Orbital Ordering and Spin Gap in Ruthenate $La_4Ru_2O_{10}$

Z. Hu (胡志偉)[1], T. Burnus[1], H. Wu[1], J. D. Denlinger[2], P. G. Khalifah[3], L.-Y. Jang (張凌雲)[4], H. Hsieh (謝輝煌)[5], D. I. Khomskii[1], A. Tanaka[6], K. S. Liang (梁耕三)[4], and L. H. Tjeng[1]

[1]II. Physikalisches Institut, Universität zu Köln, Köln, Germany
[2]Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California, USA
[3]Department of Chemistry, University of Massachusetts, Amherst, Massachusetts, USA
[4]National Synchrotron Radiation Research Center, Hsinchu, Taiwan
[5]Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan
[6]Department of Materials Science, Faculty of Science, Hiroshima University, Higashi-Hiroschima, Japan

The role of orbital degree of freedom in determining the properties of materials with strongly correlated electrons attracts now more and more attention [1]. In particular, there are now many indications that the orbital degree plays an important role in metal-insulator transitions [2]. One interesting example is $La_4Ru_2O_{10}$ in which a strong first-order structural transition at T_S = 160 K accompanied by a rare 4*d* orbital ordering and a spin-gap opening were found [3]. It was proposed that a strong crystal-field splitting (CFS) of the Ru-t_{2g} levels due to the lattice distortion below T_S forces each Ru^{4+} ion to transform from the usual low-spin state $t_{2g}\uparrow^3 t_{2g}\downarrow^1$ (S = 1) to an ultra-low-spin state $t_{2g}\uparrow^2 t_{2g}\downarrow^2$ (i.e., $d_{xy}^2 d_{xz}^2$, S = 0) [3]. However, for the transition from an S = 1 to an S = 0 state of the Ru^{4+} ion, the CFS must be larger than the Hund's exchange energy J_H, which for Ru is about 0.5 eV. For t_{2g} levels this seems to be rather unlikely.

To settle these questions and to find the origin of the spin-gap state, we undertook a joint experimental and theoretical study on the Ru-$L_{2,3}$ x-ray absorption spectroscopy (XAS) spectrum of $La_4Ru_2O_{10}$ as well as LDA+U calculations. Fig. 1 shows the Ru-$L_{2,3}$ XAS spectra of $La_4Ru_2O_{10}$ taken at 220 K (black line) and 110 K (red line), and the inset shows the O-*K* XAS spectra measured at 200 K (black line) and 85 K (red line). The O-*K* XAS spectra are sensitive to the surrounding and thus the considerable spectral change across T_S evidences the structural change. However, the Ru-$L_{2,3}$ spectrum is very sensitive to the valence and spin state [4]. The Ru-$L_{2,3}$ spectrum of $La_4Ru_2O_{10}$ is at the same energy position as Ca_2RuO_4 (not shown), indicating the Ru^{4+} ($4d^4$) state. Note that there is no change of the *Ru*-$L_{2,3}$ spectra across the transition, indicating no change of the valence and spin state of Ru crossing T_S. To extract further information of the spin state from the Ru-$L_{2,3}$ spectrum, we have also performed cluster-model calculations. The experimental Ru-$L_{2,3}$ XAS spectrum can be well reproduced with the Ru-O transfer integral $pd\sigma$ = –2.8 eV and the O *2p*–Ru *4d* charge-transfer energy Δ = 0 eV. This simulation gives S = 1 in the ground state for both the high and low temperature phases. Theoretically we expect an intensity $I(L_3)/[I(L_3)+I(L_2)]$ branching ratio change of 6.4 % from S = 1 to S = 0 as distortion *Ds* changes from –0.09 to –0.8 eV, where $I(L_3)$ and $I(L_2)$ represent spectral intensity of the L_3 and L_2 edges, respectively. However, Fig. 1 shows that the branching ratio is only slightly changed (< 0.5 %) from 220 K to 110 K.

Furthermore, the theoretical Ru-$L_{2,3}$ spectrum with S = 0 [Fig. 1(c)] strongly disagrees with the experiment at 110 K. Therefore we can rule out the original model of orbital-ordering-induced spin-state transition from S = 1 to S = 0 [3].

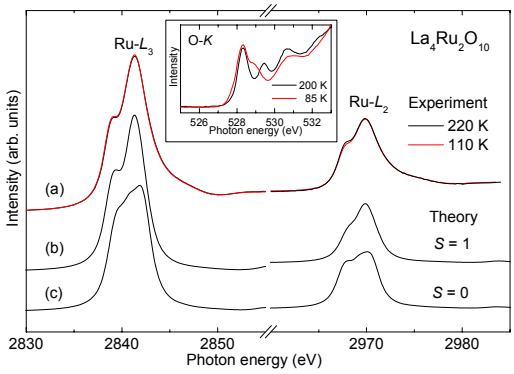

Figure 1. The Ru-$L_{2,3}$ XAS spectra of $La_4Ru_2O_{10}$ (a) measured at 220 K (black line) and 110 K (red line); theoretical spectra either for Ru^{4+} S = 1 (b) or S = 0 (c). The inset shows O-*K* spectra measured at 200 K and 85 K.

Our LDA+U band calculations further confirm that the Ru^{4+} ions in $La_4Ru_2O_{10}$ remain in the normal S = 1 state both above and below the structural phase-transition temperature T_S. Associated with the lattice distortion below T_S, the Ru^{4+} ions undergo a t_{2g} orbital ordering and produce drastically anisotropic antiferromagnetic couplings. The resultant spin-gap opening is due to the formation of spin-singlet dimers of two strongly antiferromagnetically coupled Ru^{4+} ions. Thus, $La_4Ru_2O_{10}$ is – in the class of 4*d* transition-metal oxides – a new example demonstrating the important role of the orbital degree of freedom and orbital ordering in determining the electronic and magnetic properties.

We acknowledge the NSRRC staff for providing us with an extremely stable beam.

[1] Y. Tokura and N. Nagaosa, Science **288**, 462 (2000).
[2] M. W. Haverkort *et al.*, Phys. Rev. Lett. **95**, 196404 (2005).
[3] P. Khalifah *et al.*, Science **297**, 2237 (2002).
[4] Z. Hu *et al.*, Phys. Rev. B **61**, 5262 (2000).