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MELTING AND POLYMORPHISM OF BARIUM AT HIGH PRESSURES*

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The fusion curve of barium has been determined up to pressures of 65 kbar by means of differential thermal analysis (DTA); no previous investigations of the melting under pressure have been reported. Bridgman has reported volume[1] and resistance[2] discontinuities, presumably indicative of polymorphic transitions, near 17 kbar and 59 kbar (revised pressure scale) at room temperature. The former transition was not detected in the present experiments, while the trajectory of the latter has been approximately delineated. In room-temperature work to higher pressures, Balchan and Drickamer[3] have reported a sharp discontinuity in resistance near 144 kbar—indicative of a further polymorphic transition.

Pressures were generated in single-[4] and double-stage[5,6] piston-cylinder apparatus. Friction corrections were made as before,[7,8] and pressures are believed accurate to ±1.0 kbar up to 45 kbar and ±3 kbar at higher pressures. DTA[4,8] determinations were accomplished with chromel-alumel thermocouples (without any corrections for the pressure effect on thermal emf) for samples in tantalum containers.[9] The signals obtained upon heating were taken for the melting points, and these temperatures were determined with a precision of ±3°C in the range up to 40 kbar and ±5°C elsewhere; the freezing signals were much sharper, although some undercooling was obvious. All of the barium samples were from high-grade commercial stock (purity >99.5%), except one, which was from vacuum-distilled material of the highest purity.[10] This sample was loaded in an argon-filled dry box. The other samples were handled in air but with sufficient care to minimize contamination, particularly oxidation. The results of the several runs are plotted in Fig. 1, no difference being obvious between the sample of highest purity and the others.

In an effort to reproduce the volume discontinuity of ~0.6% reported[1] by Bridgman near 17 kbar, compression runs were made with both grades of barium at room temperature. A column about 0.50 in. diam by 1.5 in. long was compressed at rates of ~1 kbar/min, while the displacement vs pressure was continuously recorded. Other details of the technique have been presented elsewhere.[9,11] Although a discontinuity of ~0.2% would have been detectable,

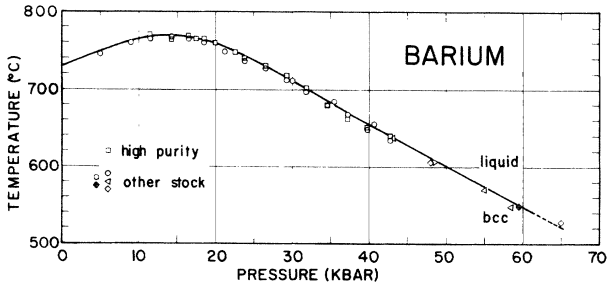

FIG. 1. Melting curve of barium.

none was apparent in the several compressions up to about 37 kbar, strongly suggesting that the transition reported near 17 kbar for barium does not exist. Bridgman does not report the purity of his material but comments that the batch on which the volume[1] discontinuity and the 0.35% discontinuity in resistance[2] were observed was probably less pure than the previous[12] material in which no discontinuities were detected to about 50 kbar. The fusion curve (Fig. 1) does not reflect the triple point that would occur if this transition had existed with the trajectory indicated by Bridgman.[1]

The present fusion curve connects satisfactorily with the zero-pressure melting point of 729°C,[13] and an initial slope of ~4°C/kbar is suggested. The maximum in the fusion curve is located near 14 kbar and 770°C.

The first maximum in the melting curve of an element was that reported by Bundy[14] for Rb, although there was some hesitation in its interpretation as such. Kennedy, Jayaraman, and Newton[15] clearly established the existence of maxima in the fusion curves of Cs I and II. The present results for Ba indicate that the occurrence of such maxima may be a more widespread phenomenon.

The present data reinforce the previous proposal[15] that an understanding of the fusion curve maxima must be sought primarily in a consideration of the structure and coordination obtaining within the liquid phase. No structural investigations of liquid barium or of the other alkaline earths—calcium and strontium—have been published. In lieu of such studies, some consideration may be directed to the results of the neutron diffraction studies of the liquid alkali metals, as carried out by Gingrich and Heaton.[16] These workers found similar coordinations of 9.0-9.5 for Li, Na, K, Rb, and Cs near the respective melting points. For Rb and possibly Cs, subsidiary peaks in the radial distribution function were detected, the relative magnitude of these peaks increasing with increasing temperature. Since the compressibilities of liquid Rb and Cs are known to be abnormally high, as strikingly manifested in the fusion curve maxima, it may be that the subsidiary peaks indicate a drastic, possibly discontinuous, change in coordination within the melt. A similar situation may exist for barium.

Some points for the solid-solid phase boundary were also obtained with DTA and these are plotted in Fig. 2. The thermal arrests associated with

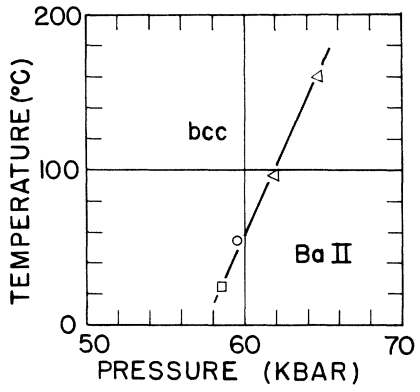

FIG. 2. Coordinates of solid-solid transition in barium. The room-temperature point (square) was obtained by resistance measurements, the others by DTA.

the transition were very weak, and hence the data cannot be considered very precise. The room-temperature point was obtained by the resistance discontinuity method[5,8] and has been precisely located because of the sharp resistance increase accompanying the transition. This is the first direct determination of this transition, which is widely used as a calibration point. For a linear fit of the four experimental points (Fig. 2), a slope of ~22°C/kbar is suggested. For a volume change[17] of ~1.9% or 0.72 cm^3/mole, the entropy difference between the body-centered cubic (bcc) polymorph and Ba II may be estimated as ~0.8 entropy unit. By linear extrapolation of both the fusion curve and the approximate solid-solid boundary, a triple point between liquid, bcc, and Ba II may be estimated to occur near 80 kbar and 450°C.

It is impossible to predict the slope and trajectory of the Ba II fusion curve. If Ba II melts with a slope only slightly less negative than the approximately linear slope ($dT/dP \approx -5.3$°C/kbar) of the melting curve of Ba I (Fig. 1), it is altogether possible that the discontinuous increase in resistance[3] near 144 kbar and 25°C is indicative of melting. The relative abruptness[3] of the resistance change at this point is certainly not incompatible with this interpretation. The existence of a liquid would have considerable significance, since investigations under completely hydrostatic conditions at such high pressures and relatively low temperatures may now be feasible.

Preliminary results from experiments now in progress in this laboratory with calcium and strontium do not immediately indicate any ob-

vious similarities with the phase diagram of barium. It may be that the solid- (and liquid-?) state transitions in Ba are more closely related to those in Cs,[15] both being intimately connected with the band structures corresponding to the closely spaced[18] $6s$, $5d$, and $4f$ atomic energy levels. In support of this viewpoint, it may be noted that the volume changes across the I-II transition for Cs and Ba are ~0.6%[19] (0.43 cm^3/mole) and ~1.9%[17] (0.72 cm^3/mole), respectively. The Cs II-III transition is known to be rapidly reversible and with a rather large volume change of ~5.6%[19] (4.0 cm^3/mole); present published speculations[20,21] are that Cs II and III are isostructural and that a discontinuous change in the character of the valence electron(s) is involved. The volume change for the Ba transition near 144 kbar and 25°C is not known, but its ready reversibility[3] does not rule out the possibility of its being an "electronic" transition.

The crystal structures of Cs II and III and of Ba II have not been determined, although most speculations[20,21] have assumed both of the former to be face-centered cubic (fcc). If the reasonable working hypothesis of a close-packed structure for Ba II is embraced, it is more likely that the structure is fcc rather than hexagonal close-packed (hcp). This statement is based on the experience that all bcc-hcp transitions studied so far[5,6] occur at different temperatures upon heating and upon cooling and that no such hysteresis was detected in the present measurements for the Ba I-II transformation.

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[1]P. W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 220 (1938).

[2]P. W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 187 (1938).

[3]A. S. Balchan and H. G. Drickamer, Rev. Sci. Instr. 32, 308 (1961).

[4]G. C. Kennedy and R. C. Newton, Solids Under Pressure (McGraw-Hill Book Company, Inc., New York, 1963), pp. 163-174.

[5]A. Jayaraman, W. Klement, R. C. Newton, and G. C. Kennedy, J. Phys. Chem. Solids 24, 7 (1963).

[6]A. Jayaraman, W. Klement, and G. C. Kennedy (to be published).

[7]W. Klement, A. Jayaraman, and G. C. Kennedy, Phys. Rev. 129, 1971 (1963).

[8]W. Klement, A. Jayaraman, and G. C. Kennedy, Phys. Rev. (to be published).

[9]W. Klement, A. Jayaraman, and G. C. Kennedy, Phys. Rev. (to be published).

[10]Major impurities (in ppm): H, 200; N, 90; C, 80; etc., as supplied by Professor D. T. Peterson of the Ames Laboratory of the U. S. Atomic Energy Commission. Thanks are due to Professor Peterson and Professor Spedding for their generous cooperation.

[11]A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. 130, 540 (1963).

[12]P. W. Bridgman, Phys. Rev. 48, 903 (1935).

[13]D. T. Peterson and M. Indig, J. Am. Chem. Soc. 82, 5645 (1960); D. T. Peterson (private communication).

[14]F. P. Bundy, Phys. Rev. 115, 274 (1959).

[15]G. C. Kennedy, A. Jayaraman, and R. C. Newton, Phys. Rev. 126, 1363 (1962).

[16]N. S. Gingrich and L. R. Heaton, J. Chem. Phys. 34, 873 (1961).

[17]P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 425 (1942); Phys. Rev. 60, 351 (1941).

[18]G. Herzberg, Atomic Spectra and Atomic Structure (Dover Publications, New York, 1944), p. 141.

[19]P. W. Bridgman, Proc. Am. Acad. Arts Sci. 76, 55 (1948).

[20]J. Bardeen, J. Chem. Phys. 6, 372 (1938).

[21]R. Sternheimer, Phys. Rev. 78, 235 (1950).