Inhomogenities of the CDW vector at the (-201) surface of Quasi-1D blue bronze Rb$_{0.3}$MoO$_3$

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Inhomogenities of the $b^*$ surface component of the CDW wave vector, probed by LT-UHV-STM, were observed at the (-201) surface of quasi-1D blue bronze Rb$_{0.3}$MoO$_3$ cleaved in-situ. Whereas on the scale of tens of nanometers, the CDW wave vector might be constant, significant changes were observed on the scale of microns in STM measurement. On the basis of first-principles DFT calculations, it is found that these inhomogenities could be due to a change in the stoichiometry of surface alkali atoms taking place after the cleavage process. It is shown that differences in the stoichiometry of surface alkali atoms change the filling of the partially filled bands of the top most layer. Consequently, in equilibrium with the bulk layers, this results in a local surface potential that changes the surface nesting vector and hence the periodicity of the CDW modulation. The DFT predictions for the changes in surface nesting vector are consistent with the observed experimental inhomogenities probed by STM.

1. Introduction

Low-dimensional molybdenum and tungsten oxides and bronzes have been the focus of much attention because of the Peierls transition and fascinating associated phenomena they exhibit [1]. The blue bronzes, $A_0.3$MoO$_3$ ($A = K$, Rb, Tl), are quasi-one-dimensional metals exhibiting a metal to insulator transition leading to a charge density wave (CDW) ground state and are among the most intensely studied of these materials. Their crystal structure is built from MoO$_3$ layers in between which the cations reside (see Fig. 1) [2]. Despite many attempts, observation of the CDW in these materials by scanning tunneling microscopy (STM) has been elusive. Only very recently, high resolution STM images of an in-situ cleaved (-201) surface of the rubidium blue bronze have been obtained at low-temperature and in ultra-high vacuum (UHV) [3]. Both the molecular lattice and the CDW superlattice were observed simultaneously at temperatures well below the CDW transition temperature. In average, the value of the projected CDW wave vector onto the cleavage plane measured by STM was in agreement with measurements from bulk and surface sensitive techniques.

We report experimental results concerning the existence of inhomogenities in the CDW vector at (-201) in-situ cleaved surface of the rubidium blue bronze Rb$_{0.3}$MoO$_3$ probed by STM. Whereas 0.75$b^*$ is the bulk in-chain component value of the CDW wave vector, the STM probed values ranged from about 0.65$b^*$ to about 0.80$b^*$. As many of the alkali atoms, and particularly the Rb 1 indicated by the filled circles in Fig. 1 b), are expected to leave the surface after cleavage hence forming a disordered surface distribution, first-principles DFT calculations were performed to study the influence of alkali
concentration at surface on the electronic band structure. It is found that in materials like low-dimensional bronzes it is a key issue because surface alkali concentration directly affects the surface nesting vector and hence, the nature of the CDW modulation observed. The calculated changes in the surface nesting vector are in good agreement with the experimental deviations observed by STM.

![Idealized room temperature surface structure of the blue bronze Rb$_{0.3}$MoO$_3$ in the (-201) plane showing the three different MoO$_6$ octahedra. Alkali atoms are not represented in this top view. b) Idealized side view of the blue bronze projected onto the plane perpendicular to the b axis (chain axis). Filled circles correspond to Rb atoms at the uppermost position of the “surface” (labeled 1) and empty circles correspond to the Rb atoms located 1.2Å below.](image)

**FIG.1:** a) Idealized room temperature surface structure of the blue bronze Rb$_{0.3}$MoO$_3$ in the (-201) plane showing the three different MoO$_6$ octahedra. Alkali atoms are not represented in this top view. b) Idealized side view of the blue bronze projected onto the plane perpendicular to the b axis (chain axis). Filled circles correspond to Rb atoms at the uppermost position of the “surface” (labeled 1) and empty circles correspond to the Rb atoms located 1.2Å below.

### 2. Experimental Set-up and Results

We report here experimental results concerning inhomogeneities of $q_b$ measured by STM in rubidium blue bronze. Three in-situ cleaved Rb$_{0.3}$MoO$_3$ single crystals from the same batch were investigated with mechanically sharpened Pt/Ir tips. All samples were prepared in a very similar manner. They were cleaved at room temperature in UHV and rapidly introduced into the cold STM head. All the STM measurements consisted of constant current mode topographical images and were performed at 77K or at 63K, well below the transition temperature ($T_c$=180K). Optically large and flat plateaus were carefully selected to perform our measurements. Typical experimental conditions were +/-450mV for the bias voltage applied to the sample and from 50 to 150pA for the tunneling current set-point. In a previous work [3] we showed that with careful STM experiments the nearly commensurate value of the projection of $q_{CDW}$ onto the (-201) plane could be observed. Hence, defining $N=q_{b}/b^*$ where $q_{b}$ is the $b^*$ component of $q_{CDW}$, $N=0.75$ is the bulk reported value and $1-N=0.25$ is the quantity reported by STM experiments (see part II and III in Ref. 3). However, it was noticed that, on some optically flat terraces, $1-N$ deviates from the 0.25 value yielding inhomogeneities for $q_{b}$. To
allow systematic accurate measurements of the 1-N ratio for a typical 512*512 pixels image resolution, much care was taken to achieve molecular resolution and CDW resolution with scanning areas ranging from 20*20nm$^2$ to 50*50nm$^2$. This 1-N ratio was directly extracted from the two dimensional (2D) Fourier transform of the STM image. At a given tip location several measurements were always performed to ensure that the measured 1-N value was reproducible within an error bar better than 10%. The extracted CDW wave vector is found to be independent upon bias voltage polarity in the above mentioned energy range.

It is found that optically distinct plateaux (of several 100$\mu$m$^2$ area) could yield distinct values of 1-N significantly different from the 0.25 bulk value. Moreover, on the same plateau, different locations estimated to be at least several $\mu$m from each other yielded differences in 1-N values that were much greater than the typical error bar for a single location 1-N measurement, leading to clear deviations of the surface CDW wave vector with respect to the projected bulk one. On the contrary, displacements along $b$ or $a+2c$ on the scale of tens of nanometers from a given position of measurement, did not lead to noticeable changes of $q_b^*$. On the same plateau the greatest change in 1-N value ranged from 0.21 to 0.32. Figure 2 illustrates this situation for STM measurements performed on two different samples with similar imaging conditions: in a) N=0.75, the bulk value, in c) N=0.70. As a result of our study all 1-N values were found in the range 0.21 to 0.35, as indicated by the empty circles in Fig. 3 (for the N value).

FIG. 2: a) Constant current STM image of about 30*30nm$^2$ of an in situ cleaved (-201) surface of Rb$_{0.3}$MoO$_3$ in the CDW ground state at 63K with molecular and CDW resolution. Tunneling conditions are $V_{bias} = +420$mV and $I_t=110$pA. b) 2D Fourier transform of a) showing surface lattice spots indicated by vectors 2$b^*$ and 2$(a+2c)^*$ and CDW superlattice spots around each lattice spot. In this scanned zone the $b^*$ component of $q_{CDW}$ equals the bulk value, 0.25. c) Constant current STM image with similar parameters as indicated in a) but measured on another sample. d) 2D Fourier transform of c) showing the same spots as those appearing in b) but with the $b^*$ component of $q_{CDW}$ equal to 0.30, showing a clear deviation from the 0.25 bulk value.
3. First-principles DFT Calculations

The present calculations were carried out using a numerical atomic orbital DFT [4] approach, which has been developed and designed for efficient calculations in large systems and implemented in the SIESTA code [5]. We have used the generalized gradient approximation to DFT and, in particular, the functional of Perdew, Burke and Ernzerhof [6]. Only the valence electrons are considered in the calculation, with the core being replaced by non-local norm-conserving scalar relativistic pseudopotentials [7] factorized in the Kleinman-Bylander form [8]. Nonlinear partial-core corrections to describe the exchange and correlations in the core region were included for Mo [9]. We have used a single-\(\zeta\) basis set including polarization orbitals for Mo atoms, as obtained with an energy shift of 0.02 Ry [5]. We verified that the description of bulk bands for this and related bronzes using this basis size, especially at the Fermi level, is essentially the same as when using a split-valence double-\(\zeta\) basis set including polarization for all atoms. The energy cutoff of the real space integration mesh was 300 Ry. Calculations for slabs of different thickness (containing from one to four octahedral layers) were carried out. For the superlattice we used the structure of reference [10] assuming a commensurate value (0.75) of the \(b^*\) component of the CDW modulation wave vector. The Brillouin zone (BZ) was sampled using grids of (2x21x1) and (2x21x6) \(k\)-points for the slabs and the bulk, respectively [11]. The energy cutoff and \(k\)-points values were tested against well converged values.
FIG. 4: Band structure for: (a) bulk Rb$_{0.3}$MoO$_3$; (b) a slab preserving the bulk stoichiometry at the surface, and (c) a slab with a defect of Rb atoms (one every three) at the surface. In (a) $\Gamma$=(0,0,0), X'=(0.5,0,0) and Y'=(0,0.5,0) in units of the $a'^*\$, $b'^*$ and $c'^*$ reciprocal lattice vectors (see Ref. [15]). In (b) and (c) $\Gamma$=(0,0), X=(0.5,0) and Y=(0,0.5) in units of the corresponding rectangular reciprocal lattice vectors.

The band structure for bulk Rb$_{0.3}$MoO$_3$ contains two partially filled bands (see Fig. 4(a)). The CDW in this material is due to the interband nesting among these quasi-one-dimensional bands so that the CDW wave vector $q_{\text{CDW}}$ is given by $k_f^1 + k_f^2$ where $k_f^i$ is the Fermi wave vector of band $i$ [12,13,14,15]. Since there are three electrons per unit cell to fill these bands, a $q_{\text{CDW}}$ component along the chain direction of 0.75$b^*$ is predicted, which is the observed value at low temperature [16]. In order to appropriately model the (-201) blue bronze surface we carried out calculations for slabs including different number of octahedral (and rubidium) layers as well as different distributions and concentration of surface rubidium atoms. There are three rubidium atoms per repeat unit of a layer, two of them (type 2, empty circles in Fig. 1(b)) are very near the octahedral layers and the third one (type 1, filled circles in Fig. 1(b)) is equidistant of the two layers. Among all these interlayer Rb atoms, only the type 2 Rb atoms closest to the cleaved layer and the type 1 Rb atoms might remain at the surface after cleaving the sample. However, due to their position exactly in between the layers, type 1 Rb atoms have in average only 0.5 probability to remain at surface after cleavage. Since these atoms are expected to relax from their bulk crystallographic position, we optimized their position with respect to the surface. These positions were the basis for all remaining calculations.
The main conclusions of our calculations were: i) the number of octahedral layers used in the computations is irrelevant; ii) the key factor in controlling the shape of the surface bands near the Fermi level is the number of Rb atoms at the surface. Shown in Fig. 4(b) is the band structure for a surface which preserves the stoichiometry of the bulk (i.e., 1.5 Rb atoms per repeat unit). Despite the folded-like shape of the bands, due to the fact that we used a unit cell twice larger along \( b \) in order to model the partial occupation of the Rb sites, the partially filled bands are nearly identical to those of the bulk. In contrast, when the repeat unit of the cell at the surface is covered by just one Rb atom, i.e. 0.5 less than in the stoichiometric case, the band structure is noticeably different (Fig. 2(c)); the corresponding surface bands are shifted upwards with respect to those of the bulk. Calculations for the case of an excess of Rb atoms with respect to the stoichiometric situation led to an opposite band shift. After carrying out computations for several situations we conclude that different concentrations of Rb atoms at the surface generate a nearly rigid energy shift of the surface bands with respect to those of the bulk. This result has the important implication that the nesting vector at the surface changes with the Rb content since \( \mathbf{q}_{\text{CDW}} = \mathbf{k}_f + \mathbf{k}_R \). It is then possible to infer the concentration of Rb atoms at the surface that produces a given surface nesting vector (see Fig. 3).

4. Discussion

According to the present calculations, the experimental deviations observed by STM would correspond to an excess of surface alkali atoms ranging from about 0.1 to -0.35 per repeat unit. These predictions would be consistent with the hypothesis that inhomogeneities in the distribution of type 1 alkali atoms is mainly responsible for the experimental inhomogeneities observed in the CDW wavevector value at the surface. The effect on the electronic properties induced by losing surface alkali atoms has been studied by photoemission combined with Ne\(^+\) sputtering [17]. It was found that induced alkali desorption decreases the electronic spectral weight around the Fermi level and shifts away from \( E_F \) the onset of the valence band. Our experimental and theoretical studies are consistent with these observations. On the other hand the present results could seem in disagreement with angular resolved photoemission and grazing incidence x-ray diffraction [18,19] showing both that \( \mathbf{q}_b \) almost equals 0.75\( b \) under 100K. This is because STM probes \( \mathbf{q}_{\text{CDW}} \) only at the uppermost layer of the compound and locally at the nanometer scale. Both x-ray and photoemission experiments probe \( \mathbf{q}_{\text{CDW}} \) over a macroscopical in-plane scale and over deeper layers (for x-ray), which remain unaffected by the inhomogeneities present in the first layer according to the present calculations. This leads to an averaged value of \( \mathbf{q}_{\text{CDW}} \) in a macroscopical volume showing no surface inhomogeneities.

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