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Melting of sodium and potassium in a diamond anvil cell

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Melting temperatures of sodium and potassium to 110 and 145 kbar, respectively, were determined by optical property changes with an externally heated diamond anvil cell using mineral oil as the pressure medium. The pressure was obtained from the known pressure and temperature shifts of the ruby fluorescence line. Sodium shows a continuous rise in the melting temperatures with pressure. The melting temperature of potassium remains nearly constant above about 70 kbar and the melting curve changes its slope drastically at 110 kbar. This is attributed to the bcc-fcc phase transformation that has been recently reported at room temperature around 110 kbar using the diamond anvil technique.

INTRODUCTION

Recent interest in the pressure induced electronic $s \rightarrow d$ transfer in the heavy alkali metals potassium, rubidium, and cesium has led to the discovery of a number of new phases at high pressure using reflection spectroscopy and x-ray diffraction in diamond anvil cells.[1-3] Based on similarities in the electronic structure a systematic sequence in this phase transition has been suggested. The structural bcc-fcc transition that occurs at 110, 70, and 22 kbar for K, Rb, and Cs, respectively, is closely related to the degree of $s \rightarrow d$ transfer. To better understand such a phase sequence a more detailed study of the phase diagrams and especially the temperature effects on the phase transitions is required.

Because Cs has low transition pressures, its phase diagram has been studied extensively. The bcc-fcc transition at 22 kbar and the electronic, isostructural transition at 42 kbar each cause a considerable depression in the melting curve. Owing to the complex physics of the $s \rightarrow d$ electron transfer, this phenomenon is not well understood and a theoretical treatment of a melting phase diagram near the electronic transformation is not yet possible.[4]

Recent improvement in liquid model calculations has led to the theoretical prediction of the melting curves for lithium, sodium, and potassium.[5] The results, however, depend strongly on the type of model. More experimental melting data, especially near and beyond the phase transitions, are required in order to provide a basis for developing better theoretical models.

The melting behavior of the lighter alkali metals near the solid-solid transitions has not been studied experimentally due to the pressure limitation of piston cylinder devices.[6] We now report on the melting curves for sodium and potassium using a diamond anvil technique.

Sodium has not shown any experimental evidence of a phase transition at room temperature to 300 kbar and therefore can allow relatively simple theoretical treatment to very high compression. Thus, melting data to very high pressures provide a valuable test for various models.

Potassium has been recently studied in a diamond anvil cell by optical reflectivity measurements[3] and x-ray diffraction,[2] revealing a bcc-fcc transition at 114 and 110 kbar, respectively. A further transition to an unknown structure (K III) was observed in the vicinity of 200 kbar. A similarity in the structural behavior of the heavy alkali metals thus predicts melting curve depressions in potassium at about 110 and 200 kbar similar to those observed for Cs at 22 and at 42 kbar. Behavior predictions for potassium under extreme pressures and temperatures are important in geophysical modeling of the outer core of the earth, especially since potassium is a possible miscible candidate in iron melts.[7]

EXPERIMENT

An externally heated diamond anvil pressure cell of new design was used. The new features are the tungsten carbide seats for the diamonds which are supported by steel binding rings. This provides permanent alignment of the diamonds. Details are published elsewhere.[8] The pressure is generated by a small, self-aligning lever that allows small pressure adjustments during the optical measurement. The optical arrangement is shown in Fig. 1. Melting was observed in both reflected and transmitted light by monitoring changes in shape, surface texture, and reflectivity of small samples of alkali metals surrounded by mineral oil. The use of mineral oil as a pressure medium minimized chemical reac-

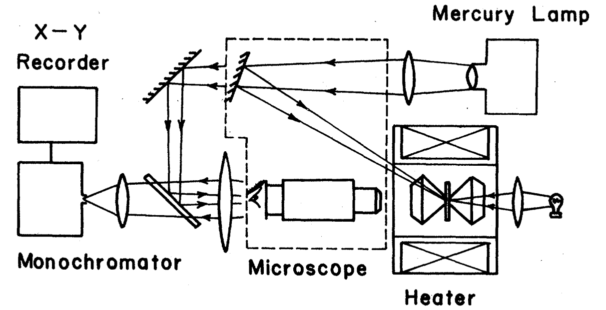

FIG. 1. Diamond cell and optical arrangement to measure melting at high pressure.

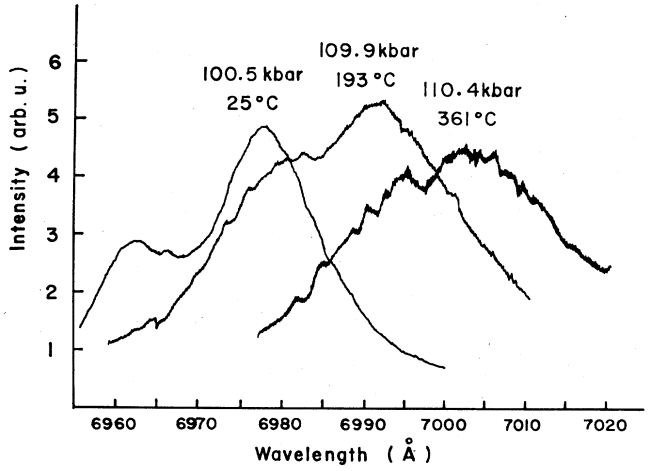

FIG. 2. Ruby spectra at high pressures and high temperature.

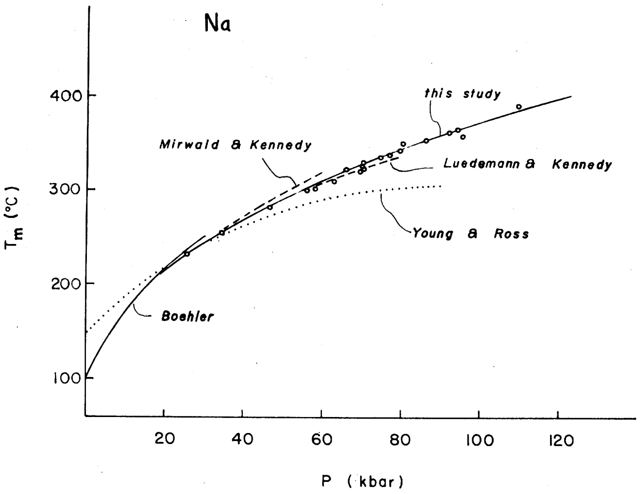

FIG. 3. Melting of sodium as a function of pressure.

tion of these highly reactive metals with the 301 stainless-steel gasket.

The temperature was measured with a 0.1-mm-diam thermocouple mechanically attached to the diamond. Temperature gradients within the diamond cell were measured during several calibration experiments with an additional thermocouple located in the gasket hole. These measurements were reproducible within ±1 °C. An uncertainty in the melting temperatures of ±6 °C is due to the observed melting range of the sample. The melting temperatures are taken at the onset of one or more of the melting phenomena that are described above. A possible source for the data scatter may be surface contamination of the sample. Effects of pressure gradients within the sample are considered unimportant due to the small melting slopes.

Pressures were obtained from previously calibrated shifts of the ruby fluorescence line with pressure and temperature. Since pressures did not exceed 200 kbar, the linear conversion factor of 0.365/kbar at room temperature was used.[9] The ruby line shift with temperature is $\Delta\lambda(\text{Å}) = 0.068T(°\text{C}) - 2.42$.[10] This temperature shift is reported to be pressure independent within the experimental uncertainty.[10,11] Above 300 °C line broadening becomes severe but location of the peak maximum is possible to at least 350 °C. Typical ruby spectra at high pressure and high temperature are shown in Fig. 2. The separation of the two ruby peaks disappears at about 250 °C from thermal line broadening. To check pressure estimates above 300 °C, we estimated the pressure-temperature function in the pressure cell at constant load during several temperature cycles below 250 °C. Extrapolated pressures from these P-T functions are in agreement with those obtained from the lower quality spectra at higher temperatures. Above 300 °C, our estimated uncertainty at 100 kbar is about +3 kbar. Difficulties such as sample spreading and thinning, and chemical reaction of the sample with the gasket material start above about 100 kbar. Pressure estimates for sodium become unreliable above 110 kbar due to its relatively high melting temperature.

RESULTS AND DISCUSSION

The melting temperatures for sodium to 110 kbar and for potassium to 145 kbar are shown in Figs. 3 and 4. At lower pressures our measurements agree well with estimates using a piston-cylinder apparatus[4,12] and with *in situ* measurements using hydrostatic fluid cell technique.[13] Recent theoretical estimates are shown by the dotted lines. Our smoothed melting temperatures are summarized in Table I. Sodium shows a continuous rise in the melting temperature with pressure. At low pressures, the slope of the melting curve starts at about 9 °C per kilobar to about 1.3 °C per kilobar at 110 kbar. Although the data by Luedemann and Kennedy from piston cylinder work to 80 kbar lie within our data scatter, they overestimated the pressure, which leads to significantly lower slopes of the melting curves. This overestimation of pressure is most likely associated with problems that occur in a piston cylinder apparatus above about 60 kbar such as the bore dilation of the pressure vessel, and the possible closing of the small gap between piston binding ring and pressure cylinder.

Theory[5] predicts a maximum in the melting curve of potassium at around 60 kbar. We do not observe a melting maximum but nearly constant melting temperatures above 70 kbar. The melting curve of potassium changes its slope at 110 kbar from nearly zero degrees per kilobar to about

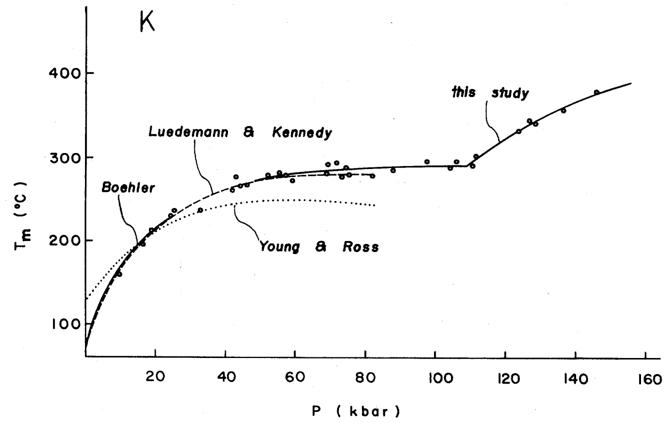

FIG. 4. Melting of potassium as a function of pressure.

TABLE I. Melting temperatures of sodium and potassium at high pressures. Values to 30 kbar are from Ref. 13.

Sodium		Potassium	
Pressure (kbar)	Temperature (°C)	Pressure (kbar)	Temperature (°C)
0	97.8	0	63.7
10	167.5	10	167
20	214.0	20	214
30	249.0	30	243
40	269.0	40	262
50	291.0	50	273.5
60	310.5	60	281.0
70	327.5	70	284.0
80	343.5	80	286.5
90	359.0	90	288.5
100	373.0	100	290.0
110	386.5	110	294.5
		120	323.5
		130	347.5
		140	367.0
		145	375.5

3 °C per kilobar. Based on the room-temperature transition from bcc to fcc structure around 110 kbar as described above, we attribute this change in slope of the melting curve to this transition and estimate a bcc-fcc-liquid triple point at 110 kbar and 295 °C. We note that the bcc-fcc phase boundary is temperature insensitive within the experimental uncertainty. The same phenomenon has been observed for Cs with a bcc-fcc transition at room temperature at 22.4 kbar, and a bcc-fcc-liquid triple point at 22.8 kbar.[14]

In Fig. 5 we compare the phase diagram of Cs with that of potassium. The solid lines are based on experimental data. An extension of the phase diagram of potassium to over 200 kbar is shown by the dashed lines. Based on the assumption of a temperature insensitive fcc–K III transition that has been found at room temperature below 200 kbar we would expect a melting maximum of potassium between 150 and 180 kbar. This, of course, remains subject to further investigation.

Recent spectroscopic work on the Rb bcc-fcc transition at room temperature shows evidence of a similarity to the Cs bcc-fcc transition.[1] This is interpreted to be due to the similar electronic structures of the two metals. We therefore expect a similar melting curve behavior of Rb at the bcc-fcc transition. A study of the melting curves of Rb and Cs using the diamond anvil cell and our techniques is possible to higher pressures than for Na and K because of the lower melting temperatures. This study would provide an important basis for theoretical development of melting temperature predictions beyond the pressure range of the electronic transition.

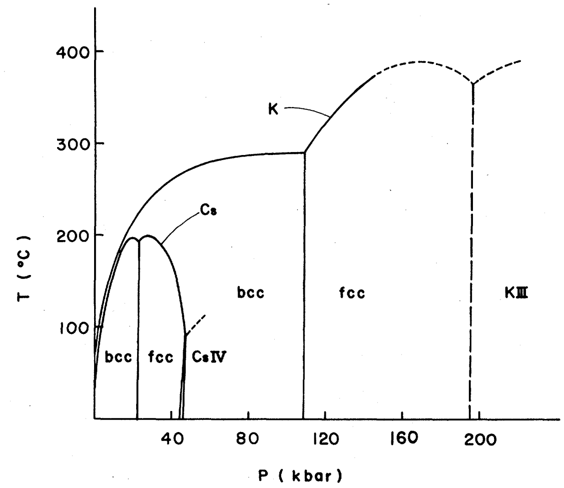

FIG. 5. Phase diagrams of Cs and K. A proposed extension of the phase diagram of K is shown by the dashed lines.

In summary, we show melting curve estimates in a diamond anvil cell by simple optical property measurements are possible. We found the sodium melting curve is continuously rising to 110 kbar with no sharp breaks in the slope, the location of the potassium bcc-fcc-liquid triple point, and similarities in the phase behavior of potassium and cesium at their triple points.

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