Beam time report

Experiment CH – 1098: “The origin of mixed valence alkaline earth guest atoms in thermoelectric clathrates”

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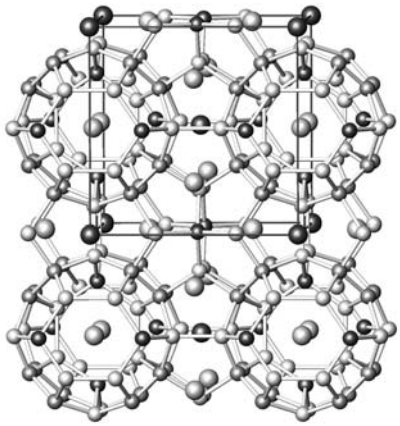
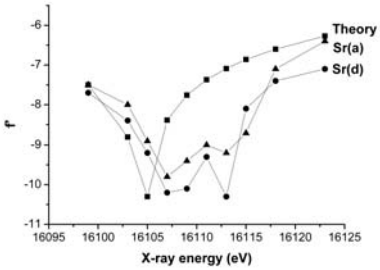


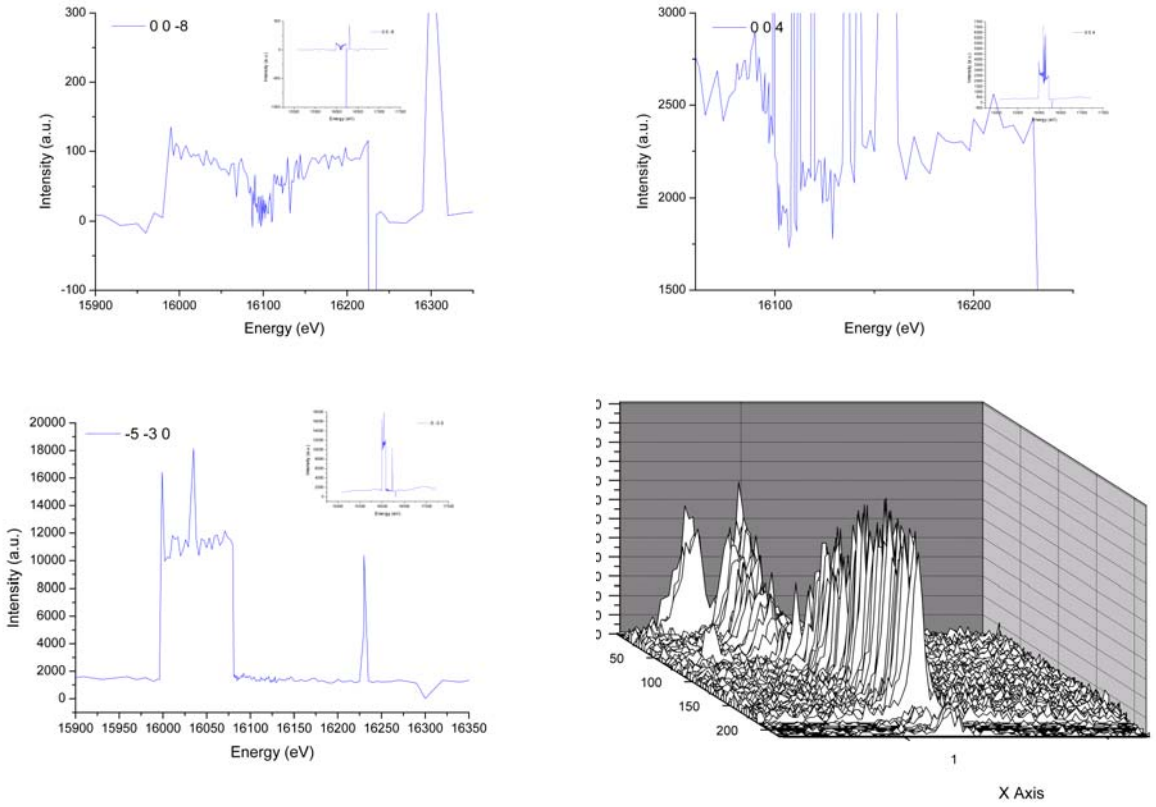


The variation in the anomalous part of the atomic scattering factor f(S), ($f(S) = f^0(S) + f' + if''$), across an absorption edge can be used to create contrast between atoms of the same element in different valence states. This is because the ionization energies and thus the position of the absorption edge depend on the oxidation state of the system. The energy dependence of the Bragg reflection intensity near and above the absorption edge of some atomic level forms the basis of the DAFS (diffraction anomalous fine-structure) method. This technique combines the long-range order sensitivity typical of the x-ray diffraction method with the local character and site selectivity of absorption spectroscopy. The DAFS technique, if applied to a selection of reflections in an energy range near and above the absorption edge should represent a valuable experimental tool to shed light, in a site-specific manner, on the guest valence states in clathrates, Figure 1. In a previous experiment (CH-893) we used a somewhat different approach than in the typical DAFS experiment. Instead of collecting few reflections at many different wavelengths and relying on i) somewhat crude absorption correction and ii) the Kramers-Kronig transformation to obtain f’, we have collected many reflections at relatively few wavelengths around the Sr k-edge. This allowed us to obtain f’ directly as a parameter in the crystallographic refinements, Figure 2. Full structural diffraction data were collected at 10 wavelengths across the Sr K-edge as well as at one very short wavelength (off-edge). The theoretical curve was calculated for a neutral Sr using a free-atom model. While this model is able to reproduce the most evident structure of f’, like the cusp, it cannot calculate the fine-structure oscillations observed in the experimental data. A model that takes these oscillations in account has been recently developed in terms of the tensor formulation of the multiple scattering theory (M. Benfatto, R. Felici, *Phys. Rev. B* **2001***, 64*, 115410)

The problem with the results of experiment CH-893 was that the energy resolution was not sufficiently good, and the esd on the individual data points is typically around 0.5 e. In the presenr experiment CH-1098 we aimed at carrying out a conventional DAFS experiment in order to validate the f’ curve. We collected on average 30 reflections at a very large number of wavelengths extending from about 1000 eV below the Sr k-edge to 3000 eV above. In the region around the edge an energy resolution of 1 eV was used. For several reflection, e.g. the 008 reflection, which is predicted to have a very large anomalous effect, we also collected intensities at different azimuthal angles to probe the angular dependence of the anomalous scattering signal (tensor property). However, we encountered problems which make the newly measured data difficult to interpret.

All reflections measured have wildly varying integrated intensities as a function of energy. A few examples are shown. The data suffer from sudden huge drops in intensity as well as unexplainable large spikes. Even the best reflections are extremely “noisy”, and the intensity changes are unrelated to the edge position (16105 eV). When plotting the azimuthal scans the problems in the data become even clearer. Besides the strange drops in intensity, it is also evident that the center of the reflections is moving.

There are a number of possible explanations for the problems. One is the monochromator, which at 16105 eV has problems with adequate energy resolution. This may affect the stability and/or reproducibility of the angle setting? Another is that we had severe problems with the centering of the reflections and calculation of an accurate orientation matrix. In fact more than a day of beam time was spent just finding an initial orientation matrix. The diffractometer software for establishing an orientation matrix was poor, and we never succeeded in getting a reliable matrix. This creates severe problems when centring the reflections, and the trajectory of the mosaicity cap through the Ewald sphere may have varied a lot for the same reflection at different energies. Overall, we must conclude that the proposed experiment was unsuccessful due to instrumental problems.



The integrated intensity as a function of energy for the 008, 004 and the 530 reflections. The 3D plot shows the peakprofile as a function of energy for the 008 reflection