The study of Manganese compounds $K_\beta$ spectra and spin-polarized XANES at BSRF

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Outline

- X-ray $K_\beta$ fluorescence yield spectra of Mn compounds
- Spin-polarized X-ray absorption near edge spectra (SPXANES)
Introduction

In last twenty years, high-energy resolution inelastic x-ray scattering and valence band relative emission spectroscopy have excited interest in the scientific world. Its use has been made possible with the availability of high flux synchrotron radiation sources. Many experiments have now been carried out in research fields such as physics, chemistry, material science and biology.
Crystal, sample and detector was aligned on the Rowland circle geometry.

The Rowland circle has a diameter $d=2R$.

Bragg's law: $2d \sin \theta = n \lambda$.

**The energy resolution**:

$$\frac{\Delta E}{E} = \Delta \theta \cot \theta$$

In a conventional fluorescence experiment is not possible to resolve the $K_\beta$ structure.
High-Energy Resolution layout at BSRF

Detector

Sample

X-ray

Crystal analyzer
The strong coupling between the 3p core hole and the partially filled 3d orbital yield atomic multiplets which are spread over about 15eV energy range.
The line positions and detailed spectral shapes of Mn K\textsubscript{\beta} spectra depend on the oxidation and the spin state of the Mn site. For example: The Mn K\textsubscript{\beta} spectra of MnF\textsubscript{2} and MnO\textsubscript{2}...
Mn K$_\beta$ spectra MnO$_2$ and SrMnO$_3$ oxides

SrMnO$_3$ is slightly more covalent than MnO$_2$. 
Mn Kβ spectra of La$_{1-x}$Ca$_x$MnO$_3$ perovskites system with different Ca doping
\[ x=1.0, 0.8, 0.67, 0.5, 0.3, 0.2, 0 \]

Mn Kβ spectra of La$_{1-x}$Sr$_x$MnO$_3$ system with different Sr doping:
\[ (x=0, 0.3, 0.5, 0.8, 1.0) \]

A logarithmic scale is used for comparisons between the weak satellite and the main line

La$_{1-x}$Sr$_x$MnO$_3$ system is more covalent than La$_{1-x}$Ca$_x$MnO$_3$
SPXANES were obtained by monitoring the $K_{\beta}$ fluorescence yield at two energies—-the main line, $K_{\beta_{1,3}}$ (e.g., spin-down) and the satellite line, $K'_{\beta}$ (e.g., spin-up) for each Mn valence while the incident energy was scanned across the near edge region (Partial Fluorescence Yield)
Spin-polarized XANES of LSMO system for x=0, 0.3, 0.5, 0.8, 1
The dash-dotted line correspond to spin-up electrons excited from the 1s state, while the solid line correspond to spin-down spectrum.

we can see a clearly splitting between the spin up and spin down spectrum.
The main line varied systematically with doping Sr.

Data collection at 4W1B @ BSRF
**Left:** SPXANES at RT and HT of \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) for \( x=0.3, 0.5, 0.8 \). The solid line corresponds to spin-up electrons excited from the 1s state (RT) while the dashed line is the HT spin-up spectrum. The dotted line corresponds to a spin-down electron excited from 1s state (RT) while the dash-dotted line is the HT spin-down channel.

**Right:** SPXANES of \( \text{La}_{1-x}\text{Ca}_x\text{MnO}_3 \) for \( x=0,0.3,0.5,0.7,1.0 \) (Q. Qian, T.A. Tyson et al, PRB 68 (2003) 014429)
For $x=0.3$, the pre-edge intensity of spin-up absorption increased from room temperature to high temperature. On the other hand, it is reversed about the spin-down absorption. For other doping, there are not obvious change.

The main line of both spin-up and spin-down absorption are broadening slightly along with the increasing of temperature.

We want to obtain the change of the pre-edge of the LSMO system when the local magnetic ordering varied.

The interpretation of the pre-edge will be studied theoretically further.
Conclusions

- Comparison of covalency between MnO$_2$ and SrMnO$_3$: SrMnO$_3$ is slightly more covalent than MnO$_2$
- Comparison of K$_\beta$ spectra and SP-XANES of La$_{1-x}$Ca$_x$MnO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$ systems: La$_{1-x}$Sr$_x$MnO$_3$ system is more covalent than La$_{1-x}$Ca$_x$MnO$_3$ system
- Comparison of Mn SP-XANES of the La$_{1-x}$Sr$_x$MnO$_3$ system. It needs multiplet and band structure calculations further
Thanks for your attention!