ESRF	**Experiment title:** Local structure of ionic and super-ionic solid and liquid ternary solutions probed by XAS	**Experiment number:** CH-1079
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Shifts: 15	**Local contact(s):** S. Ansell	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):
E. Principi, A. Di Cicco, A. Trapananti, M. Minicucci, (INFM - University of Camerino, ITALY)
J. Bosko (University of Gdansk, POLAND)
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Report:

Accurate EXAFS (Extended X-ray Absorption Fine Structure), energy-scanning x-ray diffraction, and single-energy temperature scans of $RbBr_{1-x}I_x$ solid (RT) and molten ($T > 1000$ K) ionic alloys have been collected exploiting the highly automated experimental setup available at BM 29. Preliminary measurements have been realized for $Ag_{1-x}Cu_xI$ and $CsBr_{1-x}I_x$ solid alloys. The measurements were performed in a high vacuum furnace which allows for the collection of high-temperature x-ray absorption and diffraction data. Energy-scanning x-ray diffraction, single-energy x-ray absorption temperature scans and a transmission x-ray camera were used in-situ to monitor sample changes, melting temperature, and homogeneity. Measurements have been also performed at low temperatures using the He cryostat.

EXAFS data of $RbBr_{1-x}I_x$ alloys have been already analyzed using the GNXAS data-analysis package and the results have been submitted for publication [1]. Multiple-edge simultaneous refinement was performed taking proper account of double-electron excitations in the atomic background shape, particularly intense for Rb, Br, and I. The fitting was obtained by floating only six structural parameters, which represent the average distances R, variances σ^2, and skewness β of the Rb-I and Rb-Br bond length distributions. R and σ^2 for the solid case are showed in fig. 1. The short-range distribution functions of the $RbBr_{1-x}I_x$ solid (RT) and molten ($T > 1000$ K) ionic alloys have been accurately measured using multiple-edge refinement of the K-edge EXAFS (Extended X-ray Absorption Fine Structure) spectra. The local structure of $RbBr_{1-x}I_x$ is characterized by two well-defined first-neighbor peaks associated with the Rb-I and Rb-Br distributions, both for solid and liquid alloys [fig. 1].

The distribution of distances in solid alloys departs from a simple linear function of the concentration, giving first experimental evidence to available theoretical models. The variances of the pure compounds differ at room temperature, due to the different masses and interactions [fig. 1].

These parameters include both thermal and structural (disorder) contributions, the latter being clearly larger at intermediate compositions in agreement with several previous results and theoretical predictions.

In the liquid, the two distance distributions are found to be practically independent of the concentration x as it can be seen from the partial pair distribution functions g_{RbBr} and g_{RbI}, reported in the lower panel of Fig. 2. The total $g_{+-}(r)$ pair distribution function measured by EXAFS reported in the upper panel of Fig. 2 shows an almost continuous variation of the average first-neighbor peak position as a function of the concentration x.

The availability of all this novel experimental results stimulates several fundamental questions. The careful analysis of the experimental data for the characteristics bond lengths Rb-Br and Rb-I could suggests a departure from a linear behavior, as a function of x, in both the solid (Fig. 1) and the liquid phases. It is not obvious that these effects have the same physical origin. In the case of the liquid alloys. The average Rb-Br bondlengths decreases (from the constant RbBr value) for $x \geq 0.6$ (low Br concentration), and similarly the $R_{\mathrm{Rb-I}}$ increases for $x \leq 0.2$ (low I concentration). A qualitative explanation of this behavior can be given in terms of the mutual screening of the ionic charges [1]. The assessment of the validity of this argument and its potential importance for the explanation of solid state data (Fig. 1) requires specific theoretical investigations.

[1] A. Di Cicco, E. Principi, and A. Filipponi, Phys. Rev. B 65, 212106 (2002).

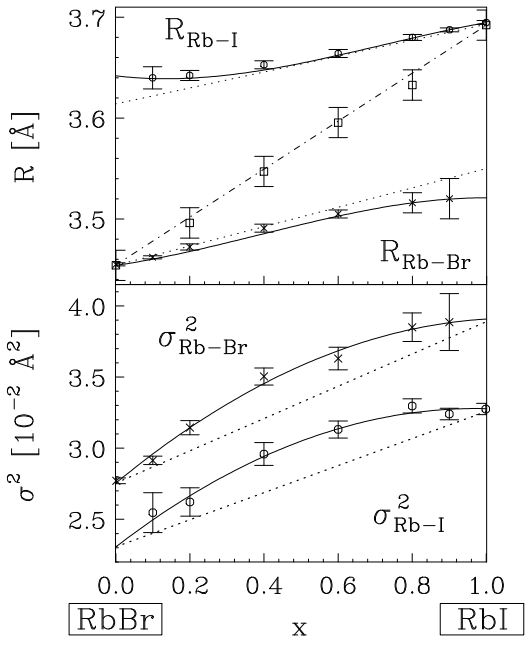

fig. 1

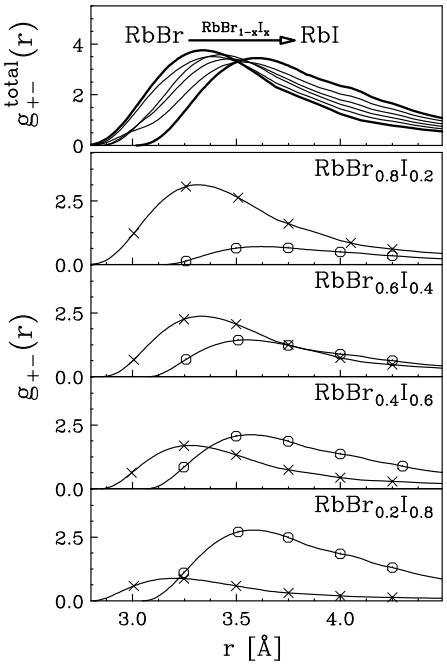

fig. 2