ESRF	**Experiment title:** Structural Studies of Solid and Liquid Potassium	**Experiment number**: HS-4719
Beamline: ID09a	**Date of experiment**: from: 08/02/2013 to: 11/02/2013	**Date of report**: 15/09/2013
Shifts: 9	**Local contact(s)**: Michael Hanfland	*Received at ESRF:*

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Report: The melting curves of the alkali elements all show "anomalous" behaviour with increasing pressure [1-4]. Na in particular has a dramatic minimum at 118 GPa and 300 K before the melting temperature increases sharply [2, 5]. Determining the melting curve of Na above 118 GPa is at the extremes of current static experimental capabilities, but we have shown in our recent studies at the ESRF and Diamond Light Source, that the melting curve of K is *remarkably* similar to that of Na, with a sharp minimum at 19 GPa, and that K is an excellent model system for gaining insight into the behaviour of Na [3]. The very close similarities in the phase diagrams of K and Na will allow us to investigate behaviour in K that lies beyond current experimental limits in Na. Such studies not only allow the investigation of the fundamental structural and electronic behaviour of high-density metals, but also provide essential equation of state information for hydrodynamic simulations of the behaviour of the alkali metals under dynamic compression.

The aim of the experiment HS-4719, which was awarded 3 days of beamtime, was to investigate the melting curve of K between 20 GPa and 70 GPa and temperatures up to 1000 K. Membrane driven diamond anvil cells were combined with external resistive heating techniques to control pressure and temperature respectively. As heating to temperatures in excess of 650 K in air can lead to the burning and hence failure of diamond anvils, the diamond cells were to be placed in a purpose-built vacuum vessel. Unfortunately, a unfixable vacuum leak developed in the heating vessel during the experiment, curtailing its use. We therefore used the remaining beamtime for a high-temperature study of potassium at lower temperatures that did not require the vacuum vessel.

In our previous studies of the melting curve of K (HS-3940), we observed, and detail in the accompanying report, that when K is in the composite incommensurate host-guest phase above 19 GPa we observed an interesting phenomenon. As pressure was held constant and temperature increased the Bragg reflections arising from the guest substructure grew increasingly broad before disappearing entirely, whereas the scattering arising from the host substructure remained entirely unchanged. This indicated an order-disorder transition occurring in the guest structure. Crucially, this order disorder transition was observed to occur some 100 degrees below the melting transition at this pressure. To investigate the pressure dependence of this phenomenon we conducted polycrystalline diffraction studies of *tI*19-K up to 50 GPa and 650 K, mapping out the order-disorder transition.

The structure of the host-guest phase of potassium changes under pressure via a series of intra-phase transitons occurring in both the host and guest structures. These have been detailed at room temperature by Lundegaard *et al.* [6] and we observe the same phenomenon at elevated temperature. Azimuthally integrated 1D diffraction profiles (Fit2D) are shown in Figure 1. There are several things to note. As pressure is increased from 25.3 GPa to 32.2 GPa, a peak appears at low angle which is ascribed to the host structure losing its *c*-glide symmetry; this peak is highlighted by the "*" symbol. Furthermore, the guest reflections, indexed on a tetragonal lattice and indicated by the "†" symbol, decrease in intensity and disappear entirely as the sample is heated at 25.3 GPa. At higher pressures and temperature (33.6 GPa, 458 K) the guest reflections reappear, but here they are indexed on an orthorhombic lattice, and are indicated by the "‡" symbol. At further compressions the guest undergoes a re-entrant phase transition back to the tetragonal structure it adopts at lower pressures, and the host regains its *c*-glide symmetry.

Through a series of small increases of pressure and temperature the order-disorder transition was mapped out up to the *tI*19-*oP*8 phase transition, and there is evidence which suggests that the series of intra-phase transitions in the host and guest structures have an influence on this order-disorder transition. Figure 2 represents the order-disorder line in the guest structure of *tI*19-K to 50 GPa and 650 K. Above 43 GPa it was not possible to disorder the guest chains up to temperatures of 650 K. To investigate this phenomenon at higher pressures would require the use of a vacuum vessel.

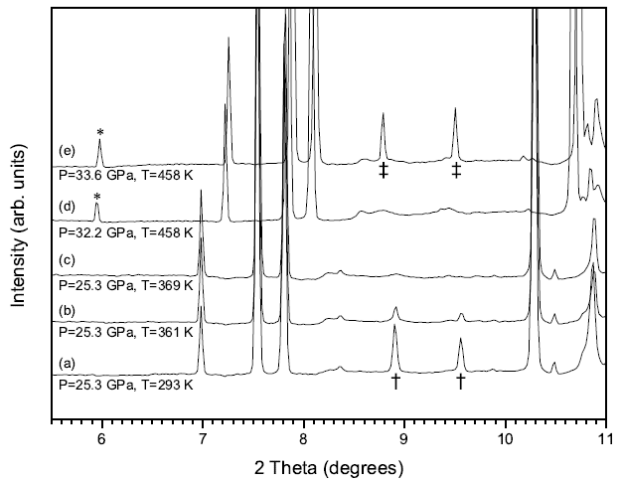

Figure 1: Azimuthally integrated 1D diffraction profiles of tI19-K indicating an order disorder transition in the guest chains, and a series of intra-phase transitions occurring in the host and guest substructures.

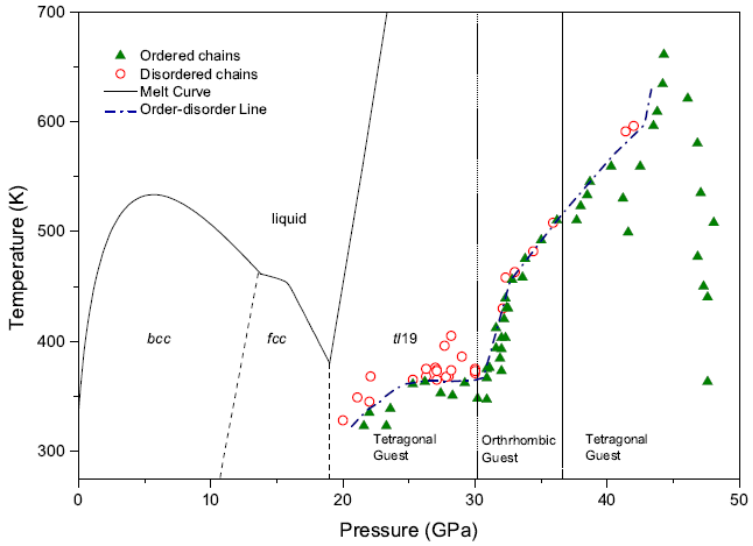

Figure 2: Pressure dependence of the order-disorder transition observed in *tI*19-K to 50 GPa and 650 K. Triangles indicated P-T points where the guest chains are ordered and open circles indicate where the guest chains are disordered. The series of intra-phase transitions in the host and the guest may influence the gradient of the order-disorder transition.

References

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