

# Ultra-high Resolution Low-energy Resonant Raman Scattering at the Cu 3p-Resonances of several Insulating Cuprates

L.-C. Duda<sup>1</sup>, T. Schmitt<sup>1</sup>, J.H. Guo<sup>2</sup>, S.E. Canton<sup>2</sup>, J.D. Bozek<sup>2</sup>, P. Kuiper<sup>3</sup> and J. Nordgren<sup>1</sup>

<sup>1</sup>Department of Physics, Uppsala University, Box 530, 75121 Uppsala, Sweden

<sup>2</sup>Advanced Light Source, Ernest Orlando Lawrence Berkeley National Laboratory, University of California, Berkeley, California 94720, USA

<sup>3</sup>Department of Physics, Växjö University, S-351 95 Växjö, Sweden

## INTRODUCTION

Crystal field (CF) excitations of cuprates may only be probed indirectly with standard techniques such as midinfrared absorption spectroscopy (by phonon- and/or magnon-assistance) or in electron energy loss spectroscopy. By contrast, CF excitations are very prominent in resonant soft x-ray emission at L- and M-edges of 3d-transition metals cations of many correlated 3d-transition metal materials [1]. The energy of these excitations simply correspond to the effective energy loss between the incoming and outgoing x-ray photons of two dipole-allowed electronic transitions, and therefore we call this process resonant inelastic x-ray scattering (RIXS). The dominating spectral features originate from it dd- and charge transfer excitations that are reached by two dipole-allowed photon transitions in the RIXS process. This is a coherent scattering process that can be described by the Kramers-Heisenberg formula. RIXS is distinct from non-resonant (so-called "ordinary") soft x-ray emission spectra (SXES) where the excited core electron leaves the vicinity of the atom and local energy conservation is lost. At resonance the excited electron is promoted into rather localized orbitals and therefore the intermediate state of the atom has a well-defined energy. Thus, whenever these conditions hold, the coherent scattering process dominates and RIXS will be prominent. Note that there are cases in which both RIXS and ordinary SXES have similar spectral weight, indicating simultaneous localized and itinerant character of the intermediate state. Such behavior has been found for several vanadium oxide compounds.

## EXPERIMENTAL

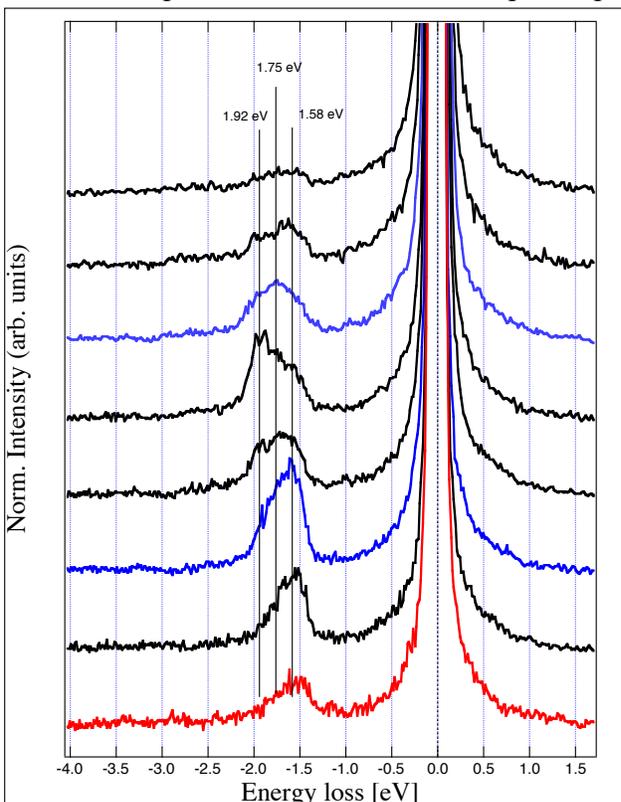
The experiments reported here have been performed at beamline 10.0.1, comprising a 10-cm-period undulator and a spherical grating monochromator BL10, at the Advanced Light Source of the Lawrence Berkeley National Laboratory, USA. The detection system for the secondary beam of scattered ultrasoft x-rays was a grazing incidence grating spectrometer in the Rowland geometry spectrometer. We used the following spectrometer settings for the present experiments: 300-lines/mm, 3m grating, at a grazing angle of 5.4 degrees. The spectrometer entrance slit width was chosen to be 10 $\mu$ m, yielding a spectrometer resolution of about 80 meV at 75eV and the monochromator spectral band width was chosen to have a corresponding or a somewhat smaller value. The combined resolution is reflected by the full width at half maximum (FWHM) of the elastic peak that appears in the RIXS spectra.

The SrCuO<sub>2</sub> and CuGeO<sub>3</sub> samples were large single crystals grown from the melt by a floating zone method. The crystal dimensions were approximately 10mmx5mmx5mm. The CuO and

$\text{La}_2\text{CuO}_4$  were commercially large obtained single crystals. All data were taken with the samples at room temperature. Energy calibration of the RIXS spectra was done by relating the elastic peak positions and the monochromator calibration.

## RESULTS

Polarization and energy dependent resonant inelastic x-ray scattering experiments at the Cu 3p absorption resonances of the insulating cuprates  $\text{CuGeO}_3$ ,  $\text{SrCuO}_2$ ,  $\text{CuO}$ , and  $\text{La}_2\text{CuO}_4$ . For  $\text{CuGeO}_3$  (see Fig. 1), we observe three close-lying excitations that agree well with energy values of dd excitatopns found in infrared absorption spectroscopy: 1.58 eV, 1.75 eV, and 1.92 eV. For



$\text{CuO}$  and  $\text{La}_2\text{CuO}_4$  we observe two close-lying structures, the energies of which are somewhat higher than previously published values using other spectroscopies. For  $\text{SrCuO}_2$ , we observe three well-resolved excitations at 1.9eV, 2.2eV, and 2.8eV. Especially the last Raman shift value is extraordinarily large compared to the values of the other cuprates. Nevertheless a new ab initio calculation [2] for the dd-excitations of this compound shows very good agreement to the experimentally determined values. We attribute this feature to the unique one-dimensional and compact structure of the cuprate  $\text{SrCuO}_2$ .

Figure 1. Energy dependence of Cu 3p RIXS of  $\text{CuGeO}_3$ . The excitation energies range from 73 eV to 80 eV in 1 eV steps.

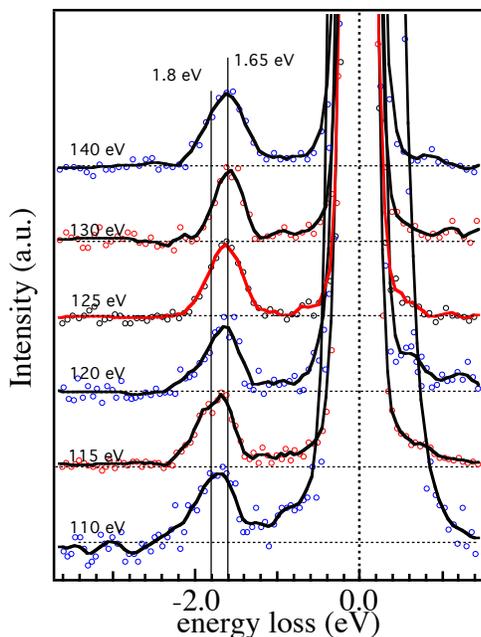
The intensity ratio between the elastic peak and the dd-excitation peaks depends on several factors, such as orientation of the crystal axes and surface roughness, among other things. Our spectra have typical ratios of  $10^5 : 1$ . The width of the dd-excitation peaks (Gaussian fits with FWHM of up to 430meV for some compounds) is larger than the spectral resolution indicative substantial broadening effects. Any phonon broadening could possibly be reduced at lower the sample temperature and this is subject of ongoing work.

## DISCUSSION

The absorption at cuprate L- and M-edges is very simple, because the excited p-electrons have only a single state to make a transition, namely the empty  $\text{Cu } 3d(x^2-y^2)$ . The electronic transitions involved are very few and therefore the RIXS spectra can be readily written out on paper [3]. Energetically less favorable transitions involving charge transfer from oxygen sites are substantially weaker and can be neglected in our discussion. The spin-orbit splitting of the 3p levels in Cu is about 2 eV and therefore we observe two energies at which the dd-excitation peaks

have a resonance (Fig. 1). At the Cu 3p<sub>1/2</sub>-resonance spin-flip transitions become allowed and

this modifies the spectral weight of the dd-transition peaks and explains partly the observed excitation energy behavior of the dd-subcomponents.



Strong correlation effects are present in these compounds which can be illustrated by the observation [4] of dd-excitation “echoes” in Cu 3s-RIXS of CuGeO<sub>3</sub> (Fig. 2). At the Cu 3s-resonance an electron from the 3s-level is excited to a p-like state. The RIXS spectra show that energy loss features appear in the same energy region. This indicates that there is a strong correlation between the Cu 4p-like and Cu 3d-like valence states.

Figure 2. Energy dependence of Cu 3s RIXS of CuGeO<sub>3</sub>.

Doped cuprates, especially superconductors, as well as temperature dependent studies will present the next stage of investigation. Also other 3d-transition metals

have their 3p resonances well below 100 eV and the crystal field excitations of their correlated oxide compounds can be addressed with this unique experimental method.

## SUMMARY

Ultra-high resolution low-energy RIXS at Cu 3p-resonances has been performed on several insulating cuprates and we have determined their dd-excitation energies.

## ACKNOWLEDGMENTS

We thank G. Dhalenne and A. Revcolevschi for the CuGeO<sub>3</sub> and SrCuO<sub>2</sub> crystal samples and we thank G. Dräger for the CuO, and La<sub>2</sub>CuO<sub>4</sub> crystal samples.

## REFERENCES

1. see Journal of Electron Spectroscopy and Related Phenomena 110–111 (2000).
2. Coen de Graaf, private communication.
3. L.-C. Duda, T. Schmitt, P. Kuiper et al., in preparation.
4. L.-C. Duda, T. Schmitt and J. Nordgren et al., Surface Review and Letters, Vol. 9, No. 2 (2002) 1103.

This work was supported by the Swedish Research Council (VR) and the Göran Gustafsson Foundation (GGS).

Principal investigator: Laurent Duda. Department of Physics, Uppsala University, Box 530, 75121 Uppsala, Sweden Email: Laurent.Duda@fysik.uu.se. Telephone: +46-18-4713512.