

Resonances at the 4d thresholds of Lanthanum

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INTRODUCTION

The electronic properties of the d and f electrons, as in the transition metals and the Lanthanides, give rise to such phenomena as magnetism, Kondo resonances and mixed valency. In order to understand these properties, it is important to study the electronic states of the d and f electrons. Lanthanum does not have any 4f electrons in the ground state and in the elements following Lanthanum in the periodic table the 4f shell is being filled. As a result the decay process in La can directly provide information about the character of the 4f (and 5p) wave functions. La is also an ideal system to study the charge transfer to empty 4f states. In the present study we address the decay mechanisms of 4d core holes of La.

EXPERIMENT

The experiments were performed at Beamline 8.0 of the Advanced Light Source at Lawrence Berkeley National Laboratory. Spherical gratings monochromatize the undulator radiation. The resolving power of the monochromator is set to about $E/\Delta E = 300$ (at 97 eV) for our measurements. The fluorescence end station [1] is equipped with a Rowland circle grating spectrometer that provides a resolving power of about 700 (at 97 eV). In order to lower the amount of elastically scattered radiation (for excitation at the 4d-4f resonance) the incident angle of monochromatic beam is about 20° to the sample normal. The plane of incidence is the plane of polarization.

RESULTS

Fig. 1 shows three experimental soft x-ray emission spectra (XES) of LaAlO₃. The excitation energy is tuned to the three absorption features (97.4, 101.7 and 119 eV) that correspond to excitations of 4d electrons to the 4f-shell ($4d^{10}4f^0 \rightarrow 4d^9 4f^1$). Arrows in the partial fluorescence spectrum (shown in the insert) indicate the excitation energies selected for the XES spectra. The emission features show dramatic differences in energy and intensity for selected excitation energies. Calculated spectra are shown below the experimental data. The intensity I of inelastic and elastic scattering as well as of resonant fluorescence is described by the Kramers-Heisenberg formula [2]. The scaling factor for the Slater integrals was set to 80% [3] and the life-time broadening Γ to 0.5 eV [4]. The transition rates then are summed incoherently in Eq. 1 and broadened with a Gaussian profile of 0.4 eV, which is approximately the resolution of the spectrometer. When exciting at 97.4 eV, the elastic peak dominates the spectrum. The 5p-4d decay of the 3P_1 term of the $4d^9 5p^6 4f^1$ configuration results in the single peak at 78 eV. At an excitation energy of 101.7 eV (intermediate state 3D_1) the emission is strongly enhanced and shows three features that are due to 5p-4d transitions to different final states (3F_2 , 1D_2 and $^3D_{1,2}$). For this excitation energy it is necessary only to include the 3D states with $J=1$ in order to obtain

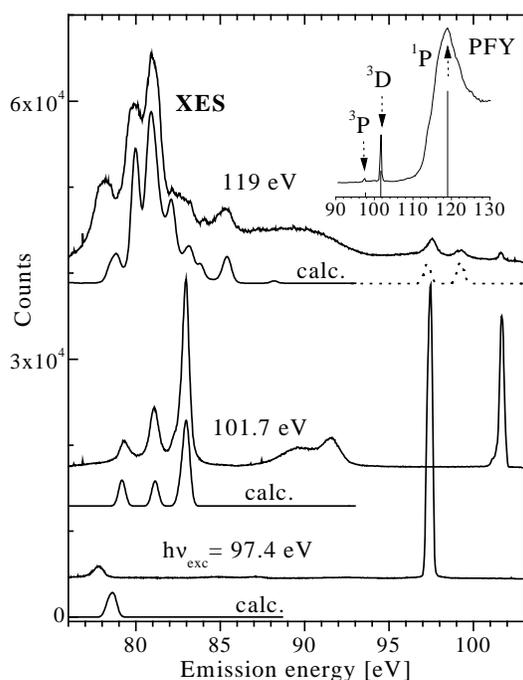


FIGURE 1. Soft x-ray emission spectra of LaAlO_3 . The excitation energy is given above each experimental spectrum. It is tuned to the three features of the partial fluorescence spectrum, PFY, (shown in top right insert) corresponding to weakly dipole allowed 3P_1 (at 97.4 eV) and 3D_1 (at 101.7 eV) and dipole allowed 1P_1 (at 119 eV) terms of the intermediate configuration $4d^9 4f^1$. Calculations are shown below the experimental data.

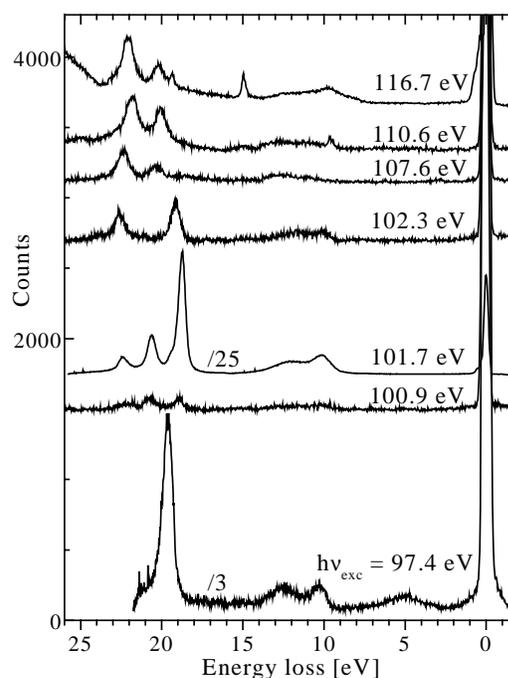


FIGURE 2. Energy loss spectra of LaAlO_3 for excitation energies near the 4d-4f resonance. Two groups of loss features at 10 to 13 eV and 19 to 23 eV are prominent. For clarity the spectra in both Figures have been displaced along the y axis. In order to display all spectra on the same scale, the spectrum for 101.7 eV has been divided by a factor of 25 and the spectrum at 97.4 eV by a factor of 3.

good agreement between calculations and measurements, because only the terms with $J=1$ are populated in the absorption process. When tuning the excitation energy to 119 eV two groups of emission features in the range at 96 to 102 eV and much stronger ones at 77 to 85 eV are observed. The 5p-4d emission through only the 1P_1 intermediate state is shown in Fig. 1 as the dotted part of the calculation below the measured spectrum for 119 eV. The much stronger additional features dominate the emission in the range from 77 to 85 eV, which is about 18 eV below the features resulting from the 1P_1 intermediate states. In order to reproduce this part of the measured spectrum by the calculations, the matrix elements of *all* intermediate terms ($4d^9 5p^6 4f^1$ configuration) to all final state terms ($4d^{10} 5p^5 4f^1$) have been taken into account. The fact that all terms of the intermediate state rather than only the 1P_1 terms have to be taken into account shows the strong mixing of terms that are separated by about 17 eV (more than 15% of the 4d ionization energy). The strong hybridization of the intermediate terms is also emphasized by the fact that (weak) 4d-4f emission from the 3P_1 and 3D_1 intermediate states is observed (97.4 and 101.7 eV respectively) when exciting at the 1P_1 term (119 eV). The lower one of these two features

overlaps in energy with the 5p-4f emission through the 1P_1 intermediate state though. Non-resonant 4d-4f emission excited by photons is observed only in La. Usually the emission of the Lanthanides near the giant resonance is dominated by inelastic scattering due to 5p-4f net transitions and 4f inner-shell excitations as well as elastic scattering. The peak at 85.4 eV is due to 5p-4d emission from the four times ionized atom La^{4+} . This peak appears at an excitation of 119 eV only because the ionization thresholds for 4d electrons lie in the range of 110 to 117 eV (for La atoms) [5].

In order to demonstrate the resonant character of the emission, soft x-ray emission spectra for various excitation energies are displayed in Fig. 2. The energy loss is obtained by subtracting the emission energy for each spectrum from the excitation energy. The emission intensity is highly resonant when tuning the excitation energy to the sharp absorption feature that corresponds to the 3D_1 term of the $4d^9 4f^1$ configuration (at 101.7 eV). The intensity of this emission spectrum is divided by a factor of 25 in order to display all of the spectra on the same scale. Detuning of the excitation energy by only 0.6 eV above or 0.8 eV below the 3D resonance (101.7 eV) leads to a drop in emission intensity by two orders of magnitude. Two groups of loss features are found: A double-peak energy loss feature is found in the range of 18 to 23 eV and another weaker double-peak loss structure appears around 10 and 12.5 eV below the excitation energy. The energy losses in the range 18 to 23 eV correspond to net transitions in which a 5p electron is promoted to the 4f level. These are usually the strongest energy loss mechanisms at the 3d and 4d thresholds and they have been observed for La (at 3d threshold), Nd (at 3d and 4d) and Gd (4d). The weaker band-like loss features around 10 and 12.5 eV is assigned to charge transfer transitions in which electrons from the O 2p valence bands are promoted to empty 4f states through the intermediate state configuration $4d^9 5p^6 4f^1 VB$. This is described in detail elsewhere [6].

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