Resonant photoemission at the 2*p* edge in compounds containing Mn with different valencies

M. C. Richter[1], J. M. Mariot[2], O. Heckmann[1], L. Kjeldgaard[3], B. S. Mun[4], C. S. Fadley[4], K. Hricovini[1]

[1]LMPS, Université de Cergy-Pontoise, Neuville/Oise, 95031 Cergy-Pontoise, France, [2]LCPMR (UMR 7614), Université Pierre et Marie Curie, 75231 Paris Cedex 05, France
[3]MAX-lab, Lund, Sweden, [4] Materials Sciences Division, LBNL, Berkeley, CA 94720, USA

Introduction

Resonant photoemission permits to probe hybridization and localization of photo-excited electrons. Two different behaviors are observed: in the radiationless Raman regime, the kinetic energy of the outgoing electrons follows the incoming photon energy, while in the Auger regime the electrons are detected at constant kinetic energy.
The comparison between the photon energy E_c at which Raman and Auger behaviors cross and the energy E_X at which absorption is at a maximum (resonance energy) contains information not only on the electronic band structure but also on the dynamics of its electrons as an answer to the photon created core hole. We report here on a study of manganese in various environments, i.e. with different nominal valencies. The purpose of our study is to link the influence of the Mn valency and insulating/metallic character of the compound to the Raman/Auger behavior and to search for some general trends in order to use resonant photoemission in a more powerful way for elucidating the electronic structure of matter.

Experimental

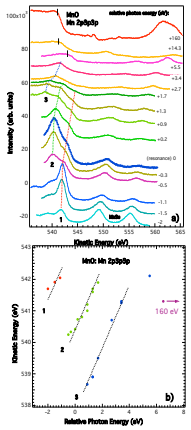
The experiments on bulk MnO were performed on the beam line I511-1 of the MAX-lab storage ring (Lund) using a modified SX-700 monochromator, which gives a flux of 10^{12} photons/s at a typical resolving power of 5000. Therefore the width of the incoming radiation is small compared to that of the resonance. Annealing to 800 K cleaned the MnO surface, as checked by photoemission, which show that no carbon was present on the surface. The Mn 2*p* absorption spectrum was typical of manganese in a d^5 configuration. The LSMO sample was measured on the beam line 9.3.2 of the Advanced Light Source (ALS) at the Lawrence Berkeley National Laboratory using a SGM monochromator with 10^{11} - 10^{12} photons/s at a resolving power of about 5000. Thin-film samples of LSMO (~1000 Å thickness) deposited on $SrTiO_3$ (STO) were produced by laser ablation in the CRISMAT laboratory, Caen, France.

Mn 2p3p3p decay

(beam line I511-1 of the MAX-lab, Sweden)

a) raw spectra
b) kinetic energy of the different transitions as a function of the photon energy
the dotted straight lines have a slope of one, indicating pure Raman behaviour.

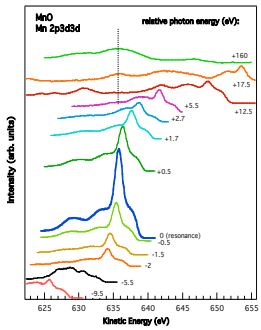
In b) we plot the kinetic energy of each of the three 2*p*3*p*3*p* features indicated in fig. a) as a function of the incoming photon energy. In this representation a line with slope unity indicates Raman behavior and a horizontal line corresponds to a classical Auger transition. Only from ≈ 4.2 eV above E_X on we find a classical Auger behavior.



Mn 2p3d3d decay

(beam line I511-1 of the MAX-lab, Sweden)

The Mn 2*p*3*d*3*d* decay does have the shape of the direct valence band photoelectron spectrum, which has been recorded at 9.5 eV below resonance. Approaching the resonance the dominant peak in this feature increases stronger than the other transitions. It takes the shape, with the same proportions of features contained in it, of the direct photoemission from the valence band only at about 20 eV above E_X. At photon energy of about 5 eV above resonance, one clearly detects the appearance of the classical 2*p*3*d*3*d* Auger transition, the shape of which is different from that of the Raman transition but has the same kinetic energy as the resonance spectra.



Mn 2p3p3d decay

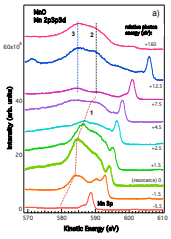
MnO, peak 1: Raman behavior up to ≈ 5 eV above resonance. Peaks 2 and 3 appear in the spectra approximately at ≈ 5 eV above resonance. They seem to be the final classical Auger transitions which we find far above (160 eV) resonance at the same kinetic energy as the resonance spectra. The 2*p*3*p*3*d* resonance feature is broad and has the same structure at resonance as what we have found for 0.2 ML Mn/Cu (M.C. Richter et al, Phys. Rev. B 63 (2001) 205416.)

0.2 ML Mn/Cu thin film: "pure" 2*p*3*p*3*d* Auger electrons only from about 1 eV above resonance on, with quite a large area of transition around resonance .

MnO/Cu thin film: Raman behavior stops just below resonance, the metallic substrate under the oxide thin film allows faster delocalization of the photon-excited 3*d* electrons, explaining the difference from the bulk MnO crystal.

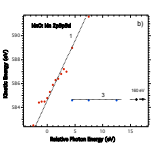
Mn thick film: the 3*d* band is implied in the auto-ionization process and plays an important role. for the metallic sample the decay feature is less structured (not shown) than for the Mn thin film or the insulating MnO crystal. Also the Raman/Auger behavior indicating the degree of 3*d* electron localization on the timescale of auto-ionization is characteristic for metallic/insulating systems with more or less localized 3*d* electrons. For the Mn thick film we found a classical Auger behavior from 1.65 eV below resonance on.

$La_{0.7}Sr_{0.3}MnO_3$ (LSMO) perovskite, (Mn in mixed valence 3+ / 4+): Raman-Auger crossing at E_c = 1.3 eV below resonance. The shape of the 2*p*3*p*3*d* feature is similar to that observed for MnO, i.e., it shows atomic character. Three transitions, plus the direct Mn 3*p* photoelectron peak, can be distinguished. The peculiarity of the Raman-Auger curves is the oscillation about the straight lines. We explain it qualitatively by a variation of intensity of the different multiplet terms.

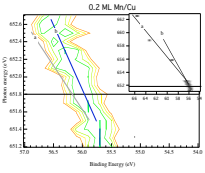


MnO crystal

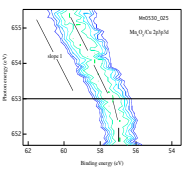
(ALS, Berkley)



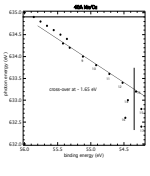
0.2 ML Mn/Cu thin film



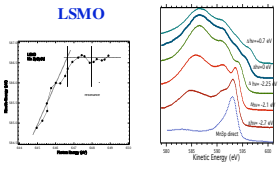
MnO/Cu thin film



Mn/Cu thick film



LSMO



Conclusions

In conclusion, the Raman-Auger characterization of three main radiationsless decays consecutive to the creation of a Mn 2*p* hole is complicated by the appearance and disappearance of different transitions. The long persistence of a Raman behavior above resonance for bulk MnO samples is a surprising result meaning that the photo-excited 3*d* electron stays in the vicinity of the core hole and gives its surplus energy to the outgoing electron. The comparison of the results obtained for various Mn compounds underlines the interplay of the valency and the metallic/insulating character of the material in the determination of the spectral response. The valency understood in terms of the number of electrons in the Mn 3*d* orbital influences the screening dynamics of the Mn 2*p* core hole and the insulating character of the material reinforces the atomic character of the transitions.