



	Experiment title: A determination of the structure of heavy alkali halide melts using X-ray anomalous dispersion and neutron diffraction	Experiment number: CH1003
Beamline: ID01	Date of experiment: from: 29/8/01 to: 4/9/01	Date of report: 24/2/03
Shifts: 21	Local contact(s): Dr Myles HAMILTON	<i>Received at ESRF:</i>

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Report:

The structures of many molten salts have already been studied in detail [1]. A single diffraction measurement gives a weighted average of all the possible pair correlations in the system and in order to separate these it is necessary to vary the scattering power of each element in a controlled manner. This can be done with neutrons by varying the isotopic composition of the sample (for an example using Cl isotopes in molten CsCl see [2]). If no isotopes are available then an alternative is to use the variation of the x-ray form factor at energies close to an atomic absorption edge. By tuning the incident energy close to the edge the scattering power of the element is changed. Indeed Cs, Na and I do not have naturally occurring isotopes making CsI and NaI ideal candidates for this technique. Note that for binary systems such as these we need three contrasting diffraction measurements in order to determine the three partial $S(Q)$ (e.g. I-I, Na-I, Na-Na). During this beamtime we have measured diffraction patterns for molten CsI, NaI and CsCl- in each case data was collected at 2 incident energies (-10 and -200 eV) below the Cs (36 keV) or I (33 keV) K-edge (the third measurement being a neutron $F(Q)$). Si(311) crystals were used at the monochromator but the mirrors were removed from the beam in order to obtain a larger beam size at the sample position. The resulting harmonic contamination was rejected by the NaI scintillation detector. The samples were held in sealed thin-walled 0.3mm SiO₂ capillaries which were heated by a stream of hot air to above the melting point ($T_{\text{measure}} = 720$ C). This setup has the advantage that there is no sample environment in the beam. The container correction can be made by measuring the scattering from an empty sample container. Background scattering was also measured. In each case multiple datasets were collected in order to confirm the stability of the sample and optics. However the major concern is the inelastic x-ray scattering such as Compton and most importantly resonant Raman scattering as the cross-section for RRS increases dramatically as the absorption edge is approached. The crystal analyser at ID1 allows most of this unwanted intensity to be rejected and the recent introduction of a bent crystal in focusing geometry has resulted in a 50 times increase in countrate if compared to our previous measurements at ID1 [3]. This advance makes it possible to make an energy scan (by rocking the analyser crystal) for each angular point. Initial analysis of the data shows that even with the high energy resolution of the Si(111) crystal that was used further analysis must be carried out to remove the K-N RRS contribution that is only partly resolved from the elastic peak and that would result in an intensity error of around 5%. These energy scans are therefore essential for accurate intensity measurements. Note that because of the effect that local environment has on the dispersive parts of the form factor we measured the absorption spectrum for each sample around the edge. This gives f'' and f' can then be obtained via the Kramers-Kronig relation.

Unfortunately these measurements which were some of the first with the new focusing analyser revealed a drift of the Bragg angle of the analyser crystal as the detector rotated in 2θ . It is suggested that this is due to

alignment errors in the diffractometer itself such that the center of rotation of the detector and analyser arm (DEL) is not concentric with that of the sample rotation (PHI) (within the circle of confusion).

As an example of the data collected we show $I(Q)$ for molten CsI at the Iodine K-edge -10 eV and -200 eV (figure 1). The line is a fit to the data with the form factor. An analyser rocking curves is also shown to demonstrate the energy spectrum from the sample (figure 2). Note the shoulder due to the K-N transition- this must be corrected for. These figures demonstrate that good quality structure factors can be obtained in this way and that the new analyser helps greatly in removing the inelastic scattering. Careful analysis is now underway to determine f' and f'' as accurately as possible, to correct the data for absorption, container and background scattering and to determine the error that has been introduced by the shifting analyser peak.

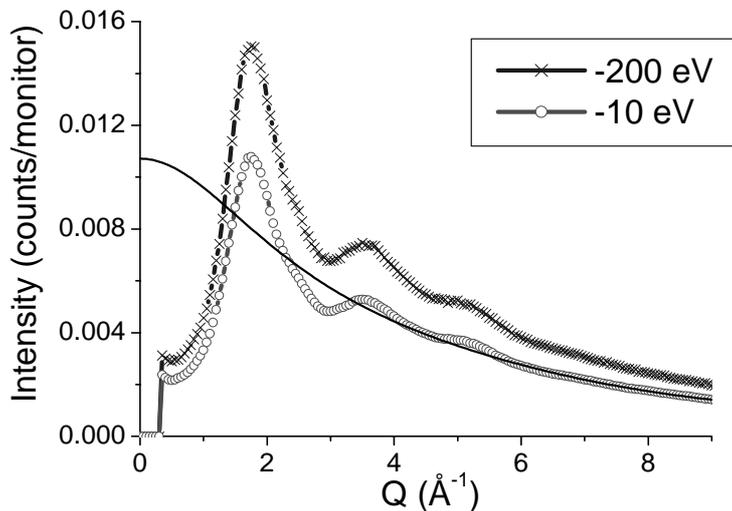


Fig.1 $I(Q)$ for molten CsI at 2 energies below the Iodine K-edge and at 720 C.

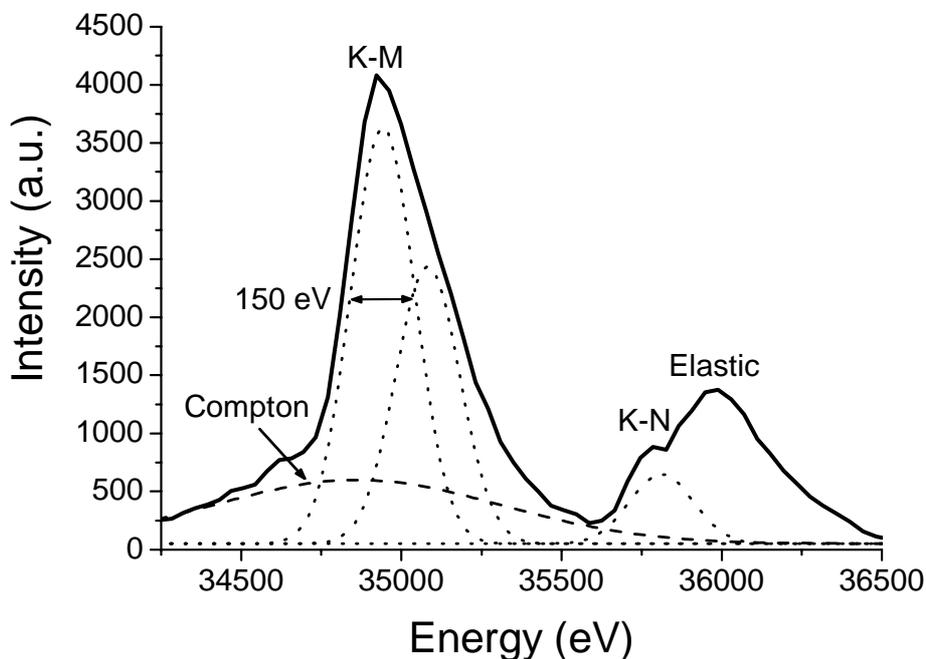


Fig.2 An analyser rocking curve at 10 eV below the Cs K-edge for molten CsCl.

References:

- [1] McGreevy RL, Pusztai L (1990) P. Roy. Soc. London A Mat 430 p241-261
- [2] Locke J, Messloras S, Stewart RJ, McGreevy RL, Mitchell EWJ (1985) Phil.Mag.B 51 p301-315
- [3] Hamilton MA, Metzger TH, Mazuelas A, Buslaps T (2003) J.Synchrotron Radiation *accepted*