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Experimental equations of state for calcium, strontium, and barium metals to 20 kbar from 4 to 295 K

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Piston-displacement measurements have been used to determine the equations of state of high-purity calcium and strontium (both fcc) and barium (bcc) metals to 20 kbar from 4 to 295 K. For each metal, the results have roughly 1% accuracy for the $P=0$ bulk modulus at 295 K and for the total volume change with pressure. The results also give the change with temperature of both the $P=0$ volume and the isothermal bulk modulus for these metals. While the bulk moduli for calcium and strontium are dependent only on the volume, those for barium show a significant temperature dependence with decreasing volume. Specifically, the bulk modulus for barium at 10 kbar is roughly 3% smaller at 295 K than would be predicted from the 0-K value at the same volume. Differences between the pressure-volume relations for bare samples and for those which were jacketed with indium metal are not understood.

I. INTRODUCTION

The experimental thermodynamic properties of the alkaline-earth metals, calcium, strontium, and barium, have not been studied in any detail, even though they are theoretically interesting two-electron systems which are ameanable to first-principles calculations.[1,2] Calcium and strontium under normal conditions (near room temperature and $P=0$) have a fcc structure which transforms into the bcc structure at higher temperatures before melting. Barium, on the other hand, retains the bcc structure at moderate pressures from melting to, presumably, 0 K. The high-temperature–high-pressure phase diagrams of calcium and strontium[3] (which trace the fcc-bcc transition and the melting line) and of barium[4] have been determined, with barium showing a transition from the normal bcc phase to a hcp phase at room temperature and 55 kbar. This transition moves towards lower pressures as the temperature is lowered. Bridgman[5] has described an additional sluggish phase transition in calcium at 25–35 kbar (2.5–3.5 GPa), and, along with Voronov and Stal'gorova,[6] has reported a 17-kbar transition in barium which moves to lower pressures as the temperature is increased. Olijnyk and Holzapfel[7] report room-temperature x-ray diamond-anvil-cell (DAC) results to 46 GPa (460 kbar) for alkaline-earth metals. These show a fcc-to-bcc transition in calcium at 19.5 GPa, the 3.5-GPa as well as higher-pressure transitions in strontium, and the 5.5-GPa and higher-pressure transitions in barium. The strontium and barium transitions, but not that for calcium, are apparent in shock-wave data.[8] The existence of these transitions has not been confirmed by other studies.[3,4,9]

Moriarty[1] has shown in a first-principles calculation that the normal bcc structure of barium metal differs from the normal fcc structure of calcium and strontium because of the importance for barium of three-ion effects and transition-metal behavior which is related to d-band contributions. Chen *et al.*[2] also have used a first-principles calculation to study the bcc-hcp transition in barium, which they show is caused by a softening of the lowest TA mode as the pressure is increased. They predict that although this transition should occur at roughly 11 kbar at low temperatures, an energy barrier will cause the bcc phase to be metastable until at least 30 kbar. These theoretical studies were triggered to a great extent by data from neutron-scattering, lattice-dynamics experiments for single-crystal[10] and polycrystalline fcc calcium,[11] polycrystalline fcc strontium and bcc barium,[12] and single-crystal bcc strontium[13] and bcc barium.[14] The lattice-dynamics calculations give good agreement with the phonon spectra from these experiments, and also have the potential to give elastic constants and pressure-volume relations at $T=0$ K.

Outside of the shear constants which follow from the lattice-dynamics representations, early room-temperature, linear-compression data by Bridgman,[15–17] and piston-displacement results to 45 kbar by Bridgman[5] and by Vaidya and Kennedy,[9] the only elastic data, either single crystal or polycrystalline, available for any of these three metals are those of Voronov and Stal'gorova[6] (VS) for barium. The only analysis of shock-wave data which has been reported is that for calcium.[18] White[19] has reported 280-K, 80-K, and low-temperature expansivities and Roberts[20] low-temperature heat capacities for calcium, strontium, and barium metals of commercial purity. Other low-temperature heat-capacity data for better-documented calcium metal exist,[21,22] although the internal agreement is not satisfying. Dzhavadov[23] has measured the pressure dependence to 25 kbar (2.5 GPa) of the isentropic expansion coefficient for strontium at temperatures through the fcc-bcc transition, and also gives expansivities for strontium at these temperatures.

The reasons for the scarcity of data for these three metals are at least twofold. First, they have been difficult to obtain in high purity, and are difficult to work with because of rapid oxidation when exposed to air. Even good-quality metals tend to contain relatively large amounts of hydrogen as a major impurity. Second, the transition from the bcc to the fcc phase when either calcium or strontium is cooled from the melt makes the growth of single crystals very difficult. The lattice-dynamics experiments of Stassis *et al.*[10] are unique in that they involved single crystals of calcium which were grown by careful cycling of the sample through the transition at 720 K. Even though no transition occurs for barium metal upon cooling from the melt, the only single-crystal data appear to be those from the lattice-dynamics study of Mizuki *et al.*[14] Of the samples used in the experiments cited above, those of Bridgman[5] appear to be the least well characterized.

The objective of the present experiments was to obtain piston-displacement data for high-purity, well-degassed calcium, strontium, and barium metals to establish their equations of state from room temperature to 4 K at pressures to 20 kbar. Similar experiments for the alkali metals[24,25] gave relative volume expansions and bulk moduli at $P=0$ which are in good agreement with other, more direct measurements. The room-temperature portions of these experiments also were intended to confirm or supercede earlier pressure-volume measurements on these metals, and possibly to determine whether or not the relatively minor transitions observed by Bridgman[5] and Voronov and Stal'gorova[6] were associated with impurities.

II. EXPERIMENTAL DETAILS AND ANALYSIS

A. High-pressure system

The apparatus and procedures used for these piston-displacement experiments have been described in detail elsewhere.[26] Very briefly, the sample is placed in a cylinder, the ends of which are closed by tightly fitting pistons. Force is applied to the pistons by a 10-ton hydraulic press and the relative motion of the pistons (the change in length of the sample) is measured as a function of the force applied by the press. The press has long compression and tension members so that its base may be held at any temperature from 4 K to above room temperature using liquid helium, liquid nitrogen, or a heater. Sample holders of two diameters are used. The smaller, "high-pressure," sample holder has a 6.35-mm (0.250-in.) -diam bore, and can be used to nominal sample pressures of roughly 22 kbar, while the second, "low-pressure," sample holder has twice the area, and can be used to roughly 13 kbar. The maximum pressure limit is determined by the lifetime of the piston-cylinder combination, since a given sample may be cycled to maximum pressure as many as 40 times at temperatures from 300 to 4 K in the course of an experiment. Each sample holder is carefully calibrated as a function of temperature and pressure in terms of a "known" equation of state for indium,[26] so a failure results in considerable loss of data.

Data are taken isothermally in the form of piston motion with increasing and then decreasing stress to compensate for friction effects in the sample.[26] The maximum width of the hysteresis loop for indium-jacketed samples (it is only slightly greater for the unjacketed samples) varies from roughly 1.5 kbar at room temperature to 3 kbar at low temperatures, roughly independent of sample length and material. The basic assumption in these experiments is that the shear-yield stress of the sample is small compared with the applied stress, since the sample diameter remains constant while the length may change by as much as 12%. Much sample flow and shear are involved in the compression. The low-shear-yield-stress condition definitely was met for the heavier alkali metals,[24,25] and we hoped that it also would be met for these alkaline-earth metals. The first series of data (two sample holders, all temperatures) for all three metals suggested that this might not be the case, so a second series of data was taken with the samples jacketed on all sides by a minimum of 0.5 mm of pure indium metal to provide a pseudohydrostatic medium.[26]

Every effort is made to ensure that the piston-motion measuring system remains stable as the sample-holder stress and the temperature are varied. Data were taken systematically at 295, 200, 115, 80, 155, 250, and 295 K, and then at 80, 45, 20, 4.2, 60, and 80 K to verify the internal consistency of the data. Small shifts in the measuring system could be detected with this procedure, and corrections made. Other experiments and the calibration runs suggest that the sensitivity and reproducibility of the measuring system is appreciably better than 1.5 μm. This leads to the expectation that for the (3–6)-mm-effective-length samples used in these experiments, significant relative volume changes, $\delta(V/V_0)$, will range from ±0.0005 to ±0.0003. The "raw" data are graphically smoothed in correcting for relatively large friction effects (see above), after which a smooth "press correction" (which can be less than 25% or as much as 50% of the observed piston motion, depending on the sample material and sample length) is applied.[26] As a result, the concept of "raw data" has no meaning. The crucial verification of the validity of the procedures which are used[26] is given by the agreement between independent data which are taken for each material for a minimum of two sample holders of different size in order to detect systematic errors. The overall agreement between these independent data sets generally is within the above estimates of accuracy. For samples such as calcium, strontium and barium, this implies that total compressions $(1-V/V_0)$ should be accurate to better than 1% from 2 to 20 kbar.

The experimental P-V relations for each metal were quantitatively different for the experiments with unjacketed and with indium-jacketed samples (see below). The total compressions for calcium and barium were smaller for the jacketed than for the unjacketed samples, with only a small effect on the shapes of the isotherms, while the differences appear primarily in the shapes of the strontium isotherms. Since data for each configuration (unjacketed, indium-jacketed) were in agreement for the different-diameter sample holders for each metal, these differences, which are well outside our experimental accuracy, appear to be related to the existence of the indium jacket, and are not understood. They could be associated with a lack of hydrostatic pressure in the sample (most likely to be true for calcium) and with the greater shear which must occur in the unjacketed samples, and/or to problems in our corrections for friction effects. There is no evidence from these data that hydrogen impurities (up to 4 at. %) had a significant effect on the results, although two experiments with inadvertently oxidized strontium samples gave compressions which were too small.

The results obtained with the indium-jacketed samples have been assumed to be correct, since the system was calibrated with indium samples, and other experiments with indium-jacketed samples have given consistent results.[26] The relatively small pressure differences between the isotherms at constant volume for a given sample, which determine the temperature-dependent thermodynamic properties, are the same for the jacketed and unjacketed samples, as well as for the pure and slightly contaminated samples.

A room-temperature density was determined for each sample from measurements of the mass of the cylinder-sample combination, the piston separation, and the masses and known densities of the other parts of the sample assembly. The precision was estimated to be ±0.2%, but systematic differences were found between the unjacketed and jacketed samples (unjacketed always larger) which were several times greater than this. The source of this discrepancy is not known.

B. Samples

A discussion of the preparation of high-purity calcium, strontium, and barium metals similar to those we used is given elsewhere.[27] The total metallic impurity content of each of the starting metals was as follows: calcium, 0.02 at. %; strontium, 0.03 at. %; barium, 0.16 at. %. The oxygen, nitrogen, and carbon contents are very difficult to determine accurately, but the sums of these elements are as follows: calcium, 0.05 at. %; strontium, 0.21 at. %; barium, 0.25 at. %.

The initial sample material was sealed into a tantalum capsule and was heated for several days under high vacuum at 900 °C to remove interstitial hydrogen. The tantalum capsule acts as a semipermeable membrane and retains the alkaline-earth metal while allowing hydrogen to pass through almost without resistance. Hydrogen evolves quite rapidly at the start of the heating, but the hydrogen pressure, which is proportional to the square of the concentration, decreases dramatically with time; a very large decrease in the rate of hydrogen evolution signals a relatively modest decrease in concentration. In one isothermal degassing run, the hydrogen-evolution rate decreased by a factor of 3000, indicating a ratio of initial to final hydrogen concentration of 55; a (reasonable) initial hydrogen content of 7 at. % would have been reduced to 0.13 at. %. The extremely reactive nature of all three metals makes handling them without significant contamination by hydrogen almost impossible. Water vapor permeates though the dry-box gloves and reacts with these metals to increase hydrogen concentration during the entire time of exposure in the glove box. The best estimates for ultimate hydrogen concentrations in these metals, based on likely initial concentrations and degassing rates, are the following: calcium, 0.02 at. %; strontium, 0.14 at. %; barium, 0.14 at. %.

The tantalum jacket was removed in a helium-filled dry box after degassing and cooling to room temperature, and the degassed material was fabricated into short cylinders which were either placed directly into the sample holder or were wrapped with indium before being placed in the sample holder. Typical hydrogen contents which were determined by vacuum fusion for small portions of the sample material probably overestimated the concentrations due to contamination in handling the small analysis samples. No analyses were obtained for the calcium samples, which, as the above discussion suggests, are most likely to have low hydrogen concentrations. The strontium samples had hydrogen concentrations of less than 2 at. %. The maximum hydrogen concentration for the original unjacketed barium samples was 4 at. %, while for the indium-jacketed and final unjacketed barium samples it was less than 1 at. %. The 295-K results for the original unjacketed (4 at. % hydrogen) barium samples and for the final low-concentration hydrogen sample were identical, which suggests a negligible effect of hydrogen content (up to 4 at. %) on the compressions.

The indium-jacketed barium experiments were complicated by what was postulated to be a "chemical reaction" between the barium and the indium jacket, although this has not been verified by chemical analysis. The effects were small, and appeared as a systematic measuring system shift after several cycles of the sample to full pressure. This first was observed with the low-pressure sample holder and only at 295 K, so the high-pressure jacketed sample was not compressed at temperatures above 250 K until a final 295-K run was made. Vaidya and Kennedy,[9] who took room-temperature data on indium-jacketed barium samples to 45 kbar, do not report seeing this effect. We did not observe it for the indium-jacketed calcium or strontium samples. The ratio of the atomic radius of barium to that of indium is sufficiently large that indium might well be a "fast-diffusing" solute in barium and have appreciable mobility at 295 K.

C. Analysis, thermodynamics

The temperature-dependent equation of state of a solid can be expressed conveniently as the sum of the pressures along a reference isotherm (295 K in these experiments), P_R, and a thermal pressure, P^*,[24,28]

$$P(V/V_0,T)=P_R(V/V_0,T_R)+P^*(V/V_0,T)\ . \tag{1}$$

The major contribution to the right-hand side of Eq. (1) is given by the reference isotherm (the 295-K isotherm for each metal in Fig. 1), with P^* (the horizontal separation in Fig. 1) typically only a few kbar. In the following, a reference isotherm was established for each sample of each material, after which the thermal contributions were characterized by P^* as

$$P^*(V/V_0,T)=P(V/V_0,T)-P_R(V/V_0,295\text{ K})\ . \tag{1a}$$

While P_R for a given metal may be slightly (but significantly) sample dependent, P^*, which is defined in terms of differences between isotherm data *for a given sample,* is the same for all samples of that metal to the accuracy with which it can be determined (a few percent). For most solids, a useful first approximation is to assume that P^* depends only on the temperature.[24-26] This is equivalent to postulating that the bulk modulus is a function only of volume, with no temperature dependence.

Piston-displacement data give volume (sample length) changes as a function of pressure $[\Delta V(P)]$ over a range of pressures which (because of friction effects) does not extend to $P=0$. The $P=0$ volume (length) of the sample (V_0) is known, so the volume change from the lowest-pressure data points to $P=0$ (ΔV_{ext}) must be determined to obtain the volume change with pressure, $V(P)=(\Delta V_{\text{ext}}+\Delta V(P)$. This can be accomplished by using a physically reasonable relationship to represent $V(P)$, and then to vary ΔV_{ext} until the best fit is obtained. In the past, we have used the Murnaghan and related equations, which are based on a series expansion of the bulk modulus as a function of pressure.[24,25] The barium data clearly required the use of second-order terms in this equation (three parameters), yet the scatter of the data prevented convergence of the nonlinear least-squares-fitting program which was used. An alternative is to use the more complex two-parameter relation proposed by Vinet *et al.*,[29,30]

$$P(V)=B_0[3(1-x)/x^2]\exp[\eta(1-x)] , \tag{2}$$

where B_0 is the $P=0$ bulk modulus, $x=(V/V_0)^{1/3}$, and $\eta=3(B_0'-1)/2$, with $B_0'=(\partial B_T/\partial P)_{T,P=0}$. The volume dependence of the bulk modulus for Eq. (2) is given by

$$\begin{aligned} B_T &= -(\partial P/\partial \ln V)_T \\ &=(B_0/x^2)[2+(\eta-1)x-\eta x^2]\exp[\eta(1-x)] . \end{aligned} \tag{3}$$

Equations (2) and (3) are equivalent to the first- and second-order Murnaghan (ME-1, ME-2) relations at moderate compressions (such as those for barium to 20 kbar), and have the advantage that they give reasonable (finite) extrapolations in the very-high-pressure limit. Vinet *et al.*[29,30] demonstrate that the fitting of experimental data (P_i and x_i) to Eq. (2) can be accomplished most readily by using a logarithmic representation,

$$\ln[x_i^2 P_i/3(1-x_i)]=\ln(B_0)+\eta(1-x_i) , \tag{4}$$

after which linear-regression techniques will give B_0 and η. This procedure effectively minimizes

$$\sum_i \{[P_i-P_{\text{calc}}(x_i)]/P\}^2 ,$$

and hence is very sensitive to data in the low-pressure region. We have preferred to select the optimum extrapolation, ΔV_{ext}, by minimizing the standard deviation of the volume,

$$N[\text{STD}(V)]^2=\sum_{i=1}^{N} \{V_i[P_i-P_{\text{calc}}(x_i)]/B_T(x_i)\}^2 , \tag{5}$$

where N is the number of data points. This requires iterative or nonlinear least-squares procedures which, by the sharpness of the standard-deviation–versus–ΔV_{ext} relation, also can give the nonuniqueness of B_0 and η (and B_0'). In the following, we will be consistent in applying the same procedure to both our data and other published results,[5,9] where the method used to extrapolate the lowest data to $P=0$ is not specified, and apparent inconsistencies exist.

The calculation of related temperature-dependent thermodynamic quantities follows from the experimental values of P^* [Eq. (1a)]. The volume expansion at constant pressure (for $P=0$, the normal volume expansion) is given by Eq. (1a) with $P=$const. These volumes then can be used in Eq. (3) to obtain the temperature dependence of the bulk modulus. The volume thermal expansivity, $\beta=(\partial \ln V/\partial T)_P$, can be calculated using a standard thermodynamic relation,

$$(\partial P/\partial T)_V=(\partial P^*/\partial T)_V=\beta B_T . \tag{6}$$

Since B_T depends primarily on the volume, this suggests that the temperature dependence of $(\partial P^*/\partial T)_V$ will resemble that of the thermal expansivity, and will be relatively constant at high temperature and approach zero at $T=0$.

The lattice (vibrational) contribution to P^* is expected to dominate at high temperatures ($T>\Theta$, the Debye temperature). The Grüneisen model then can be used to write Eq. (6) as[28]

$$(\partial P/\partial T)_V=(\partial P^*/\partial T)_V=\beta B_T=(\gamma/V)C_V=(\gamma/V)3R . \tag{7}$$

Here, γ is the Grüneisen parameter, R the gas constant, and $3R$ the classical value of C_V. In this limit, P^* is expected to be linear in T for a classical solid, with a temperature dependence which is proportional to the Grüneisen parameter. These considerations can be used to rationalize[28] the experimental observation that, for most solids, P^* is independent of volume and B_T is a function of volume only.

III. RESULTS

A. General

The results of these experiments are summarized in Table I, where the relevant parameters for Eqs. (1) and (2) are given for 295 and 0 K, and in Figs. 1–4. Figure 1 and the bottom part of Table I give the pressure-volume relations for calcium, strontium, and barium for these temperatures, and illustrate the relatively small magnitudes of the thermal contributions. The 0-K curves for calcium and strontium (both fcc) are identical in shape with their 295-K relations, but are shifted to the left by an amount equal to a constant (volume-independent) thermal pressure, P^*, in agreement with our first-order postulate. This is not true for barium (bcc), for which the magnitude of P^* decreases by 30% from $P=0$ to 20 kbar.

Figure 2 summarizes the temperature dependence of P^* for the three metals. P^* is volume independent for calcium and strontium, while the low-pressure values are

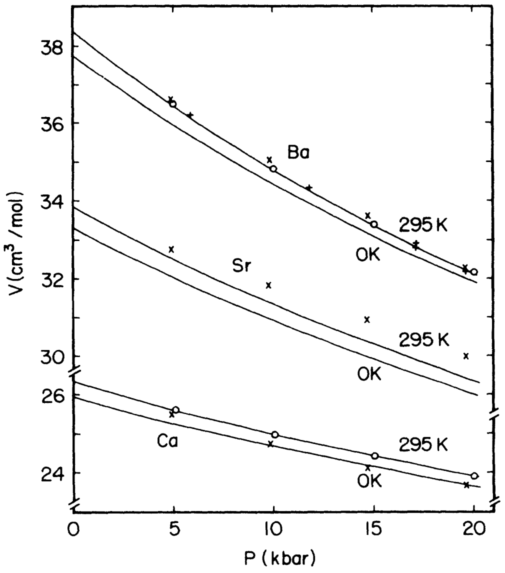

FIG. 1. Smooth pressure-volume relations for calcium, strontium, and barium metals for 295 and 0 K. See Table I. The data points are from Refs. 5 (×), 6 (+), and 9 (○).

plotted for barium; a more detailed discussion will be given in the following sections. In each case, the linear temperature dependence [see Eq. (7)] extends well below $T=\Theta_0$ and, for barium, extends to 4 K. The expressions for the linear regions are

$$P^*=-3.33(3)+0.0112(1)T[\mathrm{K}]\ \text{kbar}\quad(\text{for Ca})\ , \tag{8a}$$

$$P^*=-2.12(9)+0.0072(3)T[\mathrm{K}]\ \text{kbar}\quad(\text{for Sr})\ , \tag{8b}$$

$$P^*=-1.42(1)+0.00483(4)T[\mathrm{K}]\ \text{kbar}\quad(\text{for Ba})\ , \tag{8c}$$

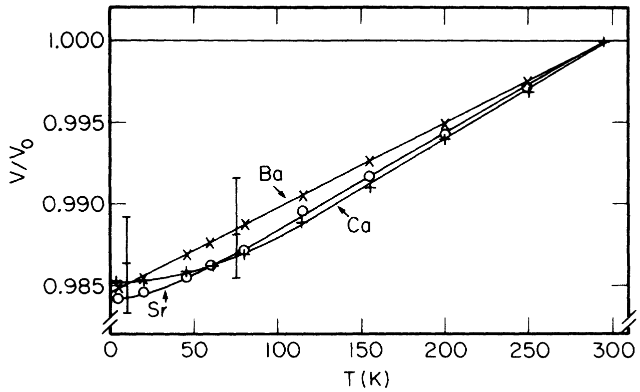

FIG. 3. Temperature dependence of the $P=0$ relative volumes as calculated from the P^*'s in Fig. 2, Eq. (1a), and the data in Table I. The two data points with large error bars are from Ref. 35. See text for details.

In these equations and elsewhere in this paper, the numbers in parentheses represent the uncertainty in the last digit shown.

The actual data were used with Eqs. (1a) and (2) to calculate the $P=0$ volume thermal expansions in Fig. 3, which, in turn, were used with Eq. (3) to calculate the temperature dependence of the $P=0$ isothermal bulk modulus in Fig. 4. In view of the very different reference isotherms for the three metals, the similarities in the expansion relations in Fig. 3 must be fortuitous. In comparable experiments with potassium metal,[24] the volume expansion which was obtained could be compared with a directly determined expansivity. The agreement was better than 0.001 in V/V_0 at all temperatures; a similar accuracy should be expected for the present results.

The measured densities (d_{expt}) in Table I, which are

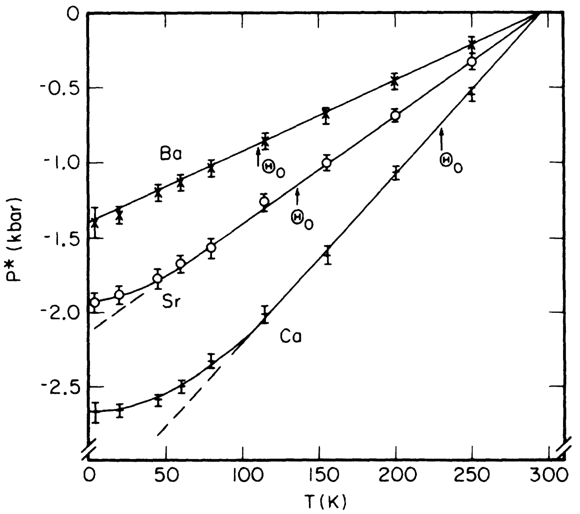

FIG. 2. Temperature dependence of the thermal pressure, P^*, for calcium, strontium, and barium metals [Eq. (1a)]. These are pressure-independent average values for calcium and strontium, and low-pressure values for barium. The straight lines are given by Eqs. (8a)–(8c).

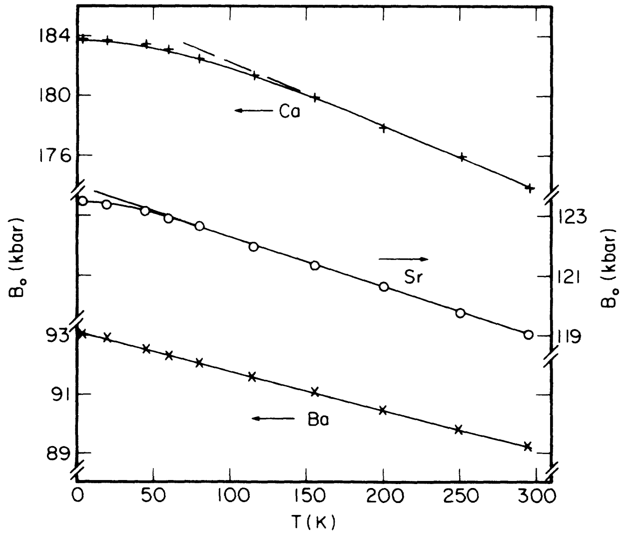

FIG. 4. Temperature dependences of the $P=0$ isothermal bulk moduli as calculated from the results in Fig. 3, Eq. (3), and the data in Table I. The scale for the Ca results is one-half as sensitive as that for the Sr and Ba results.

averages over at least four samples, appear to be in reasonable agreement with the x-ray lattice-parameter values (d_x). For both strontium and barium, however, densities from the unjacketed samples were systematically greater than those from the indium-jacketed samples. These differences, which are within the uncertainties given in Table I, nevertheless are 2 or 3 times greater than our estimated experimental precision, and are not understood.

The values of B_0 and B'_0 for each metal in Table I are from an analysis of the data for the indium-jacketed samples which used Eqs. (4) and (5). The uncertainties (in parentheses) are for the nonuniqueness of this analysis; if a *positive* uncertainty is taken for B_0, a *negative* uncertainty should be taken for B'_0. In addition, there is, we believe, an overall uncertainty of roughly ±1% in the volume changes $(1-V/V_0)$ which are calculated from these parameters. The data for the different-sized, indium-jacketed sample holders for calcium and barium agreed well within these limits; unfortunately, the only indium-jacketed data for strontium were to 20 kbar for the smaller-diameter sample holder.

Figure 1 contains actual data from the papers of Bridgman,[5] of Voronov and Stal'gorova,[6] and of Vaidya and Kennedy (VK),[9] while Table II gives a comparison of the room-temperature parameters B_0 and B'_0 for the present experiment (for jacketed and unjacketed samples, see Sec. II A) and other published results. A major difficulty in these comparisons is that none of the previous papers has documented the methods used for extrapolating the results from the lowest experimental data point (nominally 5 kbar) and $P=0$. In Bridgman's early work,[16,17] length changes to 12 kbar were determined directly, and did not suffer from the need for friction corrections which occurs in his later work[5] and that of VK.[9] Bridgman's 1923 data for calcium and strontium[16] agree well with our results, as do his later results for barium.[5] His corresponding results for calcium and strontium[5] (see Fig. 1) do not appear to be reasonable. The results of VK (Ref. 9) for calcium and barium (they did not report data for strontium), and of Voronov and Stal'gorova[6] for barium, can be made to agree almost exactly with the present smooth relations if the extrapolations of these data from the lowest data points to $P=0$ are increased in magnitude (see Table II).

TABLE I. Thermodynamic parameters and P-V relations for calcium, strontium, and barium at 295 and 0 K. The P-V relations (see Fig. 1) were calculated from Eqs. (1) and (2) using the parameters listed. See text for details.

	Calcium		Strontium		Barium	
	295 K	0 K	295 K	0 K	295 K	0 K
d_x (g/cm^3)	1.5254[a]		2.595[b]		3.621[c]	
d_{expt} (g/cm^3)	1.522(8)[d]		2.60(2)		3.61(3)	
V_m (cm^3/mol)	26.330	25.940	33.847	33.312	38.372	37.789
B_0 (kbar)	174(1)	183.6	118.8(5)	123.5	89.3(6)	93.0
B'_0	3.7(1)	3.6	2.41(5)	2.37	2.76(5)	3.06
P^* (kbar)	0.00	−2.67(6)	0.00	−1.93(8)	0.00	$P^*(P)$[e]
Θ_0 (K)		229(2)[f]		147(1)[f]		110.5(20)[f]
γ	1.2[g]	0.62[h]	0.98[g]	0.43[h]	0.74[g]	1.16[h]
P (kbar)			V/V_0			
−2.67		1.0000				
−1.93		0.9958		1.0000		
−1.40		0.9928		0.9956		1.0000
0.00	1.0000	0.9852	1.0000	0.9842	1.0000	0.9848
2.00	0.9888	0.9747	0.9836	0.9687	0.9785	0.9644
4.00	0.9782	0.9647	0.9681	0.9539	0.9586	0.9455
6.00	0.9680	0.9552	0.9534	0.9399	0.9401	0.9284
8.00	0.9583	0.9461	0.9394	0.9266	0.9228	0.9124
10.00	0.9491	0.9373	0.9261	0.9138	0.9066	0.8972
12.00	0.9402	0.9289	0.9134	0.9016	0.8914	0.8830
14.00	0.9317	0.9209	0.9012	0.8899	0.8770	0.8695
16.00	0.9235	0.9131	0.8895	0.8796	0.8634	0.8566
18.00	0.9156	0.9056	0.8783	0.8679	0.8505	0.8444
20.00	0.9081	0.8983	0.8675	0.8575	0.8383	0.8328

[a] Reference 31.

[b] Reference 32.

[c] Reference 33.

[d] The numbers in parentheses are uncertainties in the last digit of the number given.

[e] For barium at 0 K: $P^*=1.4(1)$ kbar for $P\leq 4$ kbar, and $P^*=-1.52(10)+0.030(5)P$ kbar for $P>4$ kbar.

[f] Reference 20.

[g] From Eq. (6).

[h] From Ref. 19, recalculated using present B_0 and V for $T=0$.

This is qualitatively apparent in Fig. 2. The results of VK for both calcium and barium show compressions above 35 kbar greater than would be expected from fits to Eq. (2). These deviations could be either physical or experimental in origin, and suggest caution in the use of Eq. (2) for extrapolation of the present data to pressures above 25 or 30 kbar. The shock-wave isotherm[18] shows approximately 10% less compression in 20 kbar than we find, as is characterized by the fit parameters in Table I.

B. Calcium

The agreement between the present 295-K isotherm for calcium and the (extrapolation-adjusted) results of VK is gratifying. The temperature dependence of the equation of state for calcium [$P^*(T, V/V_0)$, Eq. (1a)] is given in Fig. 5 for the indium-jacketed samples. Different reference isotherms were used for the two samples; the deviations from $P^*=0$ show the quality of the individual fits for these two sets of data, and *not* the agreement between the two independent 295-K isotherms. There were no high-pressure data for unjacketed calcium for temperatures below 80 K. The horizontal dashed lines (P^* independent of volume) correspond to the + plotted in Fig. 2. The data for a given temperature, in general, do not deviate from a constant P^* by more than the equivalent of ±0.0005 in V/V_0. The unjacketed results (not shown)

TABLE II. Comparison of present fit parameters for calcium, strontium, and barium with those derived from other data.

	Note	B_0 (kbar)	B_0'	V/V_0 (adjusted)[a] (10^{-4})	Comments
			Calcium		
Present, indium		174(1)	3.7(1)		Eq. (2)
Present, no jacket		164.4(8)	3.9(1)		Eq. (2)
Bridgman, 1923	b,c	192	2.5		quadratic, to 12 kbar
Bridgman, 1938	d	141	3.14	−10	5–30 kbar, Eq. (2)
VK, 1970	e,c	183.6	2.62		quadratic, 0–45 kbar
VK, 1970	e,c	186.8	2.52		ME-1, 0–45 kbar
VK, 1970	e,f	180.4	3.14	−1.5	5–30 kbar, Eq. (2)
VK, 1970	e,g	174(1)	3.7(1)	−11(2)	5–25 kbar, present
Shock wave	h	193.3	2.61		5–100 kbar, Eq. (2)
			Strontium		
Present, indium		118.3(7)	2.47(7)		Eq. (2)
Present, no jacket		116(1)	3.0(1)		Eq. (2)
Bridgman, 1923	b	120	2.1		quadratic, to 12 kbar
Bridgman, 1938	d	148	3.05	+160	5–20 kbar, Eq. (2)
Bridgman, 1938	d	149	3.65	+170	5–45 kbar, Eq. (2)
			Barium		
Present, indium		89.3(6)	2.76(5)		Eq. (2)
Present, no jacket		87.3(6)	2.72(5)		Eq. (2)
Bridgman, 1927	i,c	96.2	2.24		quadratic, to 12 kbar
Bridgman, 1938	d,j	91.5	(2.76)	+40(1)	4.9–14.8 kbar
VS, 1965	k,j	89.3(6)	2.76(5)	−27(3)	6–17 kbar
VK, 1970	e,c	94.6	1.73		quadratic, 0–45 kbar
VK, 1970	e,c	94.3	2.19		ME-1, 0–45 kbar
VK, 1970	e,f	88.1	2.84	−22	5–30 kbar, Eq. (2)
VK, 1970	e,g	89.3(6)	2.76(5)	−15(1)	5–35 kbar, present

[a] The extrapolation adjustment is used with Eq. (2) to give an optimal representation of the data.

[b] Reference 16.

[c] Parameters as given in the publication.

[d] Reference 5.

[e] Reference 9.

[f] These data show a systematic negative deviation (excess compression) above 35 kbar when compared with the form of Eq. (2).

[g] These data correspond with the present indium-jacketed results when relative volumes are adjusted by the amount shown.

[h] Reference 18.

[i] Reference 17.

[j] A transition with 0.5% volume change is reported at roughly 17 kbar; only three data points are given below the transition.

[k] Reference 6.

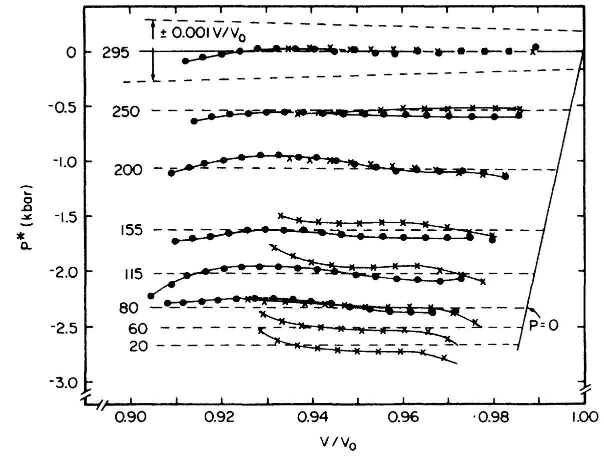

FIG. 5. Experimental P^*'s [Eq. (1a)] for the indium-jacketed calcium results. The ● refer to the high-pressure data and × to the low-pressure data. Different 295-K reference functions were used for these different sets of data (see the text). The dashed horizontal lines are the values which are plotted as + in Fig. 2. The dashed lines above and below the 295-K isotherm represent the effect on P^* of ±0.001 in V/V_0.

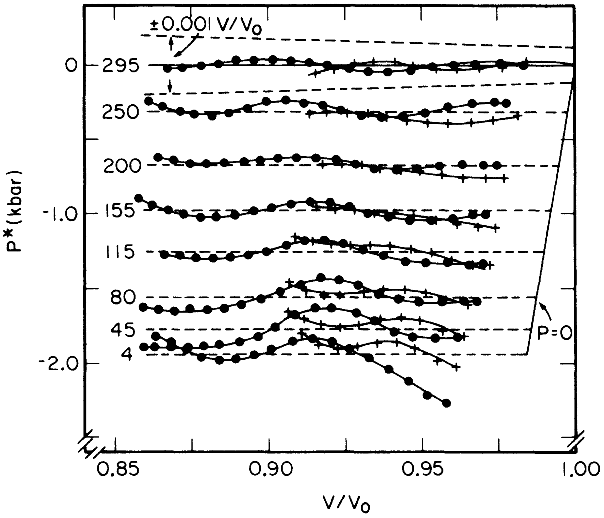

FIG. 6. Experimental P^*'s for the indium-jacketed strontium results. The ● refer to the high-pressure results and + to the low-pressure results. The dashed horizontal lines are the values which are plotted as ○ in Fig. 2. See the caption for Fig. 5 for other details.

are consistent with these within the same uncertainty limits.

The $P=0$ volume expansion of calcium metal shown in Fig. 3 can be compared with three other results. The 283-K linear-expansion coefficient given by White,[19] $\alpha=2.21\times10^{-5}\ \mathrm{K}^{-1}$, and the average α from -120 to 20 °C given by Erfling,[34] $2.08\times10^{-5}\ \mathrm{K}^{-1}$, agree well with the average linear expansivity ($\alpha=\beta/3=2.1\times10^{-5}\ \mathrm{K}^{-1}$) calculated from Eqs. (6) and (8a). Zaretsky and Stassis[35] have used neutron-diffraction measurements on their calcium single crystal[10] to determine the relative volumes of calcium at 75 and 10 K which are shown in Fig. 3. The large error bars are due to estimates of systematic errors, with the overall agreement very satisfactory. There are no other data with which to compare the temperature dependence of B_0 in Fig. 4.

C. Strontium

The present indium-jacketed data for strontium are for only one relatively small sample at pressures to 20 kbar. A complete set of data which were taken with the larger-diameter sample holder showed systematic deviations from these results which eventually were traced to impurities which were introduced into this sample during fabrication. This lack of a confirmatory experiment is unfortunate, since, as Table II shows, there are no other reliable high-pressure data for strontium. Nevertheless, the agreement between our 295-K isotherms for calcium and barium (see below) and other results indicates that the parameters given in Table I should be reliable within the limits given.

In contrast with the 295-K reference-isotherm results, the P^* results for these two jacketed samples were quite consistent, and are given for selected isotherms in Fig. 6. Again, the 295-K deviations for each sample represent differences from the reference function which applies to data for that sample, and *not* to differences from a common reference function. The systematic positive and negative deviations of the high-pressure data with decreasing temperature in Fig. 6 suggest a structure which is roughly independent of temperature, with isotherm separations which are approximately constant. The P^*'s which determined the horizontal lines and which correspond to the ○ plotted for strontium in Fig. 2 were generated as averages of the actual isotherm separations. The deviations from "ideal" [$P^*(T)$] behavior at low temperature are roughly twice as great in magnitude (0.001 in V/V_0) as those for calcium in Fig. 5. This structure is considerably enhanced in the P^* plots for the unjacketed samples (not shown), with, however, the isotherm separations remaining roughly constant and corresponding very well with those shown in Fig. 6.

The average linear expansivity of strontium metal between 80 and 295 K as calculated from Eq. (6) is $2.0(1)\times10^{-5}\mathrm{K}^{-1}$, in good agreement with the average value given by White[19] over this same temperature interval, $2.05\times10^{-5}\ \mathrm{K}^{-1}$, and with the 300-K expansivity of Dzhavadov,[23] $2.25(3)\times10^{-5}\ \mathrm{K}^{-1}$. There are no data with which to compare the $P=0$ volume expansivities in Fig. 3 nor the $P=0$ bulk moduli in Fig. 4.

D. Barium

The present 295-K data are in good agreement (Table II) with two earlier studies,[6,9] and are in essential agreement with a third.[5] We, in agreement with VK,[9] do not observe the 0.5% volume-change transition at 17 kbar in either the unjacketed of jacketed data. We do , however, observe subtle, reproducible, effects in the 295-K raw data for the indium-jacketed samples at roughly 17 kbar

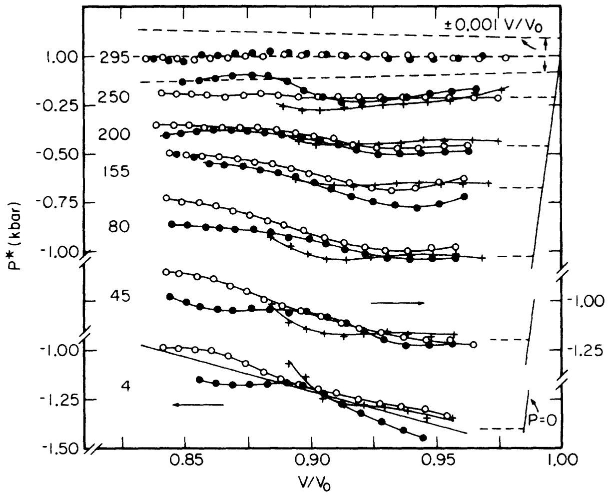

FIG. 7. Experimental P^*'s for the barium results. The ● refer to the unjacketed high-pressure data, ○ to the indium-jacketed high-pressure data, and + to the indium-jacketed low-pressure data. Different 295-K reference functions were used for these different sets of data (see the text). The dashed horizontal lines are the values which are plotted as × in Fig. 2. See the Fig. 5 caption for other details.

upon increasing pressure and at 13 kbar upon decreasing pressure. These effects are small (roughly 0.0004 in V/V_0), and they correspond to a *decrease* in the system friction (the width of the hysteresis loop) with increasing pressure. A smooth curve was drawn through them in the data analysis. These effects occurred also in the initial runs at lower temperatures, with, possibly, a decreased magnitude and an increased hysteresis. Since these samples had less than 1 at. % hydrogen, we do not feel that these effects are associated with sample purity.

Unusual effects also occur in the temperature-dependent contributions to the equation of state for barium. Figure 7 gives selected P^* isotherms for the high-pressure unjacketed (●) and jacketed (○) data, and for the low-pressure jacketed (+) data. As for Figs. 5 and 6, P^* for a sample is defined in terms of the appropriate reference isotherm *for that sample*. The 295-K deviations are from different reference functions for the unjacketed and jacketed results, and do not indicate an agreement between the unjacketed and jacketed reference functions. The important feature in Fig. 7 is that P^* for an isotherm becomes volume dependent as the temperature decreases. This is most obvious for the high-pressure data, where the effect is qualitatively independent of whether the sample is jacketed or unjacketed. The low-pressure data (only the jacketed data are plotted) are consistent with this conclusion. For a given isotherm, the magnitude of P^* begins to decrease at a pressure which varies from roughly 10 kbar at 200 K to 2(2) kbar at 4 K, with the 295- and 0-K isotherms in Fig. 1 converging for barium rather than being separated horizontally by a constant P^* as for calcium and strontium. The bulk modulus for barium at 0 K and 10 kbar is roughly 3% greater than it is for barium at the same volume and 295 K. This is characterized in Table I by the relatively large decrease of B_0' between 0 and 295 K for barium, in contrast with the slight increase for calcium and strontium. The P^* relation for $P=0$ (the horizontal dashed lines in Fig. 7, and × in Fig. 2) is well behaved, as is the volume thermal expansion in Fig. 3, so, if a phase transition exists, the volume change must be small, of the order of or less than 0.001 in V/V_0. This effect does not appear to be related to the subtle decrease in friction with increasing pressure observed in the higher-temperature data. According to Bridgman,[5] the transition at 17 kbar should occur at higher pressures at lower temperature, so should not be associated with the present observations.

The only temperature-dependent data with which the present results can be compared again are the linear-expansivity measurements of White.[19] The average linear expansivity from 80 to 295 K as calculated from Eqs. (6) and (8c) is $1.78(3)\times10^{-5}$ K^{-1}, which compares well with White's average over this same range of 1.87×10^{-5} K^{-1}. The value of B_T at 295 K (89.3 kbar) is appreciably smaller than that given by Voronov and Stal'gorova[6] from sound-velocity measurements, 94.6 kbar. Their pressure-dependent length-change measurements, however, are consistent with our indium-jacketed reference isotherm.

IV. CONCLUSIONS

Table I and Figs. 1–4 contain the basic results of these experiments. The agreement with extrapolation-adjusted results of other high-pressure, room-temperature experiments and with direct-expansivity measurements provides confidence in the reliability of the 295-K isotherm. For completeness, Table I also contains x-ray densities, limiting Debye temperatures, Θ_0, and Grüneisen parameters for both the high- and low-temperature limits. The low-temperature equilibrium volumes and bulk moduli, as well as the P-V relation for 0 K, should be useful for comparison with further first-principles energy calculations of the type reported by Chen *et al.*[2] for barium metal. Here, their calculated $B_0=110$ kbar (for a lattice parameter $a=4.8$ Å) is significantly larger than our 0-K value of 93 kbar ($a=4.99$ Å). While the value of B_0' for calcium (3.7) is similar in magnitude to that for the alkali metals (4.0),[24,25] the values of B_0' for both strontium and barium are appreciably smaller (2.5 and 2.8, respectively). First-principles energy calculations would be very useful to determine whether or not this "softness" for strontium and barium is understandable in terms of the volume-dependent electronic-structure effects commented on in theoretical treatments.[1,2]

While the temperature-dependent equations of state for calcium and strontium are consistent with the postulate that the bulk modulus depends only on volume, not temperature, the high-pressure (10 kbar) bulk modulus for barium metal at 295 K is 3% smaller than it is for the same volume at 0 K. This unusual effect occurs without a significant (less than 0.001 in V/V_0) volume change, and is independent of ambiguities or uncertainties which might exist in the specification of the 295-K reference isotherm. Chen *et al.*[2] show that the T1 (shear) -mode frequency decreases with increasing pressure, a factor which could be important in these experiments, where considerable sample shear occurs. This "abnormal" decrease in B_0 with increasing temperature may be a precursor of the bcc-hcp transition (which has a 2% volume change and moves to lower pressures as the temperature is lowered[4]), but, if so, occurs without a significant volume change. Barrett[36] cold-worked barium at low temperature in an attempt to observe using x rays the martensitic bcc-hcp transition, with negative results.

Two general features of these results are not understood. First, we do not understand why the measured densities should be greater for the jacketed than the unjacketed samples. Second, we do not understand the differences between compression data taken with indium-jacketed and unjacketed samples. The effects of nonhydrostatic-pressure environments should become more significant in the unjacketed samples as the temperature decreases, but this is not observed. Unusual effects are the rule rather than the exception for these alkaline-earth metals, however. The inconsistencies in Table II are striking, and outside reasonable experimental uncertainties. Bridgman[5] reports a phase transition and excess compression for calcium (see Fig. 1 and Table II), and, also, along with Voronov and Stal'gorova,[6] a phase transition in barium at 17 kbar. These have not been verified in other work, and the role of impurities has not been documented. We do not believe that hydrogen contents of up to 4 at. % have had a significant effect on the present results, although we have not studied this systematically. The fcc-bcc transition in strontium at 35 kbar shows considerable hysteresis at room temperature;[4,5] this presumably is why VK chose not to include strontium in their studies.

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