ESRF	**Experiment title:** A determination of the structural changes in superionic and molten AgI at high temperatures and pressures	**Experiment number**: HS-1811
Beamline:	**Date of experiment**: from: 24/04/02 to: 28/04/02	**Date of report**: 28/08/02
Shifts:	**Local contact(s)**: W. Crichton	*Received at ESRF:*

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Report:

This experiment concerned three aspects of the structure of AgI:

1. The nature of possible pressure induced ordering in the architypal superionic conducting phase, α-AgI.
2. Characterisation of the gradual superionic transition in the high-pressure rocksalt phase of AgI.
3. Determination of the changes in the liquid structure with increased pressure.

ID30 was used in its standard mode for the large volume (LV) Paris Edinburgh pressure cell with Soller collimator and Mar345 image plate. The image plate was placed to give a 2θ range between 0 and +/- 27°. With a wavelength of 0.15816Å, this should permit a theoretical maximum *Q* of around 18Å^{-1}. An important aspect of this work was to obtain high quality Bragg diffraction and total scattering from the diffraction data. Hence careful measurements were made of the background signal and rigorous data treatment was attempted. Data were collected in small pressure increments through the α-phase at ~730K and into the rocksalt phase. The sample was then cooled and further data were collected at pressure (~2.4GPa) within the rocksalt phase with small temperature steps until the sample melted. Further measurements were then made on the molten salt at a numer of pressures, although the LV cell frequently failed due to the molten sample reacting within the sample containment. This report therefore concerns the results from the crystalline material.

Results from Rietveld refinement of the Bragg powder pattern and from the radial distribution function obtained from the corrected total scattering showed no clear indictation of any significant pressure induced cation ordering within the α-phase. In contrast, there was clear evidence for temperature induced cation disorder within the high-pressure rocksalt phase. There was an anomaly in the linear expansivity at high temperature prior to melting and Rietveld refinements showed that this corresponds to in increase in cation occupation of the tetrahedral interstitial sites of the rocksalt structure (see Figure 1). In addition, the total

scattering shows a strong increase in diffuse scattering with increased temperature and a shift in the first peak in the radial distribution function corresponding to a change from octahedral (longer distances) to tetrahedral (shorter distances) co-ordination (see Figures 2 and 3). We have therefore observed clear evidence for the 'Type-II' superionic transition in rocksalt AgI in both the average and local structure. This is the first time that diffuse scattering has been used to assess the behaviour of a superionic solid at high pressure and high temperature.

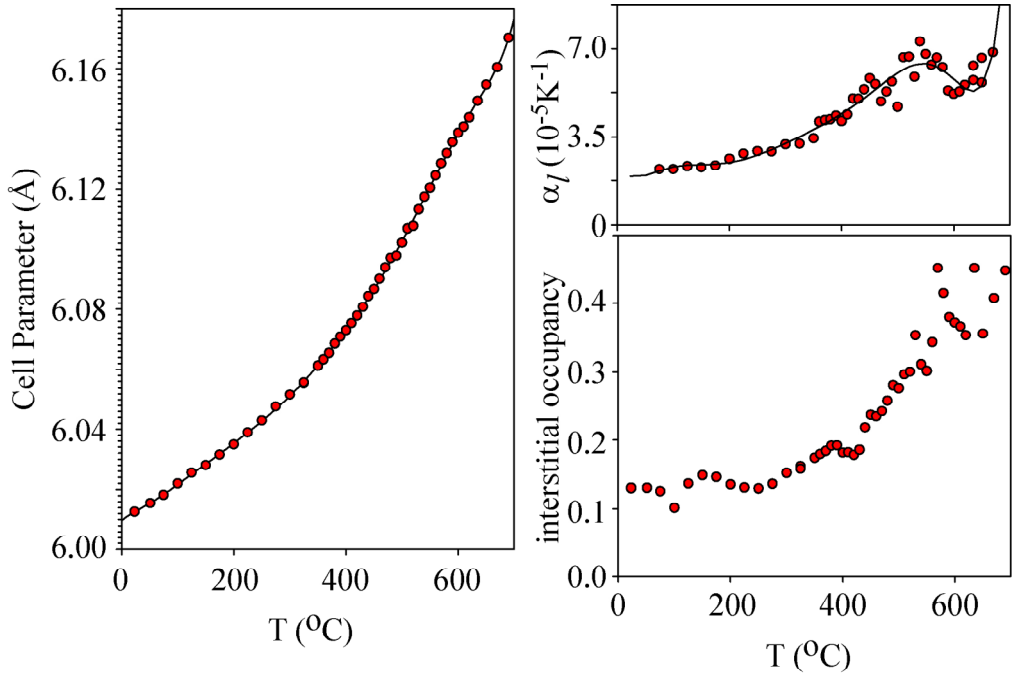

Figure 1

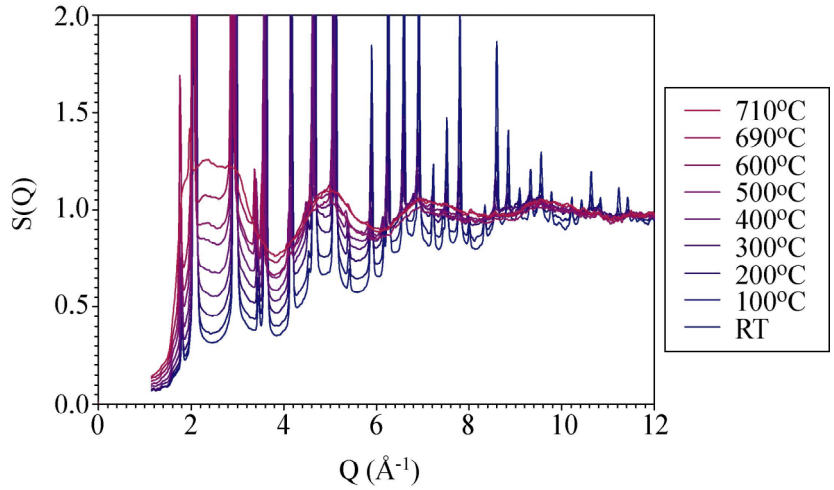

Figure 2

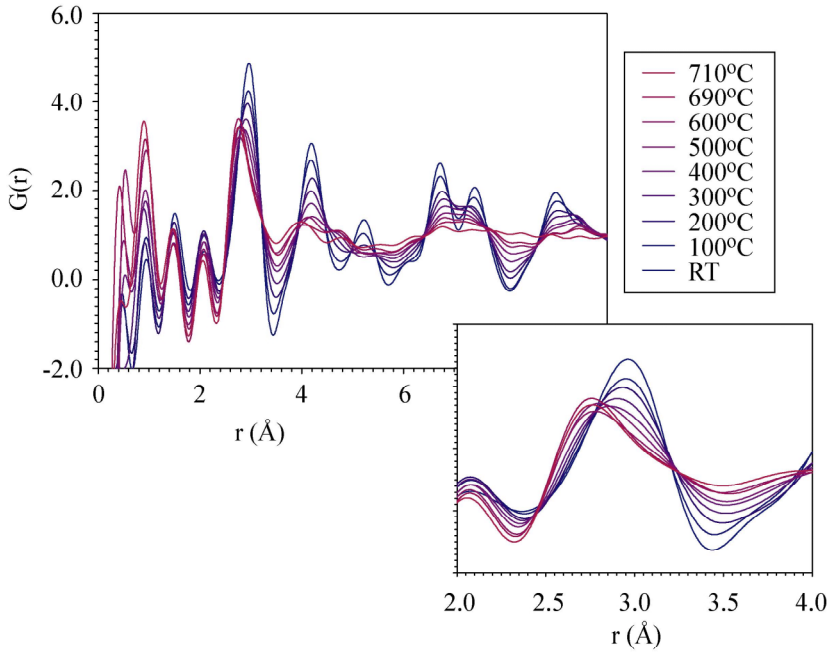

Figure 3