| ESRF | **Experiment title:** Short-range structure of binary salts and ionic alloys probed by x-ray absorption techniques | **Experiment number:** CH557 |
|---|---|---|
| **Beamline:** BM29 | **Date of Experiment:** from: 25/11/98 to: 06/12/98 | **Date of Report:** 25/08/1999 |
| **Shifts:** 30 | **Local contact(s):** M. Borowski and S. De Panfilis | *Received at ESRF:* **31 AOUT 1999** |

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## Report:

Several x-ray absorption experiments were performed on binary salts following our original proposal CH557. The last experiments were carried out at BM29 in late November 1998 and regarded AgI, AgBr, CuI, for which accurate x-ray absorption measurements in a wide temperature interval were obtained at the Ag, I, Br, and Cu $K$ -edges respectively. Single-energy x-ray absorption temperature scans [1] were measured for each sample under consideration allowing us a detailed characterization of the phase transitions taking place in those systems as a function of temperature.

In Fig. 1 we report an example of a temperature scan for an AgI sample for a high-contrast energy point (E = 25.545 eV) near the Ag $K$-edge. The solid phase transition leading to the superionic $\alpha$ phase at about 147 $^o$ C is evident both in the warming (upper) and cooling (lower) strokes.

Melting of the sample above 560 $^o$ C is clearly monitored by the absorption decrease due to the gradual evaporation of the sample. The effect of the evaporation can be minimized by collecting temperature scans at two different energies (differential absorption $\delta\alpha$, see [2] and [3]) as we have done in several cases. The right panel of Fig. 1 shows a hysteresis loop obtained for the solid-solid transition in AgI.

Samples have been also characterized in-situ by collecting diffraction patterns at fixed exit angle. High temperature XRD ad XAS scan were collected simultaneously using a setup developed by our group (see http://camcnr.unicam.it site). This sophisticated set-up (as an example of an application see [2]) has been always used and the structural transitions occurring in our samples have been monitored continuously.

Complete low-noise EXAFS scans have been collected for all of this superionic compounds in the 30-1100 K temperature interval (depending on melting point and evaporation threshold of the samples) using both the cryostat and the L'Aquila-Camerino oven installed on the BM29 beamline.

EXAFS measurements allowed us a detailed study of the local structure of these systems at high temperature. We have used multiple-edge multiple-scattering ab-initio GNXAS data-analysis giving always very accurate results on test systems.

Motivations for these measurements in these salts, as explained in the original proposal, are to study i) the short-range structure and interatomic interactions in the molten phase and ii) the anharmonic vibrations occurring in these systems even at moderate temperature. Our experimental results are compared with theoretical models provided by MD or MC simulations and with previous diffraction studies, when existing.

Our previous publications on CuBr [4] and the recent paper on liquid AgI [5], based on the present measurements, can be used as a reference to understand the potential of this research. In particular, the excellent performances of the BM29 at high energies have been exploited in present investigation. The quality of the data in the whole temperature range can be appreciated looking at Fig. 2, where the EXAFS spectra of AgBr are reported for both Ag and Br $K$-edges.

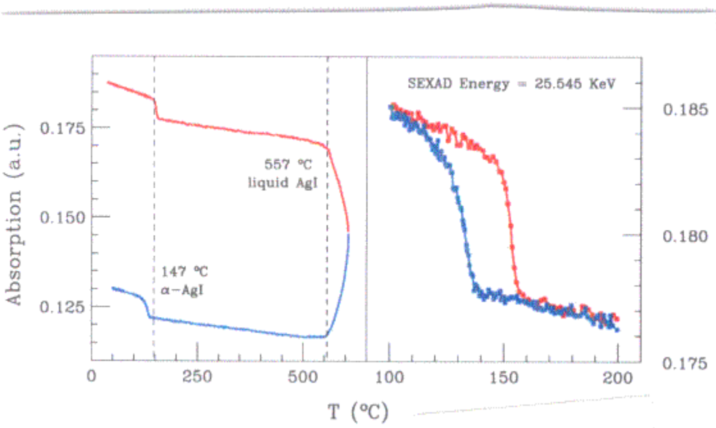


**Fig. 1**

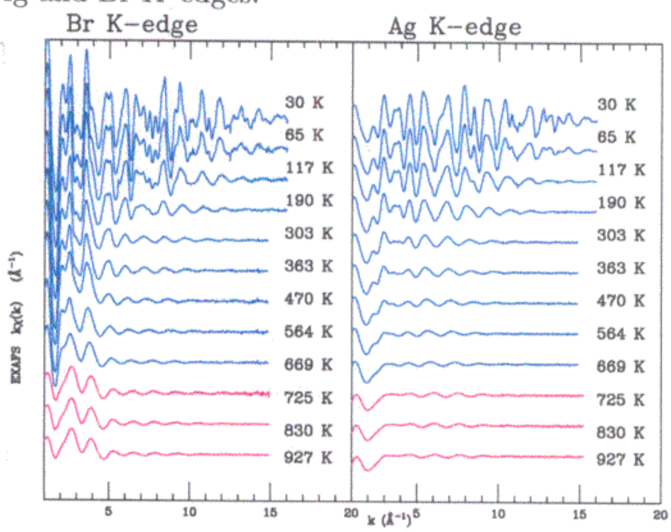


**Fig. 2**

We performed a simultaneous refinement of both Ag and its counterion $K$-edge XAFS starting from molecular dynamics (MD) results. Comparing the $g(r)$ reconstructed from XAFS data analysis, we have found a shift toward larger distances and a very clear narrowing of the peak, well outside the error limits. Our accuracy at short distances turned out to be much better than that of presently available diffraction data. The new measurements can thus help improving parametrization of the potential, presently not sufficiently accurate, in not purely ionic systems. These results are in agreement with previous investigations on CuBr and stimulate the development of new theoretical approaches taking into account non-ionic bonding in superionic compounds.

As a final comment, we have also measured, for the first time, samples of molten ionic $RbBr_xI_{1-x}$ and superionic $Ag_xCu_{1-x}$ alloys. Preliminar data are of excellent quality good and appears to be very interesting. All samples have been characterised by single-energy temperature scans. Data-analysis of these measurements is not yet finished.

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[2] A. Filipponi, A. Di Cicco, and S. De Panfilis, "Structure of Undercooled Liquid Pd Probed by X-Ray Absorption Spectroscopy", Phys. Rev. Lett. **83**, 560 (1999).

[3] A. Di Cicco, S. Fusari, and S. Stizza, "Phase Transitions and Undercooling in Confined Gallium" Philosophical Magazine B (1999, to be published).

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[5] A. Di Cicco and M. Minicucci, *Solid and liquid short-range structure determined by EXAFS multiple-scattering data-analysis*, J. Synchrotron Rad. **6**, 255 (1999).