Discovery of an Unconventional Charge Density Wave at the Surface of $K_{0.9}Mo_6O_{17}$

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We use angle resolved photoemission spectroscopy, Raman spectroscopy, low energy electron diffraction, and x-ray scattering to reveal an unusual electronically mediated charge density wave (CDW) in $K_{0.9}Mo_6O_{17}$. Not only does $K_{0.9}Mo_6O_{17}$ lack signatures of electron-phonon coupling, but it also hosts an extraordinary surface CDW, with $T_{S\_CDW} = 220$ K nearly twice that of the bulk CDW, $T_{B\_CDW} = 115$ K. While the bulk CDW has a BCS-like gap of 12 meV, the surface gap is 10 times larger and well in the strong coupling regime. Strong coupling behavior combined with the absence of signatures of strong electron-phonon coupling indicates that the CDW is likely mediated by electronic interactions enhanced by low dimensionality.

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Most known charge density wave (CDW) materials are mediated by strong electron-phonon (*e*-ph) interaction [1], as confirmed by observation of large kinks in the dispersion by angle resolved photoemission spectroscopy (ARPES) [2–6]. The role of the Fermi surface nesting in formation of the CDW is still a subject of ongoing debate [7,8]. Some of the best known examples are the layered transition-metal dichalcogenides and tellurides [9–13], where charge order often coexists and competes with superconductivity, due to their common *e*-ph origin [4,5,10,14–18]. A CDW has been discovered within the pseudogap state of the cuprates [19–28]. The observation of phonon anomalies suggests *e*-ph coupling may play a role [29–31]; however, a number of theoretical models suggest that this CDW could be electronically mediated [32–36]. Electron-electron (*e*-*e*) interactions are also likely responsible for the CDW found in related cuprate ladder compounds [37].

In some CDW materials the transition temperature is enhanced at the surface [38,39], so called *extraordinary* transition [40,41]. Recently, such effect was also reported in a monolayer [42–44]. The increased T_C has been attributed to enhanced interactions due to the decreased dimensionality [45,46]. In this Letter, we show that $K_{0.9}Mo_6O_{17}$ has an enhanced surface transition temperature by factor of 2 and a surface energy gap that is an order of magnitude larger than the bulk. More surprisingly, we demonstrate that this material lacks usual signatures of strong *e*-ph coupling. This, combined with the large ratio $(2\Delta/k_BT_C) \sim 15$ (strong coupling regime), indicates that the CDW is likely mediated by electronic interactions enhanced by low dimensionality. Despite the strong coupling nature of the surface order, $K_{0.9}Mo_6O_{17}$ shows no signatures of strong *e*-ph coupling, either in the phonon or electronic structure, making it a new candidate for an *e*-*e* mediated CDW.

$K_{0.9}Mo_6O_{17}$ is a quasi-2D CDW material with $T_{B\_CDW} \sim 115$ K [47–49]. Its crystal structure [50] consists of a stacking of molybdenum-oxygen slabs (Mo_6O_{17}) along the hexagonal *c* axis with potassium atoms intercalated in between. The Mo-O layers consist of Mo_2O_{10} zigzag chains along three directions, and the 2D Fermi surface (FS) can be constructed by superimposing three sets of quasi-1D FS lines, with a weak hybridization [51,52]. The measured CDW vectors agree well with FS nesting vectors that connect two crossing points of the quasi-1D FS sheets [53,54].

$K_{0.9}Mo_6O_{17}$ single crystals were grown by electrolytic reduction [55]. The typical size of the samples was $\sim 2 \times 2 \times 0.3$ mm^3 in ARPES measurements and $\sim 3 \times 4 \times 1$ mm^3 in the x-ray diffraction measurements. ARPES measurements were carried out using a Scienta R8000 electron analyzer and a tunable VUV laser [56]. All data were acquired with a photon energy of 6.7 eV. The energy resolution of the analyzer was 1 meV and the angular resolution was 0.13° and ~0.5° along and perpendicular to the direction of the analyzer slit, respectively. Each measurement was confirmed by temperature cycling to ensure aging effects did not affect the conclusion. The x-ray diffraction experiment was performed using the six-circle diffractometer at the 6-ID-D station at the Advanced Photon Source, Argonne. Synchrotron radiation of 100 keV with an attenuation length of 3.2 mm for $K_{0.9}Mo_6O_{17}$ was used to study the bulk. Polarized Raman scattering measurements from the *ab* surface of the single crystal were performed in quasi-backscattering geometry using the 530.9 nm excitation line of a Kr^+ ion laser with less than 15 mW of incident power focused to a $50 \times 100\ \mu\mathrm{m}^2$ spot. The data were corrected for the spectral response of the spectrometer and the CCD.

Typical band dispersion at temperatures well above the CDW transition is shown in Fig. 1(b) and is rather unremarkable. When cooled down below 230 K, still above the bulk transition temperature, T_{B_CDW}, an astonishing transformation occurs [Fig. 1(c)]. The single conduction band present at high temperatures splits into two branches. One branch follows the high-temperature dispersion, while the other reaches only -150 meV, then bends back towards higher binding energies marking the presence of an energy gap with its minimum located at the metallic k_F value. The dispersion extracted from low temperature energy distribution curve (EDC) is shown in Fig. 1(e). The appearance of the lower branch coincides with the decrease of the low binding energy intensity of the other branch that crosses E_F. A detailed analysis of the intensities is presented in the Supplemental Material [57], Fig. S1. The most natural explanation of this unusual behavior is that the measured band dispersion is a combination of surface and bulk contributions. The electronic structure measured at high temperature, quite surprisingly, must be very similar for both; thus, we observe a single band. At lower temperatures, we attribute the conducting branch of the band to the metallic bulk of the crystal and the gapped branch to the surface of the crystal, where the gap is due to a CDW with a transition temperature of 230 K enhanced from the 115 K bulk value. Surprisingly, the energy value of the gap minimum of the surface CDW is temperature independent. Instead, the intensity of the gapped surface band increases with decreasing temperature. Such unusual behavior is likely a result of strong coupling, and is similar to cuprates [58].

Above the bulk CDW transition, the metallic branch crosses E_F as shown in Figs. 1(g)–1(k). Upon cooling below the bulk CDW T_{B_CDW}, the intensity at E_F decreases—a clear signature of the opening of an energy gap due to the bulk CDW also seen in EDCs [Figs. 1(j)–1(k)]. The temperature at which the bulk gap opens—$T_{B\_\mathrm{CDW}} = 115$ K and an energy of $\sim$12 meV are consistent with values expected for the bulk CDW in this material. The leading edge of the EDC's moves to higher binding energies upon cooling, in contrast with the behavior of the large gap at the surface.

To validate these conclusions, we performed extensive low-energy electron diffraction (LEED) and x-ray studies. The LEED studies, carried out with electron energies of 54 eV, are primarily sensitive to the surface electron density, whereas the x-ray measurements, with energies of 100 keV, probe the bulk of the sample. In Figs. 2(a)–2(c) we plot our x-ray data. At 5 K, we observed additional Bragg peaks, with positions consistent with the previously reported CDW superstructure [48]. A detailed temperature-dependent measurement of the diffraction peak with

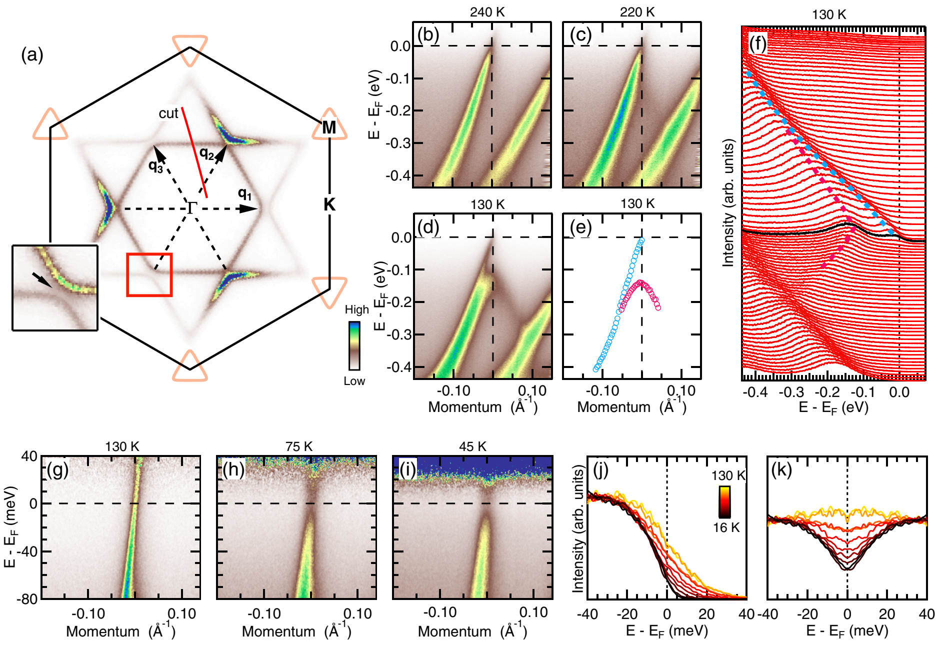

FIG. 1. Bulk and surface CDW gaps: (a) Measured FS at 130 K. Intensity is integrated within $E_F \pm 10$ meV and data are symmetrized with sixfold symmetry. Dashed arrows indicate three nesting vectors, each connecting two quasi-1D FS sheets [51]. The red rectangle is expanded in the left-bottom inset to demonstrate the FS hybridization. (b)–(d) ARPES intensity measured along the cut (red line) shown in (a). (e) Extracted band dispersion from (d). (f) EDCs along the same cut. (g)–(i) ARPES intensity divided by Fermi function close to E_F at 130, 75, and 45 K. (j) Temperature dependence of the EDCs at k_F showing opening of bulk CDW gap. (k) Same as in (j), but symmetrized about E_F.

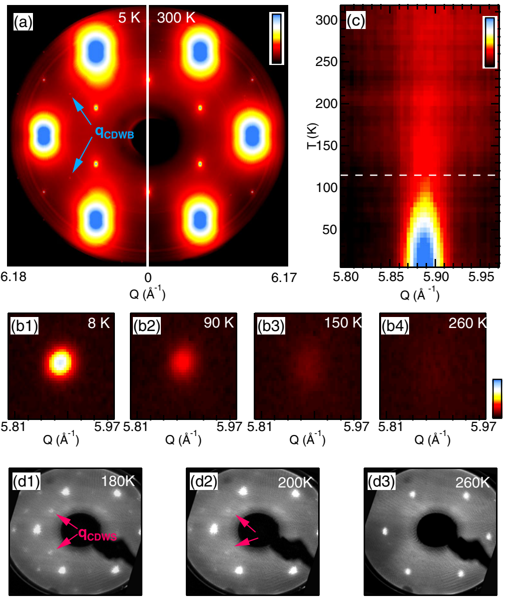

FIG. 2. Bulk and surface CDW transition. (a) High-energy x-ray diffraction patterns of the reciprocal lattice plane ($H\,K\,0$). The CDW superstructure peaks are marked by blue arrows (logarithmic color scale). (b) High-resolution diffraction patterns of the ($\frac{9}{2}$ 0 0) CDW peak (linear color scale). (c) Plot of the temperature dependence of the CDW peak (linear color scale). The intensity is obtained by summing up the high-resolution diffraction patterns of the ($\frac{9}{2}$ 0 0) peak along the transverse direction in (b), and is plotted along the longitudinal direction. (d) LEED images. Red arrows point to CDW superstructure peaks.

high resolution shows that the peaks sharpen and become more intense below the bulk CDW transition temperature T_{B_CDW} [Figs. 2(b) and 2(c)]. It should be noted that a very broad, weak peak is present at this location up to much higher temperatures, most likely due to the presence of fluctuations with correlation length limited to a few atomic unit cells. In the LEED data [Fig. 2(d)], clear CDW superstructure peaks occur already at 200 K, much higher than the bulk transition, consistent with ARPES data. Current data do not allow us to conclude whether this behavior displays any hysteresis.

To investigate the role of phonons in the formation of the CDW we conducted temperature-dependent measurements of the phonon spectrum using Raman spectroscopy [59] and show the results in Fig. 3(a) (more detailed plots can be found in the Supplemental Material [57], Fig. S2). The drop of the electronic background intensity below ~24 meV and 115 K indicates the opening of the energy gap, consistent with the "bulk" ARPES data. However, in contrast to materials where new phonon modes appear in the CDW phase [60,61], no changes in the phonon energies are observed across both the bulk and surface transitions for purple bronze. This absence indicates that any changes in the ionic positions across the CDW transition are likely very small and well below our detection limit.

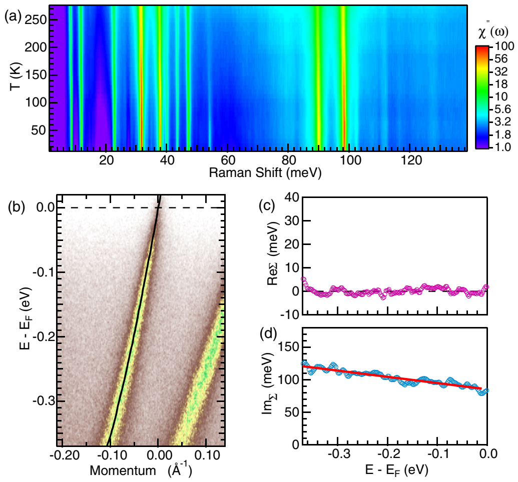

FIG. 3. (a) Temperature dependence of the Raman response in false color image (logarithmic scale) to emphasize a general trend of spectral weight suppression upon cooling due to gapping of the Fermi surface pockets. (b) Band crossing E_F at $T = 260$ K along same cut as in Fig. 1. The parabolic fit to the dispersion is plotted in black. (c) Real part of self-energy extracted from (b). (d) Imaginary part of self-energy extracted from (b). Red solid line is a linear fit.

Of course, Raman spectroscopy is only sensitive to phonons at the center of the Brillouin zone, and not all phonon modes are Raman active. To verify our hypothesis that the *e*-ph coupling is weak and does not play a leading role in formation of CDW in purple bronze, we conducted a detailed study of the ARPES dispersion. This method is very sensitive and any significant coupling is visible as kinks in the dispersion. In Fig. 3(b), the black line is a parabolic fit to ARPES data and reflects a "bare," non-interacting dispersion. Surprisingly, there is no evidence of deviations of the data from this line (i.e., kinks), signifying the absence of strong *e*-ph coupling. Real part and imaginary parts of the self energy extracted from MDCs are shown in Figs. 3(c) and 3(d), respectively. Again, there is no evidence of the coupling of electrons to phonons. Based on our ARPES data, any peaks in the real part of the self energy must be smaller than the 3 meV error bars; by contrast, $\mathrm{MgB_2}$ has an ~80 meV peak [62] and $\mathrm{NbSe_2}$ an ~30 meV peak [6] in real part of the self energy. The absence of such features is highly unusual and implies that the *e*-ph coupling does not play a significant role in the formation of the CDW.

At low photon energy (6.7 eV) the expected photoelectron escape depth is ~30 Å. Significant intensity of the surface band suggests that it originates from the top slab of the molybdenum oxide, rather than a single atomic layer. LEED measurement at 54 eV probes mostly the top atomic layer. Raman probe depth of ~250 nm is mostly dominated by bulk.

The combined ARPES and Raman data imply that *e*-*e* interaction must play a role in the CDW formation here.

Indeed, *e-e* interactions drive a CDW in the $Sr_{14}Cu_{24}O_{41}$ ladder compounds [37] and possibly in the cuprates [19,20,32–35], where magnetic interactions are deemed important. However, $K_{0.9}Mo_6O_{17}$ shows no signs of magnetism. The FS of $K_{0.9}Mo_6O_{17}$ consists of quasi-1D lines, leading to extremely good nesting. The on-site *e-e* interaction is repulsive in the CDW channel; however, further neighbor interactions are attractive. Normally, one would not expect these in a good metal; however, the quasi-1D nature of the bands reduces the screening of the Coulomb interaction. Therefore, further neighbor interactions could stabilize a CDW at wave vectors connecting two of the quasi-1D FSs, consistent with the wave vectors here. The relevance of quasi-1D physics [63] is also seen in the power law behavior of $\mathrm{Im}\Sigma(\omega) \sim \omega$. $\mathrm{Im}\Sigma(\omega)$ has been extracted from the data [Fig. 3(d)] and is linear with energy at least up to 0.4 eV. The possibility of such interactions stabilizing a CDW was examined in the related quasi-1D $Li_{0.9}Mo_6O_{17}$, which similarly shows Luttinger liquid behavior [64,65]. Although no CDW forms in $Li_{0.9}Mo_6O_{17}$, the estimated Coulomb parameters put it close to the regime where *e-e* interactions could induce a CDW. Thus, the CDW in $K_{0.9}Mo_6O_{17}$ is likely due to *e-e* interactions enhanced both by strong nesting and quasi-one-dimensionality. The screening is further reduced at the surface, explaining the surface strong coupling behavior.

The behavior of the two energy gaps, the bulk CDW order measured by x-ray and surface CDW measured by LEED are shown in Fig. 4(a). The bulk CDW gap decreases in BCS-like fashion. In contrast, the large energy gap at the surface remains open up to 230 K. Its magnitude does not change with temperature, instead the spectral weight is transferred to the metallic band that crosses E_F. The ratio $(2\Delta/k_B T_C)$ for the bulk band is ~2.5, while at the surface it is in excess of 15. We schematically illustrate the formation of the surface and bulk CDW and their corresponding band structures in Figs. 4(b) and 4(c). Perhaps the most astonishing aspect of our results is that despite such different behavior at the surface and in the bulk, the electronic structures are essentially identical at high temperature. By contrast, the single layer material with enhanced T_{CDW} has an electronic structure different from the bulk counterpart [43,66]. It is difficult to conclude whether or not the surface CDW is incommensurate based on LEED data. The gap minimum of the dispersion at the surface and the gap minimum in the bulk are both located at k_F of the normal state. This suggests that surface CDW is commensurate just like bulk. A high resolution scanning tunneling microscopy study would certainly be desired to shed light on this and other issues that still remain open.

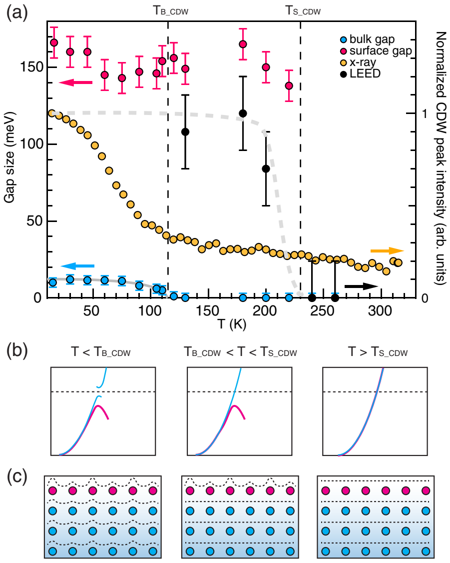

FIG. 4. Summary of the temperature-dependent CDW gap and band structure evolvement. (a) Temperature dependence of the surface (red solid circles) and bulk (blue solid circles) CDW gap. The surface gap is extracted from the back bending point of the surface band and the bulk gap is extracted from the leading edge shift of k_F EDCs [Fig. 1(j)]. The gray solid line is a BCS-like temperature dependence with $\Delta_0 = 12$ meV. The integrated intensity of the CDW peak measured by x-ray diffraction [Fig. 2(b)] is shown with yellow solid circles. Black data points represent the intensity of CDW peaks measured by LEED. Dashed line is a guide to the eye. (b) Illustration of the surface (blue line) and bulk (red line) band dispersion. (c) Illustration of surface (red) and bulk (blue) CDW formation in real space. Dashed lines represent a density distribution of conducting electrons.

In summary, we report the discovery of an extraordinary CDW at the surface of purple bronze that lacks any signatures of *e*-ph coupling and has an energy gap enhanced by more than an order of magnitude from the bulk. The strong coupling, combined with the dominant role of *e-e* interaction makes the surface charge order in purple bronze a CDW counterpart to unconventional superconductivity. Indeed, a suppression of this CDW order, if possible, may lead to an exotic superconducting state.

Raw data for this manuscript is available at [67].

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