ESRF	**Experiment title:** Studies of Chain Melting in the Incommensurate Composite Rb-IV Structure	**Experiment number**: HS-2777
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Shifts: 18	**Local contact(s)**: W. Crichton	*Received at ESRF:*

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Report: We have recently discovered a series of extraordinarily complex crystal structures in Rb, Sr, Ba, Sb, Bi, As and Sc at high pressure [1,2]. 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 [3,4] 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 experiment we asked for 4 days of beamtime on ID27 to conduct high-pressure high-temperature single-crystal diffraction studies of Rb-IV (i) to study the onset of diffuse scattering below P_c=16.5GPa as a function of T to model inter- and intra-chain disorder, (ii) to measure the intensities of the modulation reflections as a function of P and T to determine the structural modulations and the P-T dependence of the host-guest interaction, (iii) to determine the T-dependence of the ADPs of the guest atoms above 16.5GPa to ascertain the nature of their thermal motion/disorder, and (iv) to look for evidence of structural complexity in the melt phase.

Unfortunately, the failure of the CCD detector on ID27 immediately prior to the experiment meant that our planned single-crystal studies were limited significantly to room-temperature studies of Rb-IV. In addition to completing studies of the diffuse scattering on Rb-IV, the results of which were published in Phys. Rev. B in June 2006 (see below), we collected full single-crystal data sets from a high-quality single crystal of Rb-IV at 19.6GPa with the aim of studying the pressure dependence of the modulation reflections. *However, despite knowing both the lattice parameters and structure of the sample we were completely unable to either index or integrate the data using existing software.* Yet, the data from ID27 were clearly of *superb* quality, with very intense reflections and an extremely low background. It was therefore clear that if the key problem of integration and analysis software could be overcome, then the world-leading capabilities of ID09 and ID27 for high-pressure research could be utilised routinely for single-crystal studies to 100GPa and above.

The remainder of the beamtime was therefore used to collect a series of single-crystal data sets from Rb-IV and Rb-III at room temperature with the aim of devloping methods by which the data could be interpretated and analysed. The key outcome of this experiment was the successful application, in January 2006, of a Long Term Proposal at the ESRF to develop single-crystal methods on ID09 and ID27.

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X-ray diffraction study of diffuse scattering in incommensurate rubidium-IV

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X-ray diffraction data have been collected from single crystals of incommensurate Rb-IV in order to study the sheets of diffuse scattering arising from the one-dimensional (1D) guest chains. Discontinuities in both the relative intensity and width of the diffuse sheets are observed on pressure decrease below 16.7 GPa, the pressure at which the interchain correlations begin to decrease rapidly. These changes in the diffuse scattering are accompanied by the progressive disappearance of the Bragg peaks from the guest chains. By modeling the diffuse scattering as coming from either a perturbed 1D lattice or a 1D harmonic liquid, we have determined the pressure dependence of the intrachain spacing of the guest atoms and the root-mean-square (RMS) fluctuation of the guest atoms from their unperturbed sites. We have also made estimates of the sound velocity along the guest-atom chains, and their effective Debye temperature.

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