Fusion Curve of Europium, Fusion, and fcc-bcc Transformation in Ytterbium at High Pressures

A. JAYARAMAN
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 23 March 1964)

The melting behavior of Eu to 70 kbar and melting and fcc-bcc transformation in Yb to 40 kbar have been studied. Europium has a maximum in the fusion curve at about 35 kbar and 995°C and retains the bcc structure in the pressure and temperature range investigated. The fusion curve of Yb has an initial slope of 19°/kbar and rapidly flattens in the 35-kbar region. There appears to be only one fcc-bcc phase boundary and not two as proposed in an earlier study. This boundary intersects the temperature axis close to the known fcc-bcc transformation temperature at atmospheric pressure, and an initial slope of −16°/kbar is suggested. This transformation in Yb behaves exactly like the analogous transformation in Sr, exhibiting pressure and temperature hysteresis and also reversing the sign of the resistance discontinuity above 24 kbar. The striking parallelism in high-pressure behavior between Eu and Ba and Yb and Sr is discussed. The greater density of the bcc phase compared to fcc or hcp noted in several instances is rationalized. The melting behavior of Eu is discussed from the standpoint of coordination in the liquid state.

INTRODUCTION

EUROPIUM and ytterbium crystallize, respectively, in the body-centered cubic and face-centered cubic structures, are divalent and have larger atomic radii in the otherwise smoothly varying size behavior and trivalency exhibited by the lanthanide series. These two metals in many respects appear to be closely related to the alkaline earths. High-pressure experiments reveal a striking parallelism in the behavior of Eu and Yb on the one hand, and Ba[1] and Sr[2] on the other, and this will be the subject matter of this paper.

Bridgman[3] discovered a phase transition in Yb at about 40 kbar (revised pressure scale) from resistivity measurements. The relative resistance increased by a factor of 12 prior to the transition but thereafter exhibited very little variation with pressure. Vereshchagin *et al.*[4] observed a similar behavior. Recent resistivity measurements under pressure by Stager and Drickamer[5] and Souers and Jura[6] confirmed these findings and further, isobaric studies of the temperature variation of resistivity revealed that before the phase transition Yb exhibits characteristics of a semiconductor over a pressure range. Hall, Barnett, and Merrill[7] have shown by high-pressure x-ray diffraction work that the phase transition near 40 kbar is from the fcc to the bcc structure, and have hypothesized that an electronic promotion from the $4f$ to the $5d$ level must be involved in the transition. Hall and Merrill[8] have recently presented results of detailed high-pressure resistance and volume measurements. They have proposed a phase diagram showing the pressure-induced bcc phase, as distinct from the normal temperature-induced bcc phase; this is contrary to the conclusions of Souers and Jura.[6] Recent high-pressure work[2] on the fcc-bcc transformation in Sr and the identification of the high-pressure phase of Sr by x-ray diffraction[9] revealed a striking similarity in behavior between Sr and Yb under high pressures. This suggested that the fcc-bcc transformation in the latter could be analogous to that of Sr and prompted the present work.

As regards earlier pressure work on Eu, Spedding *et al.*[10] have reported a compressibility measurement up to 12.4 kbar and Stager and Drickamer[11] have recently published resistivity measurements to an estimated 700 kbar at room and lower temperatures. There appear to be no previous high-pressure–high-temperature studies on Eu.

In the present investigation, the fusion curve of Eu has been determined up to 70 kbar. The fusion curve and the fcc to bcc transformation in Yb have been studied to about 45 kbar.

EXPERIMENTAL

A piston cylinder device was used to generate high pressures. Pressures to 45 kbar were obtained by advancing an unsupported tungsten carbide piston into a pressure chamber $\frac{1}{2}$ in. in diam by 2 in. long. For generating higher pressures, a double-staging scheme[12] was adopted. Talc was used as the pressure medium. Friction correction was estimated by determining points on the phase boundary being investigated, both on the increasing and decreasing pressure cycle. Where

[1] A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. Letters **10**, 387 (1963).
[2] A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. **132**, 1620 (1963).
[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **83**, 1 (1954).
[4] L. K. Vereshchagin, A. A. Semerchan, and S. V. Popova, Doklady Akad. Nauk. SSSR **139**, 585 (1961) [English transl.: Soviet Phys.—Doklady **6**, 609 (1962)].
[5] R. A. Stager and H. G. Drickamer, Science **139**, 1284 (1963).
[6] P. C. Souers and G. Jura, Science **140**, 481 (1963).
[7] H. T. Hall, J. D. Barnett, and L. Merrill, Science **139**, 111 (1963).
[8] H. T. Hall and L. Merrill, Inorg. Chem. **2**, 618 (1963).
[9] D. B. McWhan and A. Jayaraman, Appl. Phys. Letters **3**, 129 (1963).
[10] F. H. Spedding, J. J. Hanak, and A. H. Daane, Trans. AIME **212**, 379 (1958).
[11] R. A. Stager and H. G. Drickamer, Phys. Rev. **133**, A830 (1964).
[12] A. Jayaraman, W. Klement, R. C. Newton, and G. C. Kennedy, Phys. Chem. Solids **24**, 7–18 (1963).

this was not possible, frictional corrections from previous experience were applied. The pressures are believed to be accurate to ±2 kbar up to 45 kbar and ±3 kbar at pressures above this.

The fusion curve was determined by differential thermal analysis.[13] Samples were encapsulated in niobium containers. The purity of Eu and Yb used were given as 99.9%. Suitable precautions were taken to prevent oxidation of the Eu while packing it into the container. Temperatures were measured with Chromel-Alumel thermocouples, without correction for the effect of pressure on the thermal emf. Melting points were determined at 4-kbar intervals from the thermal arrests noted upon heating. The thermal arrests were strong and sharp in both cases. The melting temperatures are believed to be within ±3° up to 1000°C and ±5° at temperatures above 1000°C.

Because the thermal arrest associated with the fcc-bcc transformation in Yb was extremely feeble and uncertain, the internally heated resistance technique[2] was employed to study this transformation. The technique was modified to extend measurements to higher temperatures than previously possible. A Teflon tube was used instead of polyethylene to enclose the Yb wire (15 mils diam), and molybdenum instead of Cu for electrical leads. To obtain accurate temperature readings the thermocouple junction was positioned near the center of the sample wire. The thermocouple and the resistance circuit were insulated from each other by inserting between them a strip of mica 20 mils thick.

RESULTS

Europium

The fusion curve of Eu is presented in Fig. 1. Melting temperatures after one cycling fell 15° lower than those obtained on the first cycle. Further experiments with the same sample revealed that the lowering resulted from a slow deterioration of the thermocouple caused by prolonged operation at temperatures above 900°C and not due to sample contamination. The situation was remedied by covering the pressure range in several runs, each time obtaining two or three melting points. The data points appearing as circles and squares in Fig. 1 have been obtained in this manner. The squares are the results of a double-stage run wherein the sample was directly pressurized to 54 kbar and melted. Two other fusion determinations at 62 and 65 kbar were also made. The filled circles are the fusion determinations of a single-stage run.

The fusion curve of Eu (Fig. 1) exhibits very definitely a maximum, located at about 35 kbar and 995°C. It begins with a steep initial positive slope, rapidly flattening in the region of 25 to 35 kbar and takes on a negative slope at higher pressures. The heat

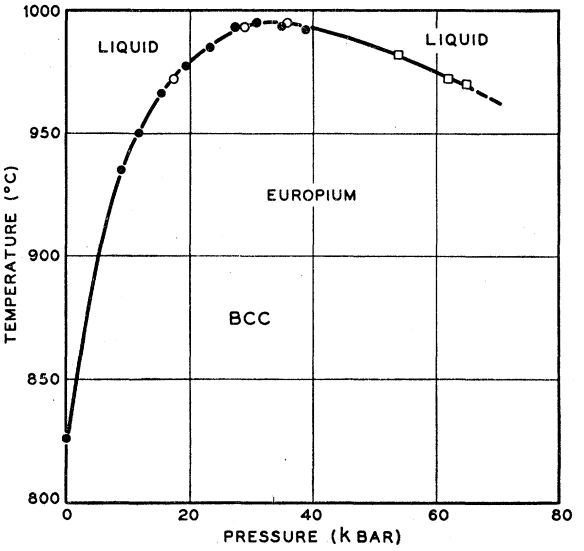

FIG. 1. The fusion curve of europium.

of melting was calculated from the presently determined slope and the known volume change[10] upon melting. The pertinent thermodynamic data are presented in Table I.

TABLE I. Thermodynamic data for Eu and Yb.

	dt/dp °C/kbar	Δv cm³/mole	Δs (Eu)
Eu fusion	+15	1.39[a]	2.23
Yb fusion	+19	1.26	1.64[b]
fcc-bcc	−16	∼−0.26	∼0.396[b]

[a] Reference 10.
[b] Reference 14.

Ytterbium

The fusion data are presented in Fig. 2 where the different symbols stand for different runs. The fusion curve has a steep positive initial slope, rapidly changing at higher pressures. Since the melting temperatures were approaching the limit of operation of the Chromel-Alumel thermocouple, further exploration at higher pressures was not attempted. From the presently determined slope and the known heat of fusion,[14] the volume change accompanying melting was calculated. The relevant thermodynamic data are given in Table I.

The fcc-bcc transformation temperatures were determined from the resistance discontinuity noticed upon heating; the data are plotted in Fig. 2. The intersection with the temperature axis at 770°C is in fair agreement with the fcc-bcc transformation temperature (>732°C,[15] <798°C [14]) reported at atmospheric pres-

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

[14] F. H. Spedding and A. H. Daane, *The Rare Earths* (John Wiley & Sons, Inc., New York, 1961), p. 185.

[15] F. H. Spedding, J. J. Hanak, and A. H. Daane, J. Less Common Metals **3**, 110 (1961).

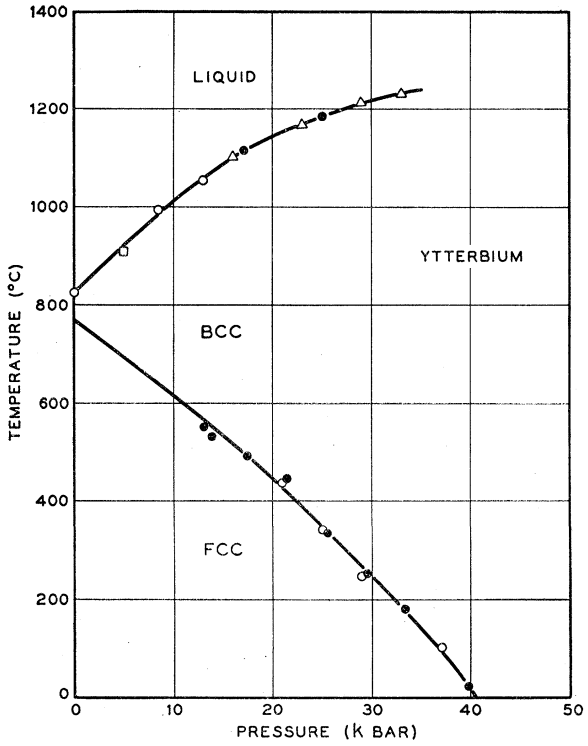

FIG. 2. The fusion curve and fcc-bcc boundary for ytterbium.

sure. As in the case of Sr[2], the character of the resistance discontinuity accompanying the transformation varies with the pressure; to about 24 kbar, it is an increase in resistance, the magnitude progressively diminishing with increasing pressure. Above 24 kbar the discontinuity is an abrupt decrease in resistance. Also, the fcc-bcc transformation has associated with it certain temperature hysteresis and sluggishness which are pressure-dependent. The transformation temperatures obtained on heating and cooling exhibit little hysteresis and the transition is sharp to about 18 kbar. Above this pressure, the hysteresis interval progressively increases and the transition is spread over a temperature range. At pressures greater than 21 kbar the fcc-bcc transition is very sluggish, and the reverse transformation does not take place on cooling. Reversion could only be accomplished by reducing the pressure to about 14 kbar. Figure 3 shows isobars at 35 and 17.5 kbar, typifying the nature of the resistance discontinuity, following the fcc-bcc transition.

The fcc-bcc boundary has an initial slope of about $-16°$/kbar. From the known heat of transformation,[14] the volume change of $\Delta v = -0.26$ cm^3/g atom was calculated. The thermodynamic data are presented in Table I. Hall and Merrill[8] report a volume change of $\Delta v = -0.65$ cm^3/g atom for the transformation, from room-temperature compression measurements. The greater volume change at the high-pressure end is to be attributed to the higher compressibility of the bcc phase.

The resistivity of bcc Yb very slowly decreases with pressure, in contrast to the fcc phase which has a very large positive pressure coefficient of resistance. The differences in the resistance discontinuity accompanying the fcc-bcc transformation owe their origin to this circumstance. At low pressures the bcc phase has the higher resistance compared to fcc, but the situation reverses at high pressures because of the rapid increase in resistivity of the fcc phase with pressure.

At pressures above 30 kbar, bcc Yb shows an anomaly in resistivity at about 470°C. In Fig. 3 is shown a plot of resistance versus temperature at 35 kbar. After transformation to bcc, the temperature coefficient of resistance is steeply rising until a well-defined break occurs at 470°C. The latter temperature is practically insensitive to pressure and is presumably connected with some kind of a transition, the nature of which is not clear. A resistance anomaly in bcc Yb was first observed by Hall and Merrill[8] but they report a temperature of 625°C.

DISCUSSION

The similarities in physical properties between Eu[10] and Yb, on the one hand, and Ba and Sr, on the other, have been pointed out. High-pressure experiments have brought out further close correlations that exist amongst them. Both Eu and Ba[1] exhibit fusion curve maxima, and have compressibilities which are about the same.[10] Likewise, the melting behavior and compressibilities of Yb and Sr are very similar. The fusion curves of Sr[2] and Yb have initial slopes of 20°/kbar, and 19°/kbar, respectively, and rapidly flatten in the 35-kbar region in either case. The most striking parallelism in the behavior of Yb and Sr is to be found in the fcc-bcc

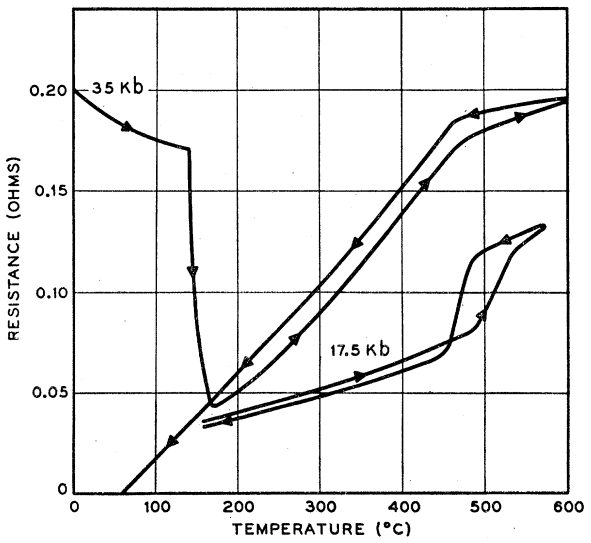

FIG. 3. Resistance versus temperature at 35 kbar and 17.5 kbar for ytterbium.

transformation and resistivity of these metals under pressure. The resistivity of both fcc Yb and Sr rises rapidly with pressure and over a certain region (around 30 kbar) exhibits a negative temperature coefficient of resistance—a characteristic of an intrinsic semiconductor. The semiconducting fcc phase is terminated in either case through a sluggish phase transformation to the bcc structure. The nature of the resistance discontinuity accompanying the fcc-bcc transformation and the temperature and pressure hysteresis associated with this transformation are very similar in the two metals. The fcc-bcc phase line has a negative slope in either case.

The similarities to the alkaline earths appear to result from the stability of half-filled and fully occupied $4f$ states of Eu and Yb, respectively, with only the two $6s$ electrons contributing to the binding. Further, their metallic nature evidently results from overlapping first and second Brillouin zones, as is found for the alkaline earths[16]; the overlaps are conceivably in the same directions in k space. To account for the large pressure coefficient of resistivity in Ca and Sr, Mott[17] proposed that a decrease in the zone overlaps occur with pressure. It is believed that a similar mechanism would account for the resistivity of Yb under pressure. The recent findings of a semiconducting region under pressure in Ca,[18] Sr,[2] and Yb[6] lend support to Mott's proposal. It may be noted that a large positive pressure coefficient of resistance and the existence of a semiconducting region under pressure seem to be characteristic of fcc metals with two electrons per atom.

Hall *et al.*[7] have suggested that the atomic radius observed in the bcc Yb at 40 kbar reflects a change in the valence state of Yb from 2 to 3, involving the promotion of a $4f$ electron to the $5d$ state. However, the observed atomic radii in bcc Yb and bcc Sr could be accounted for when corrected for the change of coordination number.[9] When the volume of 33.5 Å^3 per atom observed for the fcc Yb at 39.5 kbar[8] is used to calculate the lattice constant of the bcc Yb, one obtains 4.06 Å, while the observed value is 4.02 Å.[8] This difference almost exactly accounts for the 3% macroscopic volume change[8] observed for the transformation at 40 kbar. The bcc phase is found to be denser than fcc or hcp in several metals, e.g., the bcc phase is denser than hcp in Zr, Ti,[19] and Tl.[12] In the bcc arrangement each atom has 8 nearest neighbors and the 6 next-nearest neighbors are only 13.4% farther away. The second-neighbor interactions are much stronger in the bcc case than in fcc or hcp, leading to an effective coordination which is more than 8 and in some cases greater than 12. The effective coordination and hence the density of the bcc phase relative to that of fcc or hcp in a particular case would be determined by the nature of the binding interactions. The apparently conflicting circumstance could thus be rationalized.

Fusion-curve maxima have been reported for Rb,[20] Cs,[21] and for Ba.[1] The present study has shown the existence of such a maximum in Eu. These metallic elements have two features in common; namely, they crystallize in the body-centered cubic structure, and are all very compressible (Rb and Cs have abnormally high compressibilities). It has been suggested[21] that an understanding of the fusion curve maxima must be sought primarily from a consideration of the structure and coordination obtainable in the liquid phase. The fusion curve of Eu reflects the rapid increase in the density of the liquid; the latter eventually becomes denser than the solid. In the pressure range investigated, Eu retains the bcc structure, and therefore the coordination in the solid state is fixed, whereas there is no similar constraint in the liquid phase. It is probable that in the liquid a higher effective coordination is progressively realized, accounting for much of the increase in density.

The fusion curve of Eu above 70 kbar may be expected to continue its downward trend, in analogy with Ba. Stager and Drickamer[11] report a sharp rise in resistance at about 150–160 kbar at room temperature, indicative of a first-order transition. It is unlikely that this would be due to melting, since the fusion curve does not extrapolate near to room temperature at this pressure. It must then be a solid-solid transition, probably analogous to the Ba transition at 59 kbar.[22]

The fusion curve of Yb is rapidly decreasing in slope and may be expected to show a maximum at higher pressures.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge discussions with S. Geller and D. B. McWhan. Thanks are due to R. G. Maines for technical assistance.

[16] M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1934).
[17] N. F. Mott, Proc. Phys. Soc. (London) **46**, 680 (1934).
[18] R. A. Stager and H. G Drickamer, Phys. Rev. **131**, 2524 (1963).
[19] A. Jayaraman, W. Klement, and G. C. Kennedy, Phys. Rev. **131**, 644 (1963).
[20] F. P. Bundy, Phys. Rev. **115**, 274 (1959).
[21] G. C. Kennedy, A. Jayaraman, and R. C. Newton, Phys. Rev. **126**, 1363 (1962).
[22] J. D. Barnett, R. B. Bennion, and H. T. Hall, Science **141**, 534 (1963).