



	<b>Experiment title:</b> Resonance Diffraction Investigation of Mixed-Valence Manganese Oxosilicates and Oxyhalides.	<b>Experiment number:</b> CH-84
<b>Beamline:</b> BM16	<b>Date of experiment:</b> June 1996	<b>Date of report:</b> 08/31/98
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**Report:**

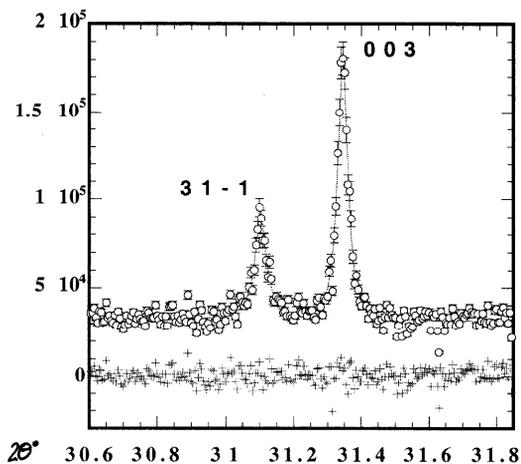
We have investigated the mixed-valence manganese oxosilicate  $\text{La}_4\text{Mn}_5\text{Si}_4\text{O}_{22}$ . This compound is an unusual system exhibiting the coexistence of three Mn valencies  $\text{Mn}^{2+}$ ,  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ . The manganese valence states have been investigated by means of **Diffraction Anomalous Fine Structure (DAFS) spectroscopy**: the same experiment probes both the local atomic environment through X-ray absorption and long-range order through diffraction. Due to the crystallographic structure, the intensities of reflections are sensitive to the relative contributions of the various Mn sites, and hence to the different valences.

Powder diffraction patterns were recorded at 20 energies around the K edge of Mn (6539 eV). Each pattern covered a 28 range of around  $50^\circ$ . The sample mounting in flat-plate geometry was rotated to average the grain contributions.

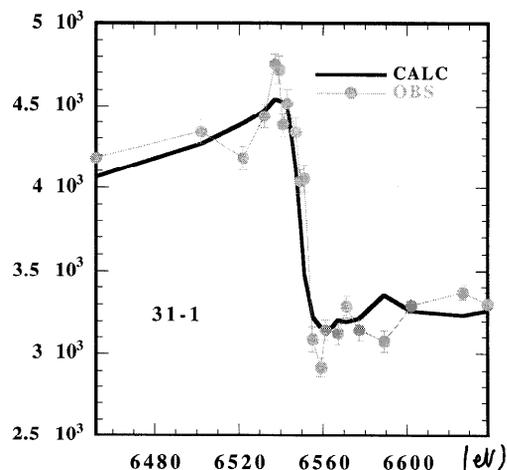
To decrease the absorption and provide an internal reference for the absorption correction, the sample was diluted with LiF powder.

The variations in intensity induced by the DAFS signal are of the order of a few percent, so the diffraction peaks must be integrated with a higher accuracy. This is why a separate integration of the peaks based on a Pearson VII function was performed instead of a Rietveld refinement (see fig. 1). The experiment was carried out on a high resolution diffractometer so that the FWHM of the peaks ( $\sim 0.045^\circ$  in  $2\theta$ ) is mainly due to the sample contribution (size and strain effects).  $\text{Mn}^{2+}\text{O}$ ,  $\text{Mn}^{3+}_2\text{O}_3$  and  $\text{Mn}^{4+}\text{O}_2$  reference spectra were also collected to extract the anomalous scattering factors and for energy calibrations.

The diffracted intensities were simulated using the valency assignment for the various Mn sites determined from the Mn-O distances and by Electron Energy Loss Spectroscopy (EELS) (see fig. 2). Due to the lack of accuracy in the measured intensities, we were not able to independently extract the valence state of each type of Mn site. However the proposed distribution of Mn valencies agrees well with the experimental data.



**Fig. 1:** Shape of the 31-1 and 003 Bragg peaks at  $E=6542$  eV (below the Mn edge)



**Fig. 2:** Simulation of the diffracted intensity for the 31-1 Bragg peak