



	<b>Experiment title:</b> <b>Melting and Phase Transitions in Potassium to 70 GPa</b>	<b>Experiment number:</b> HS-3940
<b>Beamline:</b> ID09a	<b>Date of experiment:</b> 31 Oct 2009 – 03 Nov 2009	<b>Date of report:</b> 22/03/11
<b>Shifts:</b> 9	<b>Local contact(s):</b> S. Evans	<i>Received at ESRF:</i>
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**Report:** The alkali metals, considered “simple” at ambient conditions, have very complex high pressure (i.e. high density) behaviour, which is both of fundamental interest, and the focus of current experimental and computational research. Recently, it has been shown that at high pressures Na has a dramatic minimum in its melting temperature, which first rises to 1000 K at ~31 GPa before dropping to just above 300 K at 118 GPa, and then rising again [1]. The minimum at 118 GPa is associated with the appearance of seven complex crystal structures, the unit cells and symmetries of which we have recently determined using single-crystal techniques on ID27 [2].

Very recently, we found that above 55 GPa, potassium transforms to the orthorhombic *oP8* phase found previously only in Na from 117-123 GPa (near the melting minimum) [3]. At 110 GPa potassium transforms to the orthorhombic *oC16* phase found previously in Rb and Cs – but not in Na [3]. K would thus seem to have a high-pressure behaviour that is finely balanced between that of Na and Rb/Cs. Furthermore, during unsuccessful attempts to grow single-crystals of K by high-T annealing at ~22 GPa, we discovered that the fully-ordered chains of guest atoms, in the host-guest composite structure which is stable at this pressure, became disordered at 420 K. We have previously seen this behaviour in Na and Rb [4,5].

It would therefore seem that K exhibits many of the “unique” properties of both Na (unusual melting curve at high pressures, the *oP8* structure) and Rb (order-disorder phase transition in the guest chains). A full determination of the properties of potassium at both high pressures and temperatures is now crucial to understanding the general behaviour of the alkali metals, and understanding their electronic properties.

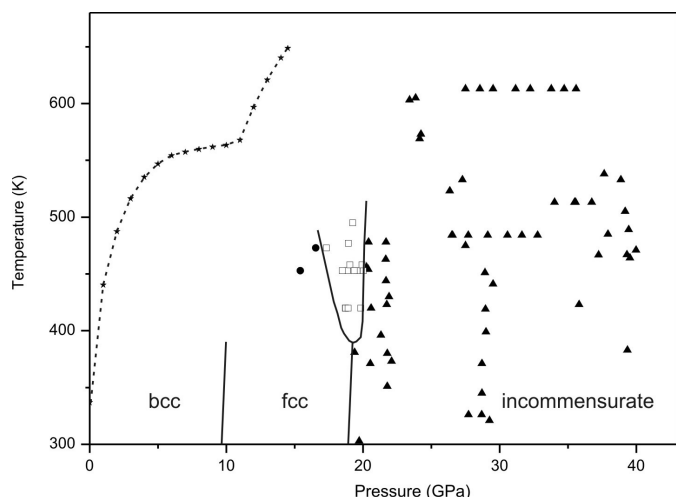
This experiment (HS-3940) was awarded 3 days of beamtime on beamline ID09 to: (i) determine the melting curve of K from 15 GPa to 70 GPa, and determine the crystal structures immediately below the melting curve; (ii) study the order-disorder transition in the guest-atom chains of the incommensurate phase of K stable in the range 20-55 GPa, and map out the phase boundary between the ordered and disordered states; and (iii) obtain high-quality diffraction data from liquid-K near the melting minimum which, we predicted (based on analogy with Na and the reported K melting curve to 15 GPa [6]) to occur near 55 GPa.

The melting line of K proved difficult to locate at high pressures: at pressures above 25 GPa we found no evidence of melting up to combined P-Ts of 36 GPa and 613 K (see Fig. 1). This was surprising, as previous diffraction images, obtained at I15, Diamond Light Source (DLS), UK, have suggested melting at a temperature as low as ~400 K at 35 GPa. At the end of the experiment, we released the pressure on a sample and finally located the melt-incommensurate phase line at 20 GPa at 435 K. Re-analysis of the data collected at I15 suggested that the pressure had been miscalibrated, and that the true pressure in that case was closer to 20 GPa than 35 GPa.

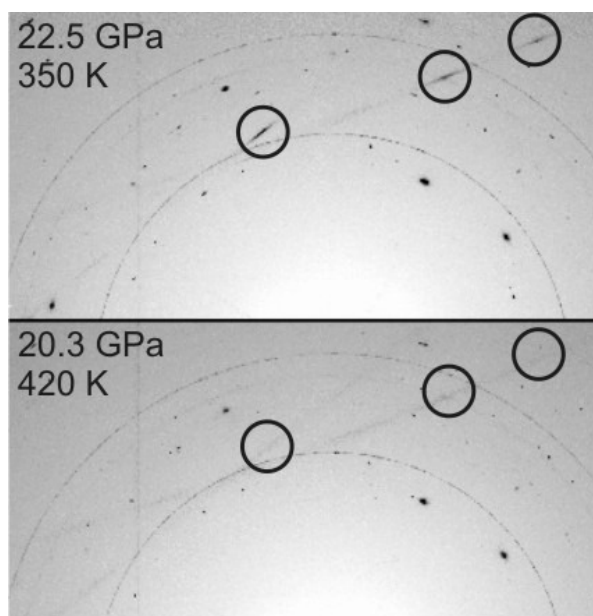
Further reductions in pressure at the same temperature located the melt-*fcc* phase boundary at 17 GPa at 435 K. A summary of the data collected is shown in Figure 1, which also shows the previous determination of the melting curve to 15 GPa [6]. Our results suggest that a melting minimum exists at the *fcc*-incommensurate phase boundary at ~19 GPa. However, constructing a melting curve that is consistent with both the current data, and that from the previous study [6], will be difficult and further data are required.

The order-disorder transition in the guest chains of atoms in the incommensurate K-III phase was clearly observed in the current experiment – as illustrated in Figure 2. But while the order-disorder transition was clearly visible at pressures near 22 GPa, where the proximity of the melting curve meant that it was possible to grow high-quality single crystals of the incommensurate phase, at higher pressures the quality of the crystals reduced markedly, and became more polycrystalline-like. As the diffuse features can only be observed from single-crystals, it was not possible to determine the onset of the order-disorder transition above 25 GPa. However, the results obtained up to this pressure suggest that the correlation length between the guest-atom chains in the disordered phase is considerably smaller than the ~30Å we have observed previously in both Na and Rb [4,5].

Our third objective, the collection of high-quality diffraction data from the liquid phase itself, was not achieved due to time constraints and our initial difficulty in locating the liquid phase. However, in further experiments at I15 (DLS) we have fully mapped the melting curve of K to 22 GPa, and the results suggest that the structural changes may occur in the liquid phase near the melting minimum. Determining these structural changes will form the case of a new proposal on ID27.



**Figure 1:** Phase diagram of K, showing the P-T points at which data were collected in this study. Triangles mark observations of the incommensurate phase, and unfilled symbols show those conditions where liquid-K was found. The dashed line shows the previously-reported melting curve of K to 15 GPa [6].



**Figure 2:** Part of the 2D diffraction profiles obtained from a single-crystal of K at ~21 GPa. In the top image, the Bragg reflections from the guest component of the structure are clearly visible, if elongated. On temperature increase to 420 K, the Bragg reflections have disappeared, as a result of the “melting” of the guest-atom chains.

## References

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