



	Experiment title: Diffraction Anomalous Fine Structure Performed on a Tin Mordenite.	Experiment number: MI-43
Beamline: ID 11	Date of experiment: from: 12-04-95 to: 17-04-95	Date of report: 21-02-97 <i>Received at ESRF:</i>
Shifts: 9 + 6	Local contact(s): Heinz Graafsma	

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Report: The aim of this study was to analyze the possibilities of utilizing Diffraction Anomalous Fine Structure in materials science for characterization of partially ordered compounds of (partially) unknown structure. The compound studied is tin-mordenite, a synthetic zeolite, which has attracted interest because of its proton conducting properties. (Crystal data: Orthorhombic Cmc₂m, a=18.1435(10)Å, b=20.4890(12)Å, c=7.4903(4)Å, chemical formula: Sn_{3.6}Si₄₀Al₈O₁₂₈H₅₆). The position of the tin ions in the zeolite is unknown, however, they are thought to reside in the channels of the zeolite with a coordination sphere of water molecules. Chemical analysis suggests a tin content of about 3.6 atoms pr. unit cell. The chemical state of tin is difficult to verify by X-ray Absorption Spectroscopy, because there is an impurity phase of SnO₂ (8 % by weight) which is present as very small particles, presumably on the surface of the tin mordenite crystallites. The sample is only available as a powder, not as single crystals.

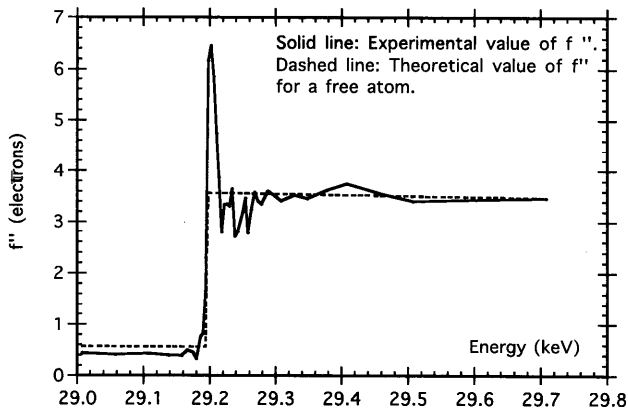
Diffraction data were collected at the ESRF Materials Science wiggler beamline (ID1 1). A bicon scintillation detector used for recording diffracted intensities was mounted on the 28 arm of the kappa diffractometer and the sample was on a flat plate powder spinner in transmission. An ionisation chamber measured transmission of the sample and a diode recorded the incoming intensity. Incoming and receiving slits were set at 0.3 mm, sample to detector distance was 98 cm. An unfocussed beam was used,

The mordenite powder was mixed with LiF to diminish bulk absorption and provide an internal standard. The powder profiles were step scanned with a resolution of 0.005° , yielding a peak FWHM of 0.03° . Three powder diffraction diagrams were recorded in the interval 1.5° to 15.0° at the energies 29.0, 29.2 (Sn K-edge) and 29.7 keV (0.42 \AA). 8 reflections were selected and measured at 47 energies bracketing the edge, with 4 eV step near the edge. The transmission was recorded to provide the absorption coefficient, $\mu(E)$. The experimental energy resolution matched well the theoretical.

The DAFS technique was developed by Sorensen et al. [1] and Pickering et al. [2]. In short, it allows extraction of site-specific absorption spectra from diffraction data collected at sequential energies bracketing an absorption edge. This formalism has been implemented in a least-squares routine, MXD [3,4]. MXD was used to refine absorption, as well as $f'(E)$, and structural distortions. The powder sample is a poor scatterer and unfortunately, there has not been enough phasing power in the data to locate all tin positions within the zeolite. Difficulties occur, because the tin atoms have partial occupation of several sites. However, one tin site in the major channel, residing in the mirror plane at $z=3/4$ is highly probable. MXD can handle uncertainties in the detailed structure and still allows extraction of the total anomalous contribution from one phase. Such an analysis was successfully performed, and the resulting anomalous scattering factor, $f''(E)$, is visualized in Fig. 1. The pronounced white line indicates, that the tin within the zeolite is in oxidation state IV, which is novel information. This zeolite is the most atom rich structure, which has hitherto been subjected to a DAFS analysis.

Figure 1.

The anomalous scattering factor, $f''(E)$ of the tin within the zeolite, calculated by Kramers-Kronig transform of the refined $f'(E)$.



We thank Dr. P. Wolfers and Dr. J. Vacinova, CNRS, Grenoble for the development of the program MXD for DAFS studies. AFJ acknowledges a post doctoral fellowship from the EU Human Capital and Mobility program.

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