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Experimental compressions for sodium, potassium, and rubidium metals to 20 kbar from 4.2 to 300 K

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Experimental piston-displacement equations of state are given for sodium, potassium, and rubidium to 20 kbar for temperatures from 4 K to just below the melting line in each case. Except for sodium at high pressures, where the low-temperature bcc-hcp martensitic transition appears to cause problems, these data can be represented by a room-temperature pressure-volume reference function and a thermal pressure which is a function of temperature only. In addition, these three solids appear to obey a reduced equation of state at both 4 K and room temperature, for which V/V_0 is a common function of P/B_0. A modification of the second-order Murnaghan equation which is well behaved at large compressions is used to extrapolate these results to 40 kbar for comparison with higher-pressure, room-temperature results. These data are compared with other high-pressure equation-of-state experiments and are extrapolated to $P=0$ to obtain thermal expansions and isothermal bulk moduli, which in turn are compared with results from other measurements. These comparisons and those with theoretical calculations show, on the whole, satisfactory agreement. The elementary form for the temperature-dependent equation of state is in agreement with a previous suggestion that the Grüneisen parameter is temperature independent and is a linear function of the volume for temperatures greater than the Debye temperature. The 295-K Grüneisen parameters for these solids, as deduced from the high-pressure results, are 1.24 for sodium and potassium and 1.26 for rubidium.

I. INTRODUCTION

A continuing interest exists in an understanding from first principles of the properties of elementary metals, with the alkali metals providing the simplest applications. The present equation-of-state data for sodium, potassium, and rubidium are intended to provide reliable results for both $T=0$ and for higher temperatures against which calculations can be tested. First-principles concepts and calculations (mostly based on pseudopotentials and free-atom configurations) have been published recently by Harrison and Wills,[1] Cheung and Ashcroft,[2] and Chelikowsky.[3] Moriarty and McMahon[4] have predicted a low-temperature hcp-bcc transition in sodium at 10 kbar and also transitions at very high pressures for Mg (hcp-bcc) and Al (fcc-hcp). López and Alonzo[5] have used an energy density functional approach similar to that of Chelikowsky[3] to calculate thermodynamic properties of alkali metals, but with a single parameter which defines the pseudopotential core radius. Soma and his collaborators[6–8] also have used pseudopotential theory to study the thermodynamic properties of the alkali metals, with a number of different screening functions. Other related papers[9–13] have used a more empirical pseudopotential approach in which the objective is to compare the application of relatively elementary models of solids in a wide range of calculations to investigate systematic differences rather than to obtain results of the highest accuracy in any one instance. This work involves, for instance, an investigation of the martensitic (bcc-hcp) and bcc-fcc transitions in sodium and lithium,[11] and of similar transitions in the heavier alkali metals,[13] for which core-core interactions are introduced, as well as the temperature-dependent equation of state.[10,12] These calculations also depend on the use of appropriate screening functions. Explicit anharmonic effects have been studied using Monte Carlo techniques by Cohen and Klein for potassium[14] and Cohen *et al.*[15] for sodium, for comparison with direct anharmonic calculations by Duesbery *et al.*[16] and Glyde and Taylor,[17] respectively, which were based on similar pseudopotentials. Swanson *et al.*[18] have used an early pseudopotential model and parameters by Wallace[19] to obtain high-temperature Monte Carlo equation-of-state results for liquid and solid sodium. In addition, the prediction by Boriack and Overhauser[20] of new excitations ("phasons") in potassium metal, in particular, and the report that they may exist for rubidium[21] has stimulated experimental work and the reinterpretation of previous data,[22–24] although these effects are too subtle to be of concern for our present purposes.

An additional objective of the present work was to attempt to resolve discrepancies which exist in published experimental results, mostly near room temperature. These discrepancies often are not serious because of limitations in the accuracy with which theoretical predictions can be made, limitations which exist because of terms which have not been included, or because, for instance, it is not clear which form of the screening function should be used. In situations such as these, accurate experimental data can provide guidance. Accurate equation-of-state data for highly compressible solids such as the alkali metals also are useful to test models for the general behavior of solids at high compressions and temperatures.[25–27] Here, the pressure scaling is in terms of the bulk modulus and temperature scaling is in terms of the Debye temperature, both of which are small in magnitude for the heavier (potassium and rubidium) alkali metals.

While no pressing immediate need exists for accurate low-temperature data to compare with first-principles theory, accurate data are needed for comparison with measurements of the zero-pressure and pressure-dependent de Haas—van Alphen (dHvA) effect in potassium, rubidium, and cesium metals,[28–33] since the bulk modulus which is deduced from the dHvA measurements and a free-electron model apparently is greater than that from the direct measurements. Discrepancies also exist between high-pressure (4-kbar) (Ref. 31) and 25-bar (Ref. 32) dHvA measurements for potassium. Elliott and Datars[33] recently have measured the dHvA effect for sodium as a function of pressure and again require reliable pressure-volume results to interpret their results. The previous equation-of-state data for sodium at low temperature[34] are not sufficiently accurate to determine whether or not a discrepancy similar to that for potassium exists for this metal.

Experimental data for the high-pressure compressions of the alkali metals near room temperature were obtained by Bridgman in a series of linear compression measurements on lithium, sodium, and potassium to 20 000 kg/cm^2 (roughly 20 kbar),[35] and then with techniques similar to ours for all five metals to 40 kbar (Refs. 36 and 37) and finally to 100 kbar.[38] Vaidya, Getting, and Kennedy[39] have published room-temperature compressions for lithium, sodium, potassium, and rubidium to 45 kbar and have compared their results with those previously published, including ours for sodium,[34] potassium,[40] and lithium.[41] Stishov and his collaborators have obtained high-temperature results for sodium,[42–44] potassium,[45] and cesium[45] in both the liquid and solid states. As will be discussed below, inconsistencies exist among the various room-temperature results, as well as with $P=0$ bulk modulus determinations.

Low-temperature compression results are important for comparison with ground-state calculations, and although rather simple procedures can be used to extrapolate the room-temperature isotherms to $T=0$,[25] actual low-temperature data are needed to confirm these. We first published low-temperature compression data to 10 kbar for the alkali metals approximately 25 years ago,[46] and then expanded the pressure range to 20 kbar for sodium,[34] potassium,[40] lithium,[41] and cesium.[47] The ever-increasing accuracy of the theoretical work, as well as inconsistencies between the results from various experiments which could be serious in the future, has led us to redetermine the equations of state of sodium and potassium metals to 20 kbar from 2.4 to 300 K, and to obtain similar data for rubidium metal. We believe that these results as given below are accurate in an absolute sense to $\pm 10^{-3}$ in V/V_0, where $V_0 = V_0(T_R, P=0)$ (here, T_R is near room temperature), at all temperatures and pressures and hence, as will be described in the following, are to be preferred to other existing high-pressure results in the same temperature and pressure region.

II. EXPERIMENTAL DETAILS

The experimental apparatus and procedures which were used in these experiments are almost identical with those described previously,[34,48,49] with improvements in the quality of the data and the results arising because of relatively minor refinements and more attention to detail. In these piston-displacement experiments, a solid sample of length L_0 is placed in a cylinder, the ends of which are closed by pistons and sealing rings. The uniaxial compression which results when force is applied is transformed into a pseudohydrostatic pressure because of the small shear yield stress of these metals. Hence the relative motion of the pistons with applied force, $\Delta L = L_0 - L$, is related directly to the volume change of the sample with pressure. That is, $\Delta L_0/L_0 = \Delta V/V_0$ to a good approximation. The pistons and the cylinder are constructed from sintered tungsten carbide (typically Kennametal K-96 and K-92, respectively) because this material has a large Young's modulus and consequent small relative deformation with stress and temperature. The relative piston motion is sensed by fused quartz feeler rods which connect the ends of the pistons to a high-quality dial indicator at room temperature.

Corrections which must be made for elastic deformation of the pistons and the cylinder with applied pressure are determined by taking compression data for indium, which serves as a relatively incompressible low shear yield stress standard material.[49] We recently have used this apparatus to redetermine the equation of state for indium to 20 kbar at room temperature and at 77 K in terms of data for sodium chloride, an indium-jacketed iron sample, and lead,[50] with results which are somewhat different from before.[49] We believe now that the use of indium as a standard material introduces a systematic error of less than 10^{-3} in the minimum values of V/V_0 which we obtain. The magnitude of this sample holder distortion correction, which is known to a few percent, was at most 10% of the total observed piston motion for these measurements on sodium, potassium, and rubidium. These distortion effects are dependent both on sample length and on temperature, so care must be taken that a given sample holder is well characterized.

Friction in the press and sample holder system and shear yield stress effects in the sample material create a hysteresis which is observed when taking data on increasing and decreasing pressure. Following Bridgman,[37] we take the average pressure for a given displacement of the pistons as the true pressure. The width of the hysteresis loop (double value of friction) varies from a maximum of approximately 5% of the maximum pressure for room temperature to as much as 8% at 4.2 K, with some dependence on the sample material and sample length. These hysteresis effects limit both the minimum and the maximum pressures at which friction-corrected data can be taken.

At least two independent sets of data are taken for each sample material to provide a test for systematic errors. These experiments involve two different sample holders which have nominal bore diameters of 0.250 and 0.354 in., respectively, and hence which differ in cross-sectional area by a factor of 2. The maximum pressures which can be generated in these sample holders are roughly 24 kbar for that with the smaller diameter (limited by piston strength and durability on pressure cycling) and 14 kbar for that with the larger diameter, which is limited by the maximum force generated by our 10-ton press. The friction-limited minimum pressures at which each of these can be used are from 1 to 2 kbar while the corresponding useful maximum pressures are 13 and 20 kbar, respectively. Among other factors, these limits depend on sample material, sample length, and temperature. As will be shown below, data taken with each of these sample holders generally agree to better than 10^{-3} in V/V_0, and often to better than 5×10^{-4} in V/V_0. This is about what would be expected from the usable sensitivity of our measuring system, 10^{-4} in., and the typical 0.3-in. length of our samples, as well as the accuracy with which these lengths can be determined.

The distortion- and friction-corrected experimental results for a given alkali-metal sample consist of a set of P-V isotherms for temperatures from 4.2 to roughly 20 K below the triple point. These results define an equation of state for the sample from which the pressure and temperature dependences of both the thermal expansion and the bulk modulus can be determined. Even though great care is taken in changing temperatures to prevent jarring of the measuring system, occasional discontinuities of 1 or 2×10^{-4} in. are observed in direct plots of dial indicator reading versus temperature at constant pressure. These discontinuities usually are the same for all pressures, and are assumed to arise due to shifts in the measuring system, and a correction is applied systematically to the data indicated.

Table I gives the details of the samples, including sizes and sources, which were used to obtain the data which are reported below. It also contains the extreme of the friction (one-half of the width of the hysteresis loop) which was observed for each series of data. The combination of sample mass, length, and actual sample holder diameter can be used to obtain a room-temperature sample density which provides a check on their consistency. Because of the sample containment configuration, a significant pressure could be locked into the sample when the sample holder and pistons are removed from the press, and, indeed, the ends of the sample need not be flat, but could be convex. Hence when inconsistencies were apparent between the calculated densities and published values, we have chosen to use sample lengths which are calculated from the sample mass and the sample holder diameter rather than the measured lengths. The accuracy of the assumed absolute room-temperature lengths is probably 0.2% or so, and should introduce a systematic uncertainty of this magnitude in the relative compressions, $\Delta L/L_0$, for a given sample. Each lot of sample material was obtained in a sealed ampoule which was opened and handled only in an inert-gas atmosphere in a dry box. Sample purities generally were the highest available commercially, or better than 99.9%.

Finally, it must be emphasized that these data are of necessity highly smoothed because of the hysteresis or friction correction. In addition, the sample holder distortion correction must be determined in a secondary experiment. No convenient procedure exists for presenting "raw" or "actual" data, so the symbols which represent data in the following figures should be connected by a smooth curve to represent a smooth relationship for measurements at a given temperature. As was stated above, the magnitudes of the various approximations and corrections are different for samples of different lengths and for measurements with sample holders of different diameter, so the agreement between the results obtained with the two sample holders for each material provides the ultimate test of the reliability of our overall results.

III. REPRESENTATION OF THE DATA

The experimental results which have been obtained in these experiments are presented graphically in Sec. IV in terms of differences from an assumed form for the tem-

TABLE I. Details of the samples used in these experiments. References to the standard densities are given in the presentation of the results for each sample.

	Mass (g)	Length at T_R (in.)		Density at T_R (g/cm^3)		Friction[a] (kbar)		Source
		Meas.	Used	Expt.	Std.	4 K	295 K	
Na-1[b]	0.2179	0.3049	0.3049	0.9692	0.9680	1.65	0.94	Alfa
Na-2[c]	0.5818	0.3711	0.3711	0.9688	0.9680	1.00	0.39	Products
K-1[b]			0.2847[d]			1.29		
K-2[c]	0.5802	0.4126	0.4145	0.8620	0.8583	0.77	0.44	Alfa
K-3[b]	0.1596	0.2296	0.2303	0.8607	0.8583	0.75[e]	0.61	Products
Rb-1[b]	0.3081	0.2481	0.2480	1.538	1.534	0.91	0.60	Fairmont
Rb-2[c]	0.9816	0.3991	0.3961	1.527	1.534	1.07	0.47	Chemical

[a] One-half maximum hysteresis.

[b] 0.250-in. sample holder.

[c] 0.354-in. sample holder.

[d] Normalized at 77 K to K-2, K-3.

[e] 77 K. Data for K-3 only for $T\geq77$ K.

perature and pressure dependence for the equation of state. This mode of presentation, which is described below, has a sensitivity which is consistent with the precision and accuracy of the data, and allows a direct comparison to be made between the results which are obtained in the various measurements for each sample material.

The free energy of a solid can be written to a first approximation as the sum of static lattice, zero-point, and thermal contributions,[25]

$$F(V,T)=U_{\mathrm{SL}}(V)+U_Z(V)+F^*(V,T)\ , \tag{1}$$

from which the equation of state is obtained as the sum of similar terms,

$$P(V,T)=-(\partial F/\partial V)_T$$

$$=P_{\mathrm{SL}}(V)+P_Z(V)+P_0^*(V,T) \tag{2a}$$

$$=P_0(V)+P_0^*(V,T)\ . \tag{2b}$$

Here F^* and P_0^* are zero at $T=0$ and $P_0(V)$ is the equation of state at $T=0$.

The thermal free energy in the quasiharmonic Mie-Grüneisen approximation has the form $F^*(V,T)=T\Phi[T/\Theta(V)]$, with the volume dependence contained in $\Theta(V)$, and with U_Z also a function of Θ. In this model,

$$P(V,T)=P_{\mathrm{SL}}(V)+\gamma U_Z/V+\gamma U^*/V \tag{3}$$

with U^* the temperature-dependent internal energy and $\gamma=-d\ln\Theta/d\ln V$. At high temperatures ($T>\Theta_\infty$, where Θ_∞ is a limiting high-temperature value of the characteristic temperature), $U^*=3RT-U_Z$, and the zero-point contributions to F^* and the equation of state disappear for the classical solid. Equation (3) then reduces to

$$P(V,T)=P_{\mathrm{SL}}(V)+(3RT/V)\gamma_\infty\ , \tag{4}$$

if explicit electronic or anharmonic terms are neglected. A comparison with Eqs. (2) gives in this limit

$$P_0^*(V,T)=(3RT/V)\gamma_\infty-P_Z\ , \tag{5}$$

with $(\partial P^*/\partial T)_V=3R\gamma_\infty/V$. We have argued previously[25] that, experimentally, the isothermal bulk modulus shows only a very small intrinsic temperature dependence, and since $(\partial B_T/\partial T)_V=-\partial(\partial P/\partial\ln V)/\partial T-V\partial(\partial P/\partial T)_V/\partial V$, $(\partial P/\partial T)_V$ must have a very small (effectively zero) volume dependence as well as a very small temperature dependence [Eq. (5)]. Hence $(\partial P/\partial T)_V=(\partial P^*/\partial T)_V$ should be independent of both V and T, and

$$P_0^*(V,T)=P(V,T)-P_0(V)$$

$$=bT-P_Z(V)\ ,\quad T>\Theta_\infty\ . \tag{6}$$

An extension of these arguments suggests that P_Z also should be volume independent.

In the Debye approximation, $U_Z=\frac{9}{8}R\Theta_\infty$, so

$$P_Z(V)=(\gamma_\infty/V)\tfrac{9}{8}R\Theta_\infty(V)\ . \tag{7}$$

For sodium, for instance, $\gamma_\infty=1.2$, $V=23.743$ cm^3/mole, and $\Theta_\infty=167$ K,[18] so $P_Z=0.80$ kbar. At low temperatures, P^* is small and has a temperature dependence which is similar to that of the Debye function for the internal energy [see Eq. (3)].

Our reference sample lengths (and hence molar volumes) are established at room temperature T_R and the room-temperature isotherm is determined most accurately by a number of runs for different samples. So, for convenience in presenting our experimental results, the thermal pressure is redefined as

$$P(V,T)=P^*(V,T)+P(V,T_R)\ . \tag{8}$$

The relationship between P^* as defined here and P_0^* as defined in Eq. (2) is

$$P^*=P_0^*-[P(V,T_R)-P_0(V)]\ . \tag{9}$$

Since, in practice, the isotherms at $T=0$ and at T_R are roughly parallel and the approximation of Eq. (6) applies at high temperatures, Eq. (9) can be written as

$$P^*=P^*(T=0)-P_Z+bT\ , \tag{10}$$

with the term in the square brackets in Eq. (9), equal to $P^*(T=0)=-P_0^*(T_R)$. The terms $P^*(T=0)$, P_Z, and $b=(\partial P^*/\partial T)_V$ in Eq. (10) are expected to be roughly independent of volume when determined for $T>\Theta_\infty$. Stishov, Makarenko, and Nikolaenko[27] have used considerations similar to those above to analyze their high-temperature data for liquid and solid alkali metals.

Figure 1 gives the smooth room-temperature pressure-volume relations for sodium, potassium, and rubidium in order to provide a frame of reference for the discussion of the results which is given in the following section. The 4.2-K isotherm is given also for sodium and rubidium (the behavior of potassium is similar) to demonstrate qualitatively that P^*, the horizontal separation between the isotherms in Fig. 1 for a given metal, is approximately independent of volume.

The procedure which will be used to present the data for each metal will be based on Eq. (8). An analytical form will be established for the room-temperature isotherm, $P_{\mathrm{calc}}(V/V_0,T_R)$, which will represent these data as closely as possible. This expression then will be used in

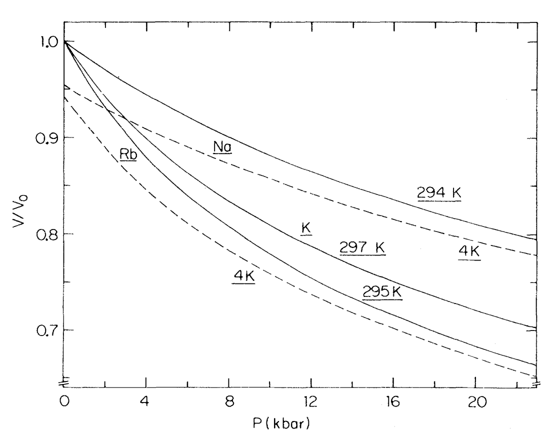

FIG. 1. Relative room-temperature compressions for sodium, potassium, and rubidium. Low-temperature (4-K) compressions are given for sodium and rubidium to illustrate the magnitude of thermal effects.

Eq. (8) to calculate a thermal pressure $P^*(V/V_0,T)$ for each experimental pressure P and relative volume V/V_0 along each isotherm

$$P^*(V/V_0,T)=P-P_{\text{calc}}(V/V_0,T_R)\ . \tag{11}$$

Here, $V_0=V_0(P=0,T_R)$, since we assume that data for a given material which are taken for samples of different lengths and measured in different sample holders can be correlated most directly by a normalization to the measured $P=0$ length at room temperature T_R;

$$L(T,P)/L_0(T_R,P=0)=V(T,P)/V_0(T_R,P=0)\ .$$

The data for each isotherm now may be displayed as a plot of $P^*(V/V_0)$, which is expected to vary slowly with volume. Since P^* typically is a few kbar and our maximum usable pressure is 20 kbar, a gain in sensitivity of approximately an order of magnitude is achieved using this procedure. The sodium results, which will be discussed in detail in the next section, are presented in this form in Fig. 2. The dashed lines on either side of the 294-K isotherm show how P^* changes due to $\pm 10^{-3}$ in V/V_0.

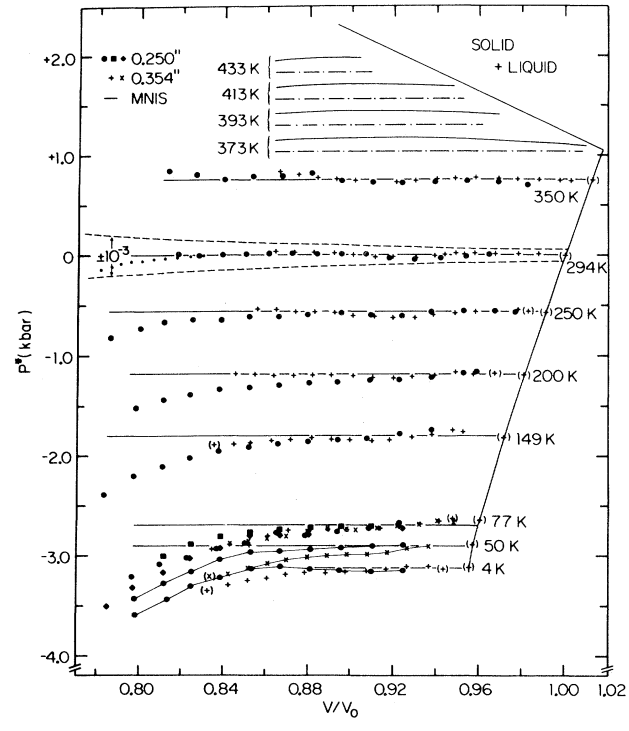

FIG. 2. Present results for sodium, as represented by Eq. (11). The solid symbols refer to data taken with the smaller diameter and the crosses to data taken with the larger diameter sample holders. The dashed lines are the equivalent in pressure of $\pm 10^{-3}$ in V/V_0. The horizontal solid lines at the top of the figure are the smooth results of Makarenko *et al.* (MNIS, Ref. 44) while the dotted-dashed lines represent an extrapolation of the present results to the same temperatures. The isotherms terminate at the right side of the figure either at the sublimation line (below 371 K) or at the melting line (above 371 K).

This type of representation also contains in the slopes of the isotherms the difference between the actual (smooth) isothermal bulk moduli along an isotherm and those calculated from the reference equation,

$$B_{T\,\text{calc}}(V/V_0,T_R)=-(\partial P_{\text{calc}}/\partial \ln V)_T\ .$$

This follows from Eq. (11) as

$$\Delta B_T=\frac{-V}{V_0}\left[\frac{\partial P^*}{\partial(V/V_0)}\right]_T$$

$$=B_T(V/V_0,T)-B_{T\,\text{calc}}(V/V_0,T_R)\ . \tag{12}$$

If P^* were independent of V/V_0 along an isotherm, the bulk modulus along that isotherm would be given by the reference equation, with no intrinsic temperature dependence. This would be the case for sodium if all of the isotherms in Fig. 2 were parallel and horizontal. Differences of the bulk moduli from the reference values appear as slopes of the $P^*(V/V_0)$ relations along an isotherm, and the actual bulk moduli can be calculated from Eq. (12). For instance, the slopes of the 250-, 200-, and 149-K isotherms at $V/V_0=0.8$ in Fig. 2 correspond to a bulk modulus which is 8 kbar less than $B_T=152$ kbar as calculated from the room-temperature reference equation for this volume.

Various functional forms have been used to represent pressure-volume results, all of which should be regarded as empirical, even though they may result from "general" theoretical considerations. Macdonald and Powell[51] have compared a number of these and have established criteria for establishing a "preferred" representation for a set of data. They conclude that the "extrapolation of a given model-parameter value set beyond the range of data on which it is based is always dangerous." Hence our choice of a specific representation to provide $P_{\text{calc}}(V/V_0,T_R)$ for our room-temperature isotherms must be regarded as arbitrary.

We have chosen to use primarily the relation which is referred to as the second-order Murnaghan relation (ME-2), and which is based on a Taylor's expansion of the isothermal bulk modulus in terms of the pressure,[51]

$$B_T(P,T)=B_0(T)+B_0'(T)P+\tfrac{1}{2}B_0''(T)P^2+\cdots \tag{13}$$

or, in reduced form,

$$B_T(P,T)=B_0(T)[1+B_0'(P/B_0)+\tfrac{1}{2}B_0B_0''(P/B_0)^2+\cdots]\ . \tag{13$'$}$$

In these relations, the parameters $B_0'(T)=B_0'=(\partial B_T/\partial P)_T$ and $B_0''=(\partial^2 B_T/\partial P^2)_T$, are evaluated at $P=0$. Equation (13) can be integrated to give[51,52]

$$P=2B_0\left[\Gamma\left[\frac{(V_0/V)^\Gamma+1}{(V_0/V)^\Gamma-1}\right]-B_0'\right]^{-1} \tag{14}$$

or

$$\frac{V}{V_0}=\left[\frac{2+(B_0'-\Gamma)(P/B_0)}{2+(B_0'+\Gamma)(P/B_0)}\right]^{1/\Gamma}, \tag{15}$$

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

$$P=(B_0/B_0')[(V_0/V)^{B_0'}-1] \tag{16}$$

and

$$V/V_0=[B_0'(P/B_0)+1]^{-(1/B_0')} \; . \tag{17}$$

The ME-1 relations are extremely useful, and it is only for relatively compressible solids, such as the alkali metals, or for very high pressures that the effects of the B_0'' term are important.[51]

The major advantages of the relations based on Eq. (13) are that they represent experimental data well, and can be expressed in closed form either to give $P(V/V_0)$ [Eq. (14)] or V [Eq. (15)]. Their disadvantage is that fits to experimental data can be achieved only by trial and error or by the use of nonlinear least-squares methods. The most important nonsystematic uncertainties in the present experiment occur in the measurement of length changes and are pressure independent. Hence, Eqs. (15) or (17) have been fit to the data with a minimization of $\sum (V_i - V_{\mathrm{calc}})^2$ for the experimental pressures.

Another useful representation is given by the Birch relation,[40,41,47,51]

$$P=y^5\sum_{n=1}^{N}A_n(y^2-1)^n \tag{18}$$

with $y^3=(V_0/V)$, $B_0=2A_1/3$, $B_0'=(4+4A_2/3A_1)$, and[51]

$$B_0''=(-1/6A_1)[\,16(A_2/A_1)^2+12(A_2/A_1)+35-24(A_3/A_1)] \; .$$

Note that $B_0''\neq 0$ even when A_2 and A_3 both are zero. Linear least-squares methods can be used to fit this relation to experimental data, with an interative procedure[48] required to minimize $\sum (V_i-V_{\mathrm{calc}})^2=\sum V_i^2(P_i-P_{\mathrm{calc}})^2/B_T(V_i)^2$.

A final problem is characteristic of piston-displacement data. Because of the hysteresis effects, the experimental length change versus pressure relation must be extrapolated from a minimum pressure to $P=0$ in order to obtain absolute compressions as a function of pressure. This problem is important primarily for the room-temperature reference isotherms. Our procedure is to use the $P=0$ room-temperature sample length together with either Eq. (15) or (17) to obtain a set of coefficients for this relation which will give sample length changes as a function of pressure which are identical with those found experimentally for an appreciable part of the lower pressure range. These parameters, preferably, will represent all of the data, but at the very least the data below 10 kbar. This relation then gives the required extrapolation to $P=0$ from the lowest reliable data point. The true test is that a fit of the equation to all of the data results in a representation which does not show systematic deviations at low pressure. The extrapolations obtained by this procedure depend only slightly on the form of the equation which is used.

This need to extrapolate the data to $P=0$ from a minimum pressure is not addressed very well in most previous reports on piston-displacement determinations of pressure-volume isotherms, and only occasionally is the extrapolation procedure mentioned. The relatively large curvature in the low-pressure region of an isotherm for compressible materials [see Eq. (13′), in which B_0' typically is close to 5] causes graphical methods or power series in the pressure to be inappropriate. Hence we have chosen to make comparisons between our data and most other data only in the region of the published pressure-volume relation which is based on actual data, and to use this comparison to redetermine an extrapolation to $P=0$ for these previous results. The differences between our extrapolations and those which are reported often are quite significant, and are appreciably greater than the estimated experimental uncertainties.

IV. RESULTS AND DISCUSSION

The present experimental results for sodium, potassium, and rubidium will be presented and compared with other results in the following sections. Our actual pressure-volume-temperature data are compared with high-pressure results when available, while $P=0$ thermal expansions and bulk moduli, which are obtained by extrapolation to $P=0$, will be compared with direct determinations of these quantities. No detailed comparison will be made with our previous work to 10 kbar for these metals,[46] nor with our earlier results for sodium[34] and potassium.[40] We have attempted to reanalyze these earlier results in terms of the most recent equation of state for indium,[50] and to include better extrapolations to $P=0$. In no instance do we find a significant difference (± 0.002 in V/V_0 at most) from the present results when the same thermal expansions are used, and it is quite clear that the quality of the present data is much higher than that for these earlier experiments. We also have compared our room-temperature isotherms with those of Bridgman[36–38] and in almost every case find that his reported extrapolation of the high-pressure results to $P=0$ shows a volume change in the first few (up to 5) kbar which is too small, as is shown by a lack of consistency with Eq. (15). An extrapolation correction brings Bridgman's linear compression results[35] in agreement with ours for sodium and potassium. His early piston-displacement results[36] (1938) generally are not consistent with ours, but in each case his final[37] (1948) piston-displacement results to approximately 40 kbar can be made to agree with ours to 20 kbar to $\pm 1.5\times 10^{-3}$ in V/V_0 by an adjustment of the extrapolation. Our room-temperature isotherms for sodium, potassium, and rubidium are compared with these 1948 Bridgman results[37] and also with those of Vaidya *et al.*[39] later in this section and suggested high-pressure equations of state to 40 kbar are presented for these metals.

A. Sodium

Data were taken for a number of sodium samples from different sources and with different sample holder configurations. The differences between these generally were small (10^{-3} or so in V/V_0 at the highest pressures) and

TABLE II. Summary of the isotherm results for sodium. The data points for the isotherms are indicated in Figs. 2 and 3.

T (K)	P^* (kbar)	$(V/V_0)_{P=0}$	B_0 (kbar) a	B_0 (kbar) b	B_0' ^{b}	B_0'' (kbar^{-1})^b	RMSD (10−4) in V/V_0)^b
350	$+0.76$	1.0130	57.4	57.3 ± 0.1	4.18 ∓ 0.02		2.23
294	(0)	(1.0000)		60.6 ± 0.2^c	4.125 ∓ 0.04^c		2.10^c
	(0)	(1.0000)		60.28 ± 0.4	4.27 ∓ 0.15	-0.021 ± 0.02	1.83
250	-0.58	0.9907	63.0	63.2 ± 0.04	4.06 ∓ 0.1		2.81
200	-1.18^5	0.9814	65.5	65.7 ± 0.4	3.99 ∓ 0.006		3.60
149	-1.80	0.9724	68.0	68.4 ± 0.4	3.93 ∓ 0.06		1.89
77	-2.69	0.9601	71.7	72.3 ± 0.1	3.78 ∓ 0.02		2.65
50	-2.89	0.9574	72.5	72.4 ± 0.8	3.91 ∓ 0.15		3.68
4	-3.10	0.9546	73.4	73.6 ± 0.6	3.90 ∓ 0.12		3.10
				73.4 ± 0.5^d	3.92 ∓ 0.1^d		2.11^d

[a] $P=0$ bulk moduli derived from the 294-K isotherm and P^*.

[b] Parameters derived from nonlinear least-squares fits of Eq. (17) to the data for each isotherm. Equation (15) was used for the alternate 294-K fit for which B_0'' is given. The 3σ uncertainties are those associated with the fitting procedure, and do not include an allowance for systematic effects. A more qualitative assessment gives minimum uncertainties of ±0.6 kbar for B_0 and ∓0.1 for B_0'.

[c] These parameters define the room-temperature reference isotherm, with $V_0(294\text{ K}, P=0)=23.743$ cm^3/mole (Ref. 53).

[d] Two "bad" points (Fig. 2, near 0.86) deleted.

the results which are presented below are those for the final and most extensive series of runs for the final sample in each of the two sample holders. Details of these samples as well as typical values for the hysteresis effects are given in Table I. The densities which are given for sodium metal for these samples agree very well with the value, 0.9680 g/cm^3, which can be calculated from the 25 °C x-ray lattice parameter of Feder and Charbnau,[53] $a_0=4.288\,60\pm0.000\,12$ Å, and which corresponds to a molar volume of 23.750±0.002 cm^3. The corresponding molar volume for our 294-K reference isotherm is 23.743 cm^3.

The first-order Murnaghan relation ME-1 [Eq. (17)] was fitted to the four sets of 294-K data (three runs to 20 kbar, one run to 13 kbar), with the coefficients and rms deviation (RMSD) given in Table II. Figure 3 gives the differences between the actual data for these four runs and this reference relation. A fit of the second-order Murnaghan relation ME-2 [Eq. (15)] to these results (see Table II for the coefficients) gave an almost identical representation for $V/V_0>0.82$, and tended to represent the data better at higher pressures, as is shown by the dotted line in Fig. 3. The uncertainties given for these coefficients in Table II, and also for all other coefficients in this paper, represent 99% confidence limits (3σ, where σ is the standard deviation) for the fits to the data by nonlinear least-squares methods, and do not include possible systematic uncertainties. The ME-1 [Eq. (17)] and ME-2 [Eq. (15)]

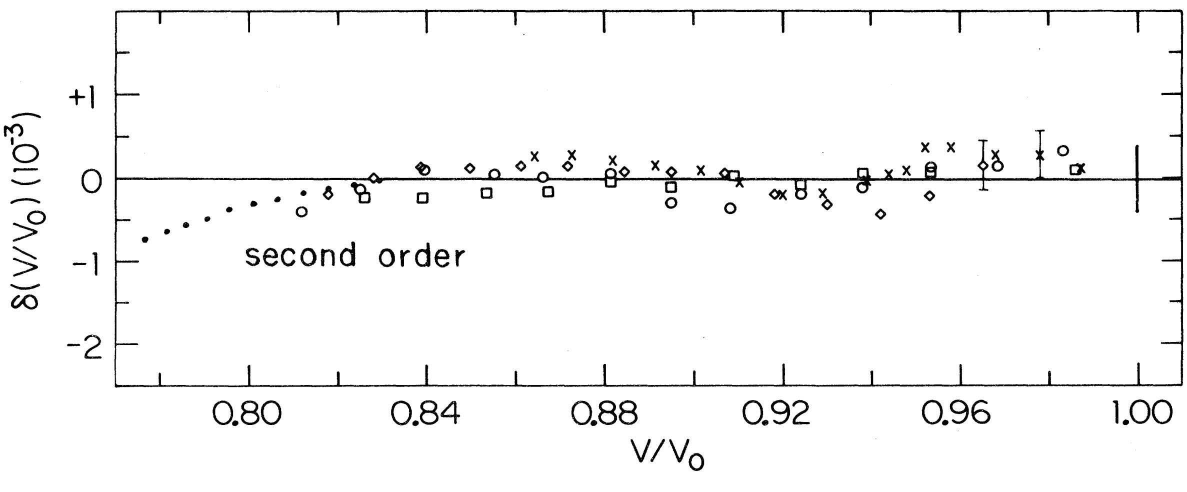

FIG. 3. Deviations of the actual 294-K data for sodium from the ME-1 reference relation (Table II). The open symbols represent data from three different small sample holder runs, the crosses data from a large sample holder run. The dotted line for $V/V_0<0.82$ is the difference between the ME-2 and ME-1 relations (Table II).

parameters agree within these limits and the improvement which is obtained with this additional parameter does not appear to warrant its inclusion. Footnote b of Table II describes more realistic uncertainties. The high-pressure ultrasonic results of Daniels[54] and of Martinson[55] give $B_0' \sim 3.8$, in better agreement with the ME-1 [Eq. (17)] fit than that for the ME-2 [Eq. (15)].

The data for all eight isotherms for sodium for each series of runs are plotted in Fig. 2 in terms of the thermal pressure P^*, using Eq. (11) and P_{calc} as defined in Table II for the ME-1 relation [Eq. (17)]. The dashed line on each side of $P^*=0$ (294 K) represents the temperature-independent variation in P^* which corresponds to an uncertainty of $\pm 10^{-3}$ in V/V_0. The dotted curve at 294 K corresponds as in Fig. 3 to the use of the ME-2 relation [Eq. (15)]. The agreement between the two independent sets of data is excellent at all temperatures, with no adjustable parameters used even to establish the 294-K isotherm. The volume dependence of P^* is small, and is in the direction which would suggest that higher-order terms should have been included in the reference equation. In no instance does this isothermal volume dependence of P^* correspond to more than 1% (2×10^{-3}) of the total compression which is observed in 20 kbar (see Fig. 1). The slopes of the low-temperature isotherms suggest that the bulk moduli which are calculated from our room-temperature reference equation for a given value of V/V_0 are approximately 5% larger than is found experimentally at high pressure and low temperature [see Eq. (12)]. This difference is approximately 5 times larger than would be expected from the use of the ME-2 relation (Table II), Eq. (15), as a reference equation.

The thermal pressure P^* is roughly constant for a given isotherm for $V/V_0 > 0.85$, and these "low-pressure" values of P^* are given in Table II and are plotted versus temperature in Fig. 4. Equation (10) suggests a linear P^* vs T relation for $T > \Theta_\infty = 167$ K, and our four data points above this temperature give (in kbar)

$$P^* = -3.805 + 0.01299T\ , \quad T > 167 \text{ K}\ . \tag{19}$$

Here, the difference between $P^*(4\text{K}) = -3.10$ kbar from Table II and the $T=0$ intercept of Eq. (19) gives $P_Z = 0.70$ kbar, in reasonable agreement with the estimate of 0.80 kbar from Eq. (7).

The normal ($P=0$) thermal expansion for sodium, $V(T,P=0)/V(294\text{ K}, P=0)$, can be obtained from Fig. 2 by setting $P=0$ in Eq. (11) to obtain $P^* = -P_{\text{calc}}$, and then using the 294-K ME-1 parameters from Table II in Eq. (17). An uncertainty of ± 0.04 kbar in P_∞^* will introduce an uncertainty of ± 0.0005 in the $(V/V_0)_{P=0}$'s which are given. The results of this procedure are given in column 3 of Table II, and are plotted in Fig. 5 for comparison with previous results. The most extensive data are those of Siegel and Quimby[56] (quartz pushrod dilatometry from 80 to 290 K), with x-ray results from Barrett[57] which have been normalized to the room-temperature results of Feder and Charbnau,[53] and other more recent data from room temperature to the melting point by Adelhart *et al.*[58] and Sullivan and Weymouth.[59] Ritter, Fritsch, and Lüscher[60] have shown that fairly large impurity con-

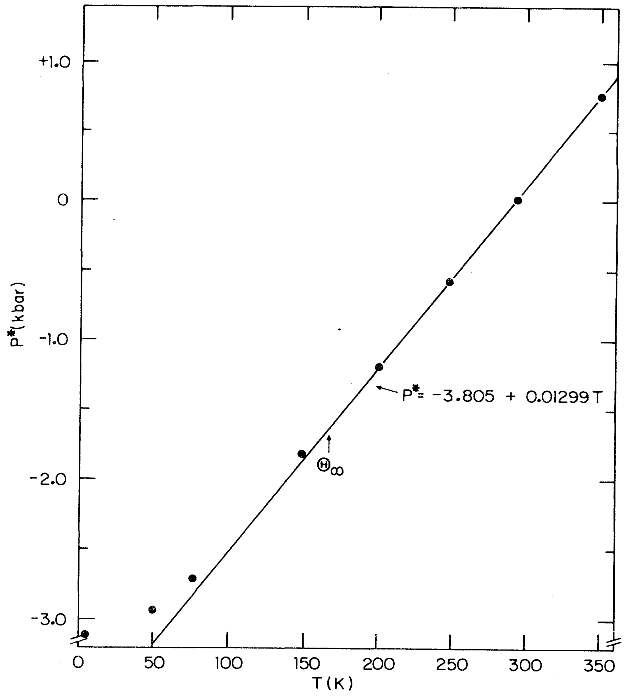

FIG. 4. Thermal pressures for sodium (the solid lines in Fig. 2) as a function of temperature.

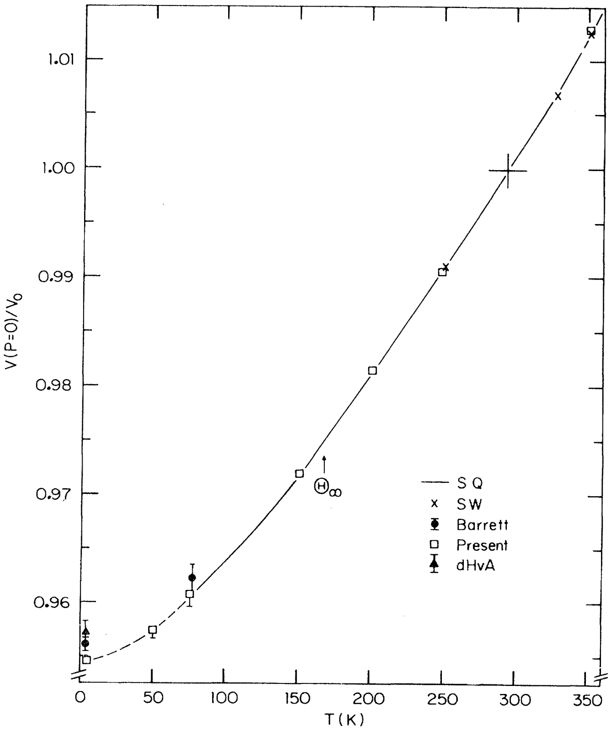

FIG. 5. $P=0$ thermal expansion of sodium. The symbols refer to published data as follows: SQ, Ref. 56; SW, Ref. 59; Barrett, Ref. 57; dHvA, Ref. 33. The error bars on the present low-temperature points represent ambiguities in the extrapolation of P^* to $P=0$ (see Fig. 2).

centrations (up to 500 ppm) have no effect on the high-temperature thermal expansivity of sodium. The low-temperature results are complicated by the existence of the bcc to hcp martensitic transition which has been investigated in some detail by Barrett,[57] Martin,[61] and Stedman.[62] Barrett,[57] initially, and then Basinski and Verdini,[63] have found that the volume of the hcp phase is greater than that of the bcc phase by approximately 0.3%. The $P=0$ dHvA results of Elliott and Datars[33] give, in the free-electron model, a $T=0$ molar volume of 22.730 ± 0.023 cm^3 for bcc sodium, which is plotted as 0.9573 ± 0.001 in Fig. 5, and is larger than our volume by 0.003. If our results were to have been affected by the bcc-hcp martensitic transition, we should have obtained a $T=0$ molar volume which is greater than the dHvA value, not smaller. If, indeed, our 4-K volume is wrong and our sample is predominantly hcp (Barrett[57] found that this phase was stabilized by cold work, and our samples are heavily cold worked with a volume change of 20% or more at constant area), the excessive softness of our 4-K isotherm at high pressures could be due to the occurrence over a range of pressure of the hcp-bcc transition which is predicted by Moriarty and McMahon.[4] Barrett[57] also suggests that the martensitic transition should appear (or could be retained) at temperatures up to 200 K when, again, severe cold work is done on a sample. But such a transition should make the isotherms appear to be harder at high pressures, and for temperatures below 200 K this is opposite to what we observe. The excellent agreement between the present results for potassium (as obtained with the same sample holders and procedures) and direct determinations of the volume changes (see Sec. IV B) gives confidence that Fig. 5 shows real, but possibly uninterpretable, effects.

As was stated at the beginning of this section, no comparison will be made with our previous high-pressure equation-of-state data for sodium,[34,46] nor with much of Bridgman's work, although a comparison with his 1948 results[37] and those of Vaidya *et al.*[39] will be given in Sec. IV D to establish a suggested extrapolation of our results to 40 kbar. A detailed comparison will be made at this point, however, with the equation of state results of Makarenko *et al.*[44,45] for liquid and solid sodium at temperatures above the triple point, 371 K, since the general features of their results are very similar to those we find. The comparison is important since they used a quite different method to obtain equivalent data. They give only smooth results in the form of pressures for a number of evenly spaced temperatures (20-K intervals) and molar volumes (0.5-cm^3 intervals) for temperatures from 373.15 to 493.15 K. We have used a 294-K molar volume of 23.743 cm^3 and our 294-K ME-1 relation to present their results for the solid as the solid lines in Fig. 2 which show that P^* is a function of temperature only. The magnitudes of their thermal pressures, however, are systematically larger by about 0.1 kbar than those given by an extrapolation of Eq. (19) (Fig. 4), and which are shown as the dotted-dashed lines in Fig. 2. This difference can be associated with a 0.12% difference in the reference molar volumes for the two experiments. The present values are related directly to the 26 °C value of Feder and Charbnau,[53] while Makarenko *et al.*[44] refer their results to a molar volume of 24.967 cm^3 for the liquid at 400 K and atmospheric pressure. Their stated uncertainty in molar volume is 0.15% or 0.03 cm^3, and is consistent with the difference in Fig. 2. If their molar volumes are reduced by 0.12%, the slight volume dependence of P^* along the isotherms in Fig. 2 disappears.

Linear relations, as suggested by Eq. (4), were fitted to the pressure-temperature values which Makarenko *et al.*[44,45] give for the various isochores for the solid. The slopes of these relations were the same for all molar volumes, with $(\partial P^*/\partial T)_V=0.0133$ kbar/K, in good agreement with our result (Fig. 4), 0.0130 kbar/K. The other, volume-dependent, parameter for these fits corresponds to $P_{\rm SL}(V)$ in Eq. (4), and should differ from the $T=0$ (effectively, 4 K) pressure-volume relation by $P_Z(V)$. A calculation of this difference, $P_0(V/V_0)-P_{\rm SL}(V/V_0)$, gives an almost constant value for $P_z=0.67\pm0.01$ kbar or 0.79 ± 0.02 kbar, with the first obtained by assuming consistency between our molar volumes and those of Makarenko *et al.*,[44] and the second by assuming their molar volumes to be too large by 0.12%. The results are consistent with $P_Z=0.70$ as deduced from our $P^*(T)$ relation, Eq. (19). The agreement is satisfactory since both our result and that deduced from the high-temperature data involve extrapolations to $T=0$ which are from one to two times the extent of the data which are fit by least squares. This additional consistency gives added confidence in the reliability of the two sets of data.

Ivanov *et al.*[42] have studied the molar volumes of sodium along the melting line and have given the data for the solid which are plotted in Fig. 2 as the boundary of the solid state. The complete results of Makarenko *et al.*[44] and of Ivanov *et al.*[42] for liquid and solid sodium are plotted in Fig. 6. The decrease in the slopes of the isotherms with increasing volume on this plot corresponds, as Makarenko *et al.*[44] point out, to a bulk modulus for the liquid which is identical to that of the solid (and to that given by our 294-K reference relation) for $V/V_0=0.88$,

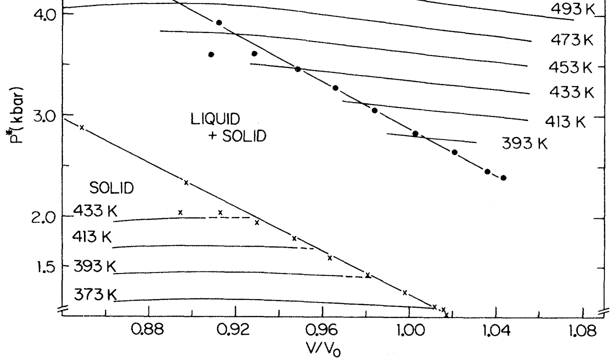

FIG. 6. Representation of the results of Makarenko *et al.* (Ref. 44) for sodium as in Fig. 2, with ● and × representing data reported by Ivanov *et al.* (Ref. 42) for the molar volumes of the liquid and solid, respectively, along the melting curve.

and which is about 3.5% greater than that for the solid for $V/V_0 > 0.95$ [see Eq. (12)]. The $P^*(V/V_0)$ relations along the melting line appear to be roughly linear and parallel for the liquid and the solid, with a constant separation of approximately 1.7 kbar at constant volume. There appears to be some inconsistency between the melting-line data for the liquid as given by Ivanov *et al.*[42] and the smoothed equation-of-state results of Makarenko *et al.*,[44] but this does not seriously affect the discussion given above.

An analysis which assumes a linear pressure-temperature relationship along the isochores for the liquid[44] is not as satisfactory as for the solid. The derivative $(\partial P^*/\partial T)_V$ is slightly volume dependent, and varies from 0.0146 kbar/K at 20 cm^3/mole to 0.0130 kbar/K at 25 cm^3/mole. $P_{\text{SL}}^{\text{liq}}(V)$ as derived from the $T=0$ intercepts of the isochores does not show a constant difference from our 4-K isotherm, but gives $P_0(V/V_0)-P_{\text{Sl}}^{\text{liq}}(V/V_0)$ varying from -0.46 kbar (-0.31 kbar) at 20.5 cm^3/mole to -0.80 kbar (-0.75 kbar) at 25 cm^3/mole (the quantities in the parentheses are for volumes adjusted by 0.12%), with a monotonic but nonuniform volume dependence. The difference in this quantity for the liquid and for the solid ($P_{\text{SL}}^{\text{liq}} - P_{\text{SL}}^{\text{sol}} \sim 1.2$ kbar) is an effective pressure which is associated with the liquid state. This is different from 1.7-kbar difference in Fig. 6 because $(\partial P^*/\partial T)_V$ is different for the liquid and the solid. Stishov *et al.*[27] have carried out a more detailed analysis of these data which is based on the Debye model, and conclude that P_{SL} for the solid is consistent with that for the liquid.

The extrapolation of our isotherm data to $P=0$ gives a $P=0$ bulk modulus which can be compared with more direct ultrasonic and bulk determinations. Two procedures have been used to obtain these results. First, if P^* is a function of temperature only (as Fig. 2 indicates for $V/V_0 > 0.85$), the bulk modulus is a function of volume only [Eq. (12)] and the $P=0$ value can be obtained by setting $P=0$ in Eq. (11) and using the resulting $P_{\text{calc}}=-P^*$ in Eq. (13) with 294-K parameters from Table II. These values are given in column 4 of Table II, where an uncertainty of ± 0.04 kbar in P^* will introduce an uncertainty of ± 0.2 kbar at most in B_T. Second, an ME-1 relation can be fitted to the isotherm data using the assumed value for V/V_0 at $P=0$ for that temperature. The resulting parameters B_0 and B_0' are given in columns 5 and 6 of Table II, together with the resulting RMSD in terms of V/V_0. No significant decrease in the RMSD was obtained when the $P=0$ value of V/V_0 was changed slightly. The agreement between the methods for obtaining B_0 is very satisfactory.

These results for the $P=0$ isothermal bulk modulus are plotted in Fig. 7, together with a summary of other results. Ultrasonic measurements were made by Diederich and Trivisonno[64] (77–95 K), Fritsch, Geipel, and Prasetyo[65] (20–95 °C), Daniels[54] (300 K), and Martinson[55] (77–300 K) to obtain elastic constants and, hence adiabatic bulk moduli which have been converted to isothermal quantities for the present comparisons using[25]

$$B_T = B_S/(1+\beta\gamma T) \tag{20}$$

with γ, the Grüneisen parameter (roughly temperature independent, $\gamma=1.2$) (Refs. 66 and 67) and β, the volume thermal expansion coefficient.[56–59,66] The agreement with Diederich and Trivisonno's[64] results is excellent, and with Daniels's[54] value is satisfactory. Fritsch *et al.*[65] quote rather large experimental uncertainties (see Fig. 7), so it is not clear that a disagreement exists. Martinson[55] indicates quite small uncertainties, however, and no obvious explanation exists for the roughly 6% systematic differences between his data and ours, and, indeed, between his data and those of Diederich and Trivisonno.[64] Ho and Ruoff[68] have published an independent analysis of Martinson's data which agrees with the smooth relation in Fig. 7 to better than 1%. The other comparison is with the direct isothermal bulk modulus determinations of Fritsch, Nehman, Korpiun, and Lüscher.[66] These show appreciable scatter at low temperature (Fig. 7) but more consistency near room temperature. They tend to agree with the results of Martinson[55] and, near room temperature, with those of Fritsch *et al.*,[65] with the error bars on the crosses in Fig. 7 indicating their stated uncertainties. It is intriguing that their results agree with ours at 350 K, and show a temperature dependence which is unexpected.

Additional support for the correctness of the present results for the $P=0$ bulk modulus near room temperature comes from Fig. 2 through the very close correlation between our results and those of Makarenko *et al.*[44] This correlation suggests that the bulk modulus has only a small, if any, explicit temperature dependence, and that the value of B_T for $V/V_0=1.000$ should be at most 1.5% greater than that given by our room-temperature reference isotherm. This difference becomes negligible if their molar volumes are decreased by 0.12%, as was suggested earlier.

The pressure dependence of the elastic constants for sodium has been measured by Daniels[54] (to 2 kbar at 300 K) and by Martinson[55] (at pressures to 9 kbar from 77 to 300 K). Daniels's[54] value for $(\partial B_S/\partial P)_T=3.60$ is somewhat smaller than the roughly temperature-independent values of Martinson,[55] 3.8. B_0' for the adiabatic bulk modulus always is less than that for the isothermal bulk

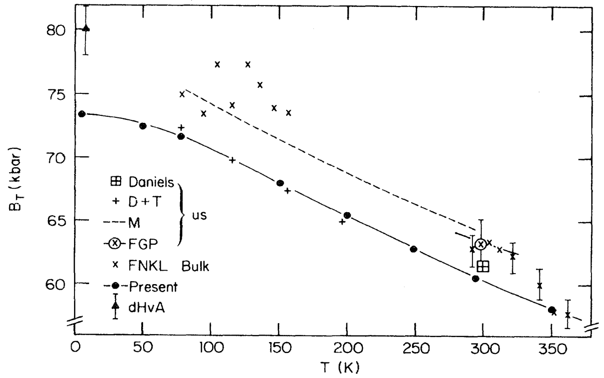

FIG. 7. Temperature dependence of the $P=0$ isothermal bulk modulus for sodium. The symbols refer to published results as follows: Daniels, Ref. 54; DT, Ref. 64; M, Ref. 55; FGP, Ref. 65; FNKL, Ref. 66; dHvA, Ref. 33.

modulus (by roughly 0.1 for sodium),[25] so a minor discrepancy appears to exist between our room-temperature results (Table II, $B_0' = 4.125 \pm 0.10$) and those from ultrasonic measurements. The temperature dependence of B_0' in Table II can be interpreted in terms of the variation with temperature of the point about which the expansion of Eq. (13) is carried out. If P^* is a function of temperature only, $P^* = -P_{\text{calc}}$ at $P=0$, and

$$B_0'[P^*(T)] = B_0'(T_R) - P^*(T) B_0'' . \tag{21}$$

A fit of this expression to the sodium coefficients in Table II gives

$$B_0' = 4.11 + 0.0857 P^* \tag{22}$$

(with P^* in kbar). The agreement with the experimental values is within the stated uncertainties (0.1 or larger). While the resulting value for $B_0'' = -0.086 \text{ kbar}^{-1}$ clearly is inconsistent with the 294-K ME-2 fit in Table II, the change in B_0' from 294 K to $T=0$ (-0.27) is just outside our estimated uncertainties, so this discrepancy perhaps is not real.

Elliott and Datars[33] have measured the average change of the dHvA frequency for sodium in 4 kbar as $(1/F_0) dF/dP = (0.76 \pm 0.02) \times 10^{-2} \text{ kbar}^{-1}$. This differs by about 9% from the average change in 4 kbar that we would predict from our data and the free-electron model $(F \sim V^{-2/3})$, $d[(V_0/V)^{2/3}]/dP = (0.834 \pm 0.01) \times 10^{-2}$ kbar^{-1}. This difference can be expressed alternatively in terms of the equivalent $P=0$ bulk modulus which would correspond to the dHvA results if the shapes of the dHvA and equation-of-state relations were directly related, $B_0 = 80 \pm 2$ kbar, to be compared with $B_0 = 73.5$ kbar in Table II.

A number of different calculations of the thermodynamic properties of sodium have appeared in recent years. A major problem in comparing actual data with many of these is that the theoretical results are displayed graphically in single-column figures, from which it it difficult to extract actual values with more than a few percent accuracy. At this level, our actual equation-of-state results for sodium metal agree with the calculations of Soma[8] and Vaks and his collaborators.[9,10] More meaningful comparisons can be made with explicit values of the $P=0$ bulk moduli [Eq. (21) has been used to convert theoretical adiabatic to isothermal values for $T>0$] and their pressure derivatives, B_0', when they are given in these papers.

The present $T=0$ (or 4-K) value of $B_0 = 73.5 \pm 0.6$ kbar is in agreement with the calculations of Chelikowsky[3] (72±13 kbar), López and Alonzo[5] (75.1 kbar), Vaks and Trefilov[9] (74.4 kbar), and Glyde and Taylor[17] (73.0 kbar), with the first[3] being a "no-parameter" calculation, two[5,17] assuming the $T=0$ equilibrium lattice parameter, and the fourth,[9] assuming as well as the elastic constant C_{44}. Soma,[8] who also assumes only the $T=0$ equilibrium lattice parameter, and Vaks and Trefilov[9] show that B_0 is very sensitive to the form of the screening function which is used, with, for the only function which is common to both parameters, $B_0 = 69.9$ kbar for Soma[8] and 76.2 kbar from Vaks and Trefilov.[9] This suggests a significant difference between these one-parameter[8] and two-parameter[9] theories. The López and Alonzo[5] calculation used a density functional method to include screening effects, while the values quoted initially in this paragraph from Vaks and Trefilov[9] and Glyde and Taylor[17] each were obtained using the Geldart and Taylor[69] screening function. Soma and Ueda[6] give $B_0' = 3.21$ while Vaks and Trefilov[9] give $B_0' = 3.75$ (almost independent of the screening function). The difference is similar to that found for B_0, with the latter much closer to the $T=0$ experimental value, $B_0' = 3.9 \pm 0.1$. Vaks *et al.*[12] calculate that for the adiabatic bulk modulus, B_0' varies from 4.07 and 3.85 for temperatures from the melting point to $T=0$ (or, roughly, from 4.2 to 3.85 for the isothermal bulk modulus[25]), in agreement with the results in Table II.

Glyde and Taylor[17] give adiabatic bulk moduli for four temperatures and use the experimental lattice parameters at those temperatures. These results, when converted to B_T, are 2% larger than ours at 90 and 160 K, 5% larger at 293 K, and identical with our (extrapolated) 361-K value. The two highest-temperature values would coincide with the Fritsch *et al.*[65,66] data in Fig. 7. Their 90-K value is in excellent agreement with that obtained at 90 K with a more refined pseudopotential.[70] The Monte Carlo calculation of Cohen *et al.*,[15] which uses a more exact potential, gave an adiabatic bulk modulus at 293 K which, when converted to B_T by Eq. (20), was within 0.5% of our result, although the 361-K value was 5% smaller than our (extrapolated) value for 361 K. Inconsistencies in the initial calculation for 361 K were removed by slight modifications to the potential, and this discrepancy now is less than 1.5% (see Ref. 15, second paper). They also calculate a Grueniesen parameter for each temperature which is slightly larger than experimental values. Vaks *et al.*[12] also have calculated the temperature dependence of the $P=0$ bulk modulus, and on a plot of B_T vs T show agreement with the results of Glyde and Taylor[17] at 90 K and then a linear behavior in temperature to 360 K, passing just between the latter's results at 293 and 361 K. The indirect agreement with our results seems to be quite satisfactory. They also give a calculation of $P_Z = 0.86$ kbar,[12] which is in reasonable agreement with our estimate [Eq. (7), 0.80 kbar], our results [Eq. (19), 0.70 kbar], the values which were deduced from the results of Makarenko *et al.*[44] (0.67 or 0.79 kbar, dependent on the reference volume) and that which was calculated by Straub and Wallace[71] (0.80 kbar) from a lattice-dynamics calculation.

Rather extensive Monte Carlo results have been presented by Swanson *et al.*[18] for three isochores which correspond, roughly, to the triple point, the equilibrium volume at $T=0$, and a somewhat higher pressure. These calculations extend from $T=0$ to the liquid at 670 K and are based on a static lattice pseudopotential model by Wallace[19] for which the three parameters are determined by the binding energy, and the $T=0$ equilibrium volume and bulk moduli, ignoring zero-point energy effects. This model gives $B_0' = 3.64$ at $T=0$. Their derivative $(\partial P^*/\partial T)_V$ is larger than ours for the solid by approximately 10%, while for the liquid it is 10% smaller than that from the data of Makarenko *et al.*[44] This large difference (20% or so) between $(\partial P^*/\partial T)_V$ for the liquid

TABLE III. Summary of the isotherm results for potassium. The data points for the isotherms are indicated in Figs. 8 and 9.

T (K)	P^* (kbar)	$(V/V_0)_{P=0}$ a	b	B_0 (kbar) c	d	B_0' [d]	B_0'' (kbar^{-1})[d]	RMSD (10^{-4} in V/V_0)
297	(0)	(1.0000)	(1.0000)		29.63±0.01	4.208∓0.003	−0.048±0.001	2.23
238	−0.40	0.9869	0.9867	31.3	31.5 ±0.1	4.16 ∓0.04	−0.050±0.01	2.85
182.5	-0.77^5	0.9755	0.9754	32.9	32.8 ±0.4	4.22 ∓0.15	−0.055±0.03	2.59
132	−1.12	0.9655	0.9660	34.3	34.6 ±0.02	4.03 ∓0.01	−0.039±0.002	3.27
77	−1.46	0.9562	0.9564	35.7	35.8 ±0.1	4.05 ∓0.06	−0.040±0.01	2.25
60	−1.58	0.9530	0.9537	36.2	36.6 ±0.1	3.92 ∓0.03	−0.027±0.01	2.91
40	−1.68	0.9504	0.9509	36.6	37.01±0.04	3.89 ∓0.01	−0.016±0.002	1.71
20	-1.72^5	0.9492	0.9490	36.8	36.93±0.03	4.05 ∓0.01	−0.037±0.002	1.55
4	−1.76	0.9483	0.9485	37.0	37.03±0.06	4.06 ∓0.03	−0.041±0.006	1.47

[a] Present results. V_0 (297 K, $P=0$) = 45.557 cm^3/mole (Refs. 72 and 73).

[b] Schouten and Swenson (Ref. 72).

[c] $P=0$ bulk moduli derived from the 297-K isotherm and P^*.

[d] Parameters derived from nonlinear least-squares fits to the data of Eq. (15) 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 assessment gives minimum uncertainties of ±0.4 kbar in B_0, ∓0.15 in B_0', and ±0.01 kbar^{-1} in B_0''. The 297-K parameters define the reference relation.

and the solid has the opposite sign when compared with experiment, and much too large a magnitude. Swanson *et al.*[18] obtain a pressure difference between the liquid and solid phases at constant volume of approximately 1.5 kbar, while that from experiment[44] is 1.7 kbar, also roughly independent of volume.

B. Potassium

The results reported below for potassium were obtained in three sets of runs, one with 0.354-in.- and two with 0.250-in.-diam sample holders. One set (the most recent) of the small-diameter sample holder data extended from 297 to 77 K, while the second, which was normalized to these at 77 K, was used for temperatures to 4 K. The details of these samples are given in Table I, where the sample lengths have been calculated from the masses of the samples and a 297-K molar volume of 45.557 cm^3,[72,73] which corresponds to a density of 0.8583 g/cm^3. In contrast with the sodium results, the measured sample lengths and masses gave densities which are systematically too large by approximately 0.5%, presumably due to the small bulk modulus for this material and a large frozen-in pressure when the pistons were removed. Potassium was the most difficult of the three materials to work with, and had a very marked tendency to bond to the sample holder and sealing assembly while the sample holder was being loaded.

A fit of the ME-2 relation [Eq. (15)] to the 297-K results gives the parameters in Table III. The use of the ME-1 relation [Eq. (17)] is far less satisfactory, with an RMSD which is about twice as large as for the ME-2 rela-

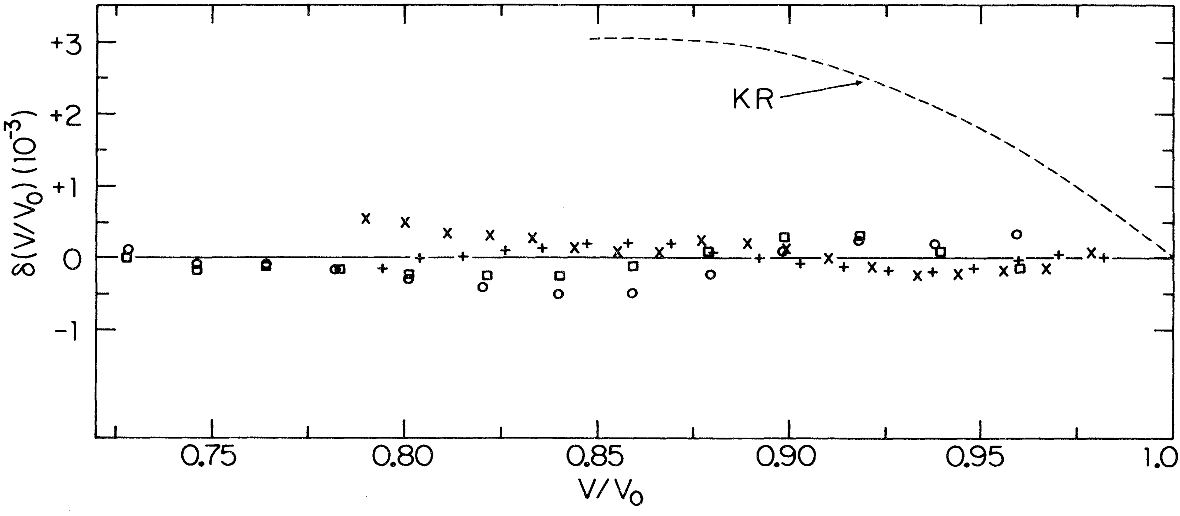

FIG. 8. Deviations of the actual 297-K potassium data from the reference relation (Table III). The symbols are as in Fig. 3. The dashed line KR refers to smooth results from Ref. 77 (see the text).

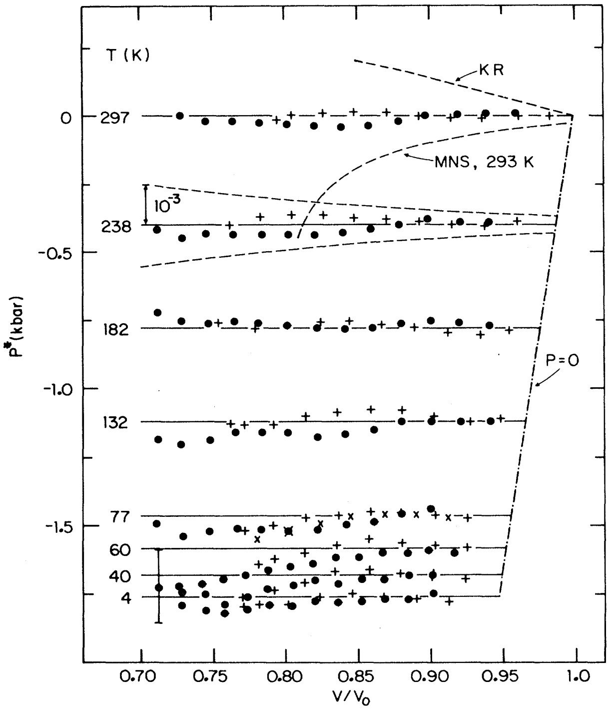

FIG. 9. Representation of the potassium data in terms of thermal pressures. See Fig. 2. KR refers to data from Ref. 77, while MNS refers to Ref. 45.

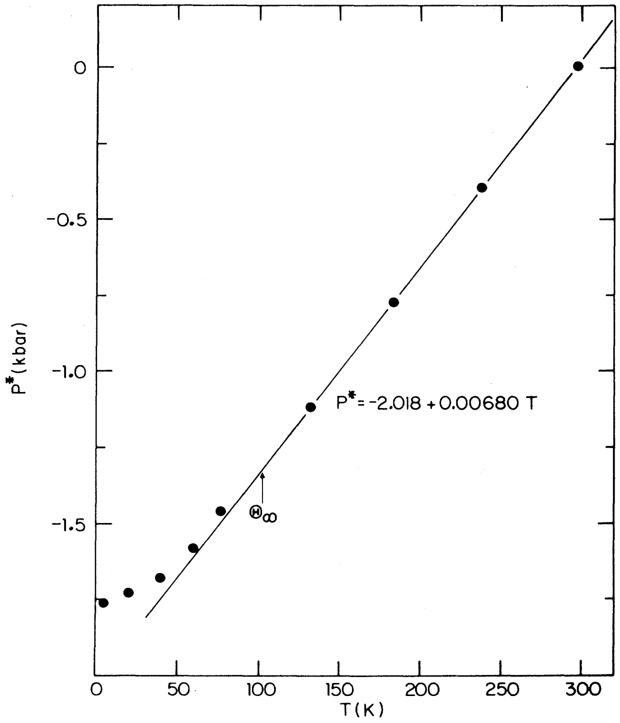

FIG. 10. Thermal pressures for potassium (the solid lines in Fig. 9) as a function of temperature.

tion. Figure 8 shows the deviations of our four 297-K runs (two for each sample holder) from this ME-2 fit, while Fig. 9 presents all of the data for potassium in the same form as for sodium (Fig. 2), with the exception of the 20-K isotherm which is very similar to that at 4 K. The agreement between the data taken for the two sample holders is excellent at all temperatures (generally better than $\pm 10^{-3}$ in V/V_0, see the dashed lines on either side of the 238-K isotherm), with none of the isotherms differing from $P^* = \text{const}$ by more than this. The 60-K isotherm contains the maximum discrepancy at high pressure which is, as the error bar at $V/V_0 = 0.71$ shows, just 10^{-3}.

The thermal pressures P^* from Fig. 9 are given in Table III, and are plotted in Fig. 10. The four thermal pressures for $T > \Theta_\infty = 102.5$ K (Ref. 67) can be represented by (in kbar)

$$P^* = -2.018 + 0.00680T \; . \tag{23}$$

This result and $P^*(4\text{ K}) = -1.76$ kbar give [see Eqs. (10) and (19)] $P_Z = 0.26$ kbar, in excellent agreement with that which can be estimated from Eq. (3), 0.25 kbar, using $\theta_\infty = 102.5$ K (Ref. 67) and $\gamma_\infty = 1.19$.[72]

The relative thermal expansions at $P = 0$ as calculated from P^* and the 297-K ME-2 relations are given in column 3 of Table III, for comparison with the direct linear expansivity results of Schouten and Swenson[72] in column 4. The agreement is excellent and well within the estimated, roughly $\pm 5 \times 10^{-4}$, uncertainties in each experiment. This corresponds 1% of the total volume change to 4 K for the direct measurement, and to an uncertainty of P^* of ± 0.02 kbar for the present experiment. Schouten and Swenson[72] give a discussion of previous molar volume determinations, and show excellent agreement between their 4-K molar volume (43.212 ± 0.02 cm^2) and that obtained from $P = 0$ dHvA measurements and the free-electron model.

As for sodium the $P = 0$ bulk moduli given in column 5 of Table III were obtained from P^* and $P_{\text{calc}}(T_R, V/V_0)$ while those in column 6 were obtained from fits of Eq. (15) to the combined data for the two sample holders for each isotherm. The agreement is very satisfactory. The uncertainties in the parameters for these fits generally (with one or two exceptions) are quite small and imply a uniqueness which may not be real. Separate fits which were made to the data for the individual sample holders show deviations from the values given in Table III which are appreciably greater than the uncertainties given in this table, and suggest more realistic uncertainties of ± 0.4 kbar in B_0, ± 0.1 in B_0'.

As for sodium, B_0' is expected to be a linear function of P^* and a fit of the results in Table III to Eq. (21) gives

$$B_0' = 4.214 + 0.141P^* \; , \tag{24}$$

with a maximum deviation at 40 K of -0.1, and $B_0'' = -0.141$ kbar^{-1}. This, as for sodium, is inconsistent with the actual isotherm fits for which B_0'' (column 8) is, within experimental uncertainties, roughly constant at -0.042 ± 0.01 kbar^{-1} if the 40 K isotherm is excluded. Similar independent analyses of the 0.250-in. and 0.354-in. data for each isotherm show systematically larger magnitudes of B_0' and B_0'' for the 0.354-in. data than are shown in Table III. The 0.250-in. analyses, on the other hand, are consistent with a temperature-independent $B_0'=4.04\pm0.05$, while $B_0''=-0.034\pm0.01$, again excluding the 40-K isotherm. It appears that the weighting of the more numerous and more precise 0.354-in. data which, however, cover a smaller range of compressions, has a large effect on the validity of Eq. (24) for potassium, and that the "inconsistency" is within experimental uncertainties. This is reflected in our estimated uncertainty of ±0.15 for B_0' (Table III).

The $P=0$ bulk moduli are plotted in Fig. 11 where they are compared with other experimental determinations. Adiabatic bulk moduli have been converted to isothermal values using Eq. (20) and summarized $P=0$ thermodynamic results.[72] Smith and Smith[74] in a 1.3-kbar high-pressure experiment at 22 °C give $P=0$ elastic constant results and pressure derivatives. A $+1\%$ correction should be made to their elastic constants to reflect the most recent 295-K density,[72] and with a revised conversion to B_T we obtain $B_T=31.0\pm0.6$ kbar at 295 K, to be compared with their value of 30.4 kbar. Their determination of $\partial B_S/\partial P_T=3.97$ probably is reliable to 2% or 3%, and reflects an average over 1.3 kbar. Our result for B_0'' (-0.05 kbar^{-1}) suggests that the $P=0$ value of B_0' which is needed for comparison with our results should be larger by approximately 0.03 to account for the averaging, while the conversion to B_T will result in an additional increase of 0.1 or so.[25] Hence we estimate for their experiment that $B_0'=4.1\pm0.1$ at 295 K, in good agreement with the results in Table III (4.21 ± 0.1). Fritsch and Bube[75] have measured the temperature dependence of the elastic constants of potassium near room temperature, with their 297-K value, $B_T=30.7\pm0.6$ kbar, and its temperature dependence plotted in Fig. 11. Marquardt and Trivisonno[76] have carried out the only low-temperature elastic constant measurements for potassium with the results shown in Fig. 11. They made a number of measurements on various samples for temperatures from 77 to 197 K with very consistent results, and then only one set of measurements on a different crystal at 77 and 4.2 K. We have chosen to normalize the second results to the other data at 77 K and hence give a 4-K value for B_T which is somewhat larger (37.55 vs 36.55 kbar) than usually is quoted for their results. These two values bracket our result. Schouten and Swenson[72] quote a single direct isothermal bulk modulus determination by Kroeger for 175 K which also is plotted in Fig. 11.

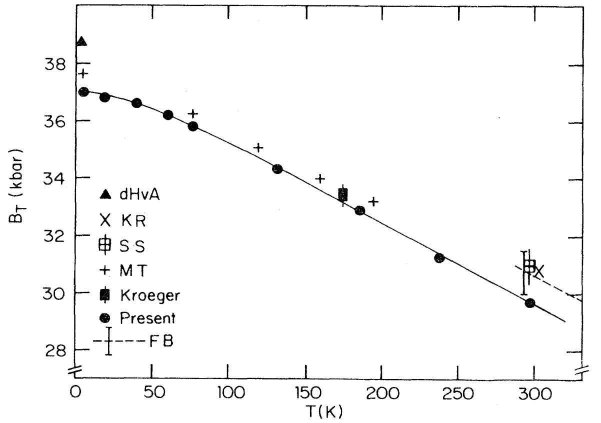

FIG. 11. Temperature dependence of the $P=0$ isothermal bulk modulus for potassium. The symbols refer to published results as follows: KR, Ref. 77; SS, Ref. 74; MT, Ref. 76; Kroeger, Ref. 72; FB, Ref. 75; dHvA, Ref. 32.

Templeton[32] has derived $B_0=38.8\pm0.2$ kbar from a free-electron analysis of the pressure dependence (to 25 bar) of his dHvA measurements, and this value is clearly larger than those obtained from direct measurements. Elliot and Datars reanalyzed the 4-kbar dHvA results of Altounian and Datars[31] and give an equivalent $P=0$ value for B_0 which, when using the present form for the 4-K P-V relation for potassium, is 40.9 ± 1.2 kbar. They are not able to understand this difference between their results and those of Templeton.[32]

The above discussion included the results of only two[74,75] of a number of room-temperature experiments on potassium metal. Makarenko *et al.*[45] have reported results for potassium which were obtained in the same apparatus as were those discussed in Sec. IV A for sodium (Figs. 2 and 6). Figure 9 gives only their smooth 293-K isotherm, and shows clearly that it is inconsistent with the present results by approximately 3×10^{-3} in V/V_0 at $V/V_0=0.82$, or 9 kbar. Their other isotherms show similar behavior. Kim and Ruoff[77] have reported very precise measurements at 28.58 °C (301.73 K) of the linear isothermal compression in 7 kbar of a 1-m-long sample of potassium metal. They present the results of several different analyses of these data, with an ME-2 analysis which is similar to that we use giving $B_0=30.86$ kbar, $B_0'=4.09$, and $B_0''=-0.073$ kbar^{-1}. We have used these parameters in Eqs. (15) and (16) together with a thermal pressure difference of 0.035 kbar [Eq. (23)] to obtain the differences between their smoothed results and ours at 297 K which are given as the smooth KR curves in Figs. 8 and 9. The deviations must have different shapes in these two representations since in Fig. 8 the relative volume differences are plotted at the same experimental pressure while in Fig. 9 the pressure differences are plotted for the same values of V/V_0. Kim and Ruoff[77] give no details of the experimental procedure nor do they give the actual experimental data. We have been informed[78] that friction effects were assumed to be small and that data were taken only on increasing pressure. The representation in Fig. 8 suggests length changes that are too small until $V/V_0\sim0.9$ ($P\sim4$ kbar), after which they are identical with our results. This would be characteristic of a friction force which increased with increasing pressure and became constant at a maximum value equivalent to 0.2 kbar or so (see Fig. 9). The alternative interpretation from Fig. 9 is that the absolute bulk modulus determinations in the two experiments differ by a constant magnitude of roughly 1.5 kbar (5% at $P=0$) as given by the slope of the KR curve in this figure. We have tested our apparatus and methods in some detail, including measurements in terms of NaCl, iron, and indium,[50] and can find no indications of potential systematic errors greater than one-fifth of those in V/V_0 which are shown in Figs. 8 and 9. The much less precise ultrasonic measurements of Smith and Smith[74] and of Fritsch and Bube[75] lend support to the Kim and Ruoff result, while the general agreement which we show with other results at low temperature for potassium (Fig. 11) indicates that our total uncertainty should not be greater than 1% or 2%. Other room-temperature results (see Sec. IV D below) are not sufficiently accurate to assist in resolving this discrepancy.

The comparison with theoretical calculations is much the same as for sodium, but possibly not as satisfactory. Chelikowsky's no-parameter calculation[3] gives B_0 -47 ± 8.5 kbar at $T=0$, to be compared with $B_0=37.0\pm0.4$ from Table III. López and Alonzo[5] in a one-parameter calculation give 33.8 kbar, while the one-parameter calculations by Soma and his collaborators[6–8] do not appear to give realistic results. Vaks and Trefilov[9] give $B_0=37.1$ kbar for their two-parameter calculation which uses the Geldart-Taylor[69] screening function. Duesbery, Glyde, and Taylor[16] in a one-parameter calculation with this same screening function obtain a comparable result for 9.2 K, 37.2 kbar. Vaks and Trefilov[9] also give B_0' varying from 3.75 to 3.79 at $T=0$, dependent on the screening function. Vaks *et al.*[12] have calculated the temperature dependence of the $P=0$ bulk modulus to 300 K, as well as a decrease in B_0' from 4.10 at 295 K to 3.84 at 0 K and $P_Z=0.25$ kbar, all in good agreement with our results. Duesbery *et al.*[16] also calculate the temperature dependence of B_S at $P=0$, with $B_T=26$ kbar at 300 K, in very poor agreement with experiment. Vaks *et al.*[12] appear to have plotted the values of Duesbery *et al.*[16] for B_S in a comparison with calculated and experimental values for B_T. Finally, Cohen and Klein[14] have used Monte Carlo techniques and a more recent version of the Duesbery *et al.*[16] potential to calculate the elastic constants of potassium at 160 and 308 K, with resulting values for B_T of 34.9 and 29.67 kbar, respectively. The 160-K value is roughly 3% larger than our experimental value, while that at 308 K is almost identical with our (extrapolated) results in Fig. 11. They also have calculated Grüneisen parameters for these temperatures which agree well with experiment.

C. Rubidium

The results for rubidium were obtained in single sets of runs with each of the sample holders. As Table I shows, reasonable agreement was found between our experimental densities and that which can be derived from the 20 °C x-ray lattice parameter (5.699 Å) which is reported by Pearson[79] and which corresponds to a molar volume of 55.74 cm^3. This result is in excellent agreement with that obtained by Copley *et al.*[80]

The ME-2 relation [Eq. (15)] was fit to the two 295-K runs for each sample holder to obtain the 295-K parameters in Table IV. Figure 12 shows the deviations from this fit to the data for each of those runs. While systematic deviations appear to exist, their magnitude ($\pm5\times10^{-4}$ maximum in V/V_0) corresponds to less than 0.2% of the total compression which was achieved in 20 kbar ($\Delta V/V_0=0.34$). The results for all of the isotherms are presented in Fig. 13 in the same form as for sodium (Fig. 2) and potassium (Fig. 9). Again, the agreement between the 0.250-in. and 0.354-in. data is excellent at all temperatures and pressures, with only the 175-K run deviating by as much as 10^{-3} in V/V_0 from the postulate of a constant P^*. Only 0.354-in. data were taken at 200 and 160 K, and the latter isotherm becomes enmeshed with the 0.250-in. data for 175 K at high pressures.

The high-pressure neutron scattering experiments of Copley *et al.*[80] give lattice parameters for rubidium as a function of temperature and pressure. These results have been expressed in the same form as the present results and have been plotted as the open circles in Fig. 13. Their es-

TABLE IV. Summary of the isotherm results for rubidium. The data points for the isotherms are indicated in Figs. 12 and 13.

T (K)	P^* (kbar)	$(V/V_0)_{P=0}$	B_0 (kbar)		B_0' [b]	B_0'' (kbar^{-1})[b]	RMSD (10^{-4} in V/V_0)[b]
			a	b			
295	(0)	(1.0000)[c]	(23.0)	23.01 ± 0.03	4.15 ∓ 0.1	-0.057 ± 0.003	2.01
250	-0.25	0.9894	24.0	$24.0\ \pm0.06$	4.16 ∓ 0.03	-0.061 ± 0.006	1.80
200[d]	-0.54	0.9778	25.2	$25.1\ \pm0.1$	4.25 ∓ 0.09	-0.087 ± 0.015	1.23
175	-0.68	0.9726	25.8	25.95 ± 0.06	4.03 ∓ 0.02	-0.052 ± 0.003	2.46
160[d]	-0.79	0.9685	26.3	$26.0\ \pm0.12$	4.28 ∓ 0.12	-0.090 ± 0.024	1.71
123	-0.96	0.9623	26.9	$26.8\ \pm0.15$	4.15 ∓ 0.06	-0.068 ± 0.012	2.05
77	-1.23	0.9528	28.1	$28.0\ \pm0.12$	4.12 ∓ 0.06	-0.066 ± 0.012	3.30
40	-1.39	0.9475	28.7	$28.4\ \pm0.3$	4.24 ∓ 0.15	-0.080 ± 0.024	3.84
21	-1.49	0.9444	29.1	$28.9\ \pm0.2$	4.20 ∓ 0.12	-0.077 ± 0.015	2.46
4	-1.51	0.9436	29.2	$29.2\ \pm0.2$	4.10 ∓ 0.12	-0.064 ± 0.018	2.46

[a] $P=0$ bulk moduli derived from the 295-K isotherm and P^*.

[b] Parameters derived from nonlinear least-squares fits of Eq. (15) 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 assessment gives minimum uncertainties of ±0.25 kbar for B_0, ∓0.1 in B_0', and ±0.01 kbar^{-1} in B_0''.

[c] $V_0(295\text{ K}, P=0)=55.74$ cm^3/mole (Refs. 79 and 80).

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

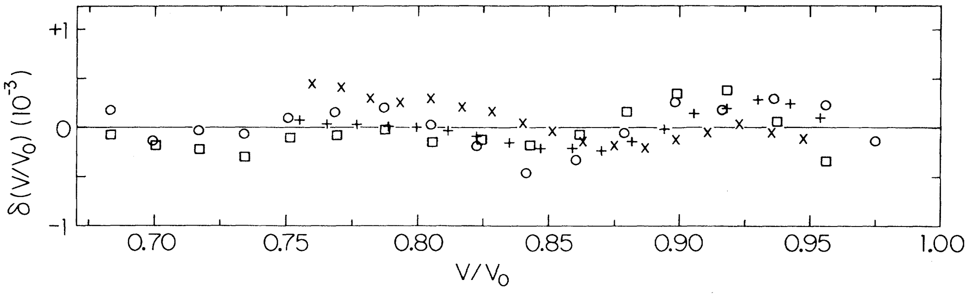

FIG. 12. Deviations of the actual 295-K data for rubidium from the reference relation, Table IV. The symbols are as in Fig. 3.

timated lattice parameter uncertainty (± 0.005 Å or 3×10^{-3} in V/V_0) appears to be quite conservative, since their 295-K lattice parameter is only 10^{-3} Å greater than that given by Pearson,[79] and the scatter of their results in Fig. 13 corresponds at worst to $\pm10^{-3}$ in V/V_0 if the high-pressure result at 230 K, for which the deviation is 2×10^{-3}, is excluded.

The thermal pressures P^* from Fig. 13 are given in Table IV and are plotted in Fig. 14. The nine thermal pressures for temperatures greater than $\Theta_\infty = 64.5$ K (Ref. 67) can be represented by (in kbar)

$$P^* = -1.664 + 0.005\,63T \tag{25}$$

with a maximum deviation of 0.025 kbar at 160 K. The agreement with the results of Copley *et al.*[80] (the open circles) is excellent. The $T=0$ intercept of Eq. (25) and $P^*(4\text{ K})$ from Table IV can be combined to estimate $P_Z = 0.13$ kbar, in good agreement with $P_Z = 0.13$ kbar as calculated by Vaks *et al.*[12] These values are consistent with Martin's estimate[67] that the Grüneisen parameter γ for rubidium is 1.4 at room temperature, which may be too large (see below).

The $P=0$ relative thermal expansions for rubidium as calculated from P^* and the 295-K reference isotherm are given in column 3 of Table IV and are plotted in Fig. 15 where they are compared with other results. Here, an uncertainty of ±0.02 kbar in P^* will affect V/V_0 by ±0.0007. There is an excellent agreement with the results of Copley *et al.*[80] for temperatures above 80 K, and also, with the x-ray results of Kelley and Pearson[81] as summarized by Pearson.[79] Barrett's[57] x-ray results appear to deviate sytematically from ours at 77 and 4.2 K, however,

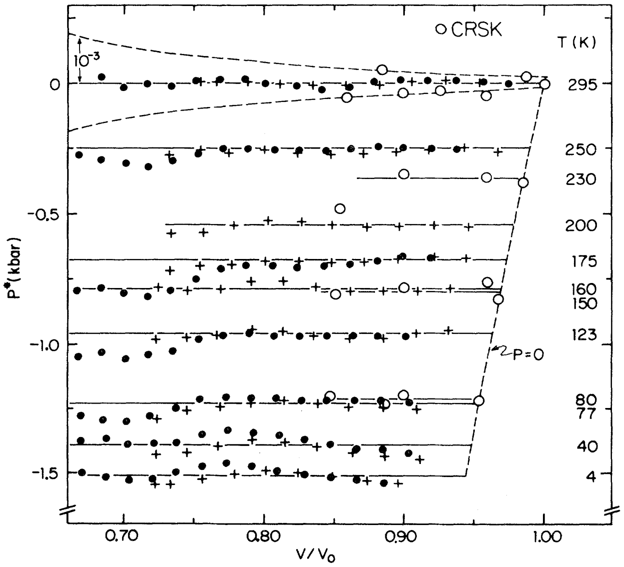

FIG. 13. Representation of the rubidium data in terms of the thermal pressure, with symbols as in Fig. 2. CRSK refers to Ref. 80.

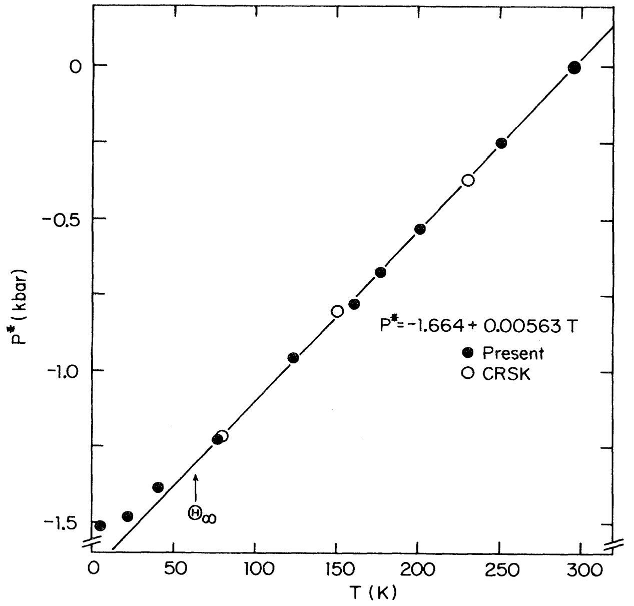

FIG. 14. Thermal pressures for rubidium (the solid lines in Fig. 13) as a function of temperature.

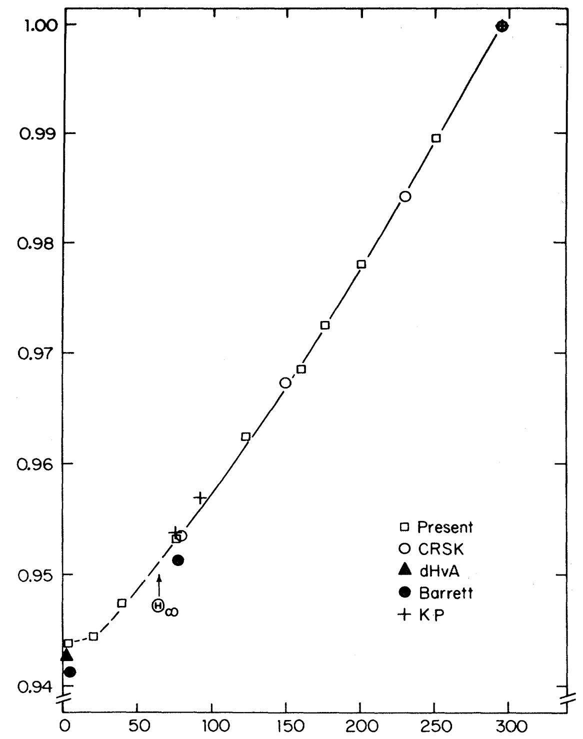

FIG. 15. $P=0$ thermal expansion for rubidium. The symbols refer to published results as follows: CRSK, Ref. 80; dHvA, Ref. 29; Barrett, Ref. 57; KP, Ref. 79.

with the volume change agreeing. Good agreement also exists with the free-electron analysis of the dHvA results of Gaertner and Templeton.[29] Templeton[82] recently has reported evidence for a martensitic transformation in rubidium, but our experiments are too crude to be able to observe these subtle effects.

The $P=0$ bulk moduli in column 4 of Table IV were obtained from P^* and the 295-K reference isotherm, while the parameters in columns 5—7 were obtained from nonlinear least-squares fits of Eq. (15) to the individual isotherm data. An uncertainty of ± 0.02 kbar in P^* will introduce an uncertainty of ± 0.08 kbar in bulk moduli derived from it. The agreement between the moduli in columns 4 and 5 is excellent, and these are compared with other results in Fig. 16. The most extensive elastic constant measurements are those of Gutman and Trivisonno[83] for temperatures from 77 to 195 K, and the agreement with our results is very good. Pauer,[84] who measured the pressure dependence of the elastic constants of rubidium at 195 K, gives a bulk modulus which is significantly greater than that of Gutman and Trivisonno, and which disagrees with our results also. Again, the bulk modulus which is derived from a free-electron model and the dHvA pressure measurements[36] (31.2 kbar) is too large by about the same factor (7%) as for potassium and sodium.

As for potassium, the values of B_0' and B_0'' which are given in Table IV are weighted somewhat by the 0.354 in sample holder data which cover a smaller compression range. This is illustrated by the 200- and 160-K isotherm results for which there are no data above 13 kbar, and for both of which the magnitudes of B_0' and B_0'' are appreciably larger than for the combined results for isotherms close to them. A reasonable temperature-independent interpretation of the combined results (excluding these two isotherms) is that $B_0'=4.14\pm0.06$ and $B_0''=-0.067$ ±0.01 kbar^{-1}. If only the 0.250-in. results are considered, $B_0'=4.11\pm0.06$ and $B_0''=-0.062\pm0.01$ kbar^{-1}, with essentially no disagreement. The high-pressure data appear to have considerable influence in determining the parameters for the combined fits. Pauer's result, $dB_S/dP=3.63$ at 195 K, is approximately 10% smaller than would be expected from our results.

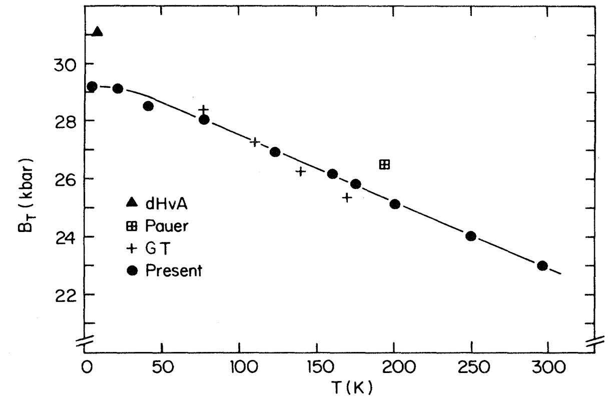

FIG. 16. Temperature dependence of the $P=0$ isothermal bulk modulus for rubidium. The symbols refer to published results as follows: GT, Ref. 83; Pauer, Ref. 84; dHvA, Ref. 29.

Fewer theoretical results exist for rubidium than for either potassium or sodium. López and Alonzo's[5] single-parameter calculation gives $B_0=25.8$ kbar at $T=0$ for comparison with our result (Table IV) of 29.2 kbar. Soma and his collaborators[6,8] give a range of values for B_0 which bracket our result and depend on the screening function which is used, and $dB_0/dP=3.19$, which is too small. Vaks and Trefilov[9] obtain excellent agreement with our result, $B_0=29.6$ kbar, when they use the Geldart-Taylor screening function. Vaks *et al.*[12] calculate a temperature dependence of the bulk modulus at $P=0$ which varies linearly from the above $T=0$ value to 23.8 kbar at 300 K, in good agreement with our temperature dependence (see Fig. 16, where $B_T=23.0$ at 295 K). They also calculate that dB_T/dP should vary from roughly 4.1 at room temperature to 3.78 at $T=0$, in rough agreement with our results. The graphical representation of the calculated $T=0$ equation of state for rubidium by Eremenko and Zarochentsev[13] which includes short-range repulsions also appears to be consistent with our results. Taylor and MacDonald[85] have used a first-principles pseudopotential calculation to obtain anharmonic phonon dispersion relations and phonon-limited electrical resistivities for rubidium, but do not calculate elastic properties.

D. Correlations, extrapolations, and comparisons with higher-pressure results

Similarities or systematic differences in the shapes of pressure-volume isotherms are characteristic of similar effects in the cohesive (or for $T>0$, the free) energy [Eq. (2a)].[47] Pressure-volume relations can be expressed in reduced form through the use of the dimensionless parameters P/B_0 and V/V_0, where B_0 and V_0 are, respectively, the bulk modulus and volume at $P=0$.[86] Equation (13′) expresses the second-order Murnaghan relation in such a reduced form, from which the related P-V relations [Eqs. (14)—(17)] also can be written in reduced form in terms of the dimensionless parameters B_0' and B_0B_0''. Since our results to 20 kbar are represented well by the ME-2 relation, common values of B_0' and B_0B_0'' for two isotherms will indicate directly that they have the same shape, and that their P-V relations differ only through B_0 and V_0. The choice of a specific form for the P-V relation will be dictated not only by how well it represents actual data, but also by its suitability for extrapolation purposes, or equivalently, the possibility that it also is valid for much greater relative pressures and compressions. The following discussion first points out a well-known inconsistency which arises in the use of the ME-2 relation at high pressures and presents an alternative which is very similar but is well behaved at all pressures. The data for sodium, potassium, and rubidium then are fit to this new relation at 4 K and at a common temperature of 295 K in order to investigate the possibility of a common reduced behavior, with these fits and their extrapolation to 40 kbar used in a comparison with other room-temperature results.[86]

Macdonald and Powell[51] have shown that the ME-2 relation [Eqs. (13)] cannot be used at high pressure because the experimentally determined negative sign for B_0'' will cause the bulk modulus to pass through a maximum and eventually decrease through zero at very high pressures. Our fits of Eq. (15) to the rubidium data, where $P/B_0\sim 1$ at 20 kbar and room temperature, do not appear to be affected by these considerations, although they could become important for an extrapolation to 45 kbar ($P/B_0\sim 2$) for comparison with the results of Vaidya *et al.*[39] The Birch relation, Eq. (18), which is well behaved at high pressure, deviates systematically from our data and gives magnitudes for B_0' and B_0'' which are appreciably larger than those in Tables II—IV. The extremely temperature-dependent behavior of $B_T(P=0,T)$ for our cesium results[47] can be associated with the use of the Birch relation to extrapolate the high-pressure results to $P=0$.[87]

An expression which is equivalent to the Murnaghan relations and which is well behaved at high pressure is given by[88]

$$B_T(P,T)=B_0(P=0,T)\left[\frac{1+\alpha P}{1+\beta P}\right]$$

$$=B_0(P=0,T)\frac{1+\alpha B_0(P/B_0)}{1+\beta B_0(P/B_0)} \qquad (26)$$

with

$$B_0'=B_0(\alpha-\beta),\quad B_0''=-2\beta B_0' \;. \qquad (27)$$

This expression, which can be integrated to give

$$V/V_0=\exp\{(-1/\alpha^2B_0)[\alpha\beta P+(\alpha-\beta)\ln(1+\alpha P)]\}\;, \qquad (28)$$

will be referred to as the modified Murnaghan equation (MME). It can be fit to the data using nonlinear least-squares methods, but is less convenient to use than the ME-1 [Eqs. (16) and (17)] or ME-2 [Eqs. (14) and (15)] relations since the pressure cannot be expressed explicitly as a function of V/V_0. Equation (26) gives $dB/dP=0$ (or $B_T=\text{const}$) in the very-high-pressure limit and hence is an improvement on the ME-2 relation [Eq. (13)]. This behavior for Eq. (26) can be modified for an even more realistic behavior by the use of an additional term in the numerator of Eq. (26),

$$B_T(P,T)=B_0(P=0,T)\left[\frac{1+\alpha P+\epsilon P^2}{1+\beta P}\right]\;, \qquad (29)$$

which now gives in the high-pressure limit $dB/dP=(\epsilon/\beta)B_0$. The resulting expression for V/V_0 is somewhat more complex than Eq. (28) and is not given here since the available experimental data are not sufficiently accurate to determine ϵ.

The appropriate P^* relation and V_0 as adjusted for thermal expansion have been used to reduce the 294-K sodium and 297-K potassium data to the 295-K temperature of the rubidium isotherm to provide a common basis for room-temperature comparisons in terms of MME relation fits. Table V contains the parameters for these MME fits as well as those for similar fits to the 4-K data for each metal. With the exception of B_0, which along with V_0 is a characteristic parameter, the parameters in Table V are expressed in dimensionless form [Eqs. (13′) and (26)]. The quality of these fits (see the RMSD's) is similar to that for the ME fits in Tables II—IV, with the corresponding values of B_0, B_0', and B_0'' agreeing within the expected experimental uncertainties (see the footnotes to Tables II—IV). Table V also contains parameters for an MME fit to a "static lattice" ($T=0$, no zero-point energy) equation of state. Data for the static lattice pressure-volume relation were generated from room-temperature data [see Eq. (4)] by subtracting from each data point the volume-independent P^* (see Table V) which is given by the $T=0$ intercept of the linear $P^*(T)$ relation for each metal for $T>\Theta_\infty$. A comparison of the 4-K and static lattice equations of state reflects the explicit effect of zero-point motion on the low-temperature properties of these metals, including the thermal pressure and $P=0$ relative volume which also are given. The calculation of the high-temperature properties of sodium by Swanson *et al.*[18] is based on the assumption of a static lattice, with the parameters derived from $T=0$ data for the actual solid.

The validity of representations in terms of the "reduced" parameters in Table V is demonstrated in Table VI, where differences between the compressions as calculated from the reduced relation and from direct fits to the data are given for 295 and 4 K, with a common (the direct fit value) B_0 used for each comparison. The agreement in

TABLE V. MME parameters [Eq. (28)] for fits to the Na, K, and Rb data for 295 and 4 K and for the static lattice (SL). Parameters for a reduced relation, which is based on the K and Rb results, are given also for each case.

	T (K)	P^* (kbar)	$(V/V_0)_{P=0}$	B_0 (kbar)	$B_0\alpha$	$B_0\beta$	$B_0'^{\text{a}}$	$B_0B_0''^{\text{a}}$	RMSD (10^{-4} in V/V_0)
Na	295	0	1	60.43	4.24	0.06	4.18	-0.5	1.98
					±0.25	±0.12	∓0.28	±1	
K	295	0	1	29.71	4.38	0.18	4.20	-1.5	2.26
				±0.02	±0.13	±0.05	∓0.14	±0.4	
Rb	295	0	1	23.01	4.34	0.18	4.16	-1.50	2.05
				±0.08	±0.08	±0.02	∓0.08	±0.17	
Reduced	295	0		B_0	4.36	0.18	4.18	-1.50	
Na	4^{b}	-3.10	0.9542^{d}	73.55	3.891	-0.007	3.90	$+0.06$	2.17
				±0.08	±0.004	±0.02	∓0.02	±0.16	
	4^{c}	-3.10	0.9542^{d}	73.05	4.40	0.27	4.13	-2.23	1.80
				±0.18	±0.11	±0.04	∓0.12	±0.3	
K	4	-1.76	0.9487^{d}	37.07	4.243	0.191	4.052	-1.55	1.48
				±0.02	±0.003	±0.005	∓0.006	±0.04	
Rb	4	-1.51	0.9436	29.24	4.311	0.238	4.073	-1.94	2.54
				±0.02	±0.004	±0.004	∓0.006	±0.03	
Reduced	4			B_0	4.29	0.22	4.07	-1.80	
Na	0,SL	-3.80	0.9457^{d}	76.38	4.18	0.05	4.13	-0.5	2.05
				±0.22	±0.08	±0.04	∓0.09	±0.4	
K	0,SL	-2.02	0.9419^{d}	38.06	4.356	0.25	4.11	-2.02	2.40
				±0.11	±0.01	±0.02	∓0.02	±0.15	
Rb	0,SL	-1.66	0.9387^{d}	29.80	4.342	0.25	4.09	-2.06	2.01
				±0.07	±0.009	±0.04	∓0.04	±0.09	
Reduced	0,SL			B_0	4.35	0.25	4.10	-2.05	

[a] B_0' and B_0B_0'' are derived from B_0, α, and β.
[b,c] Alternative nonlinear least-squares fits to the data. These data are those referred to in Table II, footnote d.
[d] Based on V_0(295 K, $P=0$).

20 kbar is quite satisfactory for potassium and rubidium (these results were weighted heavily in establishing the reduced parameters), and is marginally satisfactory for the two equivalent fits to the sodium data for each temperature. These differences are extended to 45 kbar using extrapolations of the same relations, since these extrapolations will be compared below to direct measurements of Bridgman[37] to 40 kbar and Vaidya *et al.*[39] to 45 kbar. The differences remain relatively small for both potassium and rubidium (where the 45-kbar compressions are approximately $V/V_0=0.60$ and 0.57, respectively), while the differences between the sodium representations (where $V/V_0=0.7$ at 45 kbar) are significant. The comparison with Bridgman's[37] results (see below) suggests better

TABLE VI. Differences between compressions at each temperature as calculated from the MME [Eq. (28)] using the reduced parameters, $(V/V_0)_{\text{red}}$, and the parameters obtained from direct fits to the data, $(V/V_0)_{\text{fit}}$. Parameters are as given in Table V, unless otherwise noted. Values above 20 kbar are extrapolated.

	$(V/V_0)_{\text{red}}-(V/V_0)_{\text{fit}}$ (10^{-3})							
P	Na				K		Rb	
(kbar)	295 K		4 K		295 K	4 K	295 K	4 K
10	-0.3	-0.3^{a}	$+0.4^{\text{b}}$	$+0.4^{\text{c}}$	-0.3	0	$+0.4$	$+0.1$
20	-1.1	-1.1^{a}	$+0.4^{\text{b}}$	$+0.6^{\text{c}}$	-0.5	-0.4	$+0.7$	$+0.5$
30	-2.4	-2.0^{a}	-0.5^{b}	$+0.7^{\text{c}}$	-0.6	-0.8	$+0.8$	$+0.8$
40	-4.0	-2.0^{a}	-1.9^{b}	$+1.0^{\text{c}}$	-0.7	-1.4	$+0.9$	$+1.3$
45	-4.7	-2.8^{a}	-2.7^{b}	$+1.2^{\text{c}}$	-0.8	-1.7	$+1.0$	$+1.6$

[a] $(V/V_0)_{\text{fit}}$ from the 294-K ME-2 parameters, Table II and Eq. (15).
[b] $(V/V_0)_{\text{fit}}$ from the parameters labeled b, Table V.
[c] $(V/V_0)_{\text{fit}}$ from the parameters labeled c, Table V.

agreement when the reduced relation is used for sodium (and possibly also for potassium), so a reasonable conclusion is that the MME relation, when combined with the "reduced" parameters from Table V, gives a reasonable representation of our data to 20 kbar at 295 and 4 K which also can be used for extrapolation to higher pressures.

The top and bottom halves of Fig. 17 present Bridgman's 1948 measurements[37] and those of Vaidya *et al.*[39] in terms of their differences from extrapolations of the direct MME fits [Eq. (28)] to our 295-K data [Eq. (28)] and Table V]. Up to our limiting 20-kbar pressure, Bridgman's results for all three metals can be made consistent with ours (to $\pm 1.5\times 10^{-3}$ in V/V_0) by postulating that his extrapolations to $P=0$ from his lower pressures (2.5—5 kbar) were underestimated. This is reasonable, since his extrapolations were accomplished through the use of large graphical representations.[36,89] The adjustments which must be made to his published volume changes ($\Delta V/V_0 = 1 - V/V_0$; see the dashed lines in Fig. 17) are 4×10^{-3} for sodium, 1.5×10^{-3} for potassium and 21.5×10^{-3} for rubidium, where the lowest point must be discarded also. The higher-pressure comparisons, which involve extrapolations of our results, are consistent with this interpretation for rubidium and possibly also for potassium, but not for sodium. If the reduced relation had been used to extrapolate the sodium results rather than the MME fit to the actual data (see the first sodium column in Table VI), the magnitude of the difference between the dashed line and Bridgman's results at 40 kbar would be reduced from 7×10^{-3} to 3×10^{-3}. This suggests, as was stated above, that our sodium data are not of sufficient quality to be able to determine with any accuracy the higher-order terms for the MME relation which are important for extrapolation. The above discussion indicates that our data for these three metals are consistent with Bridgman's results[37] to 20 kbar, and that the MME relations which represent these data for potassium and rubidium also are consistent with them to 40 kbar. The reduced relation could be preferable for the extrapolation of the sodium data.

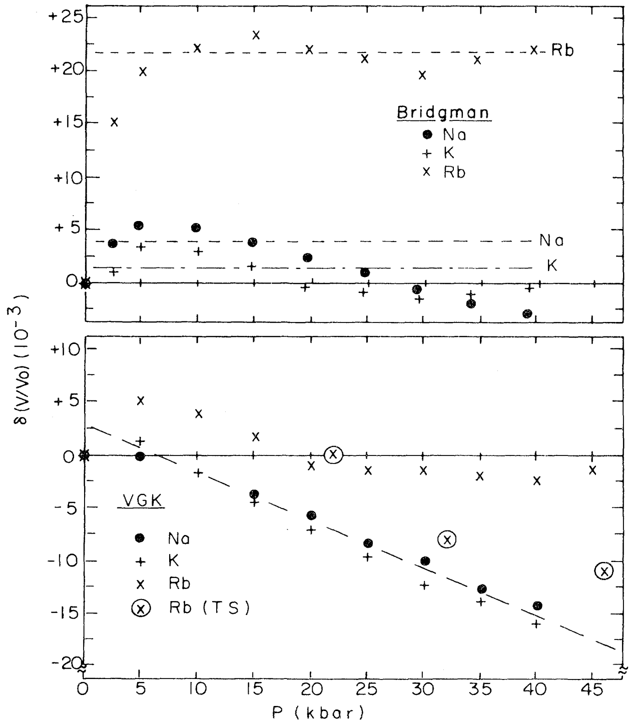

FIG. 17. Differences between the room-temperature compressions reported by Bridgman (Ref. 37) (top half) and by Vaidya *et al.* (Ref. 39) (bottom half) and the present results as extrapolated for pressures greater than 20 kbar. TS refers to Ref. 90. The dashed lines through the Bridgman results represent adjustments to the extrapolations from 5 kbar to $P=0$ which are needed to make these results consistent with the present results. See the text.

The results of Vaidya *et al.*[39] to 20 kbar cannot be made consistent with ours by an adjustment of the extrapolation to $P=0$. The deviations of these sodium and potassium results from our assumed relations (and from Bridgman's results, see Fig. 17) for each metal are consistent with a piston compression correction which is too small and which is roughly the same for both sets of data. This correlation becomes somewhat worse if the reduced relations are used in the comparison. No such elementary interpretation applies to the rubidium results which, perhaps fortuitously, agree well with ours at 20 kbar and for the extrapolation to 45 kbar. For lithium, which has one-half the compression of sodium, we find[87] good agreement with Bridgman's[37] results and a difference from Vaidya *et al.*[39] which is smaller but of opposite sign from those in Fig. 17. This suggests inconsistencies in the results of Vaidya *et al.*[39] which have no simple relationship to the magnitude of the compressions.

The lower half of Fig. 17 also contains the difference between the diamond anvil x-ray lattice parameter results of Takemura and Syassen[90] and our extrapolated rubidium relation. Again, the agreement at 22 kbar may be fortuitous since the deviations for their higher-pressure results at -13×10^{-3} at 66 kbar and -12×10^{-3} at 70 kbar, where they observe a first-order transition from the bcc to the fcc phase.

V. SUMMARY

The rather extensive equation-of-state results which were described in some detail in the preceding section provide such information for the first time for rubidium metal, and confirm with appreciably higher accuracy previously published results for sodium[34] and potassium.[40] The use of common sample holders and identical experimental procedures for all three metals provides a rather rigorous test for the existence of systematic errors in these experiments. The internal consistency of the results for a given metal, which are taken to 20 kbar over a wide range of temperature (both absolute and with respect to Θ_∞), and the correlations which exist between the results for these three metals, again for a wide range of relative temperatures (T/Θ_∞) and pressures (P/B_0), provide confirmation of a general picture of the temperature-dependent equation of state of solids which was proposed previously.[25] The overall consistency (see Figs. 2, 9, and 13) suggests an absolute accuracy of the results which probably is better than $\pm 10^{-3}$ in V/V_0. Systematic problems could arise due to an incorrect reference equation of state for indium metal or to an incorrect pressure scale, but our internal checks[50] and overall agreement with other results (see below) suggests that the above uncertainty limit probably is realistic, in spite of occasional disagreements with previous results which cannot be understood.

A number of conclusions follow from the discussions which were given in the preceding section, and these are summarized in the following. The isotherms which represent the pressure-volume-temperature relationships for potassium and rubidium, and to an understandably lower accuracy for sodium where the bcc-hcp martensitic transformation causes difficulties, can be represented by Eq. (8),

$$P(V/V_0,T)=P(V/V_0,T_R)+P^*(T)\ , \tag{8'}$$

where P^* is independent of V/V_0 (Figs. 2, 9, and 13) and has a linear temperature dependence for $T>\Theta_\infty$ [Eq. (5), Figs. 4, 10, and 14]. Once the form of the reference isotherm has been established, the simplicity of this relationship allows a sensitive display of the actual data and a straightforward means for carrying out the analyses.

The second-order Murnaghan equation [Eqs. (13)], which has been used routinely to represent our results, is unsatisfactory at high compressions where it exhibits nonphysical behavior,[52] while the commonly used Birch relation [Eq. (18)] does not represent our data at all well. Since one use of accurate data is to provide a basis for extrapolation to higher pressures, we also have reported our results for 295 and 4 K in terms of a modified form of the Murnaghan relation, the MME, Eqs. (26)–(28). This representation (Table V) has been used to extrapolate the 295-K relationships from 20 to 40 kbar for comparison with Bridgman's 1948 results.[37] The agreement is quite satisfactory (Fig. 17) if his extrapolations to $P=0$ from 5 kbar or so are made consistent with ours. The results for sodium do not fit this picture as well as do those for potassium and rubidium, most likely because the relatively smaller compressions for this metal result in parameters that are not sufficiently well defined for extrapolation purposes. The differences between the results of Vaidya *et al.*[39] to 45 kbar and both our data to 20 kbar and the extrapolations are clearly outside experimental uncertainties and are not understood.

The results in Tables V and VI show that at both 295 and 4 K the isotherms for the three metals can be represented to 20 kbar by a reduced form for the equation of state. For sodium, this reduced form probably is

TABLE VII. Smooth values for the $P(V/V_0)$ relations at 295 and 4 K using the MME [Eq. (28)] and the parameters for individual metal fits from Table V.

	P (kbar)					
	Na[b]		K[b]		Rb[b]	
V/V_0[a]	295 K	4 K[c]	295 K	4 K	295 K	4 K
1.00	0	(−3.11)	0	(−1.76)	0	(−1.51)
0.975	1.62	(−1.51)	0.79	(−0.96)	0.61	(0.89^5)
0.9542	3.13	0				
0.950	3.46	0.32^5	1.70	(−0.05)	1.31	(−0.20)
0.9487			1.75	0		
0.9436					1.51	0
0.925	5.57	2.42	2.74	0.99	2.12	0.61
0.900	7.99	4.82	3.92	2.17	3.03	1.52
0.875	10.48	7.59	5.29	3.54	4.08	2.58
0.850	14.02	10.76	6.86	5.11	5.29	3.79
0.825	17.77	14.41	8.68	6.92	6.69	5.19
0.800	(22.14)	18.63	10.78	9.01	8.31	6.80
0.775	(27.2)	(23.5)	13.21	11.44	10.17	8.67
0.750	(33.2)	(29.1)	16.03	14.25	12.33	10.83
0.725	(40.3)	(35.6)	19.31	17.52	14.84	13.34
0.700	(48.6)	(43.1)	(23.12)	(21.33)	17.75	16.25
0.675			(27.5)	(25.8)	(21.14)	19.63
0.650			(32.7)	(30.9)	(25.1)	(23.6)
0.625			(38.7)	(37.0)	(29.6)	(28.1)
0.600			(45.7)	(44.0)	(35.0)	(33.4)
0.575					(41.1)	(39.4)
0.550					(48.3)	(46.5)

[a] V_0 (295 K, $P=0$) in cm^3/mole is 23.748 for Na (Ref. 53), 45.535 for K (Ref. 72), and 55.74 for Rb (Refs. 79 and 80).

[b] Values in parentheses are extrapolated.

[c] From the second set of parameters (labeled c) in Table V.

preferable to the actual fits to the data since it gives better agreement with Bridgman's results on extrapolation (see Fig. 17, Table IV).

Table VII contains a summary of our 295- and 4-K pressure-volume results for these metals as they are calculated from direct fits of the MME relation [Eq. (29), Table V] to the data. The data which were used to obtain the representations for each metal at each temperature are independent, except that the relative $P=0$ volume change from 295 to 4 K is calculated from the room-temperature isotherm and $P^*(4\text{ K})$ using Eq. (8). The 295- and 4-K isotherm as represented by these fits are parallel to 20 kbar for potassium and rubidium (that is, P^* is constant), as would be expected from Figs. 9 and 13, but not for sodium where the martensitic transformation appears to cause problems at low temperatures and high pressures (Fig. 2). This parallel behavior persists for extrapolations of the 4-K isotherm to negative pressures (to $V/V_0=1$), and also, unexpectedly, for extrapolations of the two isotherms to 45 kbar for both potassium and rubidium. This suggests a high degree of consistency between our model (that P^* is a function of temperature only) and the extrapolation functions which we have used. The magnitude of P^* for sodium, however, increases from 3.13 kbar at $P=0$ to 5.6 kbar at roughly 45 kbar. The use of the reduced relations in this case would result in lower 295-K pressures and higher 4-K pressures (Table VI), and a decrease of the magnitude of P^* to approximately 4 kbar at 45 kbar. Because the reduced relations are only marginally unsatisfactory for sodium to 20 kbar, and, indeed, would give better agreement with Bridgman's results to 40 kbar (see Table VI, Fig. 17), we cannot conclude that the isotherms for sodium have a different shape from those of the other two metals.

Other direct comparisons of these isotherms with high-pressure results at specific temperatures give confirmation within experimental accuracy for sodium (Makarenko *et al.*,[44] see Fig. 2) and rubidium (Copley *et al.*,[80] see Fig. 14), with discrepancies of opposite sign appearing for two quite different experiments for potassium (Makarenko *et al.*[45] and Kim and Ruoff,[77] see Figs. 8 and 9). The room-temperature isotherm and the extrapolations of the lower-temperature isotherms to $P=0$ (Figs. 2, 9, and 14) give the temperature dependences of the relative molar volumes (Figs. 5 and 15) and of the $P=0$ isothermal bulk moduli (Figs. 7, 11, and 16). These are given in Tables II—IV also. Our relative volume changes for potassium at $P=0$ agree very well (to within roughly $\pm 5\times 10^{-4}$ in V/V_0) with those obtained in direct measurements by Schouten and Swenson[72] (Table IV), who also discuss previous measurements. A similar accuracy is expected for the sodium and rubidium thermal expansions, since these data were taken using the same sample holders and corrections. No differences from other results are found for sodium (Fig. 5) and rubidium (Fig. 15) above 77 K, while at lower temperatures our relative volume changes from 77 to 4 K agree with those found by Barrett[57] from x-ray measurements, although the absolute magnitudes of V/V_0 differ in opposite directions for these two metals. Our result also is consistent with the dHvA result for rubidium (Fig. 15) and perhaps a discrepancy could be expected for sodium where the dHvA result corresponds to a single-crystal, single-phase sample (Fig. 5). The discussion for sodium indicates, however, that inconsistencies appear to exist which are outside estimated experimental uncertainties. New determinations of the low-temperature lattice parameters or expansivities would be useful for sodium and rubidium to remove a reliance on the present results, and possibly also for potassium, where a difference exists between direct and neutron scattering results.[72]

The present results can be used to obtain thermal expansion coefficients $[\beta=(\partial \ln V/\partial T)_P]$ directly since

$$\left[\frac{\partial P}{\partial T}\right]_P=\beta B_T \ . \tag{30}$$

The agreement between the resulting β's and published values for sodium and potassium (roughly 4% near room temperature) reflects the good agreement in the relative thermal expansions V/V_0 which is shown in Fig. 5 for sodium and in Table III for potassium.

Equation (5), which relates P^* to the high-temperature Grüneisen parameter γ_∞, represents the present results for sodium, potassium, and rubidium very well. Since P^* is independent of volume, it follows that γ/V also must be independent of volume for a harmonic solid.[25] The P^* vs T relations in Figs. 4, 10, and 14 [Eqs. (19), (23), and (25)] can be used together with the 295-K molar volumes (Table VII) and $C_V=3R$ to calculate $\gamma=1.24$, 1.24, and 1.26 for sodium, potassium, and rubidium, respectively. These are consistent with previous results for sodium[66] and potassium,[72] with Martin's[67] early estimate for rubidium too large. Boehler[91] has determined the temperature and pressure dependence of γ for lithium, sodium, and potassium through measurements of $(\partial T/\partial P)_S$ and concludes that his results, which are tied to room-temperature thermodynamic determinations of γ (similar to those given above), are consistent with $\gamma/V=\text{const}$, as we propose. His analysis uses Bridgman's data and representations which are based on the Birch relations. He has similar data for rubidium metal which will be analyzed using the present results.[92]

A number of different measurements of low-pressure (mostly $P=0$) elastic properties give results with which our $P=0$ isothermal bulk moduli can be compared. No significant discrepancies occur for rubidium, for which only limited data exist (Fig. 16). Our results for potassium agree with other results below room temperature (Fig. 11), with a difference from the highly precise direct room-temperature measurements of Kim and Ruoff[77] (4.5%) which appears to be well outside our estimated experimental uncertainty (1.2%). The situation for sodium is even more confusing (Fig. 7), with a reasonably clear bifurcation of the results at the 5% level from 77 to 300 K and agreement at 350 K. Since our results should be accurate to 1% or so, these discrepancies for sodium and potassium, although not serious in a broad sense, should be resolved. The $T=0$, $P=0$ bulk moduli which can be derived from dHvA measurements under pressure and the assumption of a free-electron model are systematically larger than the present determinations of B_0 by $(8.5\pm 2.5)\%$, 4.6%, and 6.7%, respectively, for sodium, potassium, and rubidium (Figs. 7, 11, and 16). These differences are appreciably greater than our estimated experimental uncertainties, and are believed to be real.

Comparisons with experimental determinations of the pressure dependences of elastic constants, and hence of B_0' show that our results generally are somewhat larger, although it is difficult to decide whether or not discrepancies exist. Our parameters are determined by fitting empirical relations to data over a wide range of pressure, a range which may not be justified [see Eq. (13′)] by the termination of the power series which is used. The analysis of pressure-dependent ultrasonic results is complicated by the need to include in a self-consistent manner the changes in the sample length which occur with pressure, and also the conversion of adiabatic elastic constants to isothermal values. Our results are consistent with the very slight decrease in B_0' with decreasing temperature which would be associated with B_0''.

A comparison with theoretical calculations has been given for each metal (see the preceding section) with, on the whole, satisfactory agreement. The theoretical results, especially at high temperature, depend greatly on the use of realistic pseudopotentials and proper screening functions, with the degree of agreement increasing with the sophistication of the theory. Most of the calculations are parametrized to some extent, if only to obtain the appropriate lattice parameter for a given temperature, although "no-parameter" calculations have been reported[1-3] which are based on free-atom configurations. It is unclear whether or not our low-temperature data reflect the hcp to bcc transition in sodium which is predicted by Moriarty and McMahon.[4]

One application of the present results is to provide guidance for the extrapolation of room-temperature equation-of-state results to higher temperatures and pressures. The rubidium results, which cover a wide range of reduced pressures ($P_{\max}/B_0=0.85$, $V/V_0=0.7$) and temperatures ($T_{\max}/\Theta_\infty=4.6$), can be represented very well by Eq. (8) with the MME relation [Eqs. (26)—(28)] as the reference function and P^* calculated from Eq. (5) with the Grüneisen parameter proportional to the volume. Figure 17 indeed suggests that the MME with low-pressure parameters is valid for extrapolation to 40 kbar for rubidium ($P/B_0=1.7$, $V/V_0=0.58$). These considerations also should be applicable to other less compressible solids for which $T>\Theta_\infty$, and, to a first approximation, explicit anharmonic effects can be neglected. A rash use of these reduced limits suggests that this form of the equation of state would be valid to 1400 K and at least 900 kbar for a real metal for which $\Theta=300$ K and $B_0=10^3$ kbar. We have serious reservations about the use of the Birch relation for the accurate representation of data or for extrapolations since it cannot be fit to our present results with the same reliability as either the ME-2 or MME relations.

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