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Evidence for an anomalous redox ionic pair between Ru and Mn in $SrRu_{0.5}Mn_{0.5}O_3$: An X-ray absorption spectroscopy approach

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Received (in Cambridge, UK) 23rd September 2002, Accepted 1st November 2002
First published as an Advance Article on the web 19th November 2002

X-ray absorption spectroscopy studies of the polycrystalline $SrRu_{0.5}Mn_{0.5}O_3$ have been performed at Ru, Mn-$L_{2,3}$ edges. The $2p \rightarrow t_{2g}$ related peak at the Ru-L_2 edge is more intense than the Ru-L_3 edge and a shift of the $2p \rightarrow e_g$ related peak by ~0.8 eV to higher energy than that of the Ru(IV) compound, $SrRuO_3$ is observed. In combination with a crystal field multiplet calculation approach, a possible anomalous change in the spectral features is explained based on the existence of a redox ionic pair involving Ru(IV)/Ru(V) ↔ Mn(III)/Mn(IV).

$SrRuO_3$ is a well-studied super exchange mediated ferromagnetic metal having the saturation magnetic moment M_s = 1.1–1.3 μ_B as observed by neutron diffraction studies.[1–3] X-ray absorption spectroscopic (XAS) studies show that Ru exists only in Ru (IV): $t_{2g}{}^4e_g{}^0$ valence state and there is no signature of mixed valence.[4] Recent observations from magnetic and transport studies of Ru doped rare earth manganites and charge ordered manganites show that Ru participates in double exchange ferromagnetic interaction.[5,6] The exact role of Ru on the magnetic and the electronic properties is not fully understood, although mixed valence of Ru [Ru(IV)/Ru(V)] seems to play a vital role in showing unusual magnetic and transport properties within the frame work of Zener's double exchange model.[7] To probe the existence of the mixed valence state of the Ru ion in the presence of the Mn ion, we have performed XAS studies of the polycrystalline $SrRu_{0.5}Mn_{0.5}O_3$ at Ru, Mn–$L_{2,3}$ edges. The observed spectral features of the Ru, Mn–$L_{2,3}$ edges have been compared with the spectral features of well-studied compounds, where Ru and Mn exists in single valent and mixed valent states.

Polycrystalline sample of $SrRu_{0.5}Mn_{0.5}O_3$ along with the reference compounds were prepared by the routine solid-state method using high purity $SrCO_3$, RuO_2, MnO_2, La_2O_3 and CuO. These powders were mixed, ground and calcined at 1000 °C for 72 h with intermittent grinding. X-Ray diffraction patterns (XRD) of the compounds were taken with a Philips diffractometer using CoK_α radiation. The XRD pattern of $SrRu_{0.5}Mn_{0.5}O_3$ indicates that the sample is in single phase having orthorhombic symmetry. The Mn–$L_{2,3}$ XAS data were recorded in total electron yield at the SX700-II beam line at Berliner Elektronen Speicherring für Synchrotronstrahlung (BESSY) Berlin. The Ru–$L_{2,3}$ X-ray absorption spectroscopic data were recorded in transmission geometry at the EXAFS-II beam line at Hamburger Synchrotron strahlung labor, HASYLAB/DESY in Hamburg, Germany.

In Fig. 1a we present the Mn–$L_{2,3}$ XAS spectra of the $SrRu_{0.5}Mn_{0.5}O_3$ system together with that of $LiMn_2O_4$ and MnO_2 for comparison, where Mn exists in Mn(III)/Mn(IV) and Mn(IV) respectively. The Mn–$L_{2,3}$ XAS spectra of $SrRu_{0.5}Mn_{0.5}O_3$ is almost identical to the spectrum of $LiMn_2O_4$, implying that the ground state of Mn corresponds to mixed valent state involving both the Mn(III)/Mn(IV) oxidation states. On the other hand, for the charge neutralization Ru should exist in the Ru(IV) and Ru(V) oxidation states. Therefore, we compare the spectral features of $SrRuO_3$ and $SrRu_{0.5}Mn_{0.5}O_3$ with a well-known tetravalent Ru compound RuO_2 and a pentavalent Ru compound $Sr_4Ru_2O_9$ as shown in Fig. 1b. To ease our comparison, we shift the L_2 spectra (open symbols) in each case, such that the high-energy feature (B) is aligned with the corresponding feature in the L_3 spectra (filled symbols). The peaks A and B are assigned to $2p \rightarrow t_{2g}$ and $2p \rightarrow e_g$ related states respectively. The relative intensity of the $2p \rightarrow t_{2g}$ related peak for $SrRuO_3$ at the L_2 edge is less intense than the L_3 edge and it closely matches with the spectral features of the tetravalent Ru(IV) compound, RuO_2, indicating that the valence state of Ru in $SrRuO_3$ is Ru(IV). However, the $2p \rightarrow t_{2g}$ related peak for $SrRu_{0.5}Mn_{0.5}O_3$ at the L_2 edge is more intense than the L_3 edge. In the Ru(IV) compound, the $2p \rightarrow t_{2g}$ related peak at the L_2 edge is less intense than the L_3 edge, because of the forbidden nature of the transition to the Γ_7 and Γ_8 orbital in the energy level diagram due to the strong spin-orbit coupling effect.[8] In contrast, the relative intensity of the $2p \rightarrow t_{2g}$-related peak A for $SrRu_{0.5}Mn_{0.5}O_3$ is greater at the L_2 edge than at the L_3 edge, indicating that the transition to the Γ_7 and Γ_8 orbital becomes allowed. This is possible if Ru exists as Ru(V). Since, the spin-orbit coupling effect of the Ru(IV) ion suppresses due to the presence of the Ru(V) ion.[9] In addition to the spectral change of the $2p \rightarrow t_{2g}$-related peak at the Ru-$L_{2,3}$ edge, a shift by 0.8

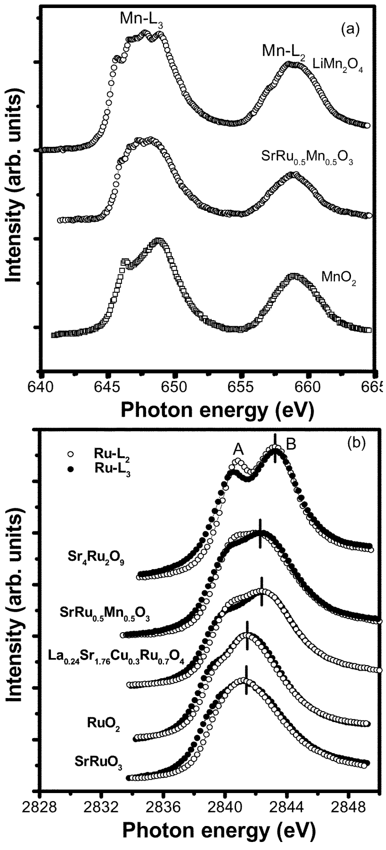

Fig. 1 Shows the Mn, Ru-$L_{2,3}$ spectra of $SrRu_{0.5}Mn_{0.5}O_3$ in comparison to the reference compound.

DOI: 10.1039/b209293j

eV to higher energy of the 2p → e_g-related peak than that of the parent compound $SrRuO_3$, suggesting a higher valency of Ru in $SrRu_{0.5}Mn_{0.5}O_3$. This change is only half way with respect to the Ru(V) compound $Sr_4Ru_2O_9$, implying that the valence of Ru in $SrRu_{0.5}Mn_{0.5}O_3$ could be in between the +4 and +5 states *i.e.* Ru exists in both Ru(IV) and Ru(V) oxidation states. The spectra of $SrRu_{0.5}Mn_{0.5}O_3$ indeed match well with the spectra of $La_{0.24}Sr_{1.76}Cu_{0.3}Ru_{0.7}O_4$, where Ru exists in both Ru(IV) and Ru(V) valence states.[4] Hence, an anomalous change in the spectral features in $SrRu_{0.5}Mn_{0.5}O_3$ could be due to the existence of redox ionic pair between Ru and Mn involving Ru(IV)/Ru(V) ↔ Mn(III)/Mn(IV).

Neutron diffraction studies clearly show that the valence state of Ru in $SrRuO_3$ is Ru(IV).[1,2] Thus, one can assume that the valence state of Ru and Mn could be Ru(IV) and Mn(IV) respectively, in $SrRu_{0.5}Mn_{0.5}O_3$ for the charge neutralization. As the ionic radius of Mn(IV) (0.52 Å) is smaller than the ionic radius of Ru(IV) (0.62 Å),[10] thus the Ru–O distance should decrease with increasing Mn content. Therefore, one would expect that the intensity distribution of the 2p → t_{2g} related peak at the L_2 and L_3 edge in $SrRu_{0.5}Mn_{0.5}O_3$ could be due to the influence of the crystal field strength (10 Dq). In order to understand, the significant changes in the spectral features of the observed XAS spectra are due to the 10 Dq effect or some other effects, we have performed a calculation within the crystal field multiplet calculation (CFMC) approach.[11] The Hamiltonian for the crystal-field-multiplet calculation is written as

$$H = H_{av} + H_{MS}$$

H_{av} gives the average energy and does not contribute to spectral splitting, while H_{MS} includes all contributions to splitting given by

$$H_{MS} = L.S\ (2p) + H_{CCF} + L.S\ (4d) + g\ (i.j)$$

For 4d transition metal compound the large spin-orbit splitting of 2p core hole separates the L_2 and L_3 edge and does not contribute to the splitting of the each edge. While, the spectral feature of the edge is determined by the cubic crystal field, H_{CCF} and the two electron coulomb term, g(i,j), as well as the spin-orbit coupling of the 4d electrons, L.S (4d). The redial part of g(i,j), is divided into direct Coulomb term F^K and an exchange term G^K is the so-called Slater integral.

Fig. 2 shows the calculated Ru-L_2 and L_3 XAS spectra for Ru(IV) and Ru(V) at different 10 Dq values by considering the Slater integral to be 40% of the atomic value for Ru(IV) and 15% for Ru(V) respectively. The values of the Slater integral obtained by Hu *et al.* for the Ru(IV) and Ru(V) compound were taken for the calculation.[9] It is observed from Fig. 2a that with a variation of the 10 Dq value from 1.8 eV to 2.8 eV for the Ru(IV) configuration, the basic spectral profiles do not change *e.g.*, the Ru–L_3 (solid line) is more intense than Ru-L_2 (dashed line) and the energy shift is within 0.2 eV. However, the higher intensity of the 2p → t_{2g}-related peak at the L_2 edge then the L_3 edge could be possible if a few percentage of the Ru(IV) can transfer to the Ru(V) state as shown in Fig. 2b. This means that the 4d spin-orbit coupling effect of the Ru(IV) ion in the presence of the Ru(V) ion suppresses due to the covalency effect, resulting in a strong transfer of intensity between the L_2 and L_3 edge. Therefore, the significant differences in the spectral features of the X-ray absorption spectra in $SrRu_{0.5}Mn_{0.5}O_3$ from that of the parent compound $SrRuO_3$ are due to the spin-orbit coupling effect, rather than the crystal field splitting energy (10 Dq) and can be attributed to the valence effect. The observed spectrum is clearly indicating the existence of mixed valence Ru(IV)/Ru(V) in $SrRu_{0.5}Mn_{0.5}O_3$. For the charge neutralization, the respective amount of Mn(IV) goes to the Mn(III) state and makes redox ionic pair with Ru as like Ru(IV)/Ru(V) ↔ Mn(III)/Mn(IV). The comparable oxidation–reduction potential of Ru(IV)/Ru(V) (1.07 eV) and Mn(III)/Mn(IV) (1.02 eV) seems to play a decisive role in balancing the charge distribution. This paper could set a reference for Ru doped rare earth manganites including charge ordered manganites, where Ru displays an unusual behavior on the magnetic and electronic properties.

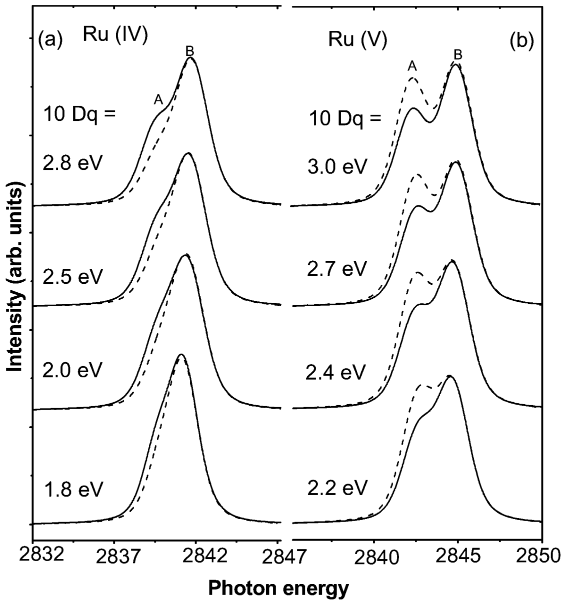

Fig. 2 Shows the theoretical multiplet spectra at the L_2 (dashed line) and L_3 (solid line) edges for (left panel) Ru (IV) and (right panel) for Ru (V) configuration with reduced Slater integrals 40% and 15% of the atomic value respectively. The values of the octahedral cubic crystal field 10 Dq used for both configurations are also given.

The authors thank Dr Z. Hu for his help in the XAS measurements.

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