ESRF	**Experiment title:** Modulations and Chain Melting in Host-Guest Structures at High Pressure	**Experiment number**: HS-2502
Beamline: ID09	**Date of experiment**: from: 18/02/2004 to: 22/02/2004	**Date of report**: 8/09/05
Shifts: 12	**Local contact(s)**: M. Hanfland	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

M.I. McMahon*
C. Hejny*
S. Falconi*
L. Lundegaard*

School of Physics and Centre for Science at Extreme Conditions
The University of Edinburgh
Edinburgh, U.K.

Report: We have recently discovered a series of extraordinarily complex crystal structures in Rb, Sr, Ba, Sb, Bi and As at high pressure [1]. These structures comprise a tetragonal "host" structure containing channels along the *c* axis. Located within these channels are chains of "guest" atoms, which form long-range ordered structures which are incommensurate with the host structure along their common *c*-axis.

A composite structure of a related kind is found in $Hg_{3-\delta}AsF_6$ where the 1D chains of Hg atoms are ordered only below 120K – at 300K they are completely *disordered*, and produce uniform sheets of intense diffuse scattering perpendicular to the chain directions. Similar chain melting might be expected in the elemental composite structures, and we have reported [2,3] that at pressure below 16.7GPa at 300K, the guest peaks in Rb-IV broaden in a way that is consistent with disordering of the chains. Further work at SRS has revealed that the broadening is accompanied by the appearance of sheets of diffuse scattering. The nature of this scattering suggests that the chains are forming an ordered 1D liquid – a highly intriguing state.

In this proposal we asked for 4 days of beamtime on ID09 to characterise the liquid state by (i) detecting higher-order layers of diffuse scattering (we could see only the first at SRS), (ii) measuring their relative widths and intensities as a function of pressure, and (iii) looking for any evidence of residual chain modulations. Finally it would be expected that the chains would melt in Rb-IV on heating at pressures a little above 16.7GPa (below which there is melting with P reduction at room temperature), and we planned to look for that and thereby establish a 'melting curve' for the chains. ***The experiment was completely successful in all respects.***

Figure 1 shows a diffraction pattern from a single crystal of Rb-IV at 19.3GPa, showing three layers of diffuse scattering. We have made detailed measurements of the diffuse scattering down to 16.2GPa, the pressure at which the sample transforms to Rb-III, and see detectable differences in the width and relative intensity of the diffuse layers above and below the onset of chain melting at 16.7GPa (Figure 2). By modelling the diffuse scattering as coming from either a perturbed lattice (above 16.7GPa) or a 1-D harmonic liquid (below 16.7GPa), we have obtained information on the sound velocity along the guest-atom chains, and on the correlations lengths within the chains. A description of this work is in preparation for submission to Physical Review [4].

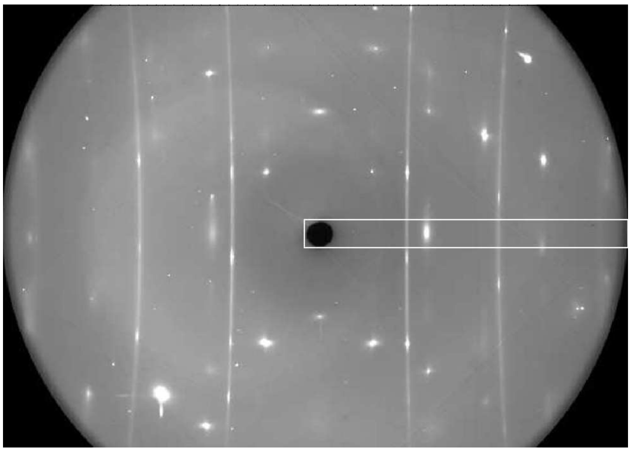

Fig 1: 2-D diffraction pattern from a single crystal of Rb-IV at 19.7GPa. Three diffuse layers are visible in each half of the diffraction pattern. The white rectangle shows the integration limits used in the integration of the diffuse scattering.

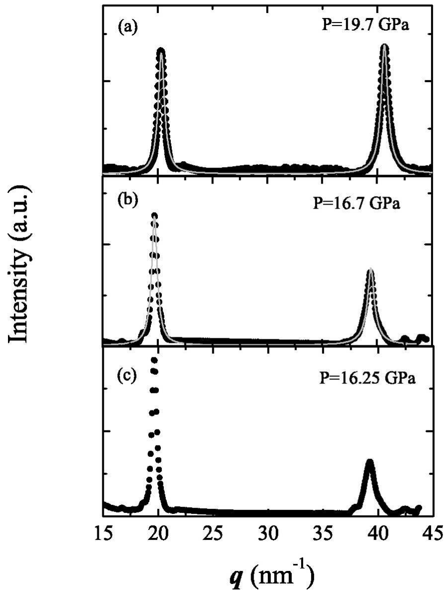

Fig 2: Integrated diffraction profiles of the diffuse scattering from Rb-IV at (1) 19.7GPa, (b) 16.7GPa and (c) 16.25GPa. The lines superimposed on the data in profiles (a) and (b) are the fits using the perturbed lattice model.

We have also made detailed studies of the P-T dependence of the chain melting. The onset of melting was found to be extremely sharp – as judged by the complete disappearance of Bragg reflections from the guest chains (see Figure 3). This enabled us to determine the melting temperature to within ±10K and ±0.1GPa up to a maximum P-T of 19.9GPa and 534K. The resulting Rb-IV phase diagram is shown in Figure 4, which shows both the strong P-dependence of the chain melting temperature and the remarkable parallel nature of the Rb-III→disordered-Rb-IV and disordered-Rb-IV→ordered-Rb-IV phase lines. This work is in preparation for submission to Physical Review [5].

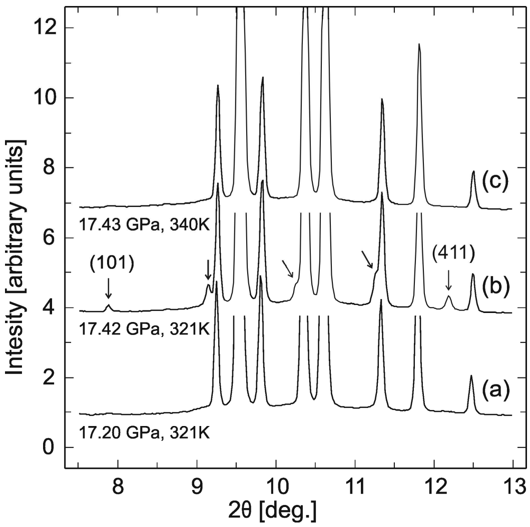

Fig 3: Diffraction profiles of disordered (profiles (a) & (c)) and ordered (profile (b)) Rb-IV. The guest reflections that disappear in the disordered phase are identified with arrows in profile (b).

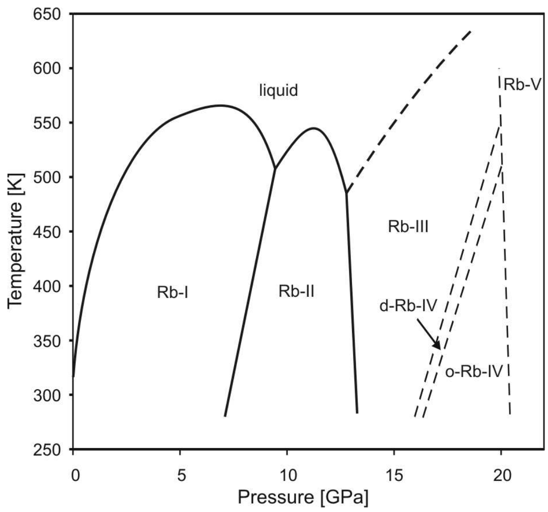

Fig 4. Phase diagram of Rb-IV to 20GPa, showing the newly determined phase boundaries (dashed).

[1] M.I. McMahon & R.J. Nelmes, Z. Kristallogr. **219**, 742 (2004), and references therein.
[2] M.I. McMahon *et al*, Phys. Rev. Lett. **87**, 055501 (2001).
[3] M.I. McMahon & R.J. Nelmes, Phys. Rev. Lett. **93**, 055501 (2004).
[4] S. Falconi, M.I. McMahon, L.F. Lundegaard, C. Hejny, R.J. Nelmes and M. Hanfland, In Preparation.
[5] L.F. Lundegaard, M.I. McMahon, S. Falconi, C. Hejny, R.J. Nelmes and M. Hanfland, In Preparation.