X-ray spectroscopy and electronic structure of MoO$_2$

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We study the electronic structure of MoO$_2$ using an extended cluster model. The calculations confirm that the compound is in a highly mixed covalent Mott-Hubbard regime. These results are then compared to other calculations and to x-ray absorption and (resonant) photoemission spectroscopies. The good agreement with the experimental spectra indicates a strong covalent character for the Mo 4d-O 2p bond. Finally, we show that, not only local charge fluctuations from the oxygen ions are necessary, but also nonlocal screenings, from the Mo dimer and from coherent (metallic) states, must be included in the description of the electronic structure of MoO$_2$.

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1. Introduction

Molybdenum compounds display a plethora of physical properties [1–6]. This is related to the wide range of oxidation states — from Mo^{2+} to Mo^{6+} — in which Mo ions appear in different systems [7]. More specifically, molybdenum oxides have attracted the attention of the scientific community for quite some time [1,7–9]. At room temperature, molybdenum dioxide (MoO$_2$) is a weakly paramagnetic conductor [2,3], which crystallizes in a distorted rutile structure (monoclinic). Because of its asymmetric structure, with Mo-Mo bonds (dimerization) along monoclinic **a** axis, this compound presents an anisotropic conductivity [8,10]. The conduction across a specific axis is also facilitated by dimerization in other Mo oxides, such as K$_x$MoO$_{2-\delta}$ [11] and MoO$_y$ [12]. It was shown that they actually present superconducting behavior at different values of T$_C$, and with a direct correlation between the anomalous behavior and the anisotropic electron doping observed in these compounds [12].

Usually, transition metal oxides show a splitting of its d orbitals into the t$_{2g}$ and e$_g$ bands, due to crystal field effect, whenever in octahedral (O$_h$) symmetry. In the case of MoO$_2$, however, the band derived from the x^2 - y^2 orbital is separated into bonding and antibonding components (so-called d$_{||}$ and d$_{||}$* bands) due to the Mo ions pairing along monoclinic **a** axis. The remaining t$_{2g}$ (xz and yz) and e$_g$ (z^2 and xy) orbitals are less affected by the dimerization and are usually labelled π* and σ* band, respectively. This is depicted in the top panel of Fig. 1.

Band structure and cluster model calculations showed that the metallic conductivity of MoO$_2$ arises from direct overlap of Mo 4d wave functions due to the distortion [8,13]. Ultraviolet and x-ray photoemission (UPS/XPS) and absorption (XAS) measurements were also made for this compound and the results agree with optical reflectivity measurements. The lowest energy Mo 4d unoccupied states are located 2.5 eV above O 2p occupied band [4,14]. The O 2p unoccupied band is composed by three peaks above E$_F$ [8]. For occupied states, the measurements show two main structures: Mo 4d and O 2p bands. The former is composed by two peaks located at ~1.5 and ~0.5 eV below E$_F$. The later band is located at higher energies, between −9.0 and −2.0 eV [7,13,15].

In this work, we study the electronic structure of MoO$_2$ via an extended cluster model. Our aim is to show the important ingredients that must be included in order to describe correctly the electronic structure of MoO$_2$. The calculation results are compared to other techniques, explicitly, band structure calculations, x-ray (Mo L$_3$ resonant) photoemission and absorption spectroscopies. There is an overall good agreement between the cluster model calculations (using the same parameters) and all the experimental spectra presented here. The results suggest that, for this compound,

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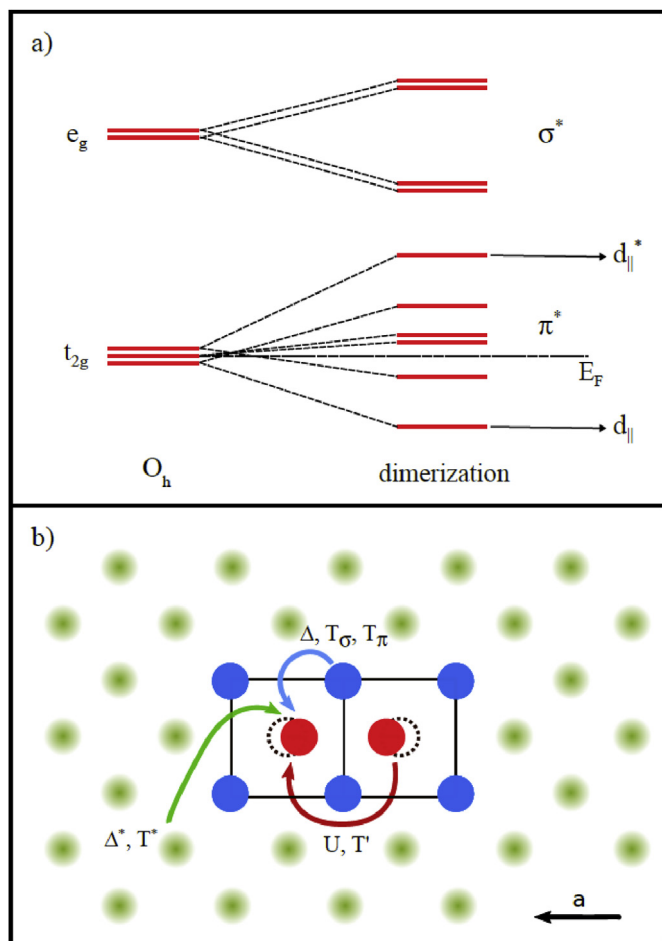E-mail address: mossanek@fisica.ufpr.br (R.J.O. Mossanek).

Fig. 1. (Top) The crystal field effect in octahedral symmetry and the expected effect on the Mo 4d levels due to the Mo-Mo dimerization along the monoclinic **a** axis. (Bottom) Schematic representation of the local (Mo 4d-O 2p) and nonlocal (Hubbard and coherent) charge fluctuations and the parameters associated with each one. The green, blue and red circles represent the coherent medium and the oxygen and molybdenum ions, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

it is necessary to include localized charge fluctuations from the oxygen states, as well as two nonlocal screening channels: (i) a Hubbard fluctuation from the neighboring Mo^{4+} site, and (ii) a delocalized (metallic) charge fluctuation from a coherent band.

2. Experimental details

Polycrystalline MoO_2 samples were prepared by solid-state re-action using Mo (Sigma-Aldrich, 99,99%) and MoO_3 (Sigma-Aldrich, 99,9%) powders. The reagents were mixed and pressed into pellets applying pressures of 300 up to 400 MPa. The pellets were encapsulated in quartz tubes under vacuum and subsequently heat treated at 400 °C for 24 h and then at 700 °C for more 72 h. The heating and cooling rates used were of 100 °C/h. The crystalline phase was confirmed by powder x-ray diffraction at room temperature and the resistivity as a function of temperature was measured as well. Further information on sample characterization can be found elsewhere [12].

The photoemission (PES) and resonant photoemission (RPES) experiments were done at the SXS beamline [16], of LNLS, Campinas, Brazil. The incident photon energies were adjusted to 1840 eV (~2500 eV) for the PES (RPES) technique, providing a resolution of

about 0.4 eV (0.5 eV), and a depth analysis of ~25 Å (~30 Å) [17]. The Fermi level was determined using a clean gold foil. The O 1s x-ray absorption spectroscopy (XAS) was performed at the SGM beamline, of LNLS, Campinas, Brazil. The overall resolution was about 0.5 eV, and the energy calibration was obtained with reference samples. The polycrystalline MoO_2 samples were scrapped with a diamond file before each measurement to eliminate any surface contamination. All the spectra were recorded at room temperature and with a base pressure of around 10^{-9} mbar.

3. Calculation details

3.1. Cluster model

The cluster model is based on an octahedron $(MoO_6)^{-8}$ with a central Mo^{4+} ion surrounded by six oxygen O^{2-} ions in O_h symmetry. In this symmetry, only two linear combinations of O 2p atomic orbitals interact with Mo 4d orbitals giving rise to the t_{2g} (π bond) and e_g (σ bond) molecular orbitals [18], which are separated by the crystal field effect (10 Dq), as shown in the top panel of Fig. 1. The cluster was solved using the standard configuration interaction method [19,20], which consists in expanding the ground state beyond the ionic picture, making it a linear combination of different configurations of many particles, such as: $4d^2$, $4d^3\underline{L}$, $4d^4\underline{L}^2$, etc., where $\underline{L}$ denotes an O 2p hole (called here local screening channel). The main parameters, used in these calculations, are the d-d Coulomb energy (U = 1.8 eV), the p-d charge-transfer energy (Δ = 6.9 eV), and the p-d transfer integral (T_σ = 3.0 eV). Each configuration is further split into different multiplets due to the intra-atomic exchange (J = 0.40 eV), the crystal field splitting (10Dq = 3.6 eV), and the p-p transfer integral (Tp = ppσ - ppπ = 0.90 eV). The different final states are obtained from the ground state by removing/adding an electron for the removal/addition state. Each Hamiltonian is solved by exact diagonalization and the spectral weight A(ω) is calculated using the sudden approximation [21],

$$A(\omega) = \sum_j \left| \left\langle \psi_{FS}^j \middle| \widehat{O}_{FS} \middle| \psi_{GS} \right\rangle \right|^2 \delta\left(\omega \pm \left(E_{FS}^j - E_{GS} \right) \right) \qquad (1)$$

in which $|\psi_{GS}\rangle$ (E_{GS}) and $\left|\psi_{FS}^j\right\rangle$ (E_{FS}^j) represent the ground state (energy) and the j-th possible final state (energy), respectively, and $\widehat{O}_{FS}$ is the operator corresponding to each experimental procedure. In the case of the valence band PES, this operator is related to the removal of a Mo 4d of an O 2p electron, whereas in the case of O 1s XAS, it is related to the addition of an O 2p electron. Finally, in the case of RPES, the operator has two contributions: from the regular PES channel, and from an indirect channel (see section 4.4 for more details). The discrete final states are convoluted with a Gaussian function to simulate band dispersion or the experimental resolution, whenever appropriate.

3.2. Nonlocal screening channels

The usual cluster model was made famous for the study of the electronic structure of mostly insulating systems such as MnO [22], NiO [23] and other transition metal oxides [24]. But, the local character of its approach is not enough to threat other types of materials, in which is necessary to include different ingredients.

In the case of MoO_2, we state that it is important to include, apart from the local one, two extra nonlocal screening channels, as shown in the bottom panel of Fig. 1: a Hubbard screening channel, to simulate the dimerization between neighboring Mo^{4+} sites; and a coherent screening channel, to account for delocalized (metallic)