Isothermal equations of state of potassium

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Volume versus pressure data of 1-m-long polycrystalline potassium has been obtained as a function of hydrostatic pressure up to 7 kbars at 28.58 °C. The length change has been measured to an accuracy of less than 500 Å using a Fabry-Perot type He-Ne laser interferometer in a temperature-controlled environment with temperature variations ± 0.001 °C. The isothermal bulk modulus B_0 and its pressure derivative B_0' at atmospheric pressure and 28.58 °C are $B_0 = 31.01 \pm 0.02$ kbars and $B_0' = 3.91 \pm 0.01$, when the first-order Murnaghan equation is used; and $B_0 = 30.84 \pm 0.02$ kbars and $B_0' = 4.16 \pm 0.02$, when the Keane equation is used. The Keane equation yields $B_0'' = -0.145$ kbar^{-1} in the applied pressure range. Various two- and three-parameter equations of state have been used to fit the measured pressure-volume data. The Keane and Birch equations represent the data most closely when these equations are extrapolated into a higher-pressure region.

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INTRODUCTION

Potassium and the other alkali metals have drawn considerable theoretical interest. The measurement of their thermodynamic properties is helpful in understanding the cohesion of simple metals. However, their mechanical softness and strong chemical reactivity have made these measurements very unattractive, since extreme care must be taken in handling these materials.

Earlier measurements of volume compression of alkali metals were carried out by Bridgman[1–4] up to 100 kbars. The pressure scale he used in a higher-pressure region turned out to deviate appreciably from the present pressure scale. Swenson and his coworkers[5,6] measured volume change up to 20 kbars over a temperature range down to liquid-helium temperature. Kennedy and his collaborators[7] have measured the pressure-volume isotherms up to 45 kbars. Both of the above authors used the piston-cylinder device. But the quasihydrostatic media and corrections due to the piston compression and friction contribute to errors in their measurements. Our present measurements are under purely hydrostatic conditions.

Let V denote the volume of a specimen under pressure P and at some constant temperature T. Then an isothermal bulk modulus B is defined and expanded in terms of pressure as

$$\begin{aligned} B &= -V\left(\frac{\partial V}{\partial P}\right)_T \\ &= B_0 + B_0'(P-P_0) + \tfrac{1}{2}B_0''(P-P_0)^2 + \cdots, \end{aligned} \tag{1}$$

where

$$B_0 = V_0\left(\frac{\partial V}{\partial P}\right)_{T,P_0}, \quad B_0' = \left(\frac{\partial B}{\partial P}\right)_{T,P_0},$$

and

$$B_0'' = \left(\frac{\partial^2 B}{\partial P^2}\right)_{T,P_0}$$

are evaluated at atmospheric pressure P_0.

Although most of those measurements made by the above workers are quite adequate to describe thermodynamic behaviors at high pressures, they are not precise enough to derive reliable higher-order pressure derivatives of bulk modulus, such as B_0'' or higher. The potassium crystal is an extremely soft solid with $B_0 \cong 30$ kbars and B_0'' is expected to contribute appreciably to the value of B at higher pressures.

Accurate measurements of adiabatic bulk modulus by the ultrasonic method have been made by Smith and his coworkers.[8] The ultrasonic method yields adiabatic data which, if isothermal results are desired, must be converted by resorting to Overton's relation.[9] The Overton formulas involve a number of parameters, all of which are not accurately determined in the desired pressure range.

Given our precise length change measurements with resolution better than 500 Å for a 1-m-long potassium specimen, B_0, B_0', and B_0'' have been determined by statistically fitting the data to several isothermal equations of state. A detailed treatment and discriminations between these equations have been described by Macdonald and his coworkers.[10,11] Macdonald and Powell[11] have shown that it is statistically insignificnat to discriminate the equations of state in a

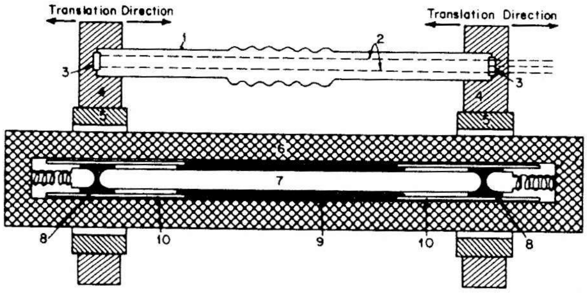

FIG. 1. Schematic of length measurement system. 1: laser path vacuum bellows, 2: laser beam, 3: interferometer mirrors, 4: coupling plates, 5: LVDT's, 6: pressure vessel, 7: specimen, 8: magnetic cores, 9: stainless-steel tube, 10: Pyrex glass tube.

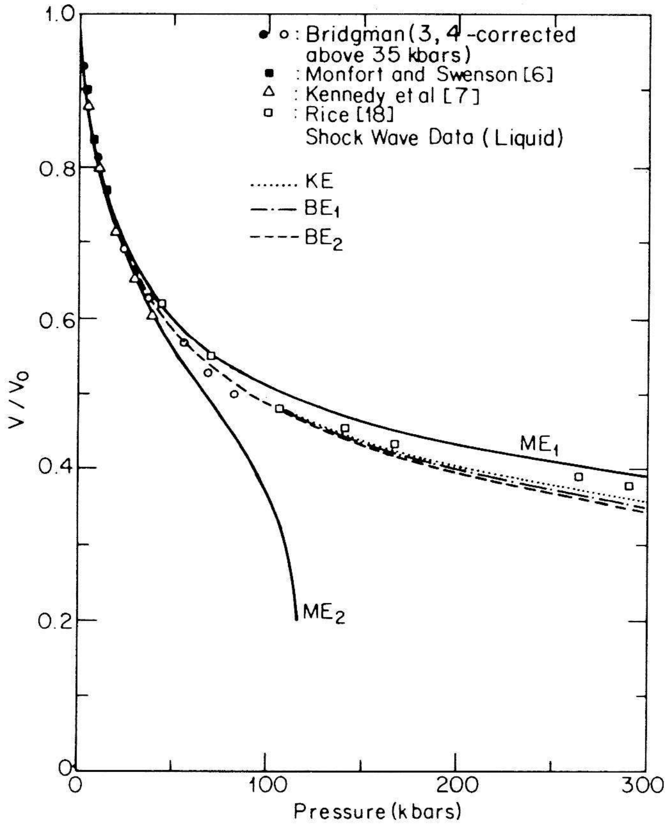

FIG. 2. Extrapolation of pressure-volume data for potassium. Bridgman's pressure scale correction above 35 kbars, 40→38 kbars, 60→56 kbars, 80→70 kbars, and 100→84 kbars. The shock data are for liquid metal.

low-pressure region ($P/B_0 \leqslant 0.01$) unless the experimental data are very accurate within an error of $\Delta V/V_0 \leqslant 10^{-6}$. The precision in our length change measurement is better than 5×10^{-8} and $P/B_0 \leqslant 0.25$.

EXPERIMENTAL METHOD

A detailed description of the experimental setup has been provided by Lincoln and Ruoff.[12] As shown in Fig. 1, a polycrystalline potassium rod which is approximately 1 m long and 7.9 mm in diameter was inserted in a tube, which in turn is held inside the 12.7-mm-diam bore of the nonmagnetic titanium alloy pressure vessel. The central portion of the tube is 304 stainless steel and the remaining part of the tube, where the magnetic cores of the linear variable differential transformer (LVDT) are slightly spring-loaded against both ends of the potassium specimen, is a Pyrex glass tube which is used to avoid any spurious magnetic effects on the H-shaped magnetic cores.

Potassium was obtained from Mine Safety Appliance Corporation and is 99.95% pure. This was extruded into a 7.9-mm die to the desired length. It is then zone refined several times to enhance purity and to anneal out defects and some dislocations. A more elaborate ball bushing arrangement for holding the specimen to minimize friction was previously used.[12–14] This was not adopted in this experiment, because the small difference in density between potassium and the pressurizing medium (liquid hexane) keeps friction sufficiently small. Dehydrated liquid hexane is used as the pressure fluid. Pressure was measured by using a manganin wire pressure sensor. The calibrating technique of the manganin gauge is described in detail elsewhere.[15]

The length measurements were made at an interval of 300 bars up to a maximum pressure of 7 kbars. Inasmuch as the linear compressibility of polycrystalline potassium is isotropic, volume measurements are obtained, using the relation $V/V_0 = (l/l_0)^3$. Resolution in the length measurements of the He-Ne laser interferometry is better than 300 Å in the temperature stabilized environment with thermal noise of 0.001 °C.

The LVDT electronics, laser interferometer, coupling plates and their translation motion, and temperature control, etc., have been described in detail in the literature.[12]

DATA ANALYSIS

For notational convenience, we shall introduce the following abbreviations: $p = P - P_0$, $\eta = B_0'$, $\Psi = B_0 B_0''$, $z = P/B_0$, and $x = V_0/V$. Note that η, Ψ, z, and x are all dimensionless quantities. Po is assumed to be 1 bar in this

TABLE I. Various equations of state.

Equation	Acronym	Form
First-order Murnaghan	ME_1	$z = \eta^{-1}(x^{\eta} - 1)$
Second-order Murnaghan	ME_2 $(\eta^2 \geqslant 2\psi)$	$z = 2(x^{(\eta^2-2\psi)^{1/2}} - 1)/[(\eta^2 - 2\psi)^{1/2}$ $\times (x^{(\eta^2-2\psi)^{1/2}} + 1) - \eta(x^{(\eta^2-2\psi)^{1/2}} - 1)]$
Keane	KE $(-\eta^2 < \psi < 0)$	$z = [\eta^3/(\eta^2 + \psi)^2]$ $\times (x^{(\eta^2+\psi)/\eta} - 1) - [\psi/(\eta^2 + \psi)] \ln x$
First-order Birch	BE_1	$z = \frac{3}{2}(x^{7/3} - x^{5/3})[1 + \frac{3}{4}(\eta - 4)(x^{2/3} - 1)]$
Second-order Birch	BE_2	$z = \frac{3}{2}[x^{7/3} - x^{5/3}]\{1 + \frac{3}{4}(\eta - 4)(x^{2/3} - 1)$ $+ \frac{1}{24}[143 + 9\eta(\eta - 7) + 9\psi](x^{2/3} - 1)^2\}$
Grover Getting, Kennedy	GGKE	$B_T = B_0^T \exp[\eta(1 - x^{-1})]$

TABLE II. Bulk modulus and its pressure derivatives for potassium at 28.58 °C.

Equation Used	B_0 (kbar)	B_0'	B_0'' (kbar^{-1})
ME$_1$	31.01 ± 0.02	3.905 ± 0.009	0
ME$_2$	30.87 ± 0.01	4.094 ± 0.018	-0.0747 ± 0.0068
GGKE	30.81 ± 0.01	4.184 ± 0.004	-0.568[a] ± 0.001
BE$_1$	30.85 ± 0.01	4.144 ± 0.003	-0.131[a] ± 0.002
BE$_2$	30.85 ± 0.02	4.151 ± 0.021	-0.135 ± 0.010
KE	30.84 ± 0.02	4.159 ± 0.024	-0.145 ± 0.014

[a] Obtained from B_0 and B_0'.

paper. Several of the two- and three-parameter phenomological equations described in detail elsewhere[10,16] are used to fit the pressure-volume data and are listed in Table I.

Table II shows the values of the bulk modulus and its pressure derivatives obtained by fitting the measured pressure volume data into the equations of state listed in Table I. ME$_1$ is the only equation of state in the list for which B_0'' is zero. The expressions for BE$_1$ and GGKE do not explicitly contain the parameter B_0''; however, this does not imply that B_0'' is identically zero. The appropriate expression for B_0'' in the case of BE$_1$ can be obtained by setting the third term in the second-order Birch equation BE$_2$ equal to zero. The result is

$$9B_0B_0'' = -\left[143 + 9B_0'(B_0' - 7)\right]. \tag{2}$$

Successively differentiating the GGKE equation with respect to pressure and taking the limit as $P \rightarrow P_0$, one obtains

$$B_0B_0'' = -B_0'^2. \tag{3}$$

GGKE, along with several other equations of state, fits the pressure-volume data well. However, a low value of B_0' (30.8 kbars) gives an unreasonably high value of B_0'', as expected from Eq. (3).

Another approach for the determination of the bulk modulus at each pressure point is to combine three neighboring data points and fit them into ME$_1$. That is,

$$\int_{V_{i+1}}^{V_i} \frac{dV}{V} = \int_{P_i}^{P_{i+1}} \frac{dP}{B_i + B_i'(P - P_i)}, \tag{4}$$

$$\int_{V_{i-1}}^{V_i} \frac{dV}{V} = \int_{P_i}^{P_{i-1}} \frac{dP}{B_i + B_i'(P - P_i)}. \tag{5}$$

Out of the two relations (4) and (5), B_i and B_i' have been numerically calculated at each pressure point (except $P = P_0$ and $P = P_{\max}$). These bulk modulus versus pressure data are statistically fitted, using the formula

$$B = B_0 + \sum_{n=1}^{N} \frac{1}{n!} B_0^{(n)} (P - P_0)^n, \tag{6}$$

where

$$B_0^{(n)} = \left(\frac{\partial^n B}{\partial P^n}\right)_{P = P_0}. \tag{7}$$

The values of B_0 and $B_0^{(n)}$ for $N = 1, 2$, and 3 are displayed in Table III.

As expected, ME$_1$ in Table II and $N = 1$ in Table III, yield essentially the same result for B_0 and B_0', and ME$_2$ in Table II and $N = 2$ in Table III also show essentially the same result for B_0, B_0', and B_0'', within experimental errors, respectively. This provides a self-consistency check for ME$_1$ and ME$_2$. It is interesting to notice that $N = 3$ inTable III provides almost identical results for B_0, B_0', and B_0'' to those which BE$_2$ and KE yield (Table II). Note that the neglect of B_0'' in ME$_1$ leads to a B_0' value which is too small.

Table IV shows the data of bulk modulus and its pressure derivatives measured by other authors together with the present work for the sake of comparison. The agreement in B_0' is only adequate when compared with Bridgman and Kennedy's static compression data, but B_0 and B_0' are in good agreement with Swenson's static compression data and Smith's values obtained by the ultrasonic technique.

DISCUSSION

As can be seen in Tables II and IV, the two- and three-parameters equations yield virtually identical results for B_0, and values of B_0' obtained from GGKE, BE$_1$, BE$_2$, and KE are also in good agreement. Although any sign of curvature is hardly noticeable in the ultrasonic mesurements of $B(P)$ vs P for potassium,[8] the three-parameter equations (ME$_2$, BE$_2$, KE) show unmistakably a negative value of $B_0'' \cong -0.1$ kbar^{-1}. Anderson[17] used Swenson's value[5,6] for B_0 and B_0'

TABLE III. Values of B_0 and $B_0^{(n)}$ for $N = 1, 2$, and 3.

N	B_0 (kbar)	B_0'	B_0'' (kbar^{-1})	B_0''' (kbar^{-2})
1	31.06 ± 0.05	3.88 ± 0.02	0	0
2	30.86 ± 0.04	4.09 ± 0.03	-0.073 ± 0.010	0
3[a]	30.81 ± 0.05	4.18 ± 0.08	-0.145 ± 0.063	0.024 ± 0.021

[a] Because of the large standard deviation associated with B_0''' and the much larger standard deviation associated with B_0'' than with the $N = 2$ case, the numbers in this row should not be given great significance.

TABLE IV. Isothermal bulk modulus and its pressure derivatives of potassium (equation used: ME_1, ME_2, ME_3).

Source	Temperature (°C)	B_0 (kbar)	B_0'	B_0'' ($kbar^{-1}$)	B_0''' ($kbar^{-2}$)
Bridgman[4]	Room	33.25	3.43		
Swenson[5]	25°	30.8	3.85		
Smith[8] [a]	Room	30.9	3.98		
Kennedy[7]	Room	34.0	2.99		
	Room	31.2	3.65	− 0.039	
This work [b]	28.58	31.01	3.91		
	28.58	30.87	4.09	− 0.075	
	28.58	30.81	4.18	− 0.145	0.024

[a] Corrected to an isothermal value from ultrasonic data.
[b] See comment in Table III regarding last row of data.

taken at low pressures on the solid and chose B_0'' which can best fit the shock wave data[18] (which is for the liquid) taken at higher pressures, using the Keane equation. He obtained the values of $B_0'' = -0.051$ $kbar^{-1}$ for potassium and $B_0'' = -0.031$ $kbar^{-1}$ for sodium. Similar procedures have been used by Fritz and Thurson[19] by using a different type of extrapolation formula. Their values of B_0'' are -0.018 $kbar^{-1}$ for potassium and 0.024 $kbar^{-1}$ for sodium. Considering that this involves mixing shock data on the liquid with low-pressure isothermal data on the solids, these values of B_0'' should not be taken seriously.

The value of B_0'' shows very sensitive dependence not only on the accuracy of the V/V_0 measurement, as pointed out by MacDonald and Powell,[11] but also on the functional form of the variation of pressure with the change in resistance per unit resistance $\Delta R/R_0$ of the manganin gauge, as indicated in the data of LiF and NaCl.[13,14] Our pressure measurements are known to a precision of 1×10^{-4}. Unless the pressure is measured to an extremely high precision of 1×10^{-6}, the error in B_0'' is going to remain relatively large unless the measurements are made to substantially higher pressure.

The extrapolation of the pressure-volume data into a higher-pressure range is displayed in Fig. 2 in order to see the discrepancies between the equations of state, despite the questionable validity of extrapolation. Bridgman's pressure scale above 35 kbars was corrected by using the recently reported values of pressure transition points of various elements.[20] His values of thallium II-III at 39 kbars, barium II-III at 59 kbars, and bismuth III-V at 89 kbars, moved down to 37,[21] 55,[22] and 74–78 kbars,[23,24] respectively. GGKE has not been shown because of its unrealistically high value of B_0'. As shown in Fig. 2, ME_1 and ME_2 begin to deviate appreciably from other equations of state at 30 kbars. The abnormal behavior of ME_2 in the higher-pressure region is due to the dominant role of a B_0'' term in the determination of $B(P)$. KE, BE_1, and BE_2 are hardly distinguishable in the entire pressure range ($P/B_0 \cong 10$) considered.

For the improvement of equation-of-state data it would be desirable to simultaneously measure pressure-volume data by the present apparatus and $B_s(P)$ by an ultrasonic technique for the same specimen. Accurate measurements over an extended pressure range will certainly contribute to improving data in the determination of B_0'' and B_0'''.

CONCLUSIONS

The value of B_0 for potassium at 28.58 °C is 30.85 ± 0.05 kbars.

The value of B_0' for potassium at 28.58 °C is 4.1 ± 0.1.

B_0'' is found to be $B_0'' \cong -0.1$ $kbar^{-1}$ and hence makes a major contribution to the value of B at high pressures. It appears that the Taylor series expansion of $B(P)$ about atmospheric pressure is a slowly converging series. This is consistent with the general conclusions of Davison and Graham[25] that fourth-order elastic constants contribute significantly to the stress-strain response even at strains of only a few per cent.

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