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	Experiment title: The electronic structure of Mn in LaMnO3 and relatives studied by RIXS in the Mn K pre-edge	**Experiment number**: HE 1916
Beamline: ID26	**Date of experiment**: from: 29 June 2005 to: 05 July 2005	**Date of report**: 28.2.2006
Shifts: 18	**Local contact(s)**: Pieter Glatzel	*Received at ESRF:*

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Report:

No reliable $LaMnO_3$ samples were available at the beginning of the beamtime and we were thus not able to perform the proposed measurement without having serious doubts concerning the quality of the samples. We thus decided to study another Mn^{3+} system. We chose to measure Mn in a single crystal of bixbyite ($Mn_xFe_{1-x}O_2$). It is a long standing controversy whether or not quadrupole transitions contribute to the K absorption pre-edge in transition metals. Bixbyite has cubic symmetry and thus serves as an ideal system to distinguish between dipole and quadrupole transitions. Dipole transitions in cubic system do not show any angular dependence.[1] The absorption scans in Figure 1 clearly show an angular dependence and thus confirm quadrupolar contributions to the spectral intensity.

These findings point to the importance of multiplet effects. However, a simple absorption scan is in many cases not enough to test a theoretical model because similar spectral shapes can be reproduced using different theoretical approaches. We thus recorded the full Mn 1s3p RIXS plane for several angles. The strong (3p,3d) interactions make this technique very sensitive to the 3d spin state and actually allows to record spin-selective absorption spectra [2-4]. However, the full RIXS plane greatly facilitates interpretation of the spectra as opposed to simple line scans. Figure 2 shows the results for two angles. The first structure of the pre-edge is almost entirely separated by the spin-selectivity while the second, broad structure shows intensity for both spin directions. Also, the first structure shows a much stronger angular dependence than the second. The intensity is considerably weaker for the spin-down direction (high larger energy transfer, s. Figure 2). This is due to the fact that many more $1s^13d^5$ final states are available for a spin down electron that is excited in a $3d^4$ high-spin configuration than for a spin-up electron (defining the 3d electrons to have spin-up direction).

We were able to simulate the spectra using ligand field multiplet calculations and obtained an admixture of about 12 % of a 3d5 configuration into the ground state due to hybridization effects. The spin-up peak at lowest incident energy is due to intra-atomic exchange-like interactions, i.e. it is a manifestation of Hund's rule. The important outcome of this study:

- unambiguous evidence for quadrupole contributions
- direct observation of intra-atomic electron-electron interactions in the K pre-edge (Hund's rule)

These findings will form the basis for future evaluation of K absorption pre-edges in the many important Mn3+ systems. They furthermore partly contradict the interpretations put forward in some studies with respect to inter-atomic (Mn-Mn) interactions[5] and confirm experiments previously performed.[6, 7]

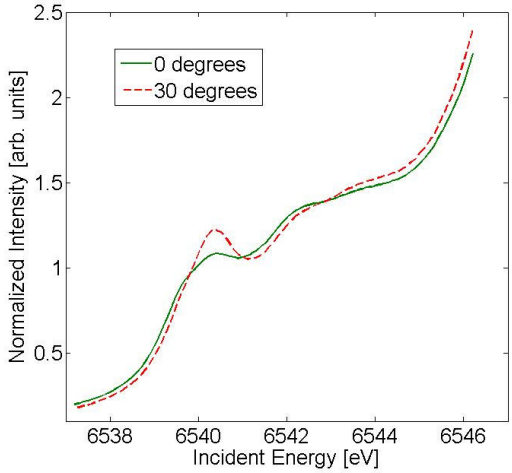

Figure 1 *:* Angular dependence of the K absorption pre-edge of Mn in bixbyite.

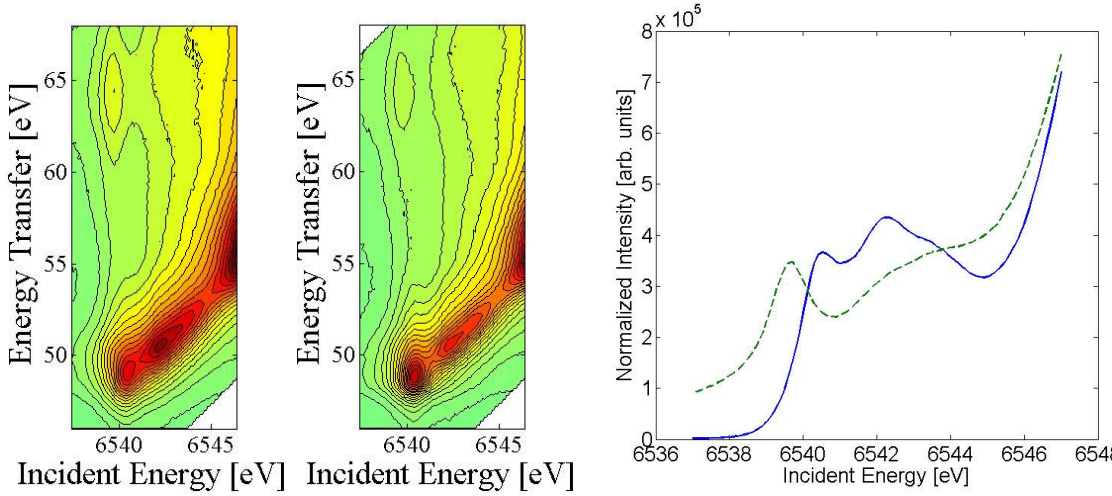

Figure 2 : left : 1s3p RIXS planes of Mn in bixbyite at 0 (far left) and 30 degrees of the incident beam relative to the crystal (110) axis. right: spin-selective absorption scans extracted from the RIXS planes: spin-down (blue solid), spin-up (green dashed)

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