Melting of potassium to 22 GPa

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Using in-situ x-ray diffraction, the melting curve of potassium was determined to 22 GPa and was found to be remarkably similar to that of sodium, and strikingly different to that reported previously. The existence of a maximum in the bcc phase was determined at 5.8(5) GPa and 530(10) K; the melting temperature was then observed to decrease over several GPa, flattening out at the bcc-fcc-liquid triple point at 13.6(3) GPa and 466(10) K, before further decreasing from 15.6(3) GPa to a minimum at 19(1) GPa and 390(10) K. It then regained a positive slope and increased rapidly at a rate of 65(5) K/GPa. In the tI19 phase it was observed that the guest chains “melted” before the host structure at 20.3(3) GPa and 420(10) K, but were solid at 22.5(3) GPa and 350(10) K.

1. Introduction
The alkali metals at ambient conditions are well described by the nearly-free electron (NFE) model but show a significant departure from this behaviour with increasing pressure. Anomalous melting, where the gradient of the melting curve becomes negative over large pressure regions, has been observed in rubidium (Rb) and caesium (Cs) [1], sodium (Na) [2] and lithium (Li) [3]. To-date, potassium (K) appears to be an exception to this trend, with no observed melting maximum, at least not to 14.5 GPa [4].

Further evidence of a departure from the NFE model is seen in the emergence of structural complexity with pressure. At atmospheric pressure, the alkali elements are all body-centred cubic (bcc), and with increasing pressure they all transform to the closer-packed face-centred cubic (fcc) structure. Further application of pressure, however, sees them depart from this “simple” behaviour, with the emergence of low-symmetry open-packed structures [5-11]. The high-pressure phases of K have much in common with its group-I neighbours, with the incommensurate host-guest structure tI19.2 (hereafter referred to as tI19) being observed in Na, K and Rb [6-8], and the oP8 and hP4 forms observed in both Na and K [6, 9-11].

Given the similar structural transitions of K and the other alkali metals, and given that anomalous melting has been observed in all others, it is remarkable that K does not follow this trend of a melting maximum. We have therefore reinvestigated its melting temperature using diamond anvil cell (DAC) techniques and in-situ x-ray diffraction.

2. Experiment
All experiments were conducted using high-purity (99.95+%) samples of K (Aldrich Chemical Company) which were loaded under argon in a dry, oxygen-free atmosphere (< 1 ppm O₂, < 1 ppm H₂O), without a pressure transmitting medium to prevent contamination. Samples were loaded into
membrane DACs with tungsten or composite rhenium-iridium gaskets. SrB$_4$O$_7$:Sm$^{2+}$ was used as a pressure calibrant.

The sample temperature was controlled using external resistive heaters and measured using a thermocouple on the back of one of the diamonds. In-situ x-ray diffraction measurements were performed at beamlines ID09a and I15 at the European Synchrotron Radiation Facility and Diamond Light Source, respectively, using MAR 555 and MAR 345 area detectors. For each x-ray exposure, the samples were rocked ±7° to ensure good powder diffraction images, and to ensure that very few crystalline Bragg reflections were missed if the sample had annealed into a single crystal.

Figure 1. Representative integrated profiles from the crystalline (a) $tI_{19}$ and (c) $fcc$ phases, and the (b) liquid phase. The background in the liquid profile has been subtracted, using the method of Sanloup et al. [12]. Tick marks below profiles (a) and (c) show the calculated peak positions for the $tI_{19}$ and $fcc$ phases, respectively. The lowest angle (111) peak from the $fcc$ phase is absent, as the sample was a single crystal and this reflection was not observed during the ±7° oscillation during the x-ray exposure.

Figure 2: The melting curve of K to 22 GPa. Unfilled circles are data to 3 GPa from refs. [4] and [13], and the solid black line below 13.6 GPa is a fit to the Kechin equation [14] using this data combined with our own. The continuation of the solid line above 13.6 GPa is a guide to the eye. Stars indicate room temperature phase transition pressures [7], and the dashed lines are proposed phase boundaries based on this study. The dot-dashed line is the previously determined melting temperature [4].

3. Results

Representative integrated x-ray diffraction profiles in figure 1 show evidence of melting. It is clear that there is a sharp transition from the $fcc$ structure at 18.3(3) GPa and 404(10) K to the liquid phase at 18.3(3) GPa and 408(10) K. By maintaining the temperature at 408(10) K and increasing pressure by 4 GPa potassium then recrystallises in the $tI_{19}$ phase. At high temperatures, K anneals easily into single crystals. As a result, integrated profiles have missing reflections, and inaccurate peak intensities. Integrated profiles were thus analysed using Le Bail rather than Rietveld methods.

The melting curve of K, as determined by our measurements, is shown in figure 2, along with the previously-determined melting curve of Zha & Boehler [4]. Our results indicate the clear presence of a melting maximum in the $bcc$ phase. Melting of the $bcc$ phase was observed at ambient pressure.
2.2(3) GPa, 4.5(3) GPa, 7.4(3) GPa, and 11.5(3) GPa at 338(10) K, 498(10) K, 536(10) K, 526(10) K and 498(10) K, respectively. There is clearly a maximum in the melting temperature between 4.5(3) GPa and 7.4(3) GPa.

Up to 3 GPa, our melting results are in good agreement with previous studies (see refs. [4] and [13]); these results are shown by the unfilled circles in figure 2. Combining these previous results with our own, and using our bcc-fcc-liquid triple point at 13.6(3) GPa and 466(10) K, we performed a fit using the Kechin equation [14] to determine the location of the melting maximum in the bcc phase. This fit locates the maximum at 5.8(5) GPa and 530(10) K.

Above the triple point the melting temperature remains (almost) flat for several GPa. It should be noted that the presence of a second maximum, like that observed in Cs [1], cannot be ruled out, but it was too slight to be observed in this study. This region of nearly constant melting temperature ends as the melting curve decreases from 15.6(3) GPa and 462(10) K to a minimum at 19.0(3) GPa and 390(10) K. The location of this minimum coincides with the transformation from fcc-K to tI19-K; the phase boundary can be seen to be almost vertical. In the tI19-K phase the melting temperature rises very rapidly, increasing at a rate of 65(5) K/GPa.

Upon heating the tI19 phase, it was observed that the guest chains “melted” before the sample, consistent with a weak host-guest interaction. This is illustrated in figure 3, which shows 2D diffraction images collected from the tI19 phase both below and above the chain-melting transition. At 22.5(3) GPa and 350(10) K (figure 3(a)) Bragg reflections from the guest phase are clearly visible, although elongated perpendicular to the chain direction, indicating only short-range inter-chain correlations. The (101) guest reflection is circled. Figure 3(b) shows the 2D image from the same sample at 20.3(3) GPa and 420(10) K. The Bragg reflections from the guest chains have disappeared, as a result of the loss of long range order, and only some diffuse scattering remains. The calculated position of the (101) reflection is circled. The change in the guest reflections is quantified in figure 4, which shows 1D integrations of the 2D images in figure 3, performed over the same small regions encompassing the (101) reflection. At 22.5(3) GPa and 350(10) K there is a distinct Bragg peak and this has clearly disappeared at 20.3(3) GPa and 420(10) K. Initial observations at higher pressures indicate the chain melting temperature is almost independent of pressure.

Figure 3: 2D diffraction images of the tI19 phase collected at (a) 22.5 GPa and 350 K, and at (b) 20.3 GPa and 420 K. The position of the (101) guest reflection is circled in both images.

Figure 4: 1D profiles obtained by integrating the 2D diffraction images over the same small region encompassing the (101) reflection. There is a distinct Bragg peak at 22.5(3) GPa and 350(10) K which is absent at 20.3(3) GPa and 420(10) K.

4. Discussion
The melting behaviour of K is remarkably similar to that of Na, where there is also a melting maximum in the bcc phase followed by a decrease in the melting temperature to a dramatic minimum
of 300 K at 118 GPa. After this, the gradient of the melting curve regains a positive slope and increases rapidly [2], although the increase does not appear to be as rapid as in K. From the Clausius-Clapeyron relation, a change in the melting curve gradient from positive to negative is an indication of densification of the liquid phase relative to the underlying solid. A change in the sign of the gradient might thus imply a structural change in either the liquid or the solid phase. In Na, as in K, the maximum in the melting temperature occurs in the bcc phase, several GPa (approximately 6 GPa in K and 30 GPa in Na) before the transition in the solid from the bcc to the fcc phase.

To further understand this anomalous melting behaviour, Raty et al. performed ab initio calculations on the evolution of the melting temperature of Na [15]. They showed that the anomalous melting could be explained by a sequence of structural and electronic transitions in the liquid phase. They found that at the maximum in the melting temperature, bcc-like to fcc-like structural transitions were occurring in the liquid. Furthermore, their study attributed the negative slope of the melting temperature above the crystalline bcc to fcc transition to electronic and structural transitions in the liquid. Not only did they report a drop in calculated co-ordination number above 60 GPa, to that of the solid above 103 GPa, but they also detailed a three-fold drop in conductivity, indicating electronic changes occurring in the liquid.

Due to the remarkable similarity of the melting curves of Na and K, we suggest that similar mechanisms to those detailed above for Na could explain the melting behaviour of K. The advantage of K is that the anomalous melting behaviour occurs at much lower, and hence experimentally accessible, pressures than Na, and so additional studies are planned to investigate the co-ordination and electronic properties of liquid-K.

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