

# Observation of Multi-Atom Resonant Photoemission via Secondary Processes: Auger Decay and X-ray Fluorescence

E. Arenholz,<sup>1</sup> A.W. Kay,<sup>1,2</sup> C.S. Fadley,<sup>1,2</sup> M.M. Grush,<sup>3</sup>  
T.A. Callcott,<sup>3</sup> D.L. Ederer,<sup>4</sup> C. Heske,<sup>5,6</sup> Z. Hussain<sup>5</sup>

<sup>1</sup> Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720

<sup>2</sup> Department of Physics, University of California-Davis, Davis CA 95616

<sup>3</sup> Department of Physics, University of Tennessee, Knoxville TN 37996

<sup>4</sup> Department of Physics, Tulane University, New Orleans LA 70118

<sup>5</sup> Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley CA 94720

<sup>6</sup> Present address: Experimentelle Physik II, Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

## INTRODUCTION

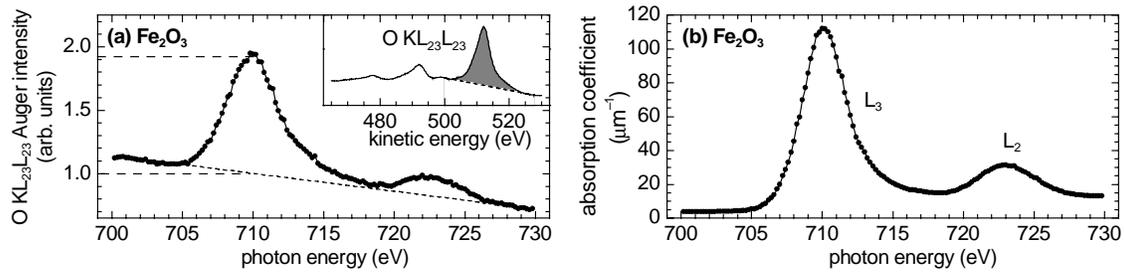
Intraatomic resonant photoemission is a well-known and powerful tool for electronic structure studies [1]. It is however only very recently that a closely related interatomic effect which has been termed multi-atom resonant photoemission (MARPE) has first been observed at the ALS [2]. MARPE occurs in photoemission from a core level of one atom as the photon energy is tuned to a deeper lying core absorption edge of another type of atom in the vicinity of the emitting atom. This interatomic resonance leads to a significant increase of up to 100% in the core photoemission intensity of the emitter as compared to excitation off resonance [2]. Since the MARPE process results in an enhanced probability of forming a particular core hole on the emitting atom, it should also be possible to detect the effect via the secondary decay processes of this hole, specifically Auger electron emission and fluorescent soft x-ray emission. To investigate these possibilities, we have studied the photon energy dependence of both the O KLL Auger intensity (inset in Fig. 1(a)) at the Fe  $L_{3,2}$  edges in  $\text{Fe}_2\text{O}_3$  and the O  $K_\alpha$  fluorescence radiation intensity (Fig. 2(a)) at the Mn  $L_{3,2}$  edges in MnO; both processes result from filling an initial O 1s hole.

## EXPERIMENTAL

Electron emission measurements were performed on beamline 9.3.2 of the ALS [3,4]. Fluorescence experiments were carried out using the grating spectrometer on ALS beamline 8.0.1 [5]. Samples consisting of an  $\text{Fe}_2\text{O}_3$  epitaxial thin film [6] and a single crystal of MnO(001) were cleaned by appropriate annealing, in oxygen for  $\text{Fe}_2\text{O}_3$  and in ultra-high vacuum for MnO. The sample temperature was ambient ( $\approx 300$  K) for  $\text{Fe}_2\text{O}_3$  in all measurements and for MnO during fluorescence experiments. Photoemission and partial electron yield measurements on MnO were performed at  $\approx 600$  K to prevent sample charging [7]. The angle of light incidence,  $\theta_{\text{in}}$ , was  $20^\circ$  with respect to the  $\text{Fe}_2\text{O}_3$  sample surface and the electrons were collected in normal emission. An angle of  $90^\circ$  was maintained between the exciting x-rays and the photoelectron/fluorescence detector for all experiments on MnO, with the incidence angle  $\theta_{\text{in}}$  being systematically varied (see inset in Fig. 2(a)).

## RESULTS

Fig. 1(a) shows the variation of the the O  $KL_{23}L_{23}$  intensity with photon energy near the Fe  $L_{3,2}$  edges. For comparison, Fig. 1(b) shows the  $\text{Fe}_2\text{O}_3$  absorption coefficient as measured with partial electron yield and an identical photon energy resolution. The O  $KL_{23}L_{23}$  intensity clearly shows about 90% enhancement at the Fe  $L_3$  edge as compared to the expected intensity without interatomic excitations, which is estimated by a linear interpolation of the Auger intensity below and above the Fe  $L_{3,2}$  edges (dashed line in Fig. 1(a)). This enhancement also is found to follow very closely the x-ray absorption coefficient in Fig. 1(b), in agreement with prior MARPE studies [2].

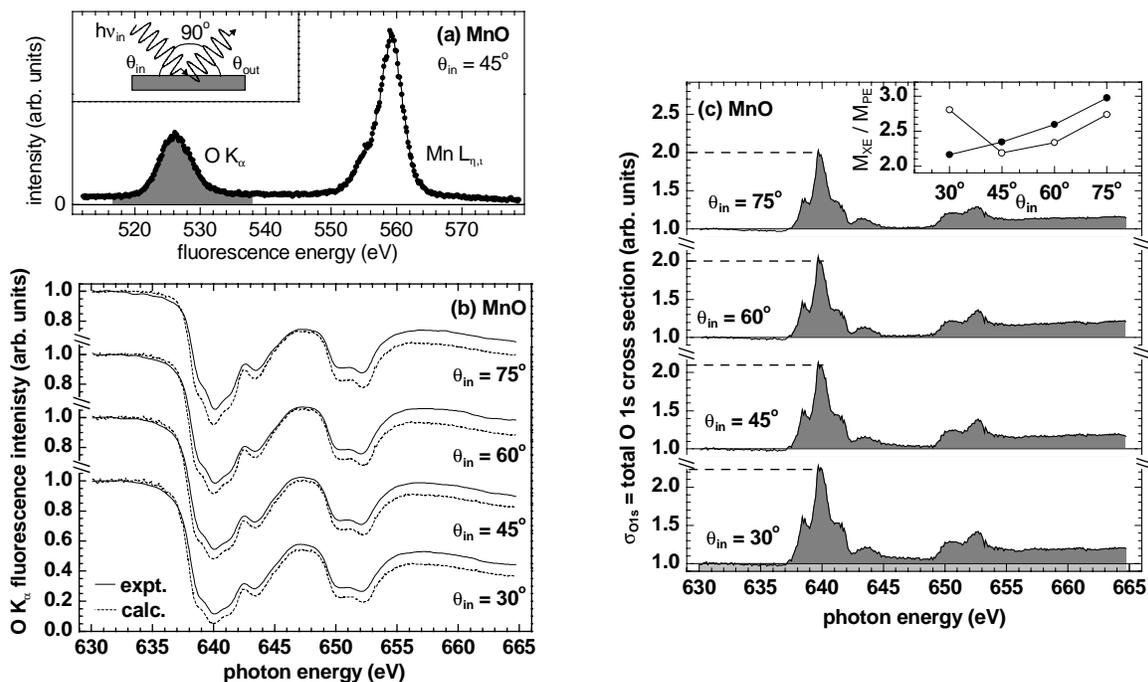


**Figure 1.** (a) O  $KL_{23}L_{23}$  intensity – as indicated by the shaded area in the inset – as photon energy is scanned through the Fe  $L_{3,2}$  edges. (b) X-ray absorption coefficient for  $Fe_2O_3$  at the Fe  $L_{3,2}$  edges as measured by partial electron yield.

In the fluorescence measurements on MnO, the O  $K_{\alpha}$  x-rays are well separated in energy from any Mn fluorescence feature, permitting us to determine the energy dependence of their intensity simply by considering an energy window of 20 eV centered at about 525 eV energy, as indicated by the shaded area in Fig. 2(a). The results of such energy scans for various experimental geometries are plotted in Fig. 2(b) as solid lines. The O  $K_{\alpha}$  intensity shows minima when the excitation energy is tuned to the Mn  $L_{3,2}$  edges instead of the maxima that might be expected based on the simplest interpretation of MARPE. However, these minima are due to well known sample absorption effects for both the exciting and emitted fluorescence intensity [8]. We can correct the O  $K_{\alpha}$  intensity for the self-absorption using the following standard expression [8]:  $I(O K_{\alpha}) \propto I_0(h\nu_{in}) \sigma_{O 1s} \epsilon_{O 1s} [\mu_{MnO}(h\nu_{in})/\sin \theta_{in} + \mu_{MnO}(O K_{\alpha})/\sin \theta_{out}]^{-1}$ , where  $I_0(h\nu_{in})$  is the incident x-ray flux at the photon energy  $h\nu_{in}$ ,  $\mu_{MnO}(h\nu_{in})$  is the absorption coefficient of MnO at this energy and  $\mu_{MnO}(O K_{\alpha})$  the absorption coefficient at the photon energy of the O  $K_{\alpha}$  radiation,  $\sigma_{O 1s}(h\nu_{in})$  is the cross section for producing an O 1s hole at the energy  $h\nu_{in}$  and  $\epsilon_{O 1s}$  is the fluorescence yield.

As an initial reference calculation, we made the assumption that the O 1s cross section  $\sigma_{O 1s}$  is constant over the entire energy range, i.e. resonant interatomic effects were neglected. The results are shown as the dashed curves in Fig. 2(b), where they are compared to our experimental results (solid curves). Although the main features around the Mn  $L_{3,2}$  edges and their variation with the angle of light incidence and exit are described correctly, there are significant percentage deviations between experiment and this non-resonant calculation. We attribute these differences to interatomic resonance effects on the O 1s cross section, and we can now estimate them simply by taking the ratio of the experimental data to the calculated curves, with both normalized to unity at an energy well below the resonance. The results are shown in Fig. 2(c) by solid lines. For all four geometries, we see clear and essentially identical curves indicating that the O 1s cross section as detected with O  $K_{\alpha}$  fluorescence radiation is enhanced at the Mn  $L_{3,2}$  edges, and furthermore that it follows the shape of the Mn  $L_{3,2}$  absorption coefficient, in agreement with prior photoemission results for MnO [2].

Fig. 2(c) indicates that the peak amplitude of the resonant enhancement at the Mn  $L_3$  edge is 100–140% using fluorescence detection, whereas for photoelectron detection 36–50% is found for different  $\theta_{in}$  [2]. This difference has its origin in the different probing depth of photoelectrons and fluorescent x rays. A typical x-ray fluorescence emitter is well below the surface, and so can experience resonant effects from atoms in a spherical cluster around itself, whereas in the case of surface-sensitive photoemission, this cluster is essentially a hemisphere extending inward from the surface. Quantitative calculations of the ratio of MARPE peak enhancement on and off the  $2p_{3/2}$  resonance in x-ray emission ( $M_{XE}$ ) and in photoemission ( $M_{PE}$ ) confirm this qualitative explanation, as shown by the comparison for experiment and theory in the inset of Fig. 2(c).



**Figure 2.** (a) Fluorescence spectrum of MnO recorded at  $h\nu = 640$  eV. The inset shows the experimental geometry. (b) Experimental (solid curves) and calculated (dashed curves) energy dependence of the O  $K_{\alpha}$  fluorescence intensity at the Mn  $L_{3,2}$  edges for different angles of light incidence,  $\theta_{in}$ . (c) O 1s cross section in MnO, including interatomic resonance effects, as derived from the ratios of the two sets of curves shown in (a). The inset shows the experimental (open symbols) and calculated (filled symbols) ratio between the resonant enhancement at the Mn  $L_3$  edge as detected via O K fluorescence radiation,  $M_{XE}$ , and via O 1s photoelectrons,  $M_{PE}$ , for different experimental geometries.

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Principal investigator: E. Arenholz, Materials Sciences Division, Lawrence Berkeley National Laboratory, MS 2-100, 1 Cyclotron Road, Berkeley CA 94720. Email: EArenholz@lbl.gov. Telephone: 510-486-4581.

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