ESRF	**Experiment title:** Development and Utilisation of High-Pressure Single-Crystal Methods at the ESRF	**Experiment number**: HS-3090
Beamline: ID09/ID27	**Dates of experiment**: 6/12/2006, 9/2/2007, 24/2/2007, 4/4/2007, 26/8/2007, 3/11/2007	**Date of report**: 8/01/2007
Shifts: 36 (6×6)	**Local contact(s)**: M. Hanfland, M. Mezouar, W. Crichton, M. Merlini	*Received at ESRF:*

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The principal aim of this Long Term Project (LTP) is to develop the diffraction methods and software necessary to enable high-quality single-crystal diffraction data to be collected and refined from samples at pressures up to and beyond 100GPa. In this first year, the stated key objectives were to (i) obtain full sets of single-crystal diffraction data, and (ii) integrate and refine crystal structures from this data. Both objectives have been met, and the stated technical and scientific year-1 milestones have been achieved.

In the first year of the LTP, we were awarded a total of 36 shifts of beamtime split equally between two allocations periods (APs) and between ID09 and ID27. In the first AP, we focused on obtaining full single-crystal data sets from both beamlines utilising high-pressure samples which we had prepared previously at SRS. These samples included high-quality crystals of low-symmetry phases (Ga-II and Rb-III), poor-quality single crystals of complex phases (Te-III and Se-IV) and crystals exhibiting a very wide range of Bragg intensities (Rb-IV and Ba-IV).

On ID09, it became clear that the MAR345 image-plate (IP) detector gave data with a very low background and an extremely high signal-to-background ratio, but that great care was required in order to determine the optimum exposure time in order not to saturate the strongest reflections. Indeed, as ~ 99% of the data collection time is devoted to the reading of the IP (a serious drawback of such detectors for single-crystal experiments), it was found that slightly de-tuning the undulator, combined with an exposure time of 1-2 seconds/frame, gave the best quality results. The size of the IP provides great flexibility – the detector can be moved closer to the sample to enable high-angle diffraction data to be collected, or it can be moved further away to further improve the signal-to-background ratio.

On ID27, we employed the CCD detector and a shorter wavelength than on ID09 (0.25Å compared to 0.41Å) in order to investigate possible advantages for extreme-pressure studies. We also utilised a highly-focused beam with dimensions of 6μm×6μm, and in the first AP we again focused on optimising data collection parameters such as exposure time, step size and sample-CCD distance. It was immediately apparent that the CCD detector was *much* more efficient than the IP for single-crystal data collections, and that optimum data collection on ID09 will also require the use of a CCD or other fast-readout area detector.

Analysis of the data collected in the first AP was conducted using the Bruker SMART/SAINT suite of software that is used in-house in Edinburgh. In order to utilise data collected from the different detectors on ID09 and ID27, we have written software to convert between the different area-detector data formats. Analysis of the test data from both stations revealed its extremely high quality – as evident from the high degree of agreement (R_{int}=3-5%) between the intensities of symmetry-equivalent reflections. The combination of very short wavelengths, or large detectors, and pressure cells with large angular apertures, also revealed the high degree of coverage of reciprocal space that could be achieved. Refinement of the data from the known structures again demonstrated the extremely high quality of the data. Of particular note was the refinement of the host-guest inter-modulation in the incommensurate composite structure of Rb-IV, which required the accurate measurement of extremely weak modulation reflections, something that we had found impossible at SRS or Hasylab. However, by combining the intensities of the strong Bragg reflections collected at SRS, with the intensities of more than 100 very much weaker modulation reflections collected on ID27, we were able to refine the full modulated crystal structure for the first time. This refinement was a stated year-1 scientific milestone of the LTP, and the results were included in the PhD thesis of Lars Lundegaard and presented at the 2007 AIPART high-pressure conference in Italy. A paper is also being prepared for submission to Physical Review.

In the second AP, we further developed and optimised data collection methods and strategies on both ID09 and ID27 using a variety of samples, uncovered some significant issues that can have a strong adverse effect on the quality of the diffraction data, and took advantage of a high-quality single-crystal of sodium at above 100GPa in order to collect single-crystal data to 150GPa. On ID09, we utilised the very high signal-to-noise ratio to study the complex behaviour of Ba-IV between 18 and 22GPa, where all our previous efforts had been unable to uncover the exact nature of the ordered of the guest chains in this previously undetermined structure. The ID09 study revealed an extremely complex pattern of weak diffuse scattering, while a complementary study of the same phase using the CCD detector on ID27 revealed previously-unobserved satellite reflections that indicate a $4\times4\times4$ superstructure of the basic unit cell. Analysis of this complex new structure is in progress.

On ID27, attempts to further explore the use of very short wavelength radiation were hampered by a technical problem on the beamline. However, again using the highly focused $6\mu m \times 6\mu m$ beam, we found that only *very* slight movement (estimated as a few microns) of the beam-conditioning pinhole resulted in dramatic variations in the intensity of the beam hitting the sample. Most importantly, this problem was *not* apparent in the raw frames of data, but only once the data had been integrated and the intensities of equivalent reflections compared. It has thus become clear that data must (where possible) be analysed in real time.

We recently reported the first single-crystal data collection and refinement above 100GPa, using a single-crystal of sodium [1]. We have since used this same sample on ID27 to push single-crystal studies to 150GPa, and have collected high quality diffraction data from *seven* different sodium phases – four of which are previously unknown. The quality of the data is much superior to that reported in [1]. It should be stressed that because of its remarkable melting curve, which drops to almost room temperature at 118GPa, sodium is the *only* material in which we expect to be able to grow high-quality single crystals above 100GPa near room temperature. However, the fortuitous availability of these remarkably complex phases at extreme pressures has proved exceptionally useful in developing data collection methods and analysis at such pressures, and for highlighting many of the additional difficulties that arise from samples at pressures above 100GPa. The results of this study have been submitted for publication, and were presented at the 2007 AIPART high-pressure conference in Italy.

In Dec 2007, MIM and LFL visited the ESRF to discuss progress of the LTP with the ID09 and ID27 station scientists. We agree with the ESRF staff that in order for the LTP to provide maximum benefit to the general user programme, and therefore to the ESRF's output, analysis and integration software that are *not* dependent on a commercial supplier (e.g. Bruker or Oxford Diffraction) will be required. Dr A. Hammersley has made some progress in this direction, using code based on the widely used and highly successful Fit2D software. We strongly urge the ESRF to provide further support and resources in this direction over the next year or two in order to maximise the benefit of the LTP to the wider user community,

In conclusion, the first year of the LTP has been very successful and we have fully achieved all of its stated technical and scientific objectives and milestones. In the second year we will focus on developing high-pressure high-temperature methods, which will also involve the growing of single crystals from the melt or by *in situ* annealing, and in pushing studies of very small ($<20\mu m$) crystals.

[1] McMahon *et al*, Proc. Nat. Acad. Sci. **105**, 17297 (2007).