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Experimental equations of state for cesium and lithium metals to 20 kbar and the high-pressure behavior of the alkali metals

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Experimental equation-of-state results to 20 kbar and from 4 K to room temperature are given for cesium and lithium metals which are comparable with those published previously for sodium, potassium, and rubidium [Phys. Rev. B **28**, 5395 (1983)]. The same generalization holds that the isothermal bulk modulus is a function of the volume only. Cesium and lithium each are slightly more compressible in a reduced sense than the other three alkali metals, and have Grüneisen parameters (1.14 and 0.878, respectively) which are smaller than the common value for the others, 1.25. Extrapolations of the present results for the alkali metals are compared with other data to 100 kbar, with these earlier results scattering about the extrapolation. It is suggested that the bcc-to-fcc transitions in potassium, rubidium, and cesium occur at common values of the ratio of the nearest-neighbor distance to the ionic or pseudopotential radius. No systematic trends are observed in these equation-of-state results which can be associated with an increase in *s*-*d* mixing effects with increasing ionic mass.

I. INTRODUCTION

A systematic study of the thermodynamic properties of the alkali metals provides an opportunity to investigate the effects of increasing core radius and of the potential mixing of electronic levels in this elementary metallic system. Takemura, Syassen, and their co-workers recently have reported bcc-to-fcc transitions in rubidium[1] and potassium[2] using diamond-anvil-cell reflectivity and x-ray studies at room temperature, and also have seen higher-pressure transitions in these metals. Olijnyk and Holzapfel[3] have used energy-dispersive x-ray diffraction in a diamond-anvil cell to confirm these results. These transitions presumably are analogs of those found by Bridgman[4–6] in cesium, with the relatively small volume change lower-pressure transition involving a reorientation of the ionic cores (bcc or fcc), which is followed by an electronic "collapse" of the cores of higher pressures. Optical studies of the potassium,[2] rubidium,[1,7] and cesium[7,8] transitions below the high-pressure transition show similar results and are interpreted commonly in terms of a mixing of the *s* and *d* states for the valence electrons in these metals. The effects of this mixing, if it takes place continuously with the application of pressure, should be apparent also as a systematic trend in the thermodynamic properties of these materials, and, indeed, our earlier equation of state (EOS) results for cesium metal[9] in the low-pressure phase were quite different in form from those for sodium[10] and potassium,[11] with the suggestion that cesium was much softer than the other metals. This appeared to be confirmed by neutron scattering measurements under pressure.[12] Lithium metal, for which no *d* states exist, also shows appreciably different behavior from that for sodium and potassium, but for different reasons.

We recently have complicated EOS measurements on rubidium metal,[13] and also have redetermined in the same set of experiments the equation of state of sodium and potassium,[13] and found very similar behavior for these three metals. We also, subsequently, reexamined our older cesium[9] and lithium[14] data, and found that their quality is, for various reasons, inferior to that of our latest measurements on the other alkali metals. Both sets of data suffer from inaccurate $P=0$ length determinations and problems in the extrapolation of the isotherms to $P=0$, while the cesium results were inaccurate due to unsuspected hysteresis at low temperature due to the bcc-fcc transitions. We, therefore, decided to redetermine the EOS for cesium metal through the bcc-fcc transition (22.1 kbar) to provide a valid comparison with the sodium, potassium, and rubidium results,[13] and to repeat the lithium measurements. The quality of the latter is improved by the use of a slightly revised EOS for the indium metal which provides the reference material in these measurements.[15] This revised reference EOS is not important for the other, more compressible, alkali metals.

The results of the cesium and lithium experiments are given in the following, along with a correlation of our results for the five alkali metals and a comparison with other room-temperature, often higher-pressure results. The reduced pressure-volume relations for lithium and cesium show an only slightly softer behavior than we found for sodium, potassium, and rubidium.[13] The suggestion is that if *s*-*d* mixing becomes more important for the heavier alkali metals as the atomic number increases, this has only a somewhat subtle effect on the low-pressure (to 20 kbar) thermodynamic properties.

II. EXPERIMENTAL DETAILS AND THE REPRESENTATION OF THE RESULTS

The procedures which were used in the new cesium measurements are identical with those described elsewhere.[13,15] As for sodium, potassium, and rubidium,[13] we will present these cesium and lithium results using the relation

$$P^*(V/V_0,T)=P-P_{\text{calc}}(V/V_0,T_R)\ , \tag{1}$$

where P^* is defined as the thermal pressure and $P_{\text{calc}}(V/V_0,T_R)$ is the analytical representation of the isotherm for the reference temperature T_R, which is 270 K for cesium and 294 K for lithium. These analytical representations will be derived from the pressure dependence of the isothermal bulk modulus $[B_T=-(\partial P/\partial \ln V)_T]$ as given by the Murnaghan relation (the ME),[13]

$$B_T(P,T)=B_0(T)+B_0'(T)P+\tfrac{1}{2}B_0''(T)P^2+\cdots \tag{2}$$

or the modified Murnaghan relation (MME), which has a relatistic high-pressure limit,

$$\begin{aligned}B_T(P,T)&=B_0(P=0,T)\left[\frac{1+\alpha P}{1+\beta P}\right]\\&=B_0(P=0,T)\left[\frac{1+\alpha B_0(P/B_0)}{1+\beta B_0(P/B_0)}\right]\end{aligned} \tag{3}$$

with

$$B_0'=B_0(\alpha-\beta),\quad B_0''=-2\beta B_0'\ . \tag{4}$$

Equation (2) can be integrated to give explicit expressions (the ME-2 relations) for $P(V/V_0)$ or $V(P)/V_0$,

$$P=2B_0\left[\Gamma\left[\frac{(V_0/V)^{\Gamma}+1}{(V_0/V)^{\Gamma}-1}\right]-B_0'\right]^{-1} \tag{5}$$

or

$$V/V_0=\left[\frac{2+(B_0'-\Gamma)(P/B_0)}{2+(B_0'+\Gamma)(P/B_0)}\right]^{1/\Gamma}, \tag{6}$$

with $\Gamma^2=(B_0'^2-2B_0B_0'')>0$. When the second-order term can be neglected ($B_0''=0$), these simplify to the ME-1 relations:

$$P=(B_0/B_0')[(V_0/V)^{B_0'}-1] \tag{7}$$

and

$$V/V_0=[B_0'(P/B_0)+1]^{-(1/B_0')}\ . \tag{8}$$

Equation (3) can be integrated to give the MME as

$$V/V_0=\exp\{(-1/\alpha^2B_0)[\alpha\beta P+(\alpha-\beta)\ln(1+\alpha P)]\}\ . \tag{9}$$

Nonlinear least-squares procedures must be used to fit each of these empirical relations to experimental data. Equations (5) and (7) are most convenient to use with Eq. (1) in presenting the actual data, since they give $P(V/V_0)$ directly, but they may not be as useful or realistic for extrapolation as Eq. (9), which is well behaved at high pressures.[13] In either case, B_0' and B_0'' represent (different) effective parameters which may not compare directly with those obtained in low-pressure ultrasonic measurements, for instance. Finally, we have found experimentally that the thermal pressure P^* [Eq. (1)] is independent of volume for most systems and that for high temperatures ($T>\Theta_\infty$) it is a linear function of the temperature. This linear temperature dependence can be understood in terms of the Mie-Grüneisen EOS for a harmonic solid for which $C_V=3R$ and the high-temperature vibrational contribution to the pressure is given by $P_{\text{vib}}=(\gamma/V)3RT$, with $\gamma(V)$ the Grüneisen parameter. A particularly useful relation is given by

$$\left[\frac{\partial P}{\partial T}\right]_V=\beta B_T=3R(\gamma/V)\ . \tag{10}$$

This is an explicit relationship between the volume thermal-expansion coefficient β and the bulk modulus at high temperatures, and, since $(\partial P/\partial T)_V$ experimentally is independent of both temperature and pressure for $T>\Theta_\infty$, suggests that γ must be proportional to the volume in this limit.

III. RESULTS

Figure 1 shows the relative compressions at room temperature for all five alkali metals and the low-temperature compressions for lithium, sodium, rubidium, and cesium. The sodium, potassium, and rubidium results are from an earlier paper,[13] while the lithium and cesium results are reported below. This figure is intended to provide a semiquantitative basis for the detailed presentation and discussion of the results which will be given in the following. The dominant factor which determines the magnitude of the relative compression for each of these metals in 20 kbar is the value of the $P=0$ bulk modulus. If these relations were to be plotted as V/V_0 versus P/B_0, they would almost fall on a common curve. Cesium and lithium are slightly different, and each show a slightly ($\sim$0.015 in V/V_0) greater compression in 20 kbar than would be predicted from the common V/V_0-versus-P/B_0 relation which applies to sodium, potassium, and rubidium.[13]

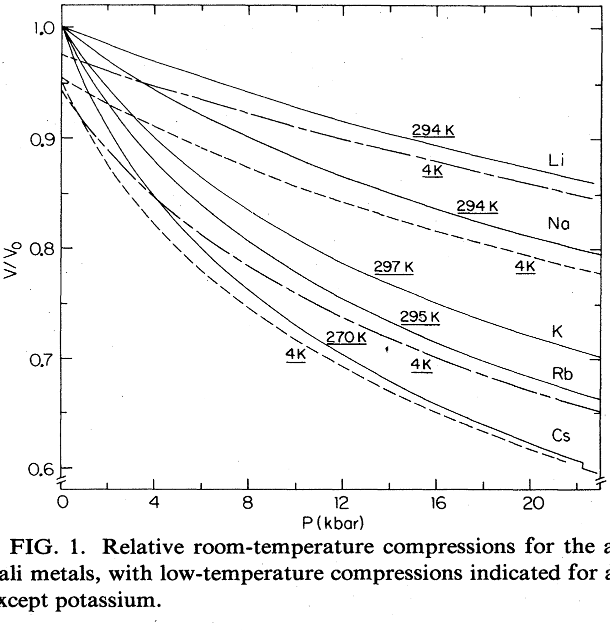

FIG. 1. Relative room-temperature compressions for the alkali metals, with low-temperature compressions indicated for all except potassium.

TABLE I. Summary of the isotherm results for cesium. The data points for the isotherms are indicated in Figs. 2 and 3. (RMSD denotes root-mean-square deviation.)

T	P^*		B_0[a]	B_0[b]		B_0''[b]	RMSD
(K)	(kbar)	$(V/V_0)_{P=0}$[a]	(kbar)		B_0'[b]	(kbar^{-1})	(10^{-4} in V/V_0)
290	+0.085	1.0050	16.90[d]	16.98±0.06	3.79∓0.02	−0.077±0.001	0.8
270	(0)	(1.0000)[c]	(17.23)	17.23±0.05[c]	3.87∓0.03[c]	−0.103±0.005[c]	2.8
				[17.13±0.03][f]	[3.98∓0.03][f]	[−0.150±0.004][f]	2.7
248	−0.09	0.9948	17.58	17.60±0.10	3.87∓0.06	−0.112±0.011	3.7
200	−0.275	0.9838	18.29	18.32±0.12	3.82∓0.07	−0.105±0.014	4.6
146	−0.505	0.9726	19.17	19.05±0.12	3.89∓0.01	−0.113±0.012	7.7
99.5	−0.69	0.9634	19.88	19.86±0.14	3.79∓0.06	−0.099±0.018	8.1
82	−0.765	0.9598	20.16	20.26±0.08	3.73∓0.04	−0.098±0.008	8.8
43	−0.915	0.9528	20.73	20.94±0.06	3.67∓0.02	−0.087±0.005	6.7
34	−0.96	0.9508	20.90[e]	20.50±0.15	3.95∓0.06	−0.125±0.012	6.1
20	−0.975	0.9501	20.95	21.09±0.06	3.69∓0.02	−0.087±0.006	7.1
4	−1.00	0.9489	21.05	21.03±0.06	3.76∓0.02	−0.096±0.006	6.8
				[20.79±0.09][f]	[3.98∓0.04][f]	[−0.168±0.009][f]	6.6

[a] Derived from the 270-K isotherm and P^*.

[b] Parameters derived from nonlinear least-squares fits of the ME-2 relation, Eq. (6), to the data for each isotherm. The 3σ uncertainties are those associated with the fitting procedure and do not include an allowance for systematic effects. A more qualitative estimate gives minimum uncertainties of ±0.3 kbar for B_0, ∓0.1 for B_0' and ±0.01 kbar^{-1} for B_0''.

[c] These parameters define the reference isotherm with V_0 (270 K, $P=0$)=70.00 cm^3/mole.

[d] 0.354-in. sample-holder data only.

[e] 0.250-in. sample-holder data only.

[f] Alternative representations of the data usng the MME relation, Eq. (9).

A. Cesium

Two new sets of cesium data were taken, one each with the 0.354-in.-diam. and 0.250-in.-diam. sample holders. The 270-K sample lengths, 0.3566 and 0.2044 in., respectively, were determined from the sample masses (1.0852 and 0.3135 g, respectively) and an assumed 270-K molar volume of 70.00 cm^3 (or a density of 1.899 g/cm^3). This is consistent with our length and mass determinations for the larger-diameter sample if, as the compression data suggest, a residual pressure of approximately 170 bars is locked into the sample when the sample holder is removed from the press and the sample length is measured directly. Very few data (either bulk or lattice parameter) exist for the density or molar volume of cesium metal at any temperature, and those that do will be discussed along with the presentation of our thermal-expansion results. The cesium metal which was used was purchased from A. D. Mackay for our previous experiments,[9] with the original 99% pure material further purified by triple distillation under vacuum before being stored in sealed glass ampoules under vacuum.

The 270-K reference relation for Eq. (1) was determined by a fit of Eq. (6) to the combined data from three large-diameter and four small-diameter sample-holder isotherms. The parameters for this reference isotherm are given in Table I, with the smooth deviations of the actual data from the reference relation presented in Fig. 2. An initial fit to these data showed an inconsistency between the large- and small-diameter sample-holder data which could be associated with an error of 0.25% in one of the sample lengths. This was within the accuracy for the 0.250-in.-diam. sample-mass determination, so this length was adjusted from 0.2044 to 0.2039 in. to obtain the agreement shown in Fig. 2. Otherwise, except for adjustments for measuring system zero shifts between runs [the time between the run labeled (17) and those labeled (1) and (7) was 2 months, with the sample holder removed from the press for weighing between these runs], the various sets of data have not been normalized in any manner. The data for all temperatures are presented in Fig. 3, where good agreement (better than 0.001 V_0) exists between the independent data for the two sample holders.

The existence of the bcc-fcc transition in cesium presents a complication in data taking, and Fig. 4 shows the actual data for 270-K and 82.4-K isotherms which were taken through this transition. The transition runs cleanly at 270 K, with the same hysteresis (separation of the pressure-increasing and pressure-decreasing curves) below, in, and above the transition. Identical lower-pressure results were obtained when a pressure cycle did not include the transition. The transition pressure,

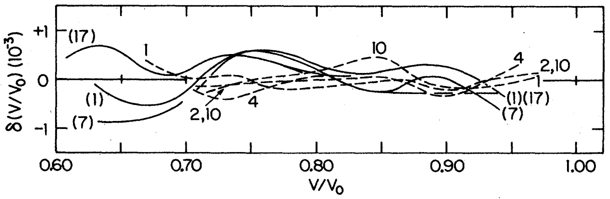

FIG. 2. Deviations of the actual 270-K data for cesium from the reference relation (Table I). The dashed lines and solid lines, respectively, represent data taken with the 0.354-in.-diam. and 0.250-in.-diam. sample holders. The numbers represent the order in which the data were taken, with 270-K runs bracketing those taken at lower and higher temperature.

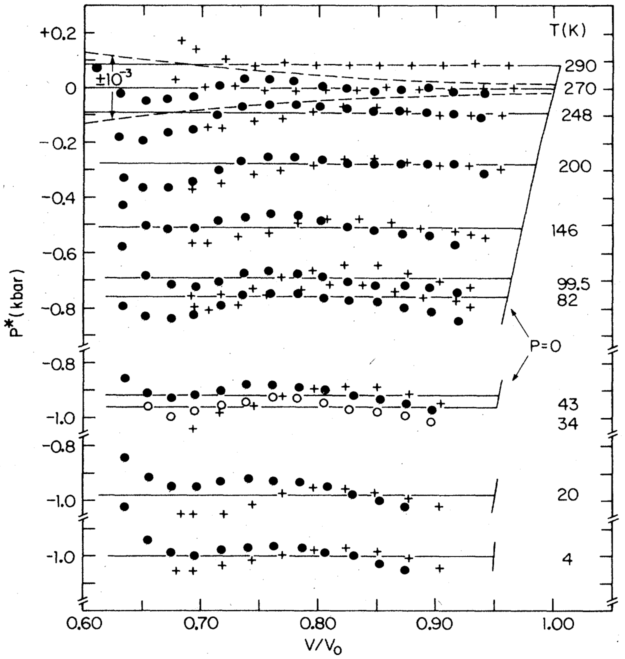

FIG. 3. Representation of the cesium data for each temperature in terms of thermal pressures [Eq. (1)]. Note the breaking of the scale for the lower temperatures. The dashed lines around the 270-K data represent the equivalent effect on the pressure of a $\pm 10^{-3}$ variation in V/V_0.

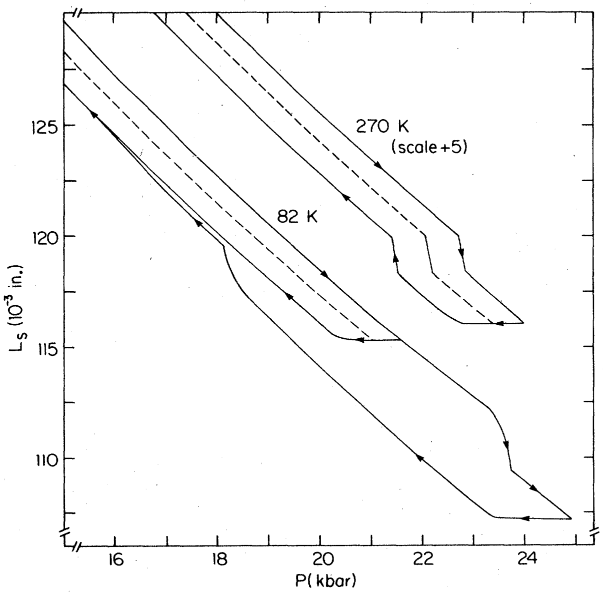

FIG. 4. Data taken through the bcc-fcc transition for cesium at two different temperatures. The hysteresis at 270 K is due to friction effects, while that at 82 K involves, in addition, sluggishness in the running of the transition.

22.1 ± 0.1 kbar at 270 K, and the volume change, $0.0063 V_0$, are in agreement with previous work.[9] A careful analysis of the 270-K isotherm suggests that the bulk modulus for the high-pressure fcc phase may be as much as 10% smaller than that for the bcc phase at the transition. This normally would not be expected for a (slightly) more dense phase.

The behavior of the 82-K isotherm in Fig. 4 (and also that of an isotherm at 146 K, which is not shown) is quite different, however, with an appreciably greater volume change on increasing pressure $(0.0095 V_0)$ than at 270 K and a hysteresis which is twice as large as the friction or normal hysteresis which is observed away from the transition. This is demonstrated in Fig. 4 by the subsequent cycle at 82 K which does not go through the transition. The combination of these two cycles suggests that the pressure-decreasing curve has two breaks, the first with $\Delta V = 0.008 V_0$ and the second with $\Delta V = 0.002 V_0$. The pressure-increasing transition at 4 K (not shown) has the same magnitude but is smeared out, while no clear break is seen on decreasing pressure. These effects were not studied in detail, and should be investigated systematically, especially in the 82 K to 270 K region.

The existence of this large, ill-defined hysteresis at low temperature was not recognized in our previous cesium experiment,[9] and it is responsible for the discrepancies which are reported there between the 0.250-in. and 0.354-in. sample-holder data. Except for the specific isotherms discussed in Fig. 4, the pressure on the sample in the present 0.250-in. sample-holder compression-determination measurements was kept at or below 20 kbar so that the sample never transformed and the hysteresis was not a problem.

The thermal pressure P^* in Fig. 3 is independent of volume to within $0.001 V_0$, with values as given in Table I. This conclusion is in agreement with our observation from the previous measurements for sodium, potassium, and rubidium.[13] Figure 5 shows that P^* varies linearly with temperature for temperatures greater than $\Theta_\infty = 46.5$ K,[16] with $(\partial P/\partial T)_V = 4.05$ bar/K. The zero-point pressure [the difference between the $T=0$ intercept of the linear relation and the $T=0$ experimental P^* (Ref. 13)], P_z, is 0.09 ± 0.02 kbar, in fair agreement with 0.06 kbar as calculated by Vaks *et al.*[17] Calculations by Glyde and Taylor[18] have shown that cesium is expected to exhibit very little explicit anharmonic behavior, even close to the melting point. Hence, we can use Eq. (10) to calculate the Grüneisen parameter ar 270 K and $P=0$ as $\gamma = 1.14$ using $(\partial P/\partial T)_V = 4.05$ bar/K and $V_0 = 70.00$ cm^3/mole. This is appreciably less than the approximately common $P=0$ value, $\gamma = 1.25$, which was obtained in a similar manner for sodium, potassium, and rubidium near 295 K. Chung and Cutler[19] in a pseudopotential calculation of the phonon dispersion relations obtain $\gamma = 1.20$ at 5 K which, they believe, should be the same as for high temperatures. The agreement with our value is reasonable.

The temperature dependence of P^* also can be used to calculate the $P=0$ temperature dependence of both the relative volume change and the isothermal bulk modulus by setting $P=0$ in Eq. (1) to obtain $(V/V_0)_{P=0}$ and hence $B_T(P=0)$, which is a function only of V/V_0.[13] These are given in Table I and also in Figs. 6 and 7, where comparisons are made with other $P=0$ results. Our previous results for these $P=0$ thermodynamic quantities[9] do not differ from the present values by more than the uncertainties which are stated in that paper. Table I also contains parameters for ME-2 [Eq. (6)] fits to the actual isotherm data which are shown in Fig. 3, using $(V/V_0)_{P=0}$ as given for the $P=0$ reference volume. The agreement between $B_T(P=0)$ as obtained in these different calculations is quite satisfactory, with no differences greater than 1%.

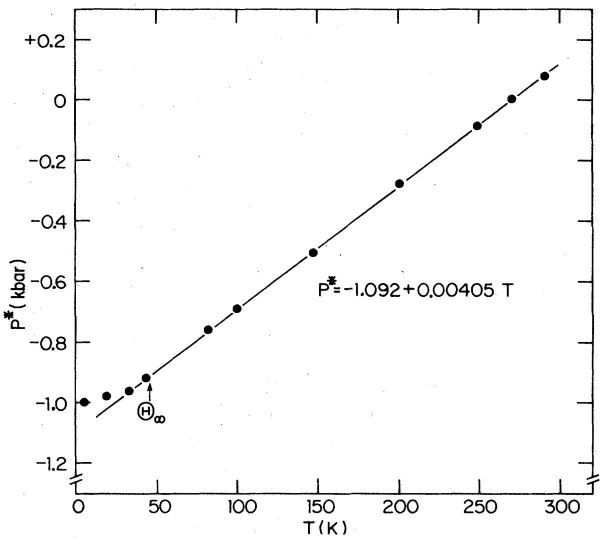

FIG. 5. Temperature dependence of the thermal pressure for cesium. See the text for details.

Figure 6 also contains a summary of existing specific volume data for cesium metal at various temperatures, with $V_0 = 70.00$ cm^3/mole at 270 K chosen as the reference volume, as was discussed above. Martin[16] quotes a

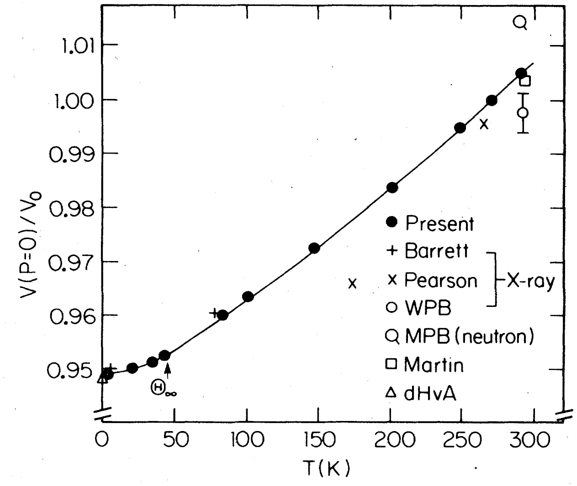

FIG. 6. The relative volume thermal expansivity for cesium metal. The references to other data are Barrett (Ref. 21), Pearson (Ref. 40), WPB (Ref. 22), MPB (Ref. 12), Martin (Ref. 16), and dHvA (Ref. 23).

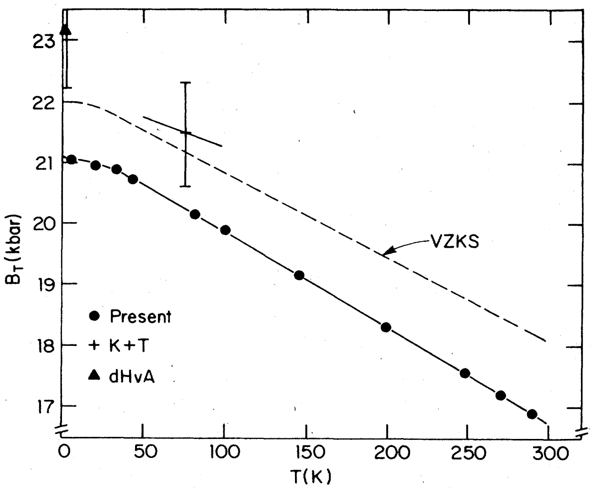

FIG. 7. Temperature dependence of the $P=0$ isothermal bulk modulus for cesium. The references to other results are K + T (Ref. 24), dHvA (Ref. 25), and VZKS (Ref. 17).

1911 density determination by Hackspill, Pearson[20] gives a summary of x-ray lattice parameter determinations, including those by Barrett[21] at low temperatures, Wier *et al.*[22] determined a $P=0$ lattice parameter at room temperature in their diamond-anvil pressure cell measurements, and McWhan *et al.*[12] used neutron scattering data to obtain a lattice parameter, again at room temperature. Finally, Gaernter and Templeton[23] have obtained $V_0=66.38\pm0.06$ cm^3/mole ($V/V_0=0.948\pm0.001$) from a free-electron analysis of their $P=0$ de Haas van Alphen (dHvA) measurements. Our assumed fiducial value for V_0 at 270 K and the temperature dependence of V/V_0 which follows from the present data appear to be consistent with other data, although modern density or lattice parameter determinations would be useful. Our equation-of-state data for potassium metal[13] gave excellent agreement with direct thermal-expansion measurements for this metal (to $\pm5\times10^{-4}$ in V/V_0), and since the same sample holders, procedures, and corrections were used in the present experiments, we would expect a similar accuracy.

Our $P=0$ (extrapolated) isothermal bulk moduli are given in Fig. 7 as a function of temperature. The only available elastic constant, and hence, bulk modulus, data are those of Kollarits and Trivisonno[24] for a range of temperatures near 77 K and for 4 K, which have large uncertainties. These disagree with our results by approximately 10% at 4 K and by more than 5% at 77 K, although the temperature dependence is roughly the same. Templeton[25] has interpreted his most recent pressure-dependent dHvA results in terms of a free-electron model, with a result ($B_0=32.20\pm0.08$ kbar) which again is 10% larger than our 4 K value and in agreement with the ultrasonic result. This agreement possibly is fortuitous, since for sodium, potassium, and rubidium, where our results show better agreement with ultrasonic data,[13] the dHvA-derived bulk moduli generally are 6% or so larger and similar, possibly greater, effects would be expected for cesium.

Figure 7 also contains the results of a temperature-dependent bulk modulus calculation by Vaks *et al.*[17] which uses the same two-parameter pseudopotential model as for sodium, potassium, and rubidium. The agreement for cesium is less satisfactory than for the other metals. Lopez and Alonzo's[26] single-parameter energy-density-functional calculation gives a $T=0$ bulk modulus for cesium which is almost identical with that of Vaks *et al.*[17]

The values of B_0' and B_0'' which are given in Table I for the various isotherms show only a small temperature dependence. These parameters should be temperature dependent since they are obtained from fits to the various isotherms for which $(V/V_0)_{P=0}$ is temperature dependent and is directly related to $P^*(T)$. This, indeed, is how the temperature-dependent bulk moduli in column 4 of Table I were obtained, and the agreement with the directly-determined values (column 5) suggests that no intrinsic temperature dependence exists for the $P=0$ bulk modulus. If B_T is a function of volume only, the temperature dependence of B_0' can be calculated as[13]

$$B_0'(P^*)=B_0'(P^*=0)-P^*B_0'' \qquad (11)$$

with the assumption that B_0'' is at most only slightly temperature dependent; that is, that higher-order terms in Eq. (2) are unimportant. A fit of this relation to P^* and B_0' in Table I gives

$$B_0'(P^*)=3.85-B_0''P^* \, , \qquad (12)$$

with $B_0''=-0.081$ kbar^{-1} if all of the data are used, and $B_0''=-0.132$ kbar^{-1} if data for the 34-K isotherm (for which only high-pressure data exist) are excluded. These results are consistent with an unweighted average over fits to all of the isotherms of $B_0''=-0.100\pm0.014$ kbar^{-1}.

While the ME-2 relation [Eq. (6)] fits our data well, it exhibits nonphysical behavior since $B_T(P)$ has a maximum value for an isotherm[13] at $P=-B_0'/B_0''\approx39$ kbar for cesium at room temperature, so the parameters B_0' and B_0'' represent effective values. The MME [Eqs. (3) and (9)] exhibits more agreeable behavior at high pressure,[13,27] and, hence, although less convenient to use with Eq. (1), should give more realistic values for these parameters for comparison with, for instance, ultrasonic results when available. Fits of our 270-K and 4-K data to this relation [Eq. (9)] give the parameters which are shown in the brackets in Table I for these temperatures. B_0, essentially, is unchanged, but B_0' increases slightly in each case, and B_0'' shows a large increase in magnitude, presumably because the form of Eq. (6) has a built-in softening as $B_T(P)$ approaches the maximum value. The lack of a temperature dependence for B_0' most likely is not real, since the expected decrease of 0.15 in B_0' between 270 K and 4 K [Eq. (11)] could be masked by the ±0.1 estimated accuracy which we assign to these B_0' values. Equation (9) can be generalized (the MME-2 relation) to provide an even more realistic very-high-pressure behavior,[13,27] but, as for rubidium, fits of this MME-2 relation to the cesium data do not result in improvements in the quality of the representation, nor in values for B_0' and B_0'' which are at all different from those given in Table I for the MME fits.

TABLE II. Room-temperature and 4 K compressions for cesium and lithium. See the text for details.

	Cs		Li	
V/V_0[a]	295 K	4 K	294 K	4 K
1.000	0	−1.083	0	−3.10
0.975	0.445	−0.645	3.06	−0.10
0.9742			3.16	0
0.950	0.950	−0.148	6.49	3.29
0.9432	1.110	0		
0.925	1.525	0.421	10.33	7.12
0.900	2.179	1.071	14.66	11.46
0.875	2.924	1.812	19.52	16.39
0.850	3.772	2.660	(25.0)	(21.98)
0.825	4.741	3.630	(31.1)	
0.800	5.846	4.741	(38.0)	
0.775	7.108	6.010	(45.8)	
0.750	8.548	7.459	(54.6)	
0.725	10.19	9.110	(64.3)	
0.700	12.06	11.00		
0.675	14.20	13.14		
0.650	16.63	15.58		
0.625	19.39	18.34		
0.6024	22.20	21.15		
0.5961	22.20			

[a] V_0 is 70.42 cm^3/mole at 295 K for cesium, and 13.02 cm^3/mole at 294 K for lithium.

Table II contains tabulations of our pressure-volume relations for cesium for 295 K and for 4 K, as derived from the MME parameters in Table I. The 295 K relation was obtained from the 270 K MME relation (Table I) and Eq. (1), with $P^*=0.101$ kbar, and $V_0(295\text{ K}, P=0) = 1.0060 V_0(270\text{ K}, P=0) = 70.42$ cm^3/mole. This change in the mode of presentation was made to be able to compare our results more directly with published room-temperature experimental values.

Vaks and Trefilov[28] have calculated the $T=0$ pressure-volume relations for cesium as well as the other alkali metals, and Eremenko and Zarochentsev[29] have repeated these calculations using the same pseudopotential and have in addition added core-repulsion effects. The calculation without core repulsion agrees almost exactly with our 4-K cesium isotherm to 20 kbar (Fig. 1 and Tables I and II), while the addition of core repulsion increases the pressure for $V/V_0=0.619$ in Table II from 20 to 23 kbar. That is, the model gives a solid which is too hard when core repulsions are included. For rubidium, on the other hand, the addition of core-repulsion effects produces very good agreement with our $T=0$ compressions to 20 kbar. The calculation for potassium is independent of core-repulsion effects for pressures to 20 kbar, and predicts a solid which is too soft at $T=0$.

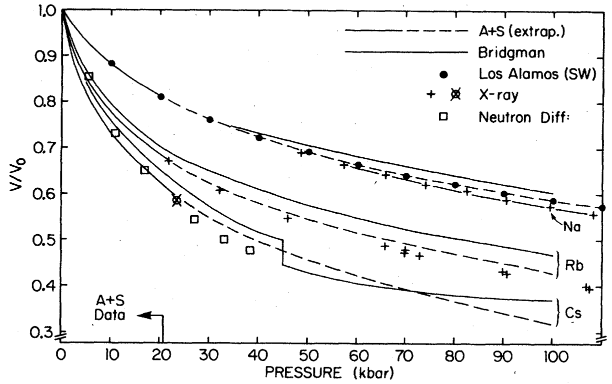

FIG. 8. Room-temperature compressions of sodium, rubidium, and cesium metals. The dashed lines refer to extrapolations above 20 kbar of the present work and that of Ref. 14. The neutron diffraction and x-ray data for cesium are from Refs. 12 and 22, respectively. Bridgman's data are from Refs. 5 and 6. See the text for a discussion of the sodium and rubidium comparisons.

Our results can be compared directly with a number of high-pressure compression measurements on cesium, with most of these being for room temperature. This is done in Fig. 8, where our relation is extrapolated for pressures in the fcc region (pressures greater than 22.1 kbar), where it serves as a smooth reference relation against which to compare other results. As for the other alkali metals,[13] we choose Bridgman's 1948 results[5] to 40 000 kg/cm^2 as being the most consistent of his several measurements. The shape of this compression curve for cesium apparently is much different from ours, although the two relations are parallel for pressures from approximately 10 to 22 kbar, with a displacement of 0.0316 in V/V_0. This suggests an "extrapolation error" in his data analysis (an underestimate of the compression of the sample in the first 5 kbar or so) similar to those which we postulated in comparisons[13] of our sodium, potassium, and rubidium results with those in this paper,[5] but of a larger magnitude. Bridgman's curve fitting was done by hand, and with no appreciation in retrospect of the very rapid change in bulk modulus which occurs at low pressure for the most compressible (rubidium and cesium) of the alkali metals. If an extrapolation error is assumed for Bridgman's data, the agreement is very good from 10 to 22.8 kbar, his transition pressure. The volume change which he gives $(0.006 V_0)$ agrees with our result $(0.0063 V_0)$, as does our observation that the fcc phase is somewhat more compressible than the bcc phase as extrapolated through the transition. The neutron scattering results of McWhan *et al.*[12] are referenced to the V_0 which we have used (Table I), since their independent determination of V_0 (see Fig. 6) appears to be too large by 1.5% or so. Wier *et al.*[22] determined the fcc crystal structure of the high-pressure phase in an x-ray diamond-anvil-cell experiment, and also gave the lattice parameter for this phase without specifying a precise pressure. All of these results are in at least qualitative agreement with Bridgman's results[5] for the fcc phase. Bridgman's extrapolation error corresponds to an excess pressure near $P=0$ of approximately 0.5 kbar, while McWhan *et al.*'s[12] lowest pressure corresponds to 3.5 kbar rather than 5.5 kbar if our results are correct.

Makarenko, Nikolaenko, and Stishov[30] have given temperature-dependent pressure-volume results for cesium in both the liquid and the solid phases. These disagree with the present results for the solid extrapolated to their lowest temperature, 313.15 K. We would expect a thermal pressure of approximately 0.18 kbar at this temperature (see Fig. 5), while the values we calculate for their data vary from -1.4 kbar at $V/V_0=0.63$ ($P=18$ kbar) to $+0.141$ at $V/V_0=0.97$ (0.7 kbar). We found a similar disagreement of the same sign with their results for potassium,[13] although their sodium results are in excellent agreement with ours.[13] We do not know the reason for these disagreements.

The reduced form of the room-temperature equations of state for sodium, potassium, and rubidium metals (V/V_0 versus P/B_0) can be characterized by common values of the dimensionless parameters B_0' (4.18) and B_0B_0'' (-1.50) [Eq. (2)].[13] The corresponding room-temperature parameters for cesium metal are 3.87 and -2.57. This suggests that cesium is relatively more compressible than the other three metals (B_T increases more slowly with increasing pressure), with an actual calculation showing a compression ($\Delta V/V_0=1-V/V_0$) in 22 kbar which is 5% greater than would be expected using the reduced parameters associated with the other metals.

B. Lithium

The lithium metal was obtained from Alpha Chemicals and was stated to be of 99.9% purity. A mass spectrometric analysis indicated natural abundance (7.1% ^{6}Li, 92.9% ^{7}Li),[31] so with the 25 °C lattice parameter given by Pearson,[32,33] $a_0=3.510\,04\pm0.000\,41$ Å, which is based on that given by Nadler and Kempter,[34] the molar volume and density at 294 K are 13.02 cm^3 and 0.534 g/cm^3. The data reported here were taken using two 0.354-in.-diam. samples (0.2269 and 0.3392 in. long, respectively) and one 0.250-in.-diam. sample, 0.2923 in. long. The densities of these samples were determined from the sample dimensions and the mass difference between the filled and empty sample holder, where in each case the measured densities were within 0.3% of the value calculated from the x-ray data. An earlier attempt to load the samples in air resulted in erroneous densities, presumably due to oxide impurities, and these final samples were loaded into the sample holders using a dry box in the same manner as were all of the other alkali-metal samples.

The sample holders which were used for these measurements were identical to those used for the other alkali-metal experiments,[13] and they were calibrated with extreme care because of the relative incompressibility of lithium when compared with the other alkali metals. They were in part the same sample holders which were used to determine the revised equation of state of indium[15] which was used in the data analysis.

Five sets of 0.354-in. sample-holder data (four with the long sample, one with the short sample, see above) and four sets of 0.250-in. sample-holder data were used to determine the room-temperature (294 K) reference isotherm. Initial fits of the ME-2 relation [Eq. (6)] to these data were unsuccessful, since the contribution of the B_0'' term is very small. We noted, however that in contrast with the other alkali metals, our data to 20 kbar agreed very well with Bridgman's 1948 compressions[5] to 40 000 kg/cm^2, so his higher-pressure results were assumed to be valid in order to establish a fixed magnitude for B_0'', with the other parameters being determined by fits of Eq. (6) to our complete results to 20 kbar. The resulting value of B_0'', -0.02 kbar^{-1}, is "reasonable" since it gives the dimensionless parameter $B_0B_0''=-2.3$, which compares with -1.5 for sodium, potassium, and rubidium,[13] and -2.6 for cesium. The resulting parameters for the 294 K fit are given in Table III, and the deviations of three typical sets of data (one each for the long and short 0.354-in. sample holders and one for the 0.250-in. sample holder) from this relation are shown in Fig. 9. The internal consistency of the data is well within our experimental accuracy, with a maximum deviation of 5×10^{-4} and an root-mean-square deviation of 2.2×10^{-4} in V/V_0. The deviations of Bridgman's 1948 results[5] from this relation also are shown in Fig. 9 as the triangles.

The reasonableness of this procedure for determining B_0'' is indicated in Fig. 10, where differences of other room-temperature results from this (in part, extrapolated) relation are given. These include piston displacement results by Bridgman[6] to almost 100 kbar and by Vaidya, Getting, and Kennedy[35] to 40 kbar, and the high-pressure

TABLE III. Summary of the isotherm results for lithium. The data points for the isotherms are indicated in Figs. 9 and 10.

T (K)	P^* (kbar)	$(V/V_0)_{P=0}$[a]	B_0[a]	B_0[b] (kbar)	B_0'[b]	B_0''[d] (kbar^{-1})	RMSD[e] (10^{-4} in V/V_0)
350	0.92	1.0081	112.3	109.44±0.04	4.52∓0.01	−0.02	0.6
294	(0.00)	(1.0000)	(115.56)	115.56±0.33[c]	3.51∓0.06[c]	−0.02[c]	2.2
238	−0.98	0.9917	119.0	118.9±0.8	3.49∓0.13	−0.02	4.1
183	−1.76	0.9853	121.7	121.3±1.2	3.55∓0.19	−0.02	5.0
132	−2.38	0.9803	123.8	123.4±0.7	3.50∓0.11	−0.02	4.6
82	−2.94	0.9759	125.7	125.1±0.5	3.57∓0.08	−0.02	2.8
61	−3.10	0.9747	126.2	125.7±1.3	3.58∓0.21	−0.02	3.8
33	−3.13	0.9745	126.4	125.0±1.2	3.71∓0.20	−0.02	3.2
4	−3.16	0.9742	126.5	124.6±1.7	3.76∓0.27	−0.02	4.9

[a] Derived from the 294-K isotherm and P^*.

[b] Parameters derived from nonlinear least-squares fits of the ME-2 relation, Eq. (6), to the data for each isotherm. The 3σ uncertainties are those associated with the fitting procedure and do not include an allowance for systematic effects. A more detailed estimate gives minimum uncertainties of ±1 kbar for B_0, ∓0.1 for B_0'.

[c] These parameters define the reference isotherm with V_0 (294 K, $P=0$) = 13.02 cm^3/mole.

[d] B_0'' was fixed, with an uncertainty of ±0.01 kbar^{-1} corresponding to ∓0.1 for B_0'.

[e] Root-mean-square deviation.

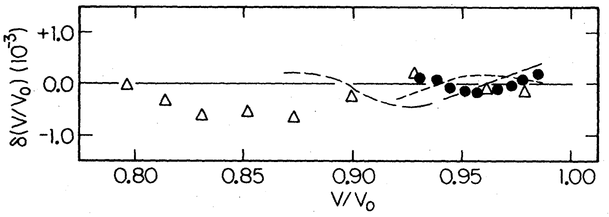

FIG. 9. Deviations of typical lithium data from the 294-K reference isotherm. The data are for the 0.250-in.-diam. sample holder (— — —), and for the long (- - - - -) and short (●●●) samples in the larger-diameter sample holder. The triangles (△) represent the deviations of Bridgman's compressions (Ref. 5) from this reference relation.

x-ray measurements of Olinger and Shaner[36] to roughly 100 kbar. The agreement with the x-ray results is excellent, as is the agreement with the work of Vaidya *et al.*,[35] if their extrapolation to $P=0$ is adjusted. The disagreement with Bridgman's very-high-pressure results is in the same direction as for the other alkali metals (see below, and Fig. 8). Table II contains smoothed values for the pressure-volume reference relation of lithium for the 294-K reference temperature and its extrapolation to the bcc-fcc transition near 70 kbar.

Figure 11 presents the results for temperatures other than 294 K in the form suggested by Eq. (1) and used for cesium in Fig. 3. The two sets of symbols at 183 and 132 K represent data taken before and after the run at 82 K, with no adjustments being made to the data. The internal consistency of the data for the two sample holders is excellent everywhere except, perhaps, at 132 K. The deviations of the results from the assumption of P^* independent of volume are nowhere greater than the equivalent of 10^{-3} in V/V_0. Table II also contains the 4-K pressure-volume relation for lithium as obtained using the 4-K parameters in Table III.

Our low-temperature results for the equation of state of sodium[13] showed inconsistencies which were interpreted in terms of the martensitic bcc-fcc transition which occurs in that metal at low temperatures. Lithium transforms spontaneously but not completely from the bcc structure to a highly-faulted hcp phase for temperatures below roughly 100 K, with both these phases being converted to an fcc phase when the sample is cold-worked at low temperature (see Refs. 21, 37, 38, and 39 for a discussion of these effects). Figure 11 does not show any suggestion of such a transition, nor of the $0.002\,V_0$ volume change due to the low-temperature portion of the bcc-fcc transition which Olinger and Shaner[36] report near 70 kbar at room temperature (see Fig. 10), and which they postulate should occur near 100 K. Possibly this transition is inhibited at high pressures and low temperature, or, more likely, it is smeared out over a range of pressures. Yet, the relatively simple behavior of the isotherms in Fig. 11 seems to preclude any effects with volume changes greater

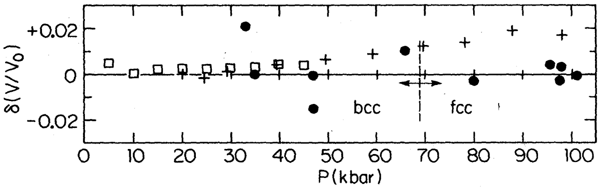

FIG. 10. Deviations of other high-pressure room-temperature data from the lithium reference relation. These include Ref. 6 (+), Ref. 35 (□), and Ref. 36 (●).

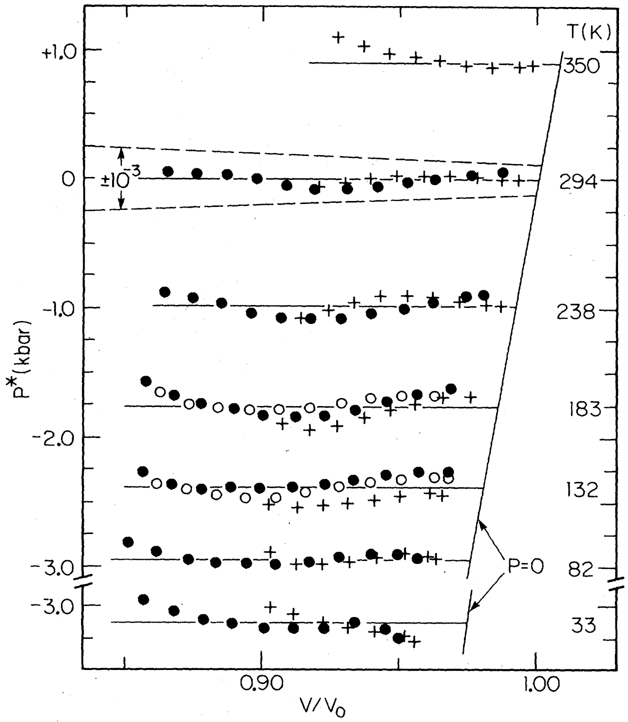

FIG. 11. Representation of the lithium data for each temperature in terms of the thermal pressure and Eq. (1). See the caption for Fig. 3.

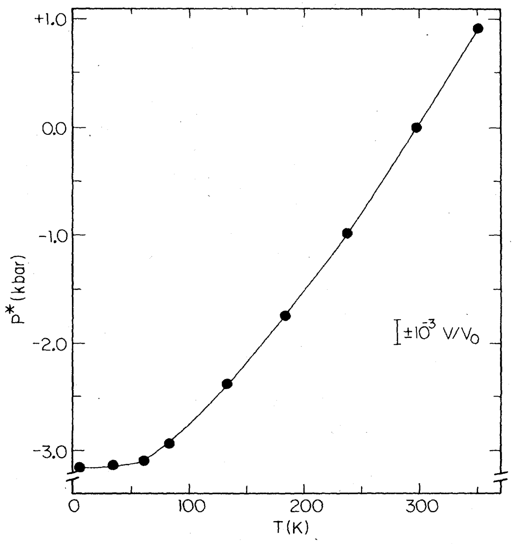

FIG. 12. Temperature dependence of the thermal pressure for lithium metal.

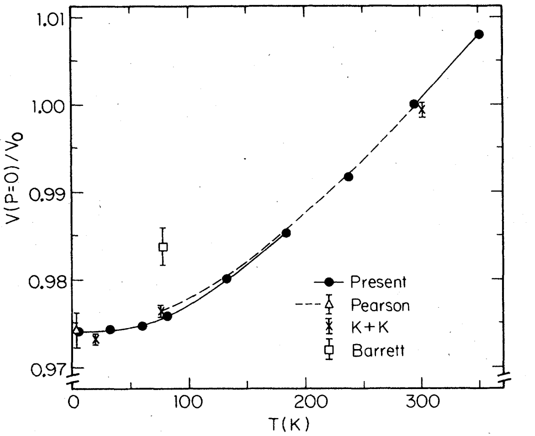

FIG. 13. Relative volume thermal expansion for lithium metal. The reference to other data are Pearson (Ref. 40), K + K (Ref. 41), and Barrett (Ref. 21).

than 0.001 V_0.

Figure 12 and Table III give the temperature dependences of the volume-independent thermal pressures P^* which are indicated by the solid lines in Fig. 11. Since Θ_∞ is approximately 400 K for lithium,[16] we do not expect to observe the same high-temperature linear variation of P^* with temperature which we obtained for the other alkali metals, since we never are in the high-temperature limit for lithium metal. We also are not able to estimate the zero-point contribution to the equation of state.

The relative volume thermal expansion at $P=0$ can be obtained from $P^*(T)$ (column 2, Table III) and the reference relation by setting $P=0$ in Eq. (1). The resulting values for $(V/V_0)_{P=0}$ are given in column 3 of Table III and are plotted in Fig. 13 for comparison with other results. Pearson[32,33] has summarized various x-ray measurements, including those of Barrett,[21] Khotkevic,[39] Pearson,[40] and Kogan and Khotkevich.[41] Most of these data are for ^{7}Li, with only a small difference from the lattice parameter of ^{6}Li (See Ref. 40). The agreement with these other data is well within our estimated accuracy of 0.001 V_0, with the exception of the single data point by Barrett[21] at 77 K. Again, the preceding discussion suggests that our samples, which undergo extreme cold-working as the data are taken, should be predominantly fcc at low temperature, but we do not observe the 0.1% to 0.2% decrease in volume which should accompany this transition, unless the slight difference from Pearson's[40] x-ray results for bcc lithium is real.

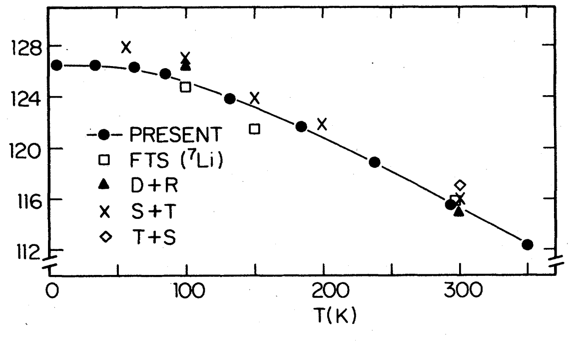

FIG. 14. Temperature dependence of the $P=0$ isothermal bulk modulus for lithium metal. The references to other data are FTS (Ref. 45), D + R (Ref. 38), S + T (Ref. 44), and T + S (Ref. 43).

The $P=0$ relative volumes in Table III were used with the reference relation to calculate the temperature-dependence of the $P=0$ isothermal bulk modulus which is given in column 4 of Table III and which is plotted in Fig. 14. Table III also contains the results of nonlinear least-squares fits of the ME-2 relation [Eq. (6)] to each of the isotherms using the $P=0$ value of V/V_0 which is given. The difference between the $P=0$ bulk moduli, which are obtained in these two different procedures, never is greater than roughly 1%, while B_0' tends to increase with decreasing temperature. Equation (1) suggests that a decrease of the order of 0.3 is to be expected on cooling to 4 K from room temperature, so a clear inconsistency exists, which may not be outside our experimental uncertainties in the low-temperature value. The effects of decreasing B_0' by 0.1 and of increasing B_0'' by 0.01 roughly compensate, and this establishes the error in limits for these parameters.

The temperature dependences of the $P=0$ elastic constants for lithium have been reported by Nash and Smith[42] for 78, 155, and 195 K, by Trivisonno and Smith[43] for room temperature in a study of Li-Mg alloys, by Slotwinski and Trivisonno[44] from 78 K to room temperature, by Day and Ruoff[38] at 100 K and room temperature, and by Felice, Trivisonno, and Scheule[45] for both ^{7}Li and ^{6}Li from 100 K to room temperature. This last study[45] shows very small isotopic effects, if any. These data, except for those of Nash and Smith[42] which were relatively imprecise, are plotted also in Fig. 14, where the agreement is very good with a scatter about our results of less than ±2%. None of the ultrasonic data extended below 78 K, the temperature below which the martensitic transformation occurs on cooling. Day and Ruoff[38] and Felice *et al.*[45] have measured the pressure dependence of the elastic constants for lithium at 300 K and lower temperatures with results which are consistent with a temperature-independent adiabatic $B_0'=3.45\pm0.1$ and an isothermal $B_0'=3.50\pm0.1$, in excellent agreement with our results.

Our directly-determined value of $(\partial P/\partial T)_V$ was used to calculate the Grüneisen parameter at $P=0$ and room temperature for each of the other alkali metals. Since this derivative cannot be determined with great precision for lithium from the data in Table III, we have used Eq. (10) and other thermodynamic data to calculate the Grüneisen parameter for lithium at 294 K. These data include Pearson's[40] value for the thermal-expansion coefficient (1.40×10^{-4} K^{-1}), the most recent ultrasonic determination of B_S (Ref. 45) (119.8 kbar) and Martin's result for C_P (Ref. 46) (24.86 J/mol K, noting that $B_T/C_V=B_S/C_P$). The resulting value of the Grüneisen parameter, 0.878, is appreciably smaller than those which we found for sodium, potassium, and rubidium,[13] 1.25, and that given above for cesium, 1.14.

López and Alonzo[26] used an energy-density-functional method to calculate $B_0=133.9$ kbar for lithium at $T=0$

and $P=0$, to be compared with our $T=0$ value of 125.5 (±1) kbar. Vaks and Trefilov[28] give $B_0=135$ kbar when using the Geldart-Taylor screening function, while Vaks *et al.*[17] calculate $B_T=116$ kbar at $P=0$ and room temperature using the same model, in good agreement with our result. These latter authors[17] also predict that B_0' will decrease from 3.79 at room temperature to 3.69 at $T=0$, somewhat in disagreement with both our results and the ultrasonic results. The low-temperature discrepancies between theory and experiment are greater for lithium than were found for the other alkali metals, and could occur because lithium does not satisfy the basic assumptions of the models which are used.

IV. DISCUSSION

The equations of state of sodium, potassium, and rubidium metals[13] are remarkably similar, since their pressure-volume isotherms differ only in values of the $P=0$ molar volumes and bulk moduli, and their Grüneisen parameters are the same to within 1%. The equations of state of lithium and cesium metals differ from these, both in the shapes of the isotherms (these solids are relatively more compressible than the others) and in the values of the Grüneisen parameters. These differences can be understood qualitatively, since, on one hand, lithium does not have a well-defined core (it has no *d* electrons) and *s*-*d* mixing effects are important for cesium. There does not appear to be a systematic effect of such mixing on the low-pressure (to 20 kbar) equation of state as the ionic mass is increased from sodium through rubidium. The question arises whether or not this mixing becomes more important as the volume decreases and thus is the cause of the various high-pressure transitions which were discussed in the Introduction to this paper.

Figure 8 was used to compare our room-temperature pressure-volume relationship and its extrapolation with existing high-pressure results for cesium, and clearly more high-pressure compression data are needed for this metal. Figure 8 also contains a comparison of our extrapolated room-temperature relation with actual high-pressure results (to 100 kbar) for sodium and rubidium. Bridgman has determined compressions for all of the alkali metals to roughly 100 kbar using a two-stage piston-displacement apparatus,[6] and in each case (see Fig. 10 for lithium: the results for potassium, which are not shown, are similar) his total compressions appear to be too small. Room-temperature diamond-anvil x-ray compression data for ru-

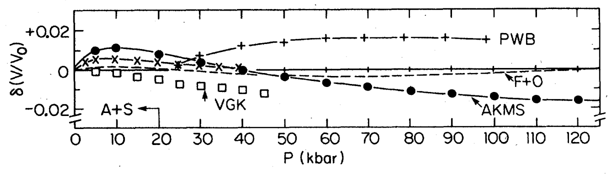

FIG. 15. Deviations of various high-pressure data for sodium from an extrapolation of the reduced reference relation of Ref. 14 (Table V) for this metal. The references to other data are A + S (Ref. 13), VGK (Ref. 35), PWB [Ref. 5 (×) and 6 (+)], AKMS (Ref. 48), and F + O (Ref. 49).

TABLE IV. Core effects in the bcc-fcc transition for the alkali metals.

	V (300 K, $P=0$) (cm³/mole)	At the bcc-fcc transition P (kbar)	V (cm³/mole)	d_{NN}[g] (Å)	$2r_I$[h] (Å)	$d_{NN}/2r_I$	$2r_{ec}$[i] (Å)	$d_{NN}/2r_{ec}$	V_{RGS}[j] (cm³/mole) $T=0$	T_{tr}
Na	23.74[a]	(1000)[c]	(8.31)[c]	(2.62)	1.96	(1.34)	2.29	(1.14)	13.43	14.02
K	45.56[a]	114±2[d]	20.7(±0.2)[f]	3.55	2.66	1.33	3.292	1.08	22.62	24.66
Rb	55.74[a]	70±2[e]	27.3(±0.3)[f]	3.89	2.96	1.31	3.691	1.05	27.18	30.0
Cs	70.0[b]	22.1[b]	42.77(±0.05)[b]	4.52	3.34	1.35	4.227	1.07	34.8	38.7

[a] Reference 14.
[b] Present results.
[c] Estimated from column 6.
[d] Reference 2.
[e] Reference 1.
[f] Calculated by extrapolation of results from Ref. 14.
[g] Nearest-neighbor (NN) distance, bcc lattice.
[h] Reference 51.
[i] Reference 28, r_{ec} denotes pseudopotential radius.
[j] Molar volumes of the corresponding rare-gas solids (RGS); neon, argon, krypton, and xenon) at $T=0$ and their triple points. See Ref. 52.

bidium[47] also are plotted in Fig. 8, in rough agreement with our extrapolation. There does not appear to be any radical change in the characteristics of this pressure-volume relation even in the region of the bcc-fcc transition.

Considerable data exist for the very-high-pressure compressions of sodium metal. These are plotted in Fig. 8 and also in more detail in Fig. 15. Bridgman's result again are high [two sets are shown, one to roughly 40 kbar (Ref. 5) and the other to roughly 100 kbar (Ref. 6), with an overlap], while, as we commented previously,[13] the results of Vaidya, Getting, and Kennedy[35] tend to give too much compression. Aleksandrov *et al.*[48] have measured the compression of sodium using diamond-anvil x-ray techniques with results which at high pressures deviate from our extrapolation by roughly the same magnitude as do Bridgman's results, but in the opposite direction. Fritz and Olinger[49] have combined x-ray compression measurements at room temperature (not shown) with shock-wave data to determine the smooth compression curve for sodium which is shown as the dashed line. The agreement to 100 kbar with our extrapolation again is quite good and indicates that no radically new physics appears as the volume is decreased.

Young and Ross[50] have used existing data to generate parameters for pseudopotential and statistical models which can be used to predict the very-high-pressure phase diagrams (melting lines, in particular) for lithium, sodium, and potassium metals. They comment that the theoretical models always were too hard for lithium and could not be made to fit the data. When compared with our extrapolated relations, their models for sodium and potassium are somewhat too soft, but within their expectations of from 3% to 5% agreement in the compressions to 100 kbar.

Olijnyk and Holzapfel[3] show that systematics exist in the relative ionic separations at which the various transitions occur in potassium, rubidium, and cesium. These can be demonstrated more quantitatively by using our extrapolated room-temperature reference relations to determine the molar volumes and, hence, ionic separations at the bcc-fcc transition where core-core interactions could be the deciding factor. The results of these calculations are given in Table IV, where it is evident that the ratio of the nearest-neighbor distance to either the ionic radius or to the pseudopotential radius at the transition pressure is the same to within a few percent for potassium, rubidium, and cesium. The pressure at which these ratios would be achieved for sodium is very large, so the analogous transition would not be observable with current techniques. Also, for reference, the molar volumes of the corresponding rare-gas solids (neon, argon, krypton, and xenon) are given in the last columns, since these each crystallize in an fcc structure, and exhibit closest packing. Again, there is a qualitative correlation between transition molar volume and the triple-point molar volumes of the corresponding rare-gas solid.

V. CONCLUSION

The equations of state of the alkali metals appear to a good first approximation to be determined by the values of B_0 and V_0 which are associated with them. The results for sodium, potassium, and rubidium, in particular, are very similar, and show no trend with increasing mass towards the somewhat softer behavior of cesium. The relationship [Eq. (9)] which we have used to represent these results can be extrapolated to provide a reference relation in each case against which other higher-pressure results can be compared. In general, these other data (see Figs. 8, 10, and 14) tend to scatter around our extrapolated relation, which suggests that in the absence of other results, the extrapolations can be used fairly reliably to 100 kbar. More high-quality data are needed at pressures above 20 kbar for potassium, rubidium, and cesium metals, in part to establish the molar volumes at which the high-pressure transitions occur.

ACKNOWLEDGMENTS

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