The SrMn$_{1-x}$Fe$_x$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.