Phase Diagrams of Calcium and Strontium at High Pressures*

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The melting temperatures for both Ca and Sr increase rapidly with pressure, reaching nearly 1200°C at 40 kbar. The only solid-solid transition in Ca below 35 kbar is that between the body-centered cubic and face-centered cubic polymorphs; the slope of the phase boundary is about 3.3°C/kbar. The phase boundary between the homologous Sr polymorphs has an initial slope of about −10°C/kbar becoming much steeper at higher pressures. Also, the hysteresis associated with the transition is a function of pressure and becomes very large above 22 kbar. The face-centered cubic Sr shows a large increase in resistance with pressure and a negative temperature coefficient of resistance prior to the polymorphic transition. The resistance discontinuity for the fcc-bcc transformation is a sharp increase at lower pressures, which progressively decreases in magnitude and sharpness and reverses sign at the higher pressures.

INTRODUCTION

THE present authors have recently[1] determined the phase diagram of barium to about 70 kbar and have found a maximum in the fusion curve of the body-centered cubic (bcc) polymorph; a phase transition near 17 kbar reported by Bridgman[2] could not be verified in this investigation. The other alkaline earths, calcium and strontium, are obvious candidates of interest for similar pressure studies. Unlike Ba, they crystallize in face-centered cubic (fcc) structure and also undergo a temperature-induced phase transition to a bcc structure at atmospheric pressure. In the purest materials, such as supplied by the Ames Laboratory of the Atomic Energy Commission for the present experiments, the transition temperatures are 448°C for Ca and 557°C for Sr.[3] Hexagonal close-packed (hcp) phases have been reported both for Ca (Ref. 4) and Sr (Ref. 5) but these are stabilized by impurities.[6,7] Bridgman,[8–10] in his pioneering volume and resistance studies, reported pressure-induced phase transitions in both Ca and Sr. The present investigation was undertaken to determine the phase boundaries and to investigate the possibility of systematic behavior among the alkaline earths at high pressures, akin perhaps to that discovered in the alkali metals.[11]

EXPERIMENTAL PROCEDURES

Pressures up to 45 kbar were generated in a piston-cylinder apparatus. Corrections for friction were made as before. The procedures have been described in detail elsewhere.[12–17] Pressures are believed accurate to ±1.0 kbar.

The fusion curves were determined by differential thermal analysis (DTA).[14,18] Temperatures were measured with chromel-alumel thermocouples, without any correction for the effects of pressure on the thermal emf. Melting points were obtained from thermal arrests upon heating.

In the attempts to determine the phase boundary and characteristics of the solid-solid transitions, the techniques of DTA, externally heated volume measurement[15] and both externally[17] and internally heated[14] resistance measurements were employed. The details of these experiments are presented in the following section.

RESULTS

Calcium

Bridgman[2] reported some irregularities in volume measurements near about 30 kbar at 25, 75, and 125°C and suggested that these were indicative of a phase transition. No discontinuity was detected in resistance measurements[8] on the same material (purity unknown). A volume discontinuity[9] of 1.3% ($\Delta V/V_0$) was reported near 63 kbar although, again, there was no corresponding clear cut discontinuity in resistance.[10] Balchan and Drickamer[19] have recently measured the resistance at

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25°C from 100 to an estimated 525 kbar; no discontinuities were detected but a pronounced maximum occurred near 375 kbar on compression. Very recently, Stager and Drickamer,[20] from results of resistance measurements to an estimated 600 kbar, have suggested two sluggish phase transitions in Ca—one above 140 kbar and another near 300 kbar.

Two grades of calcium were used in the present experiments, viz., vacuum distilled stock of the highest[21] purity and also some granules from Dominion Magnesium Ltd., claimed to be of 99.9% purity. Melting experiments were carried out in tantalum containers with stoppers of boron nitride, tantalum and iron. Samples of the highest purity stock were initially loaded in an argon-filled dry box, but later it was found that this material could be machined without visible oxidation when covered with oil. The thermal arrests for the fcc-bcc transition were faint but clear, and those for melting quite strong and sharp with the Dominion Magnesium specimens. Inexplicably, all thermal arrests were extremely weak in 6 runs with the highest purity stock. However, in one run with the thermocouple buried in the sample, a recognizable thermal arrest was noted for the fcc-bcc transition and a strong thermal arrest for the melting. The melting temperature of 928°C at 9.4 kbar obtained on the high purity stock is in good agreement with the data for Dominion Magnesium specimens. The fusion curve and solid-solid boundary (Fig. 1) are largely based on data from experiments with calcium from the Dominion Magnesium stock. Temperatures corresponding to the thermal arrests observed on heating are plotted. A hysteresis interval of about 10°C between the values for heating and cooling was noted for the solid-solid transition. The melting points for the runs using containers with BN stoppers fell progressively lower with time, an effect which is believed to be due to the contamination of the sample with boron nitride. There was no evidence of any contamination of the samples encapsulated in all Ta or Ta containers with Fe stoppers. The connection of the Ca fusion curve to the normal melting point[3] of 839°C is satisfactory and an initial melting slope of

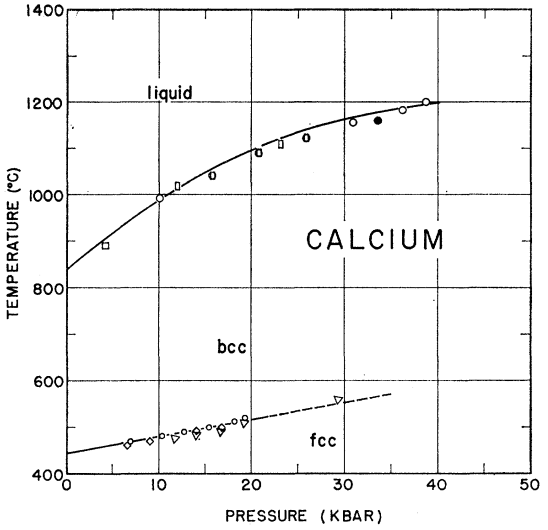

FIG. 1. Phase diagram of calcium. The filled circle represents the melting point for a sample compressed to 34 kbar at room temperature and then heated.

~17°C/kbar is suggested (Fig. 1). This slope and the published value[22] for the entropy change of $\Delta S \approx 1.75$ eu (entropy units) gives a volume change $\Delta V \approx 1.25$ cm³/mole for fusion. The thermal arrests associated with the fcc-bcc transformation were clear at the lower pressures but became progressively weaker with increasing pressure and could not be detected above 30 kbar. The appearance of a new phase boundary was considered, but a search for thermal arrests at other temperatures at these pressures was without success. The connection with the one atmosphere transition temperature,[3] on heating, of 448°C is satisfactory and a slope of 3.3°C/kbar is suggested for the fcc-bcc transition. The pertinent thermodynamic data are given in Table I.

Several compression[15,17] runs using a specimen 0.5 in. in diameter and about 1.5 in. long of the highest purity calcium were made at 25°C up to about 38 kbar. No irregularities in volume were noted, such as those reported by Bridgman.[2]

TABLE I. Thermodynamic data for Ca and Sr at one atmosphere.

	dT/dP (°C/bar)	ΔV (cm³/mole)	ΔS (eu)
Ca fusion	~17	~1.25	1.75[a]
fcc-bcc	3.3	~0.01	~0.08[a]
Sr fusion	~20	~2.0	~2.3 [a]
fcc-bcc	−10	~0.1	~0.23[a]

[a] See Ref. 22.

Strontium

Bridgman,[2] working with material of unknown purity, found a sluggish transition by volume measurements in the 20–40 kbar range. The transition was described as being "difficult to start," commencing at ~37 kbar at 25°C and slightly lower pressures at 75 and 125°C; upon release of pressure, the reverse transition ran rapidly at about 18 kbar for these three temperatures. Resistivity measurements[8] up to 30 000 kg/cm² showed that the resistance rapidly increased with pressure. Experiments[10] at higher pressures revealed that the resistance reached a maximum in the vicinity of 45 kbar, followed by a pronounced drop. No discontinuity in resistance was evident near 64 kbar where a volume

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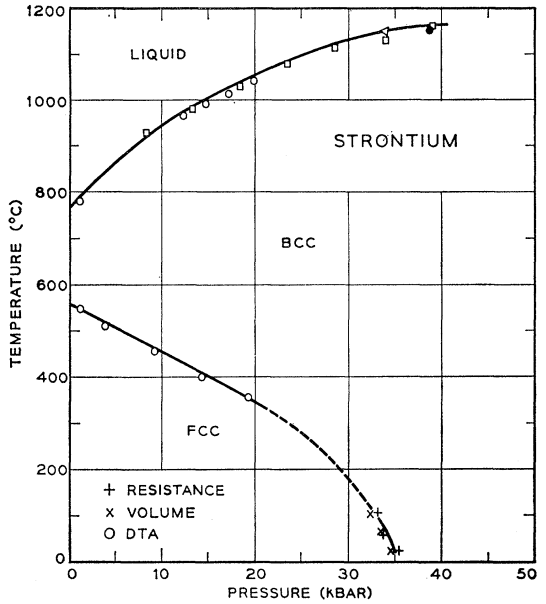

FIG. 2. Phase diagram of strontium. For the fcc-bcc boundary DTA points on heating and resistance and volume discontinuities on increasing pressures are plotted.

discontinuity[9] of 0.8% ($\Delta V/V_0$) had been detected. Bridgman[10] concluded that no discontinuity in resistance was observable corresponding to those observed by volume.

The strontium used in the present experiments was vacuum distilled stock of the highest purity.[23] Melting experiments were carried out in tantalum containers and all encapsulation was done inside an argon-filled dry box. In runs where BN stoppers were used for the containers, a progressive lowering of the melting points was obvious from repeated measurements. In an experiment with a tantalum container and stopper, such lowering was not evident. The fusion data for Sr are presented in Fig. 2. The results obtained on two runs in Ta containers where the samples were compressed directly to 34 and 39 kbar and then melted, to avoid progressive contamination, are in agreement with the fusion data obtained with all Ta containers. The connection of the Sr fusion curve to the normal melting point[3] of 768°C is satisfactory and an initial melting slope of $\sim$20°C/kbar is suggested (Fig. 2). The volume change accompanying fusion is estimated to be 2.0 cm^3/mole from the slope and the published value[22] of 2.3 eu for the entropy change on melting.

The thermal arrests associated with the fcc-bcc transition were quite feeble. In an attempt to obtain better DTA signals, the thermocouple was located in a hole drilled midway into a sample 0.22 in. in diameter and 0.40 in. long, encapsulated in iron. With the thermocouple in direct contact with the sample, the thermal arrest signals were much enhanced and consequently the transition temperatures were located with greater precision. In Fig. 2 the transition temperatures obtained upon heating are plotted. The fcc-bcc transition decreases rapidly in temperature with pressure with a slope of -10°C/kbar. For this slope and $\Delta S \approx 0.23$ eu,[22] the volume change is very nearly 0.1 cm^3/mole. In Table I the relevant thermodynamic data are given. A temperature hysteresis for this transition was noted, especially at higher pressure, but no precise measurement was made. The thermal arrests became progressively weaker with increasing pressure, similar to calcium, and could not be detected above 20 kbar.

Compression runs at room temperature (25°C) with a sample 0.5 in. in diameter and 1.5 in. long indicated a solid-solid transition at about 35 kbar on increasing pressure and at about 18 kbar on decreasing pressure in accord with Bridgman's[2] findings. The forward transition is spread over a range of about 5 kbar, while the reverse transition on release of pressure is much sharper. Other compression runs were made at 65 and 104°C in an externally heated pressure plate[15]; the transition pressures obtained on increasing pressure are plotted in Fig. 2. The transition pressure decreases slightly with temperature and the transition itself becomes slightly more distinct, although the hysteresis interval is practically independent of temperature. The volume change is estimated to be about 1%, as compared with the 0.9% decrement reported by Bridgman.[2]

Resistance measurements on extruded wires of Sr were carried out using internally and externally heated arrangements previously described.[14,17] However, in the present scheme for internally heated resistance measurements, the resistance circuit was completely isolated from the ac heater circuit. A Sr wire about $\frac{1}{2}$ in. in length and 10 mil diam enclosed in a polyethylene tube was located at the end of a four-hole thermocouple ceramic, and electrical connection was through two copper leads coming out of the ceramic and entering

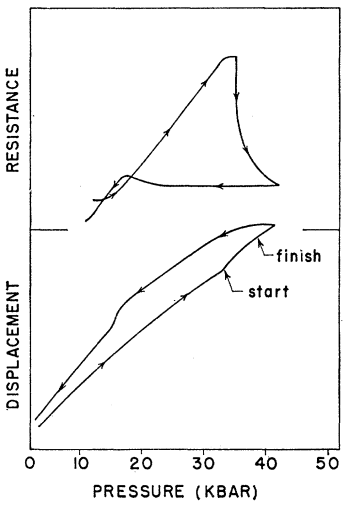

FIG. 3. Upper curve is resistance in arbitrary units versus pressure and the lower one is piston displacement versus pressure.

[23] Primary impurities (in ppm): 1000 each of Ba and Ca, 500 Mg, 350 H, etc.

the polyethylene tube. Thermocouple wires were brought through the other two holes of the ceramic and the sample temperature was read by a chromel-alumel junction. The polyethylene tube containing the Sr wire was surrounded by AgCl which served as the pressure transmitting medium and the assembly consisted of the usual graphite heater and talc sleeve. The heater current circuit through the lower piston and the insulated top plate was thus completely isolated from the sample.

The plot of relative resistance versus pressure recorded at 25° is shown in Fig. 3, where the compression curve obtained at 65°C is also displayed. The resistance of Sr increases with pressure up to about 36 kbar and then begins to drop sharply, almost at the pressure where the discontinuity in volume is initially detected. The sluggishness of the transition is further demonstrated by the slow decrease in resistance upon maintaining constant pressure; increasing the pressure slightly causes the resistance to decrease more rapidly. The transition pressure decreases slightly with temperature, as plotted in Fig. 2. The commencement of the resistance decrease with increasing pressure has been taken as the pressure of transition. Upon release of pressure, the resistance increases only slightly and the reverse transition, occurring at about 18 kbar, is marked by a hump which has approximately the shape of the curve obtained on increasing pressure, but is only about one fifth as large, a fact also noted by Bridgman.[10] This is to be expected since the reverse transition takes place nearly 20 kbar below the pressure at which the forward transition runs, and much of the steep rise in resistance for the fcc polymorph lies in this higher pressure interval. What is seen on release of pressure is the resistance of the high pressure phase—until the hump appears which marks the reverse transition (Fig. 3).

The fcc-bcc transition was also followed by the resistance technique; the advantage of larger and better signals accompanying the transition have in these experiments brought out several features. The transformation temperatures on heating and cooling do not coincide; this hysteresis interval is also dependent on pressure. Below 12 kbar, there is little hysteresis; at 17 kbar, there is about 15°C, and at 19.5 kbar, about 25°C hysteresis. At pressures greater than 15 kbar the resistance signal associated with the fcc-bcc transformation progressively becomes weaker and is spread over a temperature range. Above 21 kbar the transformation is characterized by a break in resistance only and on cooling no signal whatever appears, suggesting thereby that the hysteresis interval becomes very large and consequently the high-temperature phase remains quenched at room temperature. Reversion to fcc could be accomplished only by releasing pressure below 18 kbar.

The boundary, delineated in the range 25 to 130°C from volume and resistance measurement, exhibits a slope of about -50°C/kbar, and further the resistance discontinuity is a sharp decrease. These facts suggested that this might represent a different phase boundary and that a third form of Sr was involved. However, neither differential thermal analysis nor resistivity measurements gave any definite and reproducible signals for the existence of a third phase boundary, at pressures above 36 kbar and temperatures up to about 400°C. Recent high pressure x-ray investigations by McWhan and Jayaraman[24] have shown that the x-ray pattern of Sr obtained at pressures above 35 kbar and room temperature can be accounted for on the basis of a bcc structure with a lattice constant close to 4.47 Å. Comparing this with the lattice constant of 4.84 Å (at 600°C) for bcc Sr, it seems appropriate to regard the two bcc phases as the same. Accordingly, the phase boundary shown in Fig. 2 is between fcc and bcc Sr. Transition temperatures from thermal arrests on heating, and transition pressures on increasing pressure are plotted in the phase diagram. It should be noted that the phase boundary exhibits a steep slope at the higher pressures. The volume change through the transition at 35 kbar and room temperature is ~ 0.3 cm^3/mole which is significantly higher than the 0.1 cm^3/mole calculated from the initial slope and entropy change for the fcc-bcc transformation at 557°C. Also from the slope of ~ -50°C/kbar and $\Delta V \approx 0.3$ cm^3/mole, the entropy change for the transition near 35 kbar is $\Delta S \approx 0.14$ eu as compared to 0.23 eu for the normal fcc-bcc transformation. The strong curvature of the phase line is to be attributed to the greater compressibility of the bcc phase.

The reversal in sign of the resistance discontinuity accompanying the fcc-bcc transformation in going from lower to the higher pressures is due to the difference in the pressure coefficient of resistance for the two phases. While at the lower pressures the bcc phase has a higher resistance than fcc, the large pressure coefficient of resistance of the latter raises its resistance above that of bcc and, consequently, the fcc-bcc transition at the higher pressures is marked by a sharp decrease in resistance.

The temperature coefficients of resistance were estimated near 30 kbar, where the resistance is close to maximum, and near 43 kbar beyond the precipitous drop in resistance and in the stability field of the high pressure polymorph. At 30 kbar, the resistance decreases 5% over the interval, 25–90°C,—a *negative* temperature coefficient, while at 43 kbar, there is an approximately 10% increase from 50–104°C. These estimates do not allow for contact resistance, which cannot be readily disentangled from sample resistance.

DISCUSSION

The initial melting slopes for the bcc polymorphs of the alkali metals increase in the sequence[11]—Li, Na, K, Rb, Cs. The curvatures in the fusion curves[11] also in-

[24] D. B. McWhan and A. Jayaraman (to be published).

crease in this sequence, although the normal melting points increase in exactly the opposite order. The normal melting points of the alkaline earth bcc polymorphs decrease monotonically with increasing atomic number—as for the alkalis, but further analogous sequences are not readily obvious at present. Indeed, the melting behavior of calcium and strontium appear to be quite similar (Figs. 1 and 2) but distinct from barium.[1] One is thus rather uncertain as to whether maxima occur in the fusion curves for Ca and Sr akin to the extremum discovered[1] for Ba. If such maxima, indeed, do occur, that for Sr may be expected at lower pressures than Ca, since the curvature in its fusion curve is somewhat greater than for Ca (Figs. 1 and 2).

The present experiments have clearly established that the pronounced increase in resistance with increasing pressure for strontium is characteristic of the fcc phase and the observed drop in resistance is due to a polymorphic transition. The resistance drop and the volume discontinuity occur at the same pressure, and there is no anomalous situation of a resistance discontinuity not corresponding to the volume discontinuity as concluded by Bridgman.[10] When Bridgman's transition pressure of 44 kbar for the resistance drop is corrected in accordance with the revised pressure scale, the volume discontinuity and resistance discontinuity would appear at about the same pressure. It has also been shown that a negative temperature coefficient of resistance, similar to that characteristic of an intrinsic semiconductor, occurs in the fcc phase, prior to the polymorphic transition. Such a behavior has been reported for ytterbium[25] and also recently for calcium.[20]

Mott[26] proposed, for the large pressure coefficient of resistance observed in Ca and Sr, that a decrease in the overlap of the Brillouin zones occurs due to pressure, resulting in a decrease in conductivity. However, Manning and Krutter[27] claimed that this mechanism cannot be operative in Ca and attributed the increase in resistance to increased scattering of electrons by vacant d states, arising from an increasing overlap with pressure. The results of present study on the temperature coefficient of resistance of Sr and Stager and Drickamer's[20] observation for Ca seem to indicate that these elements show the characteristics of a semiconductor with a small energy gap over a certain pressure range. The experimental data do not seem to support the mechanism proposed by Manning and Krutter,[27] because increasing temperature would result in enhanced scattering and therefore a positive coefficient for resistance, contrary to the observations.

The occurrence of hcp phases in very slightly impure Ca and Sr suggests that the energy difference between fcc and hcp is small. The occurrence of an hcp phase may possibly be expected in the higher pressure range. However, Stager and Drickamer[20] do not report any resistance discontinuity in Sr, in work up to estimated 500 kbar.

There is a very close parallelism between ytterbium and strontium in their high pressure behavior. Yb exhibits a sluggish phase transition[28] around 47 kbar on increasing pressure and shows a big hysteresis interval; the reverse transition runs at 20–25 kbar. The resistance of fcc Yb rises rapidly with pressure and, indeed, the resistance versus pressure curve is quite similar to that for Sr; before the phase transition, both show a negative temperature coefficient of resistance.[25] An hexagonal close-packed phase has also been reported[29] for Yb and is believed to be due to very slight impurities. Hall *et al.*[31] from high-pressure x-ray investigations found that the high-pressure phase of Yb is bcc. The analogy that exists between Sr and Yb suggested that the 36 kbar transition in Sr might be to a bcc structure. Recent high-pressure x-ray investigation shows this to be true. Hall *et al.* have suggested that the phase transition in Yb involves the promotion of a $4f$ electron to the $5d$ state. However, both in Sr and Yb the radii of respective atoms in the fcc and bcc structures could be accounted for when corrected for the change of coordination number. Therefore, it does not appear necessary to bring in electronic promotion in the case of either Sr or Yb.

The present techniques are insufficient to reliably attempt to verify the volume discontinuities of 1% reported[9] near 65 kbar by Bridgman for both Ca and Sr. No corresponding discontinuities in resistance were reported[10] and this should allow some skepticism as to whether these transitions occur in high-purity material.

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