X-ray Absorption Study of Co and Mn Valence State in $LaMn_{0.5}Co_{0.5}O_3$

Tobias Burnus[1], Zhiwei Hu[1], Hui-Huang Hsieh (謝輝煌)[2], P. A. Joy[3], Hong-Ji Lin (林宏基)[4], Chien-Te Chen (陳建德)[4], and Liu-Hao Tjeng[1]

[1]II Physical Institute, University of Cologne, Cologne, Germany
[2]Chung Cheng Institute of Technology, National Defense University, Taoyuan, Taiwan
[3]Physical and Materials Chemistry Division, National Chemical Laboratory, Pune, India
[4]National Synchrotron Radiation Research Center, Hsinchu, Taiwan

Substitution of the magnetic Mn ions by Co yields ferromagnetism in the $LaMn_{1-x}Co_xO_3$ series. The Curie temperature reaches a maximum for x = 0.5 (T_C = 220-240 K) [1,2]. Explaining the appearance of ferromagnetism in the manganites by Co substitution is, however, not a trivial issue. Joy *et al*. have synthesized two different single phases of $LaMn_{0.5}Co_{0.5}O_3$ and inferred from a combination of magnetic susceptibility and x-ray photoelectron spectroscopy measurements that the phase with the higher T_C contains high-spin Mn^{3+} and low-spin Co^{3+} ions, while the lower T_C phase has Co^{2+} and Mn^{4+}.

Very recently, however, long-range charge ordering has been observed in neutron diffraction experiments on the high-T_C phase, pointing towards the Co^{2+}-Mn^{4+} scenario [3,4].

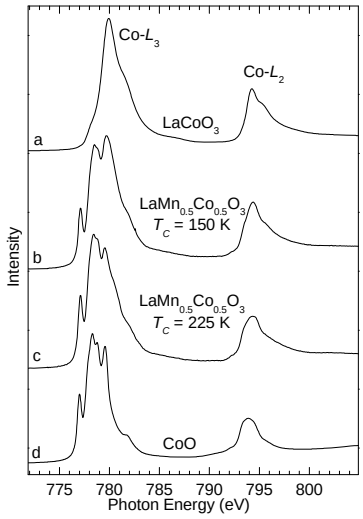

Figure 1. The Co-$L_{2,3}$ XAS spectra of $LaMn_{0.5}Co_{0.5}O_3$ with T_C = 150 K and 225 K together with $LaCoO_3$ and Co as references.

To settle the question of Mn and Co valence we have studied the Co-$L_{2,3}$ and Mn-$L_{2,3}$ XAS spectrum of $LaMn_{0.5}Co_{0.5}O_3$. Fig. 1 shows the Co-$L_{2,3}$ XAS spectra of both low-T_C and high-T_C $LaMn_{0.5}Co_{0.5}O_3$ and $LaCoO_3$ as a trivalent reference and CoO as a divalent reference.

In Fig. 1 we see a shift of the ``center of gravity" of the L_3 white line to higher photon energies by approximately 1.5 eV in going from CoO to $LaCoO_3$. The energy position and the spectral shape of the high-T_C-phase of $LaMn_{0.5}Co_{0.5}O_3$ is very similar to that of CoO, indicating an essentially divalent state of the Co ions. From the high-T_C to the low-T_C phase, the spectral weight at the main peak of $LaCoO_3$ (about 780 eV) is increased. This is natural to associate this increase with the presence of Co^{3+} species.

Fig. 2 shows the Mn-$L_{2,3}$ XAS spectra of both low-T_C and high-T_C $LaMn_{0.5}Co_{0.5}O_3$ together with MnO, $LaMnO_3$ and $SrMnO_3$ as a divalent, a trivalent and tetravalent Mn references, respectively. Again we see a gradual shift of the ``center of gravity" of the L_3 white line to higher energies from MnO to $LaMnO_3$ and further to $SrMnO_3$, reflecting the increase of the Mn valence state from 2+ via 3+ to 4+. The result is agreement with above observation of the Co^{2+} valence in the Co-$L_{2,3}$ XAS spectra, i.e. fulfilling the charge balance requirement.

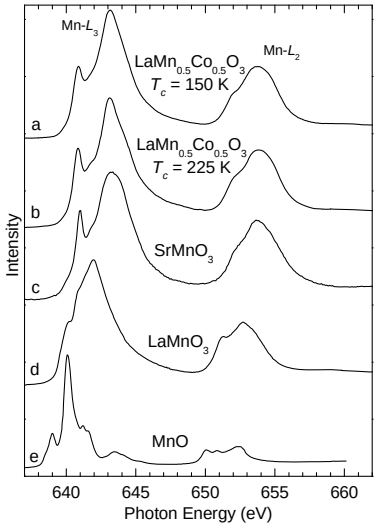

Figure 2. The Mn-$L_{2,3}$ XAS spectra of $LaMn_{0.5}Co_{0.5}O_3$ with T_C = 150 K and 225 K together with MnO, $LaMnO_3$ and $SrMnO_3$ as references.

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