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Strongly correlated transition metal compounds investigated by soft X-ray spectroscopies and multiplet calculations

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ABSTRACT

Direct probe of Mott–Hubbard (MH) to charge-transfer (CT) insulator transition in the MF₂ (M = Cr–Zn) family of compounds was observed by combining FK and ML X-ray emission spectra (XES). This transition is evident as a crossover of the F-2p and M-3d occupied states. By combining FK XES data with FK edge X-ray absorption (XAS) data we directly obtained values for the M-3d Hubbard energy (U_{dd}) and the F-2p to M-3d charge-transfer energy (Δ_{CT}). Our results are in good agreement with the Zaanen–Sawatzky–Allen theory. We also present three examples where X-ray absorption at the transition metal L_{2,3} edges is used to study the oxidation state of various strongly correlated transition metal compounds. The metal oxidation state is obtained by direct comparison with crystal field multiplet calculations. The compounds are CrF₂, members of the La_{1-x}Sr_xCoO₃ family, and the MVO₃ (M = La and Y) perovskites.

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1. Introduction

Core-level spectroscopies are well established tools to study the electronic structure of transition metal (TM) compounds [1]. X-ray absorption spectroscopy (XAS) provides information about electronic states in the conduction band [1,2] and X-ray emission gives complementary information about occupied states [1]. In the soft X-ray region the electronic transitions follow electric-dipole selection rules and therefore one probes electronic states with inherent atomic and orbital selectivity. This is particularly useful in the study of strongly correlated TM compounds for which XAS and XES at the metal L_{2,3} edge probe, respectively, the metal 3d conduction and valence bands. The absorption spectra are quite sensitive to the intra-atomic effects, including the TM oxidation state. The TM L_{2,3} absorption spectra can help to identify the TM oxidation state and ligand to metal charge transfer effects [1]. Also, a comparison of emission at the metal L_α and the ligand K_α lines gives a very good indication of the site- and symmetry-projected states of the valence band [3].

In this paper we review recent work in which we observed the Mott–Hubbard to charge-transfer insulator transition in the

MF₂ (M = Cr, Mn, Fe, Co, Ni, Cu) family of 3d-transition metal di-fluorides [3]. We also present three examples in which a combination of XAS and theory is used to determine the TM oxidation state in 3d strongly correlated compounds. The first example deals with a member of the MF₂ family, namely, CrF₂, for which there is still a significant disagreement between a single oxidation state atomic multiplet calculation for the L_{2,3} XAS spectrum and experiment [1,4,5]. In the other two examples we show how X-ray absorption at the L_{2,3} edge can be used to determine the oxidation state of transition metal perovskites which, because of their many interesting properties have attracted widespread interest [6]. There are already examples of determination of transition metal oxidation states in complex samples that is extracted by comparing their X-ray absorption data with reference experimental spectra of controlled oxidation states [7]. There is also work in which several oxidation states of vanadium compounds were determined by comparison with multiplet calculations [8].

In the second example we present XAS results for the La_{1-x}Sr_xCoO₃ (x = 0, 0.15, 0.3 and 0.5) perovskite family. This is a very interesting system with promising applications as a catalyst [9]. Its performance is linked to changes in its electronic structure induced by the strontium doping fraction x. The increase of strontium content will in principle increase the oxidation state of Co into an unphysical Co⁴⁺ [9]. The doping process is usually accompanied by oxygen loss in the compound, which would compensate for this change in the cobalt oxidation state [10]. Therefore, to understand

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the effect of strontium doping in this perovskites, a detailed determination of the cobalt oxidation state is very valuable [10].

In the third example we study the vanadium oxidation state of the MVO_3 ($M = La, Y$) perovskites. They are both antiferromagnetic Mott insulators in which the nominal vanadium oxidation state is V^{3+} . They are strongly correlated systems that have very interesting properties such as a temperature dependent metal-insulator transition, and both exhibit spin, orbital and charge ordering [11]. Evidence of the presence of V^{3+} and V^{4+} in layered $LaVO_3$ samples has been studied by X-ray absorption at the vanadium L-edge [8], where they found a strong presence of V^{4+} in the bulk.

2. Experiment

Fresh commercially available polycrystalline MF_2 samples ($M = Cr-Zn$) from Sigma-Aldrich with nominal purity greater than 99.9 % were prepared inside a N_2 flow bag and introduced inside the UHV experimental chamber. The polycrystalline samples of the $La_{1-x}Sr_xCoO_3$ ($x = 0, 0.15, 0.3, \text{ and } 0.5$) compounds were prepared by standard solid state reaction [12], using La_2O_3 , $SrCO_3$, and Co_2O_3 powders with a purity greater than 99.9% as starting materials. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) confirm the formation of the $La_{1-x}Sr_xCoO_3$ structure with inhomogeneous grain size. The morphology and crystal size of the final samples were studied by transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [13]. The MVO_3 ($M = La, Y$) samples were obtained by reduction of MVO_4 prepared by two different methods: solid state reaction and sol-gel acrylamide polymerization [14,15]. Reduction was achieved by heating the MVO_4 samples to $850^\circ C$ under vacuum, in the presence of a metallic Zr rod. The resulting powders were characterized by X-ray diffraction, and their size and morphology were studied by TEM and SEM. The only significant difference between the two samples was that the one prepared by sol-gel reaction presented a more homogeneous distribution of smaller crystals compared with the solid-state sample [14,15].

All X-ray absorption and emission measurements took place at beamline 8.0.1 of The Advanced Light Source in Berkeley [16]. Experimental X-ray absorption spectra were recorded in the total electron yield (TEY) mode. All XAS and XES spectra presented in this work were recorded at room temperature.

3. Crystal field multiplet calculations

Atomic multiplet crystal-field calculations were performed for different ionic species of the transition metal in CrF_2 , $La_{1-x}Sr_xCoO_3$ and MVO_3 ($M = Y, La$), [17,18]. In these calculations an essentially atomic view of the orbitals is considered and it does not take into account their covalent character. They included intra-atomic multiplet and crystal field effects for CrF_2 and also charge transfer effects for the perovskites [17,18]. The X-ray absorption cross sections were then normalized to the number of 3d holes [18]. These are all semi-empirical calculations for which the crystal field parameters and the charge transfer energy were varied until the best agreement between theory and experiment was obtained. The multiplet structure is calculated in terms of the intra-atomic Slater integrals which are reduced from their Hartree-Fock values to take into account some degree of electron-electron correlation [19]. For CrF_2 crystal field effects are given in D_{4h} symmetry by the 10Dq, Ds and Dt parameters [17]. For the perovskites the calculation is in O_h symmetry, and therefore only the 10Dq crystal field energy is needed. However, for these compounds we had to include charge transfer effects. The parameters used are the dd Hubbard energy U_{dd} , the 2p-3d core-hole potential U_{pd} , and the ligand-to-metal charge transfer energy Δ_{CT} [17]. Charge transfer

Table 1
Parameters used in the CrF_2 spectra calculation.

Parameter	Cr^+	Cr^{2+}	Cr^{3+}
10Dq (eV)	0.80	0.85	0.80
Ds (eV)	0	0.17	-0.20
Dt (eV)	0	-0.07	0.20
Coefficient (this work)	0.17	0.35	0.47
Coefficient (spectrum in Ref. [4])	0.24	0.38	0.38

Table 2
Parameters used in the calculation of the $La_{1-x}Sr_xCoO_3$ spectra.

x	0	0.15	0.3	0.5
10Dq (eV)	1.28	1.25	1.20	1.20
Δ_{CT}	4.0	3.7	3.3	3.20

effects induces mixing of the $3d^n$ and $3d^{n+1}\underline{L}$ configurations in the transition metal, where \underline{L} represents a configuration with a hole in the ligand 2p band. The calculation gives the energy of all irreducible representation states of the ground ($3d^n$, $3d^{n+1}\underline{L}$) and excited ($2p^5 3d^{n+1}$, $2p^5 3d^{n+2}\underline{L}$) configurations. It also gives the transition matrix element between corresponding pairs of states in these two groups. For each oxidation state the transition matrix elements are expressed in terms of a single atomic reduced radial transition matrix element, $\langle 2p||r||3d \rangle$. This approximation neglects spin-orbit and orbital relaxation effects in the transition matrix elements.

In an early crystal field multiplet calculation for CrF_2 , Theil et al. [4] used a rather large value of the Ds parameter while trying to reproduce the broad L_3 and L_2 features in their spectra. By doing this they only achieved fair agreement with their experimental results. Their interpretation was [4] that it is an effect introduced by a Jahn-Teller distortion for this $3d^4$ configuration. This large Ds parameter introduces a change in the expected ordering of the D_{4h} orbitals [4,17]. In the present work, instead, the calculation considered three oxidation states for chromium, namely, Cr^+ , Cr^{2+} and Cr^{3+} . The X-ray absorption spectrum was then a superposition of the three spectra. In this fashion much better agreement between experiment and theory for the data of ref. [4] and our data was obtained. In both cases we used the same values of the crystal field parameters. Also, no change in the orbital ordering was found. The values of the crystal field parameters used are given in Table 1. The lifetime broadening (FWHM) was 0.28 eV [20] and the experimental resolution was 0.50 eV.

For the perovskites (MVO_3 and $La_{1-x}Sr_xCoO_3$) the calculation considered the atomic multiplet and crystal field effects in O_h symmetry which only requires the crystal field energy 10Dq. However, given the presence of oxygen, charge transfer effects now play a major role. Modeling the TM $L_{2,3}$ XAS spectra requires accounting the attracting potential exerted by the 2p core hole on the valence electrons. This is captured by the difference between U_{dd} and U_{pd} , which is usually set to -2 eV for oxides [17]. The charge transfer energy Δ_{CT} and 10Dq were varied in each calculation to reach the best agreement with experiment. Three ionic states were used for cobalt, namely Co^{2+} , Co^{3+} , and Co^{4+} and two ionic states were used for vanadium, namely V^{3+} and V^{4+} . The parameters used in the cobalt calculation are shown in Table 2. The lifetime broadening was 0.50 eV and the experimental resolution was 0.50 eV.

For vanadium we performed the calculation in O_h symmetry. For the two families of compounds we only used two values of the crystal field parameter 10Dq, namely 1.7 eV for V^{3+} and 1.4 eV for V^{4+} . For the two oxidation states, the charge transfer energy was $\Delta_{CT} = 0.0$. The lifetime broadening was 0.25 eV for L_3 and twice this value (0.50 eV) to take into account the large broadening of the L_2 structure introduced by the Coster-Kronig decay of the $2p_{1/2}$ core-hole [21]. The absorption spectra of all four compounds were then

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