



	<b>Experiment title:</b> <b>Liquid-liquid Phase Transitions in High-Density Potassium</b>	<b>Experiment number:</b> HS-4470
<b>Beamline:</b> ID09a	<b>Date of experiment:</b> 12-15/11/2011	<b>Date of report:</b> 15/04/12
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<b>Names and affiliations of applicants (* indicates experimentalists):</b> <b>M.I. McMahon</b> School of Physics & Astronomy and Centre for Science at Extreme Conditions <b>E. McBride*</b> The University of Edinburgh <b>I. Loa*</b> Edinburgh, U.K. <b>G. Stinton* &amp; R. J. Husband *</b>		

The alkali metals are known to be “simple” metals at ambient conditions, and are well described by the nearly-free electron model. Under pressure, however, they all show a remarkable departure from this behaviour, and a series of complex, low-symmetry structures have been observed in lithium (Li), sodium (Na), potassium (K), rubidium (Rb) and caesium (Cs) at high pressure [1-3]. The complexity of the structures in Na and Li are such that they have only been determined recently, using the single-crystal diffraction techniques we have developed on ID09 and ID27 as part of Long Term Project HS3090 [4-5].

Recent diffraction studies have also shown the melting curves of Na and Li to be unusual: they both exhibit a melting maximum in the body-centred cubic (*bcc*) crystalline phase, followed by a negative slope in the face-centred cubic (*fcc*) phase, leading to a marked melting minimum at extreme compressions [4,6].

Raty *et al.* [7] have shown from *ab initio* calculations that the unusual behaviour in the melting temperature of Na arises from a sequence of structural and electronic transitions in the liquid phase that mirror those found in solid-Na at higher pressures. While the experimental confirmation of this in Na is at the extreme limit of current capabilities, due to the extreme P’s and T’s required, our recent discovery that the melting curve of K is very like that of Na (HS-3940 and subsequent data collected at Diamond Light Source) [8] allows us to study the same physical phenomena at much more accessible conditions.

This experiment (HS 4470) was awarded 3 days of beamtime on ID09a to (i) obtain high quality liquid diffraction data using perforated diamond anvils to search for changes in liquid-coordination that mirror phase changes in the underlying solid, but occurring at lower pressures; and (ii) to utilise x-ray absorption techniques to measure changes in density of liquid-K, which would also indicate a change in liquid structure.

The density of the sample was determined using:

$$I = I_0 e^{-(\mu_s \rho_s t_s - \mu_d \rho_d t_d)} \quad (\text{eqn. 1})$$

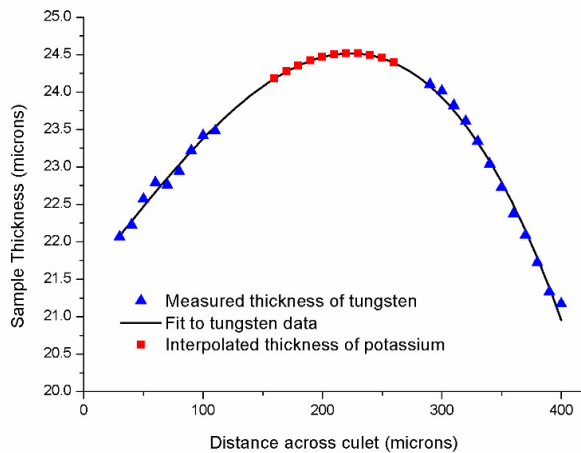
where  $I$  is the x-ray intensity transmitted through the sample and  $I_0$  is the x-ray beam intensity immediately before the sample, both measured with photodiodes;  $\mu$  is the mass absorption coefficient taken from ref. [9];  $\rho$  is the density of the sample; and  $t$  is the thickness. The subscript  $s$  indicates the values pertaining to the sample (either tungsten or potassium, depending on the position measurements were made across the culet, i.e. either on the gasket or in the sample chamber), while subscript  $d$  pertains to values connected to the diamond anvils. The thickness and density of the diamonds was taken as constant throughout the experiment.

To test the x-ray absorption technique as a method of measuring the density of liquid-K, we first applied it to solid-K and compared our calculated values of density using the x-ray absorption method with values determined

directly from the lattice parameters (obtained via x-ray diffraction). Here, the thickness of the tungsten gasket was measured as different points across the 400  $\mu\text{m}$  diamond culets. The density of the tungsten sample was determined directly from the lattice parameters and x-ray diffraction images were taken in 10  $\mu\text{m}$  steps across the culet. Substitution of these measured values into Eqn. 1 meant it was possible to calculate the gasket thickness. This data was then fitted to a third order polynomial, and then the thickness of the potassium sample was interpolated from this (see Figure 1)

Using the interpolated sample thickness, the literature value of  $\mu_K$ , and the measured values of  $I$  and  $I_0$ , the density of potassium was determined. Values in the centre of the sample were judged to be free of strontium borate (used as a pressure calibrant) and from gasket material. The density, as determined by the x-ray absorption measurement, was then compared to the density of solid-K as determined from the lattice parameters and was found to be in excellent agreement. This data is displayed in Table 1. The large difference between the density measured by x-ray absorption and that measured from the lattice parameters at position 210  $\mu\text{m}$  is most likely due to the presence of some strontium borate, used as a pressure calibrant.

We collected liquid density data at increased pressures and temperatures, covering the liquid melting curve up to 18 GPa. Analysis of the density of the liquid phase is on-going, and the results look very promising. In particular, by collecting data from the solid and liquid phases at the same pressure, and a temperature difference of only 10 K, we are able to directly determine the relative density change on melting. From our analysis we have identified several further improvements that can be made to this experimental setup, such as using ruby spheres instead of powdered strontium borate as a pressure calibrant, as the powder disperses unevenly through the sample chamber and therefore the transmitted x-ray profile from the sample is more complicated than pure K. Improved calibration of the two diodes will also improve our results still further.



**Figure 1:** The thickness of tungsten gasket across the diamond culet at 12 GPa, as determined by the x-ray absorption technique, is shown by the blue triangles. A fit to this data using a third order polynomial is shown by the black curve. The red squares indicate the calculated thickness of the potassium sample at various points across the gasket hole.

**Table 1:** Density of solid-K as determined by x-ray absorption techniques and diffraction techniques

Culet Position ( $\mu\text{m}$ )	Density from X-ray absorption ( $\text{g}/\text{cm}^3$ )	Density from lattice parameters ( $\text{g}/\text{cm}^3$ )	% difference
190	1.945	1.953	0.20
200	1.942	1.955	0.32
210	1.864	1.955	2.42
220	1.922	1.954	0.85

## References

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