the slabs of MoO_6 octahedra, perpendicular to the $(20\bar{1})$ surface.

The study of the effects of a surface on phase transitions (melting, reconstruction, order-disorder, magnetic) is an important topic in surface physics. In general, one expects critical phenomena at phase transitions (critical temperature, order parameter, correlation lengths) to be different at the surface from what they are in the bulk. These modifications are related to dimensionality and finite-size effects associated with the surface and they have been studied in several cases.[1]

Charge-density-wave (CDW) phase transitions and the associated modulated structures are good candidates for the study of these phenomena. For instance, we may expect modifications, near the surface, of the wave vector (which is usually incommensurate with the average lattice) or the amplitude of the modulation as well as their temperature dependences. Several techniques have been used to investigate CDW's at the surface of various one-dimensional (1D) or (2D) systems, typically transition-metal chalcogenides and blue bronzes. Low-energy electron diffraction (LEED) experiments were performed in $1T$-TaS_2 (Ref. 2) where the CDW-induced satellites were clearly seen and the behavior of the surface appeared to be the same as that of the bulk. Molecular-beam diffraction (helium beam) also revealed the existence of CDW's at the surface of $1T$-TaS_2 and $2H$-$TaSe_2$ (Ref. 3) crystals. Surprisingly it was found that the intensity of the CDW-induced satellites was stronger at the surface than in the bulk, indicating larger displacements. The same technique was also used very recently to study the normal-to-incommensurate CDW transition in $2H$-$TaSe_2$. The transition was found to be second order and a critical exponent $\beta = \frac{1}{3}$ was deduced.[4]

In the last five years, following the first observations by Coleman *et al.*,[5] scanning tunneling microscopy (STM) has been used extensively to image CDW's at the crystal surface of various compounds such as $1T$-TaS_2,[5–7] $1T$-$TaSe_2$,[5] o-TaS_3.[6] Contrary to the scattering experiments which probe essentially the atomic displacements coupled to the CDW, STM is sensitive to the CDW itself and is an invaluable technique for studying the CDW characteristics (discommensuration lattice, harmonicity, amplitude, gap). However, to the best of our knowledge, there is little evidence for clear and reproducible differences between the behavior of the surface and of the bulk.

Surface x-ray diffraction is a powerful technique for comparing surface and bulk structural phase transitions since one can vary the penetration depth by changing the glancing angles of the incident and scattered x-ray beams.[8] It has been utilized to investigate various types of structural transitions like reconstructive or order-disorder transitions[8,9] but no attempt has been made to study CDW phenomena so far. The aim of the present work was to study the CDW transition near the $(20\bar{1})$ surface of a single crystal of $K_{0.3}MoO_3$ (so-called blue bronze) with grazing incidence x-ray diffraction and to look for possible surface-related effects.

$K_{0.3}MoO_3$ is a low-dimensional inorganic conductor which exhibits at $T_c \simeq 183$ K a CDW phase transition that has been studied extensively (nature of the structural modulation, influence of disorder, fluctuations, dynamics) and recently reviewed.[10] However, as far as we know, there has been no conclusive observation of the CDW modulation at the surface of $K_{0.3}MoO_3$.

Our experiment was carried out at the AT&T beam line X16A at the National Synchrotron Light Source (Brookhaven National Laboratory). The incident x-ray beam was focused by a toroidal mirror and monochromated by a Si(111) double-crystal monochromator ($\lambda = 1.12$ Å). The $(20\bar{1})$ plane of the $K_{0.3}MoO_3$ crystal was freshly cleaved using a razor blade and a smooth surface, free of steps, was obtained after several attempts. Then, the sample was immediately introduced into a vacuum of 10^{-9} torr. Alignment of the surface was made using the reflection of a laser beam and the orientation of the crystal was determined from a set of bulk fundamental Bragg reflections, thus allowing the derivation of the so-called orientation matrix. For the low-temperature measurements the sample holder (copper block) was cooled by a flow of nitrogen gas. The temperature of the block was varied down to a minimum 120 K and regulated within

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0.25°.

We have studied the temperature dependence of several CDW satellite reflections. Their reduced wave vector is of the form (0,0.263,0.5) at the transition temperature $T_c \simeq 183$ K as reported previously.[11,12] The b^* component, q_b, of the wave vector is incommensurate. We measured reflections above, but close to, the $(20\bar{1})$ plane using an asymmetric glancing-incidence geometry in which the incident beam only was at grazing angle while the angle of the diffracted beam was determined by fulfillment of the Bragg condition. By varying the angle of incidence α_i, while maintaining an exact crystallographic setting, we could perform depth-sensitive measurements. The calculated x-ray penetration depth is given as a function of α_i/α_c in Fig. 1, where α_c is the critical angle for total reflection of x rays ($\alpha_c = 0.21°$ for $K_{0.3}MoO_3$ and $\lambda = 1.12$ Å). The divergence of the incident x-ray beam along the perpendicular to the crystal surface was on the order of 0.15°, while the exit beam was relatively uncollimated (0.5° divergence).

Figure 2 shows a scan along b^* (parallel to the surface) across a CDW satellite peak at (4,k,3.5) taken at $T = 161$ K and for five different angles of incidence spanning a range of depths of about 20–1000 Å (as indicated in Fig. 1). It appears that within our resolution the CDW peak is centered at a constant k value of 0.2615 ± 0.0002, corresponding to $q_b = 0.2615 b^*$ independent of the penetration depth. This value is in good agreement with that measured previously in bulk samples at the same temperature, i.e., $q_b = (0.260 \pm 0.002) b^*$.[11–13] Note that the profile and width [half width at half maximum (HWHM) $\simeq 0.00066$ Å^{-1}] of the peak are practically unchanged when the penetration depth is increased. Actually the width appears to be limited by the experimental resolution. This indicates that the in-plane correlation length in the monoclinic b direction (which is the axis of the chains of MoO_6 octahedra) is larger than 1500 Å in all cases. Similar scans were performed systematically for two different values of α_i (typically for α_i close to 0 and 0.5°) at several lower temperatures down to 125 K. They confirmed that the incommensurate wave vector q_b is not modified from its bulk value down to a 20-Å-thick layer at the surface.

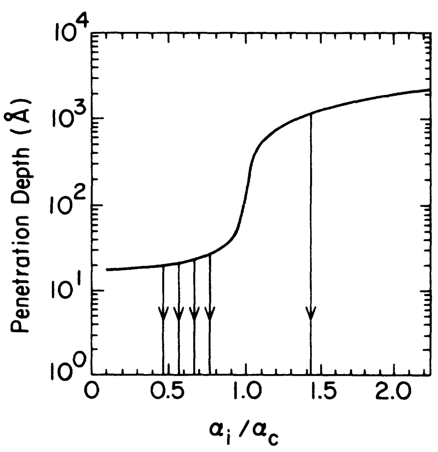

FIG. 1. Calculated x-ray penetration depth as a function of α_i/α_c above and below the critical angle $\alpha_c = 0.21°$ in $K_{0.3}MoO_3$. The arrows indicate the values of α_i corresponding to the scans of Fig. 2.

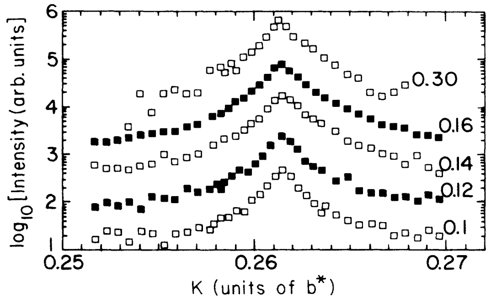

FIG. 2. Scans of the (4,0.2615,3.5) CDW satellite peak at 161 K for five different angles of incidence α_i relative to the $(20\bar{1})$ surface of a $K_{0.3}MoO_3$ crystal (note that the intensity curves have been shifted for clarity, i.e., multiplied by 5, 5^2, 5^3, 5^4 for $\alpha = 0.12$, 0.14, 0.16, and 0.30, respectively).

In Fig. 3 we show plots of the square root of the integrated intensity ($\sqrt{I}$ is proportional to the order parameter of the CDW) for the same CDW satellite reflection at (4,q_b,3.5) as a function of the temperature from 125 K to T_c for different angles of incidence below and above α_c. The intensity for each point was obtained by integrating over the rocking curve and keeping α_i fixed. All the curves in the linear plot of Fig. 3(a) extrapolate to zero for the same transition temperature $T_c = 175$ K, indicating that within an accuracy of about 1 K, T_c does not vary with the depth. Note that T_c here is about 6–8 K below

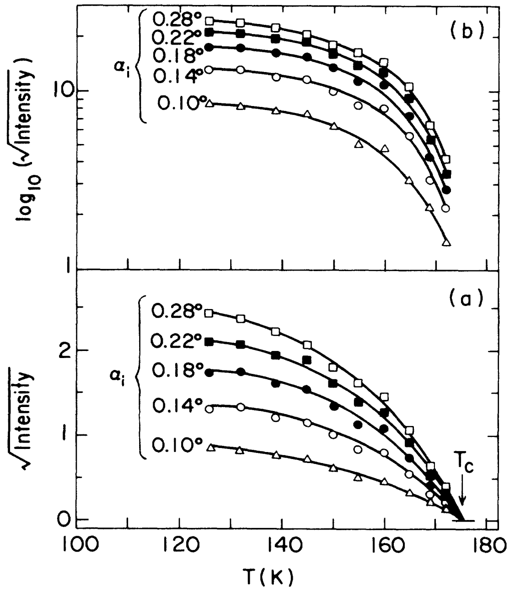

FIG. 3. Temperature dependence of the square root of the integrated intensity (arbitrary units) of the CDW satellite peak at (4,q_b,3.5) and for different angles of incidence α_i's. The linear scale (a) shows that all curves extrapolate to $T_c = 175 \pm 1$ K while the log scale (b) shows that the temperature dependence of the order parameter is unchanged when the penetration depth is varied.

the normal T_c value of 181–183 K.[11–13] This is most likely due to a technical problem such as the existence of a temperature gradient in the crystal mount or voltage offsets in the wires of the Pt resistance thermometer. Figure 3(b) shows the same intensity data plotted on a log scale. It reveals that all the curves are reasonably parallel, from which we conclude that the temperature dependence of the intensity and thus of the order parameter is very nearly the same for all the corresponding depths (i.e., from about 20–1000 Å).

In summary, the above results clearly show that the CDW modulation is present at the $(20\bar{1})$ surface of $K_{0.3}MoO_3$ (or more precisely within the outer 20-Å-thick layer). It suggests that other techniques such as STM should be able to reveal the CDW as well and such studies are much awaited. Furthermore, we find that the diffraction effects associated with the CDW exhibit the same characteristics at the surface as in the bulk, at least within the limits of our resolution and the temperature range which we probed ($T > 125$ K). Although there is no definite prediction for the influence of a surface on the characteristics of CDW transitions we can discuss the possible implications of our results.

The fact that q_b (surface) $= q_b$ (bulk) gives us information about the electronic structure near the $(20\bar{1})$ surface. In $K_{0.3}MoO_3$ the conduction electrons are provided by the monovalent K atoms (3 per $Mo_{10}O_{30}$ cluster in the basic unit) and it has been shown[14] that two quasi-1D bands, originating from groups of MoO_6 octahedra, cross the Fermi level at $k_F^1 \simeq 0.33b^*$ and $k_F^2 \simeq 0.42b^*$, respectively. The formation of the CDW is driven by the nesting of one band into the other with a nesting vector $k_F^1 + k_F^2 \simeq 0.75b^*$ (or $\simeq 0.25b^*$ when referred to the first Brillouin zone) which is close to q_b.[12] Our findings indicate that (i) the dispersion of the bands and (ii) the charge density are not significantly modified in the vicinity of the $(20\bar{1})$ surface. The first point is probably related to the quasi-1D character of the band structure and especially to the very weak coupling between the layers formed by the conducting chains of MoO_6 octahedra, i.e., perpendicular to the $(20\bar{1})$ surface. The coupling energy in this direction was estimated to be $U_\perp \simeq 2.5$ meV,[10] which is about 1 order-of-magnitude lower than the transverse interchain tunneling within the layers.[10,14]

The fact that the band filling and its temperature dependence are the same at the surface is puzzling. In bulk samples the deviation of q_b from commensurability ($\Delta q_b = q_b - 1/4$) appears to be thermally activated with an activation energy $\Delta E = 50$ meV and different mechanisms have been proposed to account for this exponential dependence. In particular, thermal activation of the conduction electrons towards a third band located above the Fermi level has been suggested.[12] Moreover, the small variations in the value of Δq_b reported for different samples are usually attributed to a slight nonstoichiometry in K or to the substitution of nonisoelectronic elements for Mo. Our values for q_b at 161 K (Fig. 2) and also in the 125–170 K range are in excellent agreement with previous measurements which means that, contrary to what one might expect, the impurity concentration and the possible nonstoichiometry are the same at the surface. Concerning the temperature dependence of Δq_b it would be interesting to measure it to low enough temperature to see whether the activation energy is different from that of the bulk.

Turning to the width of the CDW satellites along b^* we find that the associated correlation length along the chain is still long range close to the $(20\bar{1})$ surface. An analogy may be drawn with some results on the influence of the partial substitution of Rb for K [which takes place between the $(20\bar{1})$ layers of MoO_6 octahedra] in $(K_{1-x}Rb_x)_{0.3}MoO_3$ where the correlation lengths (longitudinal but also transverse) stay long range below T_c even for $x = 0.5$.[15] In this case a strong disorder is introduced between the layers as a result of the substitution but with little effect on the CDW correlation. It appears again that the weakness of the interlayer coupling might be responsible for these properties.

Similar arguments may be applied to the transition temperature T_c and the temperature dependence of the order parameter which also are unchanged at the surface. However, these arguments are mostly qualitative and it appears that a theoretical study would be necessary to better understand why the CDW is unaffected by truncation at the $(20\bar{1})$ cleavage plane in the blue bronze. On the experimental side it would be extremely useful to perform the same type of study for different surface orientations where the transverse coupling is stronger, such as (201) and (010). This could also be done in other CDW materials. Actually, to our knowledge, the successful observations of CDW's on surfaces have all been made on cleavage planes with weak transverse coupling. This is the case, in particular, for the STM studies of the 2D transition-metal chalcogenides. There are obvious practical reasons for that since the cleavage planes are easier to obtain but it is also possible that CDW's are much more perturbed or even destroyed for other surface orientations.

Finally, our results have some implications on recent work which indicates that the pinning mechanisms of CDW motion could be strongly influenced by size and surface effects.[16–21] For instance, threshold fields have been found to depend on the thickness or cross-sectional area of the sample.[16–19] It also has been proposed that carriers are scattered from the surface[19] or that they can be pinned by defects or different CDW wave vectors at the surface.[20] In the case of the $(20\bar{1})$ surface of $K_{0.3}MoO_3$ the present results do not show evidence of a sizable change of the wave-vector component q_b at the surface.

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