Mixed-valence State of Cu in $RuSr_2R(Cu_{1-x}M_x)_2O_8$ (R=Gd, Eu and M=Ni, Zn)

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Recently, D.C. Ling et al. [1] have reported the impurity induced influence both on superdonductivity and ferromagnetism for the Ni- and Zn-substituted ruthenium-based layered copper oxide, $RuSr_2RCu_2O_8$ (RuR-1212), where R=Gd and Eu. The Cu substitution by Zn exhibits the contrast reduction rate of transition temperature, T_C, between RuGd-1212 (rapid) and RuEu-1212 (slow), respectively, while Ni melts regularly the superconductivity regardless of the kind of base materials (Gd and Eu). In contrast to the pair-breaking effects by Ni and Zn impurities, the magnetic ordering, T_M, incrases in RuGd-1212 as doped regardless of the kind of impurities while it decreases in RuEu-1212

In order to elucidate the doping effects, the electronic structure of RuR-1212 (R=Gd, Eu) and doped samples has been investigated by using X-ray absorption spectroscopy (XAS), which were carried out at the 16A, 20A and 17C beamlines. All spectra were recorded in the fluorescence yield (FY) mode for Ru and Cu L-edge.

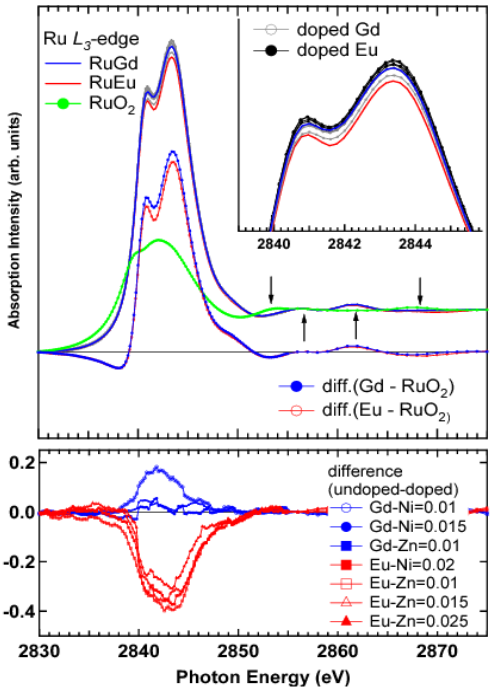

Fig. 1: Ru L_3-edge XAS spectra of RuR-1212 and doped samples in comparison with the reference compound, RuO_2 (Ru^{4+}:$4d^4$). Inset magnifies the L_3-edge XAS spectra. Bottom shows the difference between undoped (Gd or Eu) and doped samples.

It is generally believed that Ru L_3-edge XAS spectra in Ru-1212 have the mixed-valence states between Ru^{4+} and Ru^{5+} [2]. The ratio of Ru^{4+} to Ru^{5+} for both RuGd-1212 and RuEu-1212 is 0.4 : 0.6 within ± 0.05 error extent, which is in good agreement with the previous estimation despite of subtracting the spectrum of RuO_2 powder, representing Ru^{4+} valence state [2].

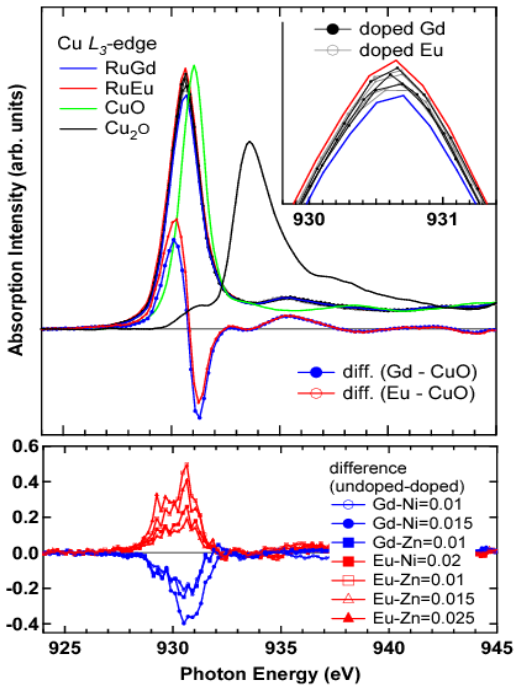

Fig. 2: Cu L_3-edge XAS spectra of Ru-1212 and doped samples in comparison with CuO and Cu_2O, representing 1+, 2+ valence state. Inset magnifies the L_3-edge XAS spectra. Bottom shows the difference between undoped (Gd or Eu) and doped samples.

Similar to the method used for Ru L_3-edge, we could estimate the amount of Cu^{3+} valence states (difference at lower energy) by subtracting the spectrum of CuO, representing Cu^{2+} valence state. Note that the white line of Cu L_3-edge spectra of Ru-1212 appears at the lower energy (-0.4 eV) than standards, CuO (931.0 eV) due to the lack of electron that fills the well-localized d shell than in CuO. The ratio of Cu^{2+} to Cu^{3+} is 0.77 : 0.23 for RuGd-1212 and 0.67:0.33 for RuEu-1212, respectively.

The inverse proportion of differences between Ru and Cu L-edge spectra suggests that there are charge transger between Cu and Ru through oxygen, in fact, Cu^{3+} and Ru^{4+} states, which are responsible for the doping effects both on superconductivity and magnetic properties.

References

[1] D. C. Ling, S. L. Wu, M. H. Lin, and F. Z. Chien, Physica C (to be published).
[2] R. S. Liu, L.-Y. Jang, H.-H. Hung, and J. L. Tallon, Phys. Rev. B **63**, 212507 (2001).