Electronic band structure and charge density wave transition in quasi-2D KMo$_6$O$_{17}$ purple bronze

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Abstract. High resolution angle-resolved photoemission of quasi-2D KMo$_6$O$_{17}$ purple bronze has been performed in the range from room temperature to 130 K, slightly above the charge density wave (CDW) transition ($T_c = 110$ K), and down to 35 K (well below $T_c$). In this paper we report a detailed study of how electronic band structure is affected by this transition driven by the hidden nesting scenario. The expected spectroscopic fingerprints of the CDW phase transition have been found and discussed according to the hidden one dimension and the development of a quasi-commensurate CDW. The excellent agreement between theory and our experimental results makes of potassium purple bronze a reference system for studying this type of instabilities.

1. Introduction

Molybdenum oxides and bronzes have been subject of intensive experimental and theoretical studies because they show a wide diversity of phenomena, mainly a variety of charge-density wave transitions owed to their electronic instabilities and low dimensional character. Specifically the potassium purple bronze, KMo$_6$O$_{17}$, is a quasi two-dimensional (2D) metal above the transition temperature $T_c = 110$ K. Below $T_c$ it undergoes a charge-density wave (CDW) phase transition, although the system remains metallic. Furthermore, X-ray diffraction and electron diffraction studies showed super-lattice spots at $a^*/2$, $b^*/2$, $(a^*+b^*)/2$ ($a^*$, $b^*$ being the in-plane reciprocal vectors) corresponding to a quasi-commensurate Peierls lattice distortion in the real space of $(2a, 2b, c)$. Its low dimensional character arises out of the fact that this compound is built with infinite slabs of distorted MoO$_6$ octahedra sharing corners terminated on both sides by a layer of MoO$_4$ tetrahedra. These slabs, perpendicular to the $c$ axis, are separated from each other by a layer of K monovalent ions [1, 2].

In order to explain the CDW instabilities in quasi-2D systems the notion of hidden nesting was introduced by Canadell and Whangbo [3]. Within this concept, the Fermi surfaces (FS) of these particular 2D materials can be seen as a superposition of several well nested quasi-1D pieces. This scenario of a hidden one-dimension has been widely supported, especially by measurements of the FS...
of these materials at room temperature (RT) [4-6]. However, two important issues remain open for future investigations. The first concerns the CDW state. Given the excellent understanding of the FS topology, these materials are ideal candidates for detailed studies of location, symmetry and size of the CDW gap and nature of the CDW transition. Preliminary low temperature (LT) measurements of KMo₆O₁₇ [6, 7] suggest some of the expected fingerprints of the development of a CDW state as it would be a partial gap opening and the backfolded bands formation instead of bands crossing the Fermi level at the $k_F$ momentum. This behavior would be indicative of the new periodicity of the real lattice. Nevertheless, the resolution of these earlier experiments was at the limit to reliably observe the expected features we were looking for. The more general second issue is related with the normal state. These materials, due to their intermediate character between 1D and 2D systems, become perfect to study how the electronic structure can be affected by dimensionality [8].

In this contribution we present a new high resolution angle-resolved photoemission spectroscopy (ARPES) study concerning the CDW state for KMo₆O₁₇. The evolution with temperature of the electronic band structure has been considered. At RT the identification of all the bands predicted by tight-binding calculation is possible, and the agreement with theory results is excellent. Slightly above the transition the effects of pre-transition CDW fluctuations should be taken into account to explain the band structure and the shape of the photoemission spectra. Well below the transition, the band structure is in agreement with the development of a quasi-commensurate CDW state, where a backfolded band, an umklapp band, and the corresponding gap opening have been identified along the $\Gamma M$ nesting direction.

![Figure 1.](image)

**Figure 1.** (Coloured online) Electronic structure along the (a) $\Gamma K$ and (b) $\Gamma M$ directions and the Fermi surface measured at RT. The insets in each panel indicate the portion of the Brillouin zone measured. Blue dashed lines correspond to the theoretical tight-binding bands and 1D-FS.

### 2. Experimental details

The photoemission experiments were performed at RT, 130 K and 35 K with a Scienta 200 high-resolution hemispherical electron-energy analyzer. The sample was illuminated with monochromatized photons of $h \nu = 40.8$ eV from a Gammadata He lamp. Total energy resolution was set to 10 meV and angular resolution to $\pm 0.1^\circ$, which corresponds to a momentum resolution of $\pm 0.004$ Å⁻¹. The samples were mounted on a He cryostat and cleaved *in-situ* at a base pressure better than $1 \times 10^{-10}$ mbar. Samples were grown-up by electrolytic reduction of a melted mixture of $K_0.3MoO_4$.
and MoO$_3$ [2], resulting in flakes whose typical size was $3 \times 3 \text{ mm}^2$. Low-energy electron diffraction (LEED) was used to check the high symmetry directions.

3. Results and discussion

Figure 1 shows photoemission intensity maps recorded at RT. The front view of each panel presents the electronic structure along $\Gamma K$ (panel a) and $\Gamma M$ (panel b), corresponding the latter to the nesting direction. On the top of each panel, the Fermi surface is shown, where the intensity has been integrated in a range of $\pm 15 \text{ meV}$ above and below $E_F$. Blue dashed lines indicate the 1D-FS and theoretical bands predicted by the tight-binding calculations and the hidden nesting condition. The agreement between the theoretical and experimental results is excellent, except slight deviations for a lower binding energy dispersive band.

It is remarkable how the two dispersive bands merge and cross as only one band the Fermi level at the $\Gamma M$ direction. This is in contrast with the electronic band structure reported for the very similar sodium purple bronze NaMo$_6$O$_{17}$ [9] where the two dispersive bands are distinguishable even at the Fermi level. This could be a significant difference with the potassium purple bronze, or just a misalignment of the sample. In fact, when we go some degrees apart from the $\Gamma M$ direction, the two bands are splitted and distinguished. As we approach the $\Gamma K$ direction the non-dispersive band at $\Gamma M$ begins to disperse, so we have three dispersive bands at $\Gamma K$.

![Figure 1](image1.png)

Given the excellent agreement between the theoretical and experimental data at RT we could cool down the sample to look for the expected fingerprints of a CDW transition, that are, the gap opening at nested FS portions, and the back-folding of the dispersive band. Also, due to the periodic lattice distortion, the appearance of umklapp bands with mirror-like dispersion relative to the original band is

![Figure 2](image2.png)
expected. In figure 2 the electronic structure along the \( \Gamma M \) direction at RT, 130 K, and 35 K is presented in panels (a), (b), and (c), respectively. In panel (d) the photoemission spectra taken at \( k_F \) from panels (a), (b), and (c) are shown. The dot lines in panel (a) indicate the two very close dispersive bands, while the dashed red line in panel (c) designates the dispersion of the CDW dispersive band. This line is also drawn in panels (a) and (b) for comparison.

The two main features to be noticed are, firstly, the backfolded band (panel c) at \( k_F \), which indicates the periodic lattice distortion after developing a quasi-commensurate CDW. The second more remarkable issue is the gap opening, expected at \( k_F \) in the nesting \( \Gamma M \) direction. The gap is seen in panel (d), where there is a well-defined shift at \( E_F \) in the LT spectrum. Moreover, the sharp drop in intensity compared with the RT data gives more evidences for the gap formation at \( k_F \). Other sign of the gap opening is the shift towards higher binding energy of the photoemission peak at LT. In panel (c) some dispersive states to the right of the \( \Gamma \) point are also visible. These states form a dispersive band that is attributed to an umklapp band, again in relation with the broken periodicity of the real lattice.

Finally in panel (b), it can be observed that while the backfolded band is still not fully developed slightly above \( T_c \), there is no more evidence of the crossing bands at \( k_F \). In panel (d), it is possible to follow how the gap seems to be already developed at this temperature. These two facts might be in relation with pre-transition CDW fluctuations that may be present in this compound, as has been shown in other Peierls materials [10].

4. Conclusions

In summary, the electronic structure of metallic quasi-2D KMo\(_6\)O\(_{17}\) have been characterized at both normal metallic and CDW state. At RT the agreement is excellent with tight-binding calculations and the hidden nesting behavior. At LT the spectroscopic fingerprints of a CDW transition have been found, pointing out also the importance of pre-transition CDW fluctuations in this material.

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