

Mn-K XAS study of $\text{SrMn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 1/3, 1/2, 2/3$) Materials

Mark Croft, Ian D. Fawcett, Gabriel M. Veith and Martha Greenblatt, Israel Nowik (Rutgers Univ.)

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The $\text{SrMn}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ ($x = 1/3, 1/2, 2/3$) phases are of interest as potential d^3/d^4 colossal magnetoresistance materials. These materials were found to occur in the cubic perovskite structure. The energies of the Mn-K main edge peaks for all x -values (see figure below right) fall close to the Mn^{4+} - CaMnO_3 standard, indicating a Mn valence close to (though perhaps just below) $4+$. The Fe substitution dependence of the Mn-K edge chemical shift is consistent with an essentially constant Mn-valence as a function of Fe content.

The Mn-K peak pre-edge features in the figure (below left), are consistent with previous results on Mn^{4+} compounds with three pre-edge features a1, a2 and a3 being quite visible. Simple crystal field and correlation arguments, along with more rigorous electronic structure and optical absorption work, support the majority-spin- e_g assignment for the a1-feature. The higher energy a2 and a3 features are associated with t_{2g} - and e_g - minority spin states with additional effects coming into play. In contrast to the Mn-main-edge results, the changes in the Mn-K pre-edge feature structure are quite dramatic, with increasing x enhancing the a1 feature intensity relative to the a2 feature.

A number of authors have argued that Fe substitutes as Fe^{3+} until the Mn has been transformed largely into Mn^{4+} ; and that the filled Fe - e_g majority spin states lie substantially lower in energy than the Mn- e_g . Within this framework, we argue that a Fe neighbor should reduce the resonant e_g overlap integrals for the Mn- e_g states. This should substantially increase the degree of localization of the Mn- e_g orbitals with increasing Fe content. It is therefore suggested, that the strong a1-feature enhancement is related to an increase in the transition matrix element with increasing e_g -state (majority spin) localization. An additional enhancement may also be related to a localization enhancement of the Coulomb interaction with the core hole.

It is worth noting that the above proposal would suggest that all perovskite-related manganite materials might show similarly dramatic Fe-substitution-induced pre-edge feature changes. Indeed XAS results in our lab have confirmed this Fe-modification trend in the 3-2-7 and 4-3-10 Ruddlesdon-Popper phases of the manganites. Further, it should be pointed out that extension of the same argument to the Fe sites would imply an analogous Mn-substitution-induced localization of the Fe-d states. Mössbauer results by our and other groups unambiguously favor such localization. Thus the mutual localization of the Mn and Fe d-states (near the Fermi energy) in the mixed (Mn,Fe) materials is supported.

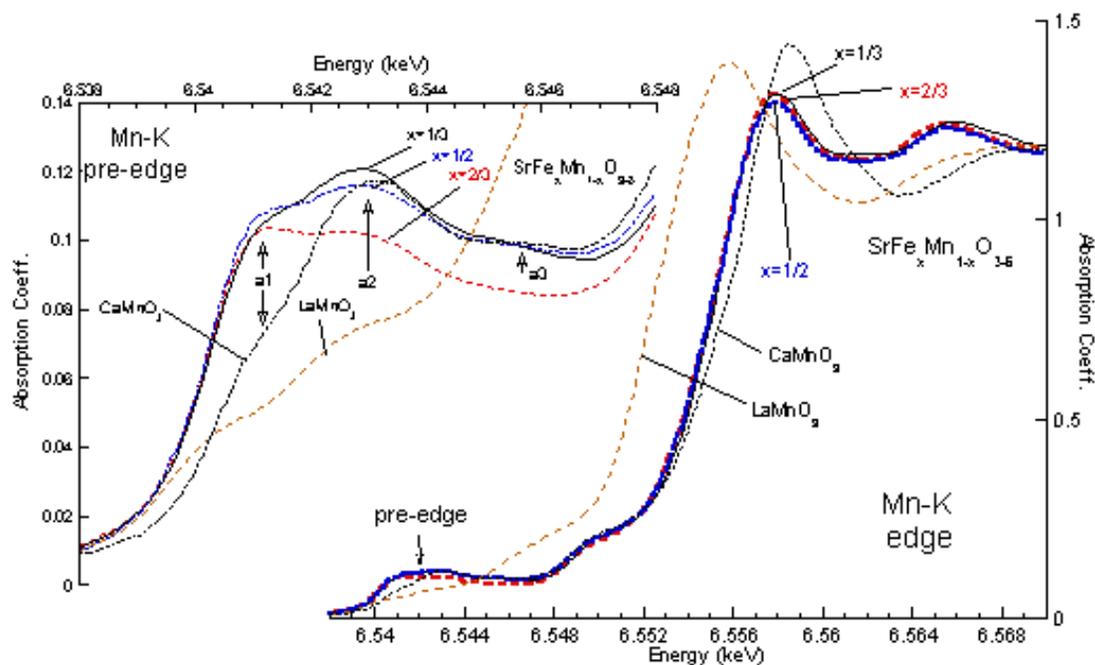


Figure Mn-K main- and pre- edges discussed in text.