

Charge-transfer excitations in lanthanum compounds measured by resonant inelastic x-ray scattering at the M_5 edge

C. Dallera,^{1,*} K. Giarda,¹ G. Ghiringhelli,¹ A. Tagliaferri,² L. Braicovich,¹ and N. B. Brookes²

¹*INFM - Dipartimento di Fisica, Politecnico di Milano, piazza Leonardo da Vinci 32, 20133 Milano, Italy*

²*European Synchrotron Radiation Facility, B. P. 220, F-38043 Grenoble Cédex, France*

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We present resonant inelastic x-ray scattering spectra from La metal La_2CuO_4 and LaF_3 . Monochromatic photon excitation with energy across the La $3d_{5/2}$ (M_5) threshold was used and the valence scattering was monitored at selected incoming energies. The spectra vs the outgoing photon energy show the elastic peak, the $5p-3d_{5/2}$ decay peak and, in between, a feature due to charge transfer excitation. This brings an electron from the ligand to the lanthanum $4f$ states (in the case of La_2CuO_4 and LaF_3) and results from a charge fluctuation from $4f^0$ to $4f^1$ occupation in the case of La metal. The energy transferred to the solid when this process occurs is remarkably different in the three cases and correlates with the difference in the electronegativity with the lanthanum neighbors. The present approach allows us to reveal features that are completely hidden in the x-ray absorption spectra.

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I. INTRODUCTION

The physical properties of rare earths and rare earth compounds are mainly determined by the $4f$ narrow-band occupancy and by the hybridization with the delocalized conduction band states, which give rise to interesting phenomena such as Kondo-like behavior, mixed valence and charge transfer. Among rare earths, lanthanum represents an important case avoiding complicated multiplet effects, thanks to the almost perfect $4f^0$ occupancy, which makes the interpretation of the spectra more straightforward. Moreover, the spatial extension of the La- $4f$ states is sufficiently large to generate a sizable mixing with the wave functions of neighbor atoms. This is interesting since the resulting hybridized states cannot be classified either as localized or extended and is at the origin of a chemical effect on the $4f$ excitations which is seen in a particularly clear way in M_5 -resonant inelastic x-ray scattering (RIXS) as it is shown in the present paper.

The electronic structure of lanthanum has already been studied by photoemission spectroscopy, which provides valuable information in particular about electronic states close to the Fermi level. The multi-component structure of the $3d$ photoemission¹ spectra in lanthanide metals has been interpreted by invoking the core-hole screening mechanism of the $5d$ conduction band electrons and of the additional $4f$ electron transferred from valence states near the Fermi level. However the information provided by this technique is highly surface sensitive. This problem is overcome in experiments of resonant inelastic x-ray scattering. In addition to being bulk-sensitive, the $M_{4,5}$ -RIXS with valence excitation in the final state has the advantage of probing the ground state and low-energy excitations. In the case of lanthanum compounds the lowest excited final states are due to energy losses resulting from the interaction of the intermediate state core-hole with $4f$ states. This interaction causes the electrons to hop from a delocalized state to a localized state, producing a net charge transfer. The energy selectivity of the RIXS technique allows us to identify the energy positions of the

charge-transfer peaks, which is important information for the understanding of the correlation in the system.

Only few soft x-ray emission experiments involving $4f$ electrons in lanthanum-containing compounds have been carried out²⁻⁶ due to intrinsic small fluorescent yields. To our knowledge only Moewes *et al.*² have used monochromatic synchrotron radiation to perform a study of the decay process of the $3d$ core hole in LaAlO_3 with resonant La $3d$ excitation. They find that the emission spectra show two inelastic features due to a final-state in the presence of either a $5p$ core hole or a $4f$ -spectator electron and ligand-hole. The energy required to produce this charge-transfer hole in LaAlO_3 has been found to be around 7.5 eV.

Previous experiments³⁻⁶ have used either electronic excitation or conventional, non-monochromatized x-ray tube photons. A theoretical analysis of measured spectra³ has allowed an evaluation of the charge transfer energy involved in the creation of a $4f^1L$ intermediate state, and the hybridization strength and Coulomb interactions characterizing the electronic states of La_2O_3 and LaF_3 . The quantitative determination of the parameters is a first step to a full understanding of the electronic states of each compound, and the systematic behavior of these parameters across the rare earth series may give more insight into the electronic states of correlated systems.

The present RIXS experiment is performed on three systems where lanthanum is involved in chemical bonds with partners of different electronegativity: metallic lanthanum, the cuprate La_2CuO_4 , and the ionic compound LaF_3 . The aim was to study the possible existence of a correlation between the chemical environment and the excitation process of the $4f$ states as seen in RIXS. This is done by relying upon the assignment of the excitation spectrum done by Moewes in LaAlO_3 . The energy of the incoming photon beam was tuned at the M_5 threshold thus promoting a $3d$ electron into the $4f$ orbital. The RIXS spectra we present give direct information about the energy required to reach the final state of $4f^1L$ configuration.

We point out that by " $4f^1L$ configuration" we denote a

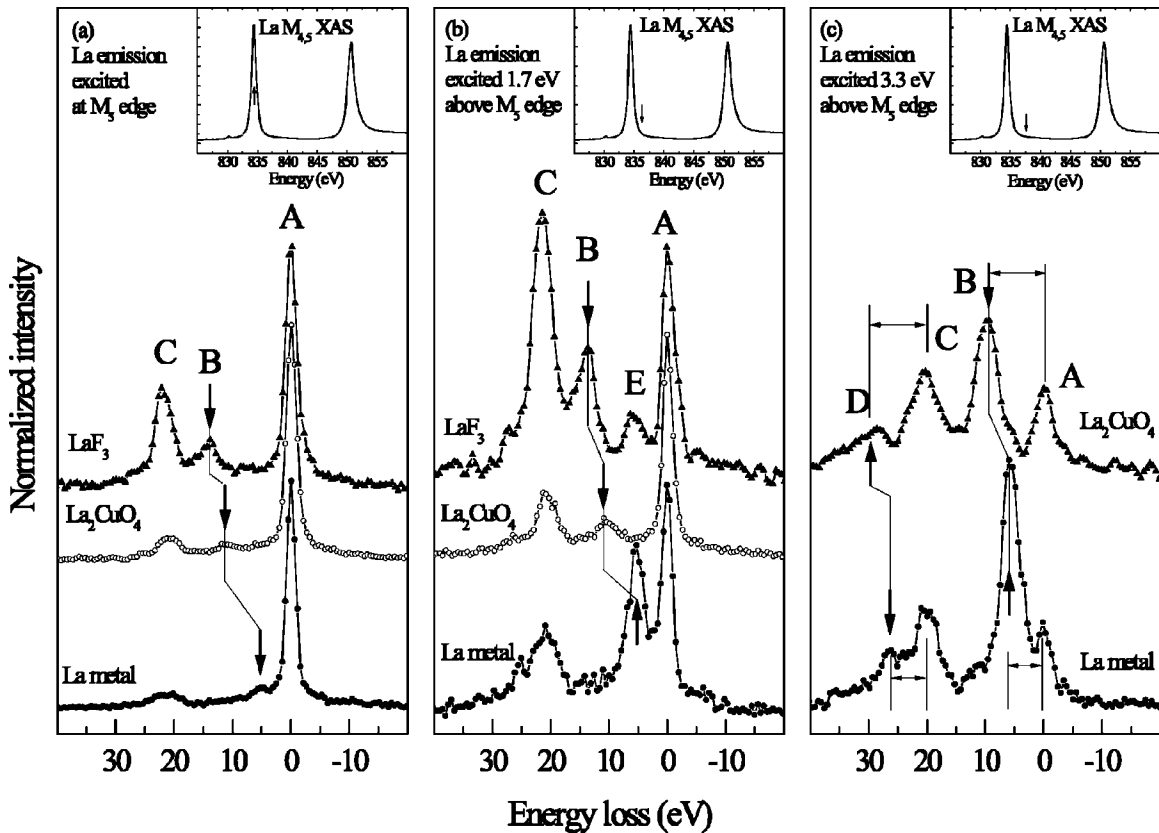


FIG. 1. Resonant inelastic x-ray scattering of La metal, La_2CuO_4 , and LaF_3 excited at the M_5 edge (panel a), 1.7 eV above the edge (panel b), 3.3 eV above the edge (panel c). All spectra have been scaled to the same height of the elastic peak to put in evidence the shape change. The arrow on the XAS spectrum in the inset indicates the excitation energy. The RIXS spectra are plotted as a function of the energy transferred to the solid. The main features are indicated by following letters: (A) is the elastic peak, (B) is the peak due to valence scattering decay towards a $4f^1L$ final state. (C) follows $5p-3d_{5/2}$ decay. Peak (D) is due to $5p-3d_{5/2}$ decay with a $4f^1L$ final state (accordingly, as shown on panel c, the distance between A and B is the same as between C and D). The feature labeled E (LaF_3 excited 1.7 eV above the edge) is attributed to a final state of antibonding nature.

state that has different nature in the case of metallic lanthanum with respect to the case of lanthanum compounds: for the metal it must be intended as a charge fluctuation from $4f^0$ to $4f^1$ occupation, in the compounds it arises from an electron transfer from the ligand to the lanthanum $4f$ state. This low energy-excitation process is not revealed by x-ray absorption spectra which are identical for the three compounds, probably due to the very low intensity of absorption towards the charge-transfer state.

II. EXPERIMENTAL

The experiment was performed at beamline ID12B at the European Synchrotron Radiation Facility (Grenoble). The x-ray beam was produced by the helical undulator Helios I. In order to set the excitation energies, absorption spectra were measured in the total electron yield mode exciting the sample with x-rays monochromatized by the beamline monochromator (Dragon type). The chosen photon bandwidth was 0.4 eV. With an electron current of 200 mA in the storage ring, the sample photocurrent was higher than $1\mu\text{A}$ at the M_5 edge. The emission spectra were measured with the AXES grating spectrometer.⁷ The x-ray beam was mono-

chromatized by a monochromator dedicated to the spectrometer.⁸ A bandwidth of 1.5 eV was chosen for the incoming photon beam, and this determined also the overall experimental resolution. With a 200 mA electron current and having set the excitation energy at the M_5 edge, the RIXS counting rate integrated over the whole spectrum shown in the figures was 25, 22, 32 counts per second for La metal, La_2CuO_4 and LaF_3 , respectively. The detector is a micro-channelplate with resistive anode encoder, 1-inch diameter. In the case of LaF_3 the counting rate was large but a big fraction of the signal was due to ultraviolet optical luminescence by the F atoms.

III. RESULTS

Figure 1 shows RIXS spectra of the three compounds excited at the M_5 edge (a), 1.7 eV (b), and 3.3 eV (c) above it. At 3.3 eV above threshold it was not possible to measure the LaF_3 spectra because the low intensity feature was lost in the background due to the luminescence by the sample. All spectra have been plotted as a function of the energy ($h\nu_{\text{in}} - h\nu_{\text{out}}$) lost by the scattered photon.

The insets display the La absorption spectra, and the ar-

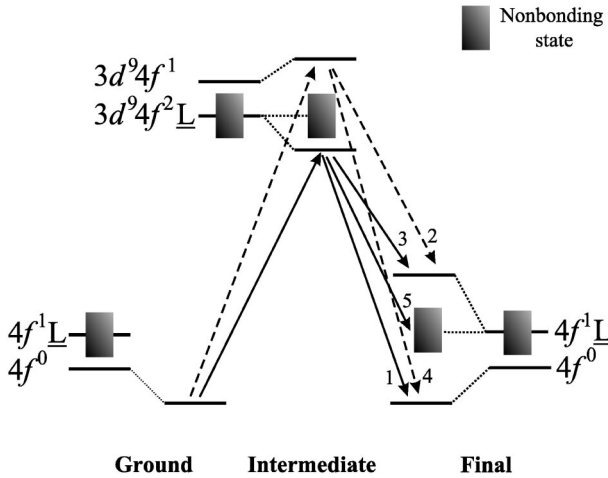


FIG. 2. Total energy level scheme in the RIXS process of lanthanum (taken from Ref. 9).

rows show the chosen excitation energy. The emission spectra have been scaled to the same height of the elastic peak in order to compare the line shapes. The total energy scheme is depicted in Fig. 2, which is based on a two-step description of the RIXS process. (The drawing is similar to that of Ref. 9 which refers to CeF_3 , and is appropriate also for the present case). The ground state of the La^{3+} ion is a mixture of the eigenstates $4f^0$ and $4f^1 L$ (where by $4f^1 L$ we refer to the state with an additional $4f$ electron and a ligand-hole in the case of the two compounds, and to the state with a charge fluctuation from $4f^0$ to $4f^1$ occupation in the case of the metal). These states give rise, in order of increasing energy, to a bonding, a nonbonding, and an antibonding state.

The $4f^1 L$ eigenstate is not a single line but has a finite width (which we disregard for simplicity in the level scheme of Fig. 2). In the ground state, only the lowest lying bonding state is occupied, having an almost pure $4f^0$ configuration.

The excitation step brings the system to an intermediate state, which is a mixture of $3d^9 4f^1$ and $3d^9 4f^2 L$ states. We refer to the Anderson Impurity Model notation,¹⁰ where $U_{fc}(3d)$ is the interaction energy between the $3d$ core hole and an f electron. The energy separation between the $4f^1$ and $4f^2 L$ configuration in the presence of the $3d$ core hole is reduced with respect to the ground state since the $4f$ level is pulled down by $U_{fc}(3d)$. Accordingly the two configurations are mixed by hybridization.

In the final state with the $5p$ hole, the distance between the $4f^0$ and $4f^1 L$ configuration is larger than in the intermediate state because the attractive potential $U_{fc}(5p)$ of the $5p$ core hole on the $4f$ electron is smaller than $U_{fc}(3d)$. The three possible final states are the bonding ground state, the antibonding, and the nonbonding state. Elastic processes (path 1 or 4) bring the system back to the ground state, transitions to final nonbonding (path 2 or 3) and antibonding states (path 5) will appear as two additional peaks in the RIXS spectra. We note that the transition to the intermediate non-bonding state is not seen in either XPS or XAS because the intensity completely cancels out due to phase factors.¹¹ In the present case, decay to the nonbonding final state of RIXS

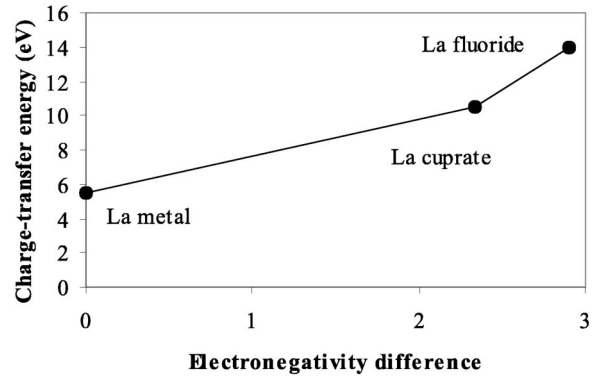


FIG. 3. Measured charge-transfer excitation energies as a function of the difference of electronegativity between La and the partner in La metal, La_2CuO_4 , and LaF_3 (see text for explanation).

is visible [peak E of Fig. 1(b)], although weak, in LaF_3 when the separation between bonding and antibonding final states is large enough.

We now discuss the peaks corresponding to the different emission paths referring to Fig. 1, where the comparison of spectra taken at the same excitation energy is presented. The main spectral features are labeled as follows: Peak A is the elastic recombination peak ($3d^{10}4f^0 \rightarrow 3d^9 4f^1 \rightarrow 3d^{10}4f^0$). The feature labeled B is due to decay towards an excited final state of mainly $4f^1 L$ nature in the presence of a charge transfer effect ($3d^{10}4f^0 \rightarrow 3d^9 4f^1 \rightarrow 3d^{10}4f^1 L$). Its intensity increases when increasing the excitation energy above the M_5 edge. Peak C is due to $5p-3d_{5/2}$ decay. As far as the charge transfer process is concerned we make the following remark: this process brings an additional electron into the $4f$ orbital, changing the occupancy from $4f^0$ to $4f^1$. In the case of LaF_3 and La_2CuO_4 $4f^1 L$ indicates the configuration with an additional electron in the $4f$ orbital and a true valence ligand hole. In the case of La metal we use the same notation but by L we indicate a charge fluctuation that occurs between equivalent atoms. The present spectral assignment is based on what has been seen for the case of LaAlO_3 .²

In addition to peaks A, B, and C, the spectra of La metal and La_2CuO_4 also show a peak D due to $5p-3d_{5/2}$ transition in the presence of a charge transfer process in the final state. This is supported by the fact that the energy distance between peaks C and D is the same as between peaks A and B and is confirmed by existing calculations.¹² In the case of LaF_3 an additional peak labeled E is visible which could be the evidence of final nonbonding states as explained above [Fig. 1(b)]. These states are expected to be only marginally sensitive to the chemistry and are not discussed here.

All peaks are seen at constant transferred energy, which is an indication of transitions between localized states.¹³ The peak C due to the $5p-3d_{5/2}$ decay is found at a transferred energy between 20 and 22 eV for the three compounds, in good agreement with previous literature.¹⁴ The peak B due to the ligand hole charge transfer excitation appears at a different energy position in the three environments: the energy transfer is 5.5 eV for La metal, 10.5 eV for La_2CuO_4 , and 14 eV for LaF_3 . The excitation energies are quite different in the three cases showing a strong chemical sensitivity of the

RIXS spectra. Starting from the value due to the $4f$ - $4f$ fluctuation in the metal, there is an increase, which correlates well with the difference in electronegativity (after Pauling¹⁵) between La and the neighbor as shown in Fig 3. Since this is a first neighbor argument we do not discuss the difference in the behavior between La_2CuO_4 and LaAlO_3 from Ref. 2 since in both cases La is coordinated to oxygen. We also note that the value of energy transfer for the three compounds agrees¹⁶ with the ε_f parameter of the Anderson impurity model (representing the energy difference between subsequent $4f$ occupation numbers) estimated for La, La_2O_3 , and LaF_3 .

IV. CONCLUSIONS

The charge transfer energy of La metal, La_2CuO_4 , and LaF_3 has been measured at the La $3d_{5/2}$ threshold by resonant inelastic x-ray scattering. The energy-transfer spectra show pronounced structures in addition to the elastic peak and the $5p$ - $3d_{5/2}$ diagram line. They are attributed to charge-

transfer excitations to the low-lying excited $4f^1L$ state due to configurational mixing in the ground and core-excited states, and their intensity increases when the incident energy is tuned above the M_5 edge. The energy transfer corresponding to the charge-transfer process correlates with the electronegativity difference between La and the chemical environment. This clear chemical sensitivity of a bulk sensitive spectroscopy as RIXS is interesting per se and deserves further systematic work aimed to establish a better correlation between bulk properties and high energy spectroscopies of rare earth systems.

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*Electronic address: claudia.dallera@fisi.polimi.it

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