Copper $L$-edge spectra: multiplet vs. multiple scattering theory

W Xu$^{1*}$, X-L. Zhang$^{1}$, Z-Y. Guo$^{1}$, C Si$^{1}$, Y-D. Zhao$^{1}$, A Marcelli$^{2,3*}$, D-L. Chen$^{1}$, and Z-Y. Wu$^{3*}$

$^{1}$Institute of High Energy Physics, Chinese Academy of Sciences, Beijing, 100049, China
$^{2}$Laboratori Nazionali di Frascati - INFN, Frascati, 00044, Italy
$^{3}$NSRL, University of Science and Technology of China, Hefei 230026, China

E-mail: xuw@mail.ihep.ac.cn; marcelli@lnf.infn.it; wuzy@ustc.edu.cn

Abstract. Cu $L_{2,3}$-edge X-ray absorption spectra of the orthorhombic La$_2$CuO$_4$ have been investigated using the multiplet method and the multiple scattering theory. We found that $d$ states of Cu$^{2+}$ are not localized and both long- and medium- range atoms contribute to the $L_{2,3}$ edge spectrum, i.e., the transition from 2p electrons to partial and local empty 3d states. The behaviour is different from that observed in many other transition metals in which localized $d$ states are merely influenced by the crystal field with a strong spin-orbit interaction.

Introduction

The transition metal $L_{2,3}$ edge X-ray absorption spectroscopy (XAS) has been widely used to investigate 3$d$ empty states in many materials and probes both the spin-orbit interaction and the crystal-field contribution. The La$_2$CuO$_4$ is the simplest cuprate, which is characterized by a LaO-CuO$_2$-LaO unit cell also known as a single-layer cuprate. [1] Cu $L_3$-edge XAS spectra of cuprates were investigated to extract information regarding their electronic structure [2,3], the valence state of copper, [4] site symmetry [5], while complementary or verified results can be achieved from interpreting both edges. [6,7] The $L_2$ and $L_3$ edge spectra probe transitions from 2p$^{1/2}$ and 2p$^{3/2}$ orbital levels, respectively, to 3d empty states. These soft X-ray absorption edges have been widely utilized to investigate charge-transfer effects, Coulomb interactions and other electronic effects in many transition metal oxides.[2-7] The theoretical framework to interpret $L_{2,3}$ edge is based either on the atomic-like multiplet method or on the single-particle approximation full multiple scattering theory.

The arrangement of CuO$_6$ octahedrons with respect to the lanthanum atoms is affected by the different oxygen atoms. As shown in Figure 1, the tilting of the distorted CuO$_6$ octahedrons is characteristic of the orthorhombic symmetry. Consequently, it is extremely
interesting to reconstruct the local structure around Cu atoms and its electronic interaction with neighbouring atoms, i.e., lanthanum and oxygen.

Figure 1 The crystal structure of the La$_2$CuO$_4$ observed from different axis (see text).

**Experiment**

The La$_2$CuO$_4$ polycrystalline ceramic was synthesized by Spark Plasma Sintering method X-ray absorption. Details about the synthesis and characterization are reported elsewhere [8]. The dense ceramic pellets were grounded into fine powders using a mortar. The powder was evenly brushed on the surface of a carbon tape that was stick to a copper sample holder for the X-ray absorption spectroscopy (XAS) measurements. XAS spectra were collected at the 4B7B endstation of the Beijing Synchrotron Radiation Facility.

**Calculation details**

Cu $L_{2,3}$ XANES spectra have been simulated using two different approaches: the multiplet theory which due to localized nature of $L_{2,3}$ edges of transition metals emphasizes crystal field effects and spin-orbit interactions; and the multiple scattering theory which describes the interactions between the central photo absorber and the coordination scatterers in the real space. For the multiplet we employed the strategy implemented in the CTM4XAS package. Details about parameters are presented and discussed in the next section. For the multiple scattering calculations we used the FDMNES code (2012). [9] The muffin-tin potential and Hedin-Lundqvist exchange potential were chosen in the Green mode, while the non-muffin-tin Finite Difference Method was also used for comparison.

**Results and discussions**

**Multiplet**

The multiplet method [10] emphasizes the atomic spin-orbit interactions of the photo absorber and the crystal field effects imposed by the coordinated ligands. Although it is easy to reproduce the $L$ edge for other metal edges as shown in Ref. [10], it is not possible to reproduce Cu $L_{2,3}$ XANES spectra of the La$_2$CuO$_4$ system by playing the orbital-charge related parameters. In Figure 2, we present here only the evolution of both shape and position of $L_2$ and $L_3$ edges with respect to different spin-orbital couplings of 2p core states and 3d valence states. The energy difference between $L_2$ and $L_3$ edges are linearly dependent by both 2p and 3d spin-orbital couplings. However, the multiplet approach is not sufficient to reproduce Cu the $L_{2,3}$ XANES spectra of the La$_2$CuO$_4$ system.

**Full Multiple Scattering Theory (FMST)**

The measured Cu $L_{2,3}$ edge XANES are shown in Figure 3(a). They are pronounced 2p$^{1/2}$-3d and 2p$^{3/2}$-3d transitions whose spectral shape can be qualitatively fitted using two lorentzian profiles and one arctangent step function. The central energy for $L_2$ and $L_3$ edges is 950.5 eV and 930.5 eV, respectively; while the weak bump feature appearing in between edges has a maximum at 938.2 eV. Besides the peak positions, the peak intensity of $L_2$ and $L_3$
edges as obtained by fitting is 6.1 and 10.7, respectively, giving rise to a branch ratio of approximately 3:5.

As shown in Figure 3(b)-(e), we compare spectra simulated using different clusters in the framework of both the full multiple scattering theory with muffin-tin potentials, as well as the finite difference method (FDM). The calculation reproduces the $L_2$ and $L_3$ peak features well, indicating that the calculations converge at 8 Å. Nevertheless, new bump features appear in between $L_2$ and $L_3$ peak for clusters larger than 8 Å. This discrepancy is due to overestimation of multiple scattering from long-distance atoms. This is reasonable due to the localization of $d$ states. The small energy shift at the $L_2$ edge for a cluster of 8 Å can be assigned to both distortion of the local structure around copper atoms or defects. The finite difference method (FDM) overcome the limitation of the muffin-tin potential but is limited by computation power. By using a small cluster, it is demonstrated the calculation can be slightly improved using full potential method, as shown in Figure 3(e).

Conclusions
We compared theoretical XAS spectra obtained with the atomic multiplet theory and the full multiple scattering approach. The multiplet theory cannot yet reproduce the experimental spectra while the full multiple scattering theory well reproduce both peaks although the calculation is limited by the localization of $d$ states and to a cluster size of ~8 Å. Simulations
point out that the full potential method have space for improvement in the description of these systems. Moreover, for this particular system, an integration of the full multiple scattering single-particle picture with the atomic screening field method appears mandatory.

Acknowledgments
The research has been supported by the National Natural Science Foundation of China (Grant No. 11105172). We thank Y. Joly for many fruitful discussions.

References
[1] N. Poccia, A. Ricci, G. Campi, M. Fratini, A. Puri, D. Di Gioacchino, A. Marcelli, M. Reynolds, M. Burghammer, N.L. Saini, G. Aeppli and A. Bianconi, Optimum inhomogeneity of local lattice distortions in La$_2$CuO$_{4+y}$, PNAS 109, 15685-15690 (2012)
[2] A. Bianconi, J. Budnick, G. Demazeau, A. M. Flank, A. Fontaine, P. Lagarde, J. Jegoudez, A. Revcolevski, A. Marcelli, and M. Verduguer, Cu $L_3$ x-ray absorption of formally trivalent Cu compounds Physica. C 153-155 (1988) 117.
[3] A. Bianconi, P. Castrucci, M. de Simone, A. Fabrizi, M. Pompa, A. Marcelli, A.M. Flank and P. Lagarde, Nuovo Cimento 25 (1990) 737.
[4] M. Grioni, J. B. Goedkoop, R. Schoorl, F. M. F. de Groot, J. C. Fuggle, F. Schäfers, E. E. Koch, G. Rossi, J. M. Esteva, and R. C. Karnatak, Studies of copper valence states with Cu $L_3$ x-ray-absorption spectroscopy, Phys. Rev. B 39 (1989) 1541.
[5] M. Pompa, C. Li, A. Bianconi, A. Congiu Castellano, S. Della Longa, A. M. Flank, P. Lagarde, and D. Udrón, Full multiple scattering analysis of linearly polarized Cu $L_3$-edge XANES of La$_2$CuO$_4$ Physica. C 184 (1991) 51.
[6] L. Braicovich, M. Moretti Sala, L. J. P. Ament, V. Bisogni, M. Minola, G. Balestrino, D. Di Castro, G. M. De Luca, M. Salluzzo, G. Ghiringhelli, and J. van den Brink, Momentum and polarization dependence of single-magnon spectral weight for Cu $L_3$ -edge resonant inelastic x-ray scattering from layered cuprates, Phys. Rev. B 81 (2010) 174533
[7] M. M. Sala, V. Bisogni, C. Aruta, G. Balestrino, H. Berger, N. B. Brookes, G. M. d. Luca, D. D. Castro, M. Grioni, M. Guarise, P. G. Medaglia, F. M. Granazio, M. Minola, P. Perna, M. Radovic, M. S. T. Schmit, K. J. Zhou, L. Braicovich and G. Ghiringhelli, Energy and symmetry of dd excitations in undoped layered cuprates measured by Cu $L_3$ resonant inelastic x-ray scattering, New J. Phys. 13 (2011) 043026.
[8] Yuan-Hua Lin, Yong Liu, Bo-Ping Zhang, Ce-Wen Nan, Jing-Feng Li, and Zhijian Shen, Electrical Transport Properties of La$_2$CuO$_4$ Ceramics Processed by the Spark Plasma Sintering J. Am. Ceram. Soc. 90 (2007) 4005.
[9] Y. Joly, X-ray absorption near-edge structure calculations beyond the muffin-tin approximation, Phys. Rev. B 63 (2001) 125120.
[10] F. de Groot, Multiplet effects in X-ray spectroscopy, Coord. Chem. Rev. 249 (2005) 31.