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Fast electron dynamics in vanadates measured by resonant inelastic x-ray scattering

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ABSTRACT

We present experimental data for the decay dynamics of a resonantly-produced $2p_{1/2}$ vanadium core-hole in YVO_4. The states produced by the fast Coster–Kronig decay are studied by resonant inelastic x-ray spectroscopy. They form groups of participant normal emission and spectator emission peaks. The spectator emission gives rise to sharp peaks whose shape and energy correspond to a screened resonant $2p_{3/2} \leftrightarrow 3d$ transition. This behavior is compared with the emission features observed in the less localized system V_2O_5. The decay lifetime of the $2p_{1/2}$ hole in YVO_4 is measured by the broadening of the sharp peaks resulting in a value of the order of 1 fs.

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1. Introduction

The lifetime of an atomic core-hole (c-h) has been successfully used as a clock to study electron dynamics [1]. This c-h clock technique compares the time of interest with the internal atomic clock when an inner shell vacancy is resonantly produced. In particular these studies are possible because the c-h decays by fast Auger or Coster–Kronig (CK) processes that take place in few femtoseconds. In a recent review, it was suggested to employ resonant inelastic x-ray scattering (RIXS) for studying fast charge transfer processes in solids [2]. In this letter we present a RIXS study of the $L_2L_3\upsilon$ CK decay in YVO_4 and V_2O_5. The lifetime of the $2p_{1/2} \rightarrow 2p_{3/2}$ CK decay in vanadium [3] is of the order of 1 fs. We are interested in the CK decay of a resonantly produced $2p_{1/2}$ hole when the excited electron remains in a localized state (spectator electron). The x-ray emission that follows this spectator decay is simplified and the lifetime τ of the $2p_{1/2}$ core hole is related to the additional broadening Γ of the emission lines by the uncertainly principle, $\Gamma\tau = \hbar$ [4]. In the CK decay the 3d excited electron may be promoted into the continuum (participant process) or it may stay as a spectator and a valence electron is the one that is ejected into the continuum [5]. In the former process one obtains normal x-ray emission, while in the latter the $2p_{3/2}$ hole can be filled by the 3d spectator electron. In the case of a localized spectator electron one would expect simpler emission features that closely resemble the $2p_{3/2} \rightarrow 3d$ absorption spectrum. Participant decay results in

changes of the normal valence emission features. YVO_4 has the closer packed zircon structure with space group of D_{4h}^{19} $I4_1/amd$ [6]. It has good thermal stability, large birefringence and a wide transparency range from the visible to the infrared as for the host lattice for rare earth ions (Re^{3+}) to produce phosphors emitting a variety of colors in color television [7], fluorescent lamps, X-ray detectors, cathode ray tubes (CRTs), and field emission displays.

2. Experiment

The experiment took place at beamline 8.0.1 of The Advanced Light Source of Lawrence Berkeley National Laboratory. The radiation is produced in a 5.0 cm period undulator and passes through a spherical grating monochromator operating at grazing incidence [8]. The relative absorption cross section is obtained by measuring the total electron yield (TEY) as the incoming photon energy is scanned. The x-ray spectrometer is based on an entrance slit less design, a spherical collecting mirror, a variable line spacing grating, and a charge coupled device detector (CCD) [9]. The V_2O_5 was a commercial powder. YVO_4 sample was prepared by sol–gel acrylamide polymerization in order to optimize the synthesis conditions and thermal treatments that reduce the temperature of crystal formation and to improve the homogeneous shape and size particle distribution in the nanometer range [10]. The monochromator energy is calibrated (with an accuracy of 0.4 eV) by comparing our V_2O_5 spectrum with those reported in the literature [11].

This calibration should be accurate to about 0.4 eV. The outgoing photon energy was calibrated with the elastic emission peaks present in all of our spectra.

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3. Results and discussion

X-ray absorption calculations were performed for YVO$_4$ and V$_2$O$_5$ using charge-transfer atomic multiplet codes [12]. The calculation was performed in a D$_{4h}$ symmetry with 10Dq, Ds and Dt as the ligand field parameters (LFP). We assumed that the ground state is an admixture of d^0 and d^1$\underline{L}$ electronic configurations ($\underline{L}$ represents a ligand hole). The Slater integrals were reduced to 70% of the Hartree–Fock values. The final values of the LFP were respectively 1.4, 0.0 and 0.24 eV for YVO$_4$ and 1.0, 0.0, and 0.5 eV for V$_2$O$_5$. The differences in these two V^{5+} compounds can be explained partly because of the change in structure which results in different LFP and charge transfer energy, Δ. However, the main effect is due to the hybridization between the V 3p and O 2p orbitals. For V$_2$O$_5$ we used $\Delta=0$. This means a strong hybridization also results in larger linewidths across all the L$_{2,3}$ region. For YVO$_4$ we used the larger value $\Delta=3.0$, which means less hybridization and narrow absorption lines.

Fig. 1a shows that the L$_3$ edge in YVO$_4$–TEY is split into two major peaks. Between 520 and 530 eV one finds a very broad L$_2$ edge due to the C–K process that reduces the lifetime of the 2p$_{1/2}$ core-hole compared to the lifetime of the 2p$_{3/2}$ core-hole [13]. In the calculated absorption spectra we indicate by a vertical line the position and relative intensity of each transition from the ground state. We then perform the convolution of these lines with Lorentzian functions to simulate the broadening from the expected atomic 0.12 eV (HWHM) [4] to a 0.26 eV hybridization-broadened for L$_3$ to 0.78 eV for L$_2$ due to the 2p c-h lifetime. The resulting spectrum is then convoluted with a Gaussian function of constant width (0.18 eV HWHM) to take into account the contribution of the monochromator finite resolution. The emission spectra are shown in Fig. 1b. They all have the elastic peak and a normal peak at about 511 eV. The region between these two is where spectator emission following the CK decay is expected. As the excitation energy goes through the L$_2$ maximum (spectra m–s) normal emission peak sharpens and also shifts upward in energy by about 1 eV. A series of new, sharp emission peaks appears between normal emission and the elastic peak. These features correspond to transitions of the localized 3d electron into the 2p$_{3/2}$ hole, the inverse transition that gives rise to the absorption features of the L$_3$ edge (Fig. 1a). However they are shifted to lower energies by about 1.0 eV, indicating a change in the screening of the 3d electron. We performed Gaussian fits to these emission spectra. The results for spectrum (r) are indicated in Fig. 1c. We have a sharp elastic peak over a broad background due to overlapping oxygen (K) emission excited by higher orders of the incoming radiation. The CK peak is constructed with two emission lines separated by the same energy interval found in the absorption spectrum (0.48 eV) and with the same intensity ratio (65/35). The central energy and the total area of this doublet were used as fit parameters. The width of the two spectator CK peaks in spectrum (r) is 1.18 eV. The elastic peak width directly gives the combined contributions of the spectrometer and monochromator, which results in an instrumental width of 0.65 eV. Subtracting these two values in quadrature gives a line width of 0.98 eV [14]. This is then the measured width of the 2p$_{1/2}$ hole in this compound and corresponds to a lifetime of 670 as. It includes the 2p Auger decay width and the CK decay width. For comparison, Fig. 1d shows the spectrum (t) taken after maximum of L$_2$. At this excitation energy the spectrum show the elastic peak and normal peak at 511 eV, but the contribution of the CK process disappeared completely.

The TEY spectrum for V$_2$O$_5$ shows two broad structures around 518 and 525 eV, which are the vanadium L$_3$ and L$_2$ edges, respectively (Fig. 2a). The O K-edge appears above 530 eV. We also present the emission spectra recorded at the vanadium L$_{2,3}$ edge for the covalent compound V$_2$O$_5$ (Fig. 2b). The spectra show the evolution of elastic peak and normal peak at about 511 eV. The region between these two is spread over a range of energies characterized by the charge transfer states. Fig. 2c shows the comparison between the
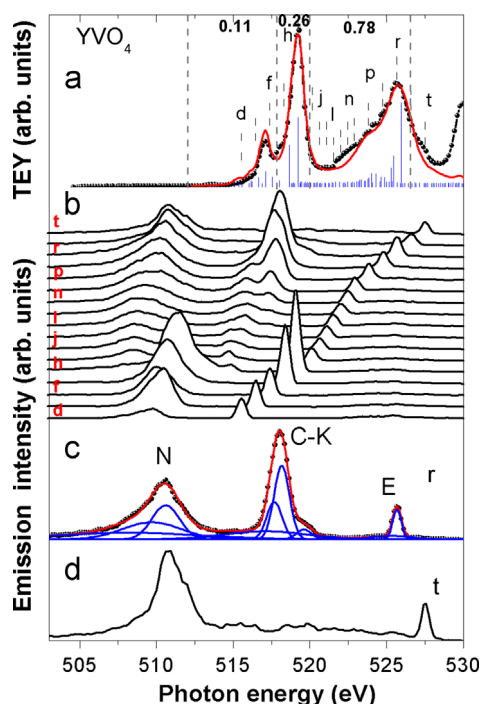

Fig. 1. RIXS results for YVO$_4$: (a) comparison between the experimental TEY spectrum (dots) and the charge transfer multiplet calculation (solid line). The values for the core-hole widths (HWHM) used in the calculations are at the top of spectrum. (b) The emission spectra recorded at the vanadium L$_{2,3}$ edge. (c) The emission spectra at the maximum of L$_2$ (r). (d) Emission spectrum (t) after the maximum of L$_2$.
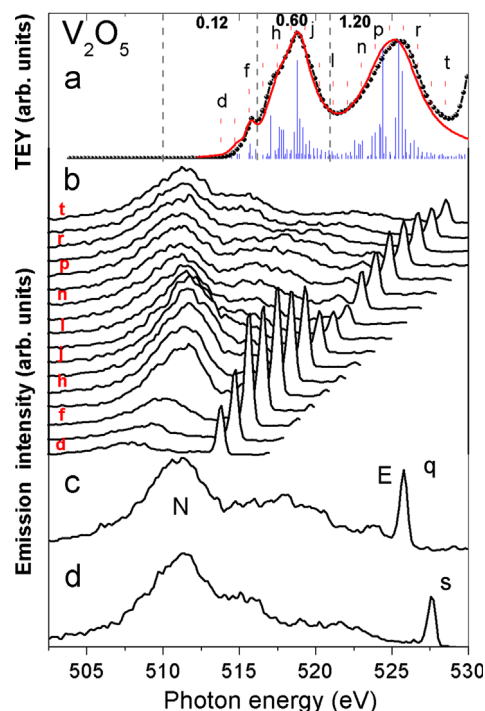

Fig. 2. RIXS results for V$_2$O$_5$: (a) comparison between the experimental TEY spectrum and the charge transfer multiplet calculation. The values for the core-hole widths (HWHM) used in the calculations are at the top of spectrum. (b) The emission spectra recorded at the vanadium L$_{2,3}$ edge. (c) X-Ray emission spectrum recorded at the maximum of L$_2$. (d) The emission spectrum recorded after the L$_2$ maximum.

spectator emission in V_2O_5 that is spread over a range of energies (delocalized states) while in YVO_4 it results in sharp emission peaks. Fig. 2d shows the spectrum (s) taken after maximum of L_2 in order to follow the charge transfer states which still remain.

4. Conclusions

RIXS experiment allowed us to study in detail the fast CK decay of the resonantly produced $2p_{1/2}$ hole in the ionic YVO_4 compound. The fact that the state is localized is reflected in the presence of sharp emission peaks with shapes that correspond to the $3d \rightarrow 2p_{3/2}$ transition in the absorption spectrum. The lifetime of the $2p_{1/2}$ hole could be measured by the broadening of these sharp spectator peaks. On the other hand, the CK behavior of the more hybridized compound V_2O_5 shows broader, less defined features that do not allow a determination of the $2p_{1/2}$ core-hole lifetime.

Acknowledgments

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