PHYSICAL REVIEW B

CONDENSED MATTER AND MATERIALS PHYSICS

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Core-hole induced charge transfer and Coster-Kronig enhanced fluorescence at the *3d* threshold of lanthanum studied by resonant inelastic scattering

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(Received 8 September 1998)

Soft x-ray emission near the *3d* threshold of La is studied with synchrotron radiation. At excitation energies above the M_{IV} edge we observe Coster-Kronig enhanced fluorescence that refills the *3d* hole via *5p* and *4f* electrons. We find a new delayed onset of the fluorescence as the 7.5-eV inelastic scattering evolves into *3d-4f* emission about 8 eV above the absorption threshold, which we attribute to the energy required to produce a charge-transfer hole. The 16.3-eV Raman-scattering loss is due to a net transition of a *5p* electron into a *4f* orbit. The results are compared with our calculations. [S0163-1829(98)50148-8]

Materials containing rare earths in general, and lanthanum compounds in particular, are of great interest because of the interaction of the localized *4f* electrons and the delocalized conduction bands. This interaction leads to such interesting phenomena as Kondo-like behavior, mixed valency, and charge transfer. The electronic structure of lanthanum has been studied by photoemission,[1] photoabsorption,[1] and electron-energy-loss spectroscopy.[2,3] Excitation with monochromatic photons is a powerful bulk sensitive probe that provides detailed and selective information about the electronic structure. Only a few soft x-ray emission (SXE) experiments involving *3d* electrons have been carried out in the lanthanides because of small fluorescent yields that are on the order of 5×10^{-3}.[4] Furthermore, the emission occurs in a spectral region that is difficult to access by either a crystal or grating spectrometer. All previous measurements of *3d* core excitations used either electron bombardment or hard x-rays for excitation. Electron bombardment lacks tunability and produces multiple excitations, which complicates the analysis of the x-ray emission spectrum (XES) spectra. Okusawa *et al.*[5] studied the $M_{IV,V}$ emission spectra of La metal with

electron excitation and 2.7-keV photons. They suggested that the *3d* core hole induces a charge transfer in which an electron from the conduction band shakes down to the *4f* level followed by fluorescence or Auger decay. Mueller *et al.*[6] measured the *4d-5p* fluorescence emission of $LaAlO_3$ and they also proposed that a charge transfer from ligand orbitals leads to *4f* level occupancy. Jouda *et al.*[7] studied the *5p-3d* transitions in LaF_3, La_2O_3, and CeF_3 excited with electrons and 23-keV photons, and found variations in the shape of the *5p* emission spectra for the different compounds. They concluded that the variations are due to the hybridization of the excited states with the *3d* core hole. Tanaka and Kotani[8] applied the Anderson impurity model[9] in a theoretical study of LaF_3 and CeF_3. They include the hybridization of $4f^0$ and $4f^1 \underline{L}$ states and predicted a double structure of the emission peak separated by about 2.6 eV when excitation occurs at the M_{IV} absorption threshold. The quantity $\underline{L}$ represents a ligand hole. We do not observe this predicted feature. Inelastic scattering experiments have become viable[10] with the availability of high brightness third generation storage rings and
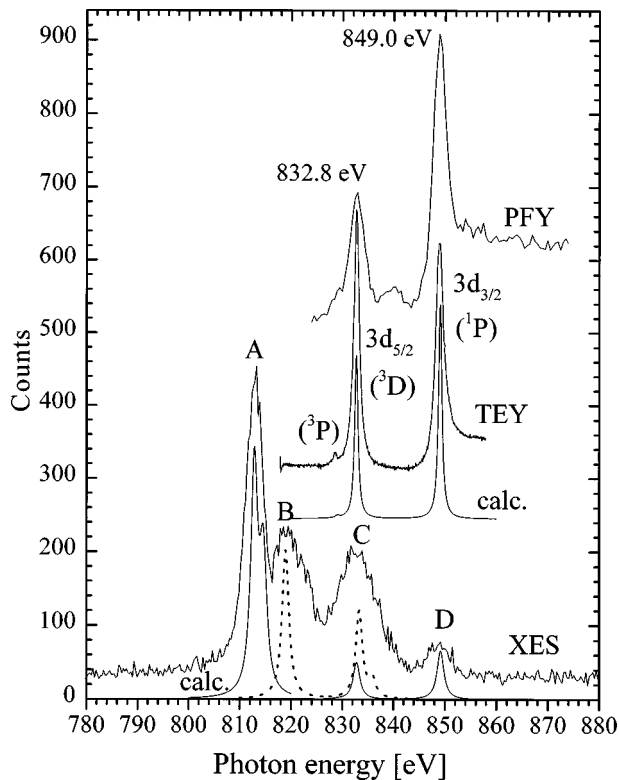
FIG. 1. Soft x-ray emission spectrum excited above threshold ($h\nu_{exc} = 858.9$ eV), total electron yield spectrum, partial fluorescence yield of $LaAlO_3$, and calculated transitions for La in the vicinity of the *3d-4f* transitions.

can be used to study correlation effects of many electron systems and in particular the *4f* electrons in rare-earth compounds.[11,12]

In our soft x-ray scattering experiments in lanthanum involving the *3d* core electrons, we find Raman scattering dominating the x-ray emission near the M_V ($3d_{5/2}$) absorption edge up to the M_{IV} ($3d_{3/2}$) absorption edge. At photon excitation energies exceeding the M_{IV} absorption edge we observe for the first time Coster-Kronig enhanced fluorescence of the M_V emission. Finally, we find a new delayed onset of the fluorescence process, where the inelastic scattering evolves into *3d-4f* fluorescence about 8 eV above the M_{IV} absorption threshold. We attribute this energy loss to the energy required to produce a charge-transfer hole. The identity of the states involved in inelastic scattering and ordinary fluorescence has been verified by our calculations.

Our emission experiments were performed at beamline 8.0 of the Advanced Light Source (ALS) Lawrence Berkeley Laboratory. The undulator beamline is equipped with a spherical grating monochromator.[13] We used an experimental resolving power of $E/\Delta E = 300$. The fluorescence end station consists of a Rowland circle grating spectrometer that provides an experimental resolving power of about 400. The incident angle of the *p*-polarized monochromatic beam on the sample was about 15°. The absorption spectrum was taken at a resolving power of 3000 using the high-resolution beamline 6.3.2 of the ALS (Ref. 14) by measuring the total photoelectron current.

Figure 1 displays the x-ray emission spectrum of $LaAlO_3$ obtained at an excitation energy above the *3d-4f* threshold

(858.9 eV). Four peaks are resolved and labeled *A* through *D*. We have also calculated the atomic transition rates to fill the hole in the M_{IV} shell for La by using Cowan's code.[15] The scaling factor for the Slater integrals was 80% and the results are shown below the XES spectrum. All calculated spectra have been broadened by 2 eV (full width at half maximum), which is about the experimental resolution of the spectrometer. Both $\mathbf{L}\cdot\mathbf{S}$ and *j-j* notation will be used for the terms of the configurations in this paper. Peaks *A* and *B* are due to emission from transitions of *5p* electrons to the $3d_{5/2}$ shells with (A: $3d_{5/2}\ 4f^1\underline{L}\rightarrow 5p_{3/2}\ 4f^1\underline{L}$) and without ($B$: $3d_{5/2}\rightarrow 5p_{3/2}$) the *4f* spectator electron and ligand hole. Peak *C* shares its intensity with $3d_{3/2}\rightarrow 5p_{3/2,1/2}$ and $3d_{5/2}\ 4f^1\underline{L}\rightarrow\underline{L}$. Peak *D* is the fluorescence from the transition: $3d_{3/2}\ 4f^1\underline{L}\rightarrow\underline{L}$. In Fig. 1, calculated fluorescence involving charge transfer are presented as solid lines while the *noncharge*-transfer transitions are given as the dashed curve. The identification of this emission spectrum is consistent with the interpretation of Jouda *et al.*[7] When exciting above the *3d* threshold, charge-transfer processes provide occupancy of the *4f* level: electrons from the oxygen valence band can shake down to the *4f* levels and then refill the *3d* hole. According to Jouda *et al.*[7] and Okusawa *et al.*[5] peaks *C* and *D* were strongly suppressed by self-absorption.

The absorption of $LaAlO_3$ in the region of the *3d* threshold has been measured by detecting the total electron yield (TEY) and the intensity of the photon emission channel was obtained by the partial fluorescence yield (PFY). The data are displayed in Fig. 1. The TEY and PFY features arise from excitations from transitions between the $3d^{10}4f^0$ ($^1S_0$) ground state to the ^3P, ^3D, and ^1P terms of the $3d^9 4f^1$ configuration. Spin-orbit splitting as well as the energy positions at 832.8 eV for the transitions $3d^{10}4f^0$ ($^1S_0$) $\rightarrow 3d^9 4f^1$ (^3D or $3d_{5/2}$) and at 849 eV and for $3d^{10}4f^0$ ($^1S_0$)$\rightarrow 3d^9 4f^1$ (^1P or $3d_{3/2}$) are almost the same as those reported for La metal [834.8 and 850.7 eV (Ref. 5)].

In Fig. 2, the measured emission spectra for $LaAlO_3$ are shown with the TEY spectrum (top) for various photon excitation energies. Above the M_{IV} threshold the emission spectra consist of four fluorescence peaks. The fluorescence evolves into inelastic scattering at excitation energies below the $M_{IV,V}$ absorption thresholds. By comparing the XES spectra shown in Fig. 2 and the partial fluorescence yield displayed in Fig. 1 one observes that as soon as the excitation energy drops below the M_{IV} absorption threshold at 849 eV, the emission from lanthanum is completely dominated by inelastic scattering.

At the M_{IV} excitation threshold, the emission corresponding to peak *C* shows strong resonant behavior. Emission, corresponding to peaks *A* and *B*, suddenly appears from the refill of the $3d_{5/2}$ hole. This is due to Coster-Kronig (CK) enhanced fluorescence from the decay of the $3d_{5/2}$ hole (peaks *A*, *B*, and *C*) that commences at the $3d_{3/2}$ threshold. The C-K transition ^1P ($3d_{3/2}$)$\rightarrow ^3D$ ($3d_{5/2}$) promotes a charge transfer *4f* $\underline{L}$ creating the $3d_{5/2}$ and $3d_{5/2}4f\ \underline{L}$ intermediate states that result in fluorescence to final states of the type $5p^5\ 4f\ \underline{L}$ (peak *A*), $5p^5$ (peaks *B* and *C*), and $\underline{L}$ (peak *C*). There is only Raman scattering that involves *4f* $\underline{L}\ 3d_{3/2}$ intermediate states and $\underline{L}$ final states (peak *D*), because the resonant energy (849.0 eV) is below the threshold to produce the *4f* $\underline{L}$ charge transfer and excite a $3d_{3/2}$ subshell electron.
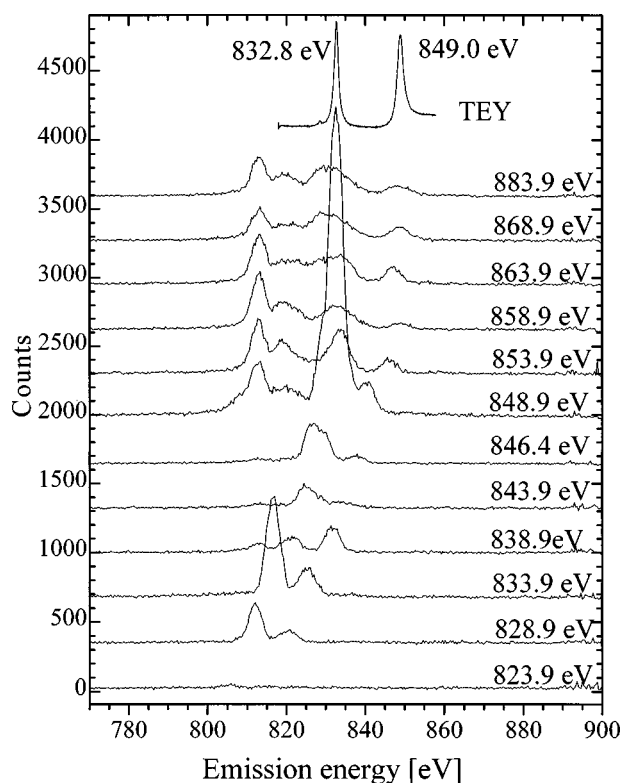
FIG. 2. Soft x-ray emission spectra and absorption spectrum (TEY) of LaAlO$_3$ in the region through the *3d-4f* threshold. The excitation energy for the spectra is given above each spectrum. The spectrum taken at an excitation energy of 858.9 eV is the same XES spectrum as displayed in Fig. 1.
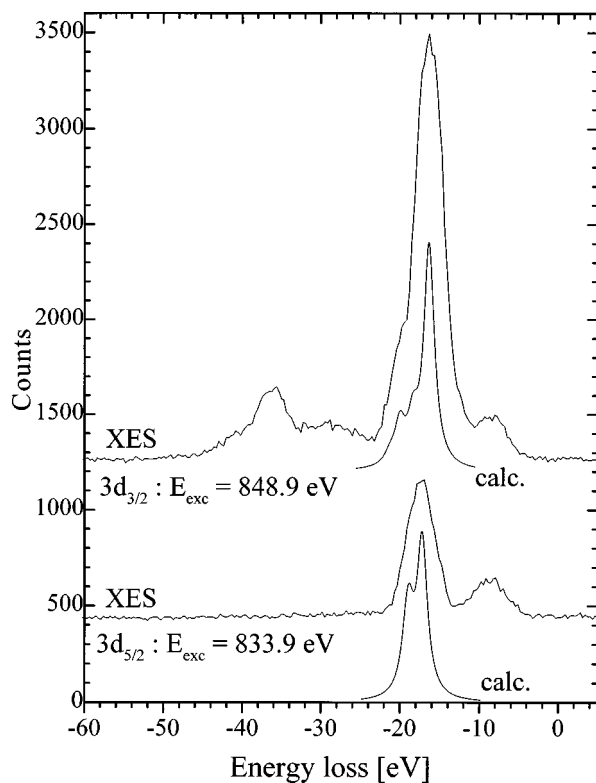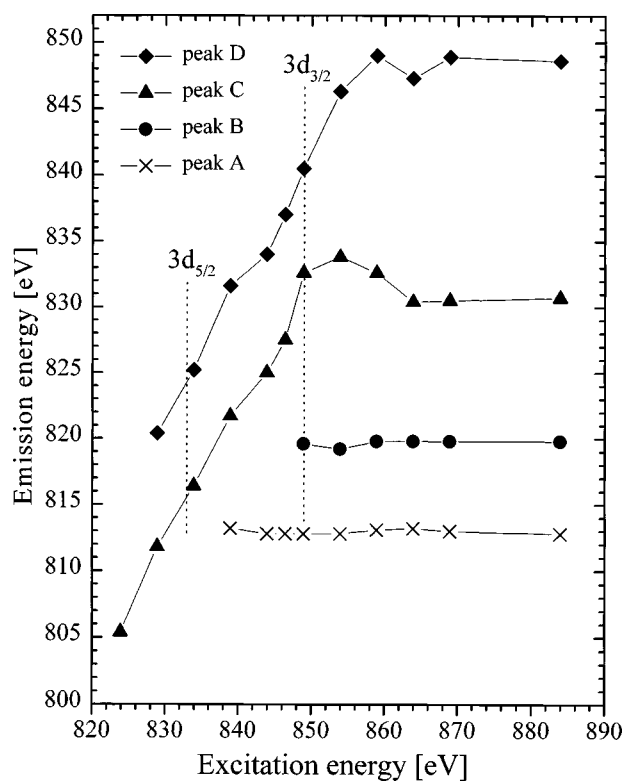

FIG. 4. Emission energy versus excitation energy for the four emission peaks of LaAlO$_3$ in the region of the *3d-4f* threshold. The dotted vertical lines indicate the energetic position of the ^3D and ^1P terms in the absorption spectrum.

FIG. 3. Energy-loss spectra of LaAlO$_3$ for excitation at ^3D and ^1P threshold and atomic calculations of the 16.3-eV loss feature.

Furthermore, the rates for $M_{IV}M_V N_{VI,VII}$ CK transitions are about two orders of magnitude greater than the rates for $M_{IV}M_V O_{II,III}$ CK transitions.[4] This is why no final states of the type $5p^4\ 4f$ are observed. Auger processes dominate photon absorption in the spectral range between the M_V and the M_{IV} absorption thresholds. Very weak fluorescence from the decay of the $3d_{5/2}$ hole is observed even when exciting at the $3d^{10}4f^0\ (^1S)\rightarrow 3d_{5/2}4f^1\ (^3D)$ absorption resonance.

Inelastic and elastic scattering intensity is described by the Kramers-Heisenberg (KH) formula:[16]

$$I(E_{in},E_{out})\propto\sum_f\left|\sum_m\frac{\langle f|pA|m\rangle\langle m|pA|i\rangle}{E_m-E_i-h\nu_{in}-i\Gamma/2}\right|^2$$

$$\times\,\delta(E_f+h\nu_{out}-E_i-h\nu_{in}). \qquad (1)$$

In this equation, pA is the dipole operator while $|i\rangle$ is the initial state of the system with energy E_i, $|m\rangle$ and E_m describe the intermediate state, $|f\rangle$ and E_f describe the final state, and Γ is the lifetime broadening in the intermediate state. In our experiment two inelastic features are observed, one at 16.3 eV and the other 7.5 eV. In Fig. 3 two emission spectra (XES) from Fig. 2 excited at resonances associated with the transition of *3d* electrons to $3d_{5/2}\ 4f$ and $3d_{3/2}\ 4f$ excited states are displayed as energy-loss spectra. The energy loss is derived from the emission spectra by subtracting the energy of the exciting photons from the energy of the emitted photons. A model of the inelastic scattering process was employed that used Cowan's[15] method to compute the transition rates and a lifetime broadening of 1 eV. The results

are summed incoherently in Eq. (1) and are shown in Fig. 3 as the solid line beneath each spectrum. In our calculation the initial state is $3d^{10} 5p^6 4f^0$ (^1S), intermediate states are $3d^9 5p^6 4f^1$, (^3D, ^1P), and the final states are $3d^{10} 5p^5 4f^1$ (^3F, ^1D, ^3D). The energy loss can be assigned to the energy difference between initial and final state or ''net transition.'' The 16.3-eV energy loss corresponds to a net transition of a $5p$ electron to a $4f$ orbit. The excellent agreement of the model and the experiment suggests that the intermediate states are not strongly coupled. We note that it was not necessary to employ the Anderson impurity model into the calculations. This indicates that there was not a significant degree of hybridization of the $4f$ states and the valence band.

Displaying the emission photon energy versus the excitation photon energy for peaks A–D, allows one to easily observe the emission change from inelastic scattered radiation to fluorescence as shown in Fig. 4. It provides clarification of the Raman energy losses of 16.3 and 7.5 eV. The 16.3-eV loss evolves into fluorescence that corresponds to a $5p$ electron filling the $3d$ hole. According to our calculations the transition energy of a $5p_{3/2}$ electron to a $4f$ level is 16.3 eV, which equals the observed energy loss. The onset of the fluorescent decay of the $3d$ hole via the $5p$ channel (peaks A, B, and C to some extent) is apparent at the corresponding $3d$ thresholds (A: $3d_{5/2}$, B: $3d_{3/2}$). The dominating energy loss (peak C) starts about 10 eV below the ^3D ($3d_{5/2}$) resonance and it tracks the excitation energy until evolving into fluorescence at the $^1P(3d_{3/2})$ threshold. On the other hand, the 7.5 eV loss corresponding to peak D follows the excitation and about 6 eV above the ^3D ($3d_{5/2}$) resonance the peak energy deviates from a straight line that represents a constant energy loss somewhat and begins to blend with fluorescence represented by peak C. This is seen more clearly above the ^1P ($3d_{3/2}$) threshold, where peak D continues to track with the increasing excitation energy. At about 6–8 eV above this threshold, the emitted photon energy approaches a constant fluorescence energy. Thus we attribute the 7.5-eV loss at a net energy to produce, <u>L</u>, a ligand hole.

To summarize, we have observed Raman scattering with a net energy loss between the initial and the final states of 7.5 and 16.3 eV. We suggest that the 7.5-eV inelastic scattering feature whose excitation energy is about 8-eV higher than the $3d$-$4f$ absorption feature arises from a $4f$ L charge transfer. According to our calculations, the 16.3-eV loss is due to the promotion of a $5p$ electron into a $4f$ orbit. Due to the high degree of localization of the $4f$ electrons, calculations based on a purely atomic model provide a consistent interpretation of the 16.3-eV energy loss and the observed fluorescence emission. One of the surprising outcomes of these measurements has been the observation that inelastic scattering provides the major contribution to the x-ray emission between the M_V and the M_{IV} absorption thresholds. This is due to the fact that the M shell fluorescence yield is of the order of 0.5%. Second, it is surprising to see how CK transitions ''switch on'' fluorescence once the threshold energy has been achieved. Studies of this effect are in progress for different rare earths.

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