

properties from shock data is that of Dugdale-MacDonald (DM) and this was used for the calculations of Fig. 1. Figure 2 shows however that each of the theories for  $\gamma$  gives a straight line over a large range of  $\Delta V/V_0$  with a relatively small variation in slopes ( $\sim 10\%$ ) between theories.

In the cases of the very soft alkali metals, direct static isothermal compression measurements are available and are to be preferred. The reason is that, except for Li, the alkali-metal shock data points are in the liquid phase and cannot be used to derive an equation of state for the solid. For this reason, we show results from static measurements for the alkali metals in Fig. 1 and reduced results from shock measurements for the remaining metals.

Room-temperature measurement of compression for the alkali metals have been reported by Vaidya *et al.*<sup>5</sup> Volumes were determined relative to gold from piston displacement measurements. Details of the technique are reported in Ref. 2 and 5. Bulk-modulus values were determined from the original piston displacement data by graphical techniques. Except for the relatively small compression of gold, no equation of state or other functional form enters the data reduction scheme. This is a unique feature of these bulk-modulus values.

The 5-kbar-spaced data of Vaidya *et al.*<sup>5</sup> were plotted, run by run, on a large scale. Graphing accuracy was typically better than  $\pm 0.05\%$  of the volume change at 45 kbar (about  $\pm 0.0002$  in  $\Delta V/V_0$ ). Smooth curves were drawn through these points with the aid of a large-radius flexible spline. Volumes were read off at 1-kbar intervals. The bulk modulus was then calculated from  $B = -(\bar{V}/V_0)[\Delta P/(\Delta V/V_0)]$ , where  $\bar{V}/V_0$  is the mean volume in the interval.  $\Delta P$  was taken at 1-, 3-, and 5-kbar intervals in search of smooth values of  $B$ . Pressure intervals were moved in 1-kbar steps over the 45-kbar range.

Relevant curvatures were sufficiently small that no systematic trend was found in the bulk modulus values as the pressure interval was increased from 1 to 5 kbar.

Straight lines of the form

$$\ln B = \ln B_0 + \alpha(\Delta V/V_0)$$

were fit by least squares to each of the original runs over an appropriate volume range. Lithium was fit to a compression of 0.15, rubidium to 0.34, and sodium and potassium over the full range of the data. One representative data set is shown with the fit line for each material in Fig. 3. Weighted averages of the slopes and intercepts were calculated for each material. The weighting factor was the inverse square of the standard deviations in each least-squares fit. The average

intercepts give Li:  $B_0 = 117.4 \pm 0.9$ ; Na:  $B_0 = 59.9 \pm 0.5$ ; K:  $B_0 = 31.0 \pm 0.2$ ; and Rb:  $B_0 = 24.9 \pm 0.3$ . Scatter of the  $B_0$  values gives an uncertainty of about 1% in each case. Agreement with the values found by a modified Murnaghan equation<sup>2</sup> fit to the original data are excellent,<sup>5</sup> within 1 kbar in every case. This accord lends strong credence to the validity of the straight-line fit over the selected volume ranges.

The average slopes are Li:  $\alpha = 3.62 \pm 0.02$ ; Na:  $\alpha = 4.06 \pm 0.07$ ; K:  $\alpha = 3.93 \pm 0.02$ ; and Rb:  $\alpha = 4.12 \pm 0.04$ . These values are remarkably similar. Except for Li they lie nearly within their mutual uncertainties.

These average straight lines are shown in Fig. 1 for comparison with the 0-deg isothermal data reduced from the shock Hugoniot.

### III. MATHEMATICAL FITS

A simple linear representation, like (1), of the data on Fig. 1 does not lead to a completely satisfactory formula for the isotherms. That is, the formula

$$B_T \equiv -V \frac{dP_T}{dV} = B_0 e^{\alpha \Delta V/V_0} \quad (L) \quad (3)$$

cannot be integrated to obtain  $P_T(V)$  in terms of simple functions. However, a slight modification of Eq. (3),

$$B_T = B_0 \frac{V}{V_0} e^{\alpha \Delta V/V_0} (T_0), \quad (4)$$

can be derived from the standard Tait equation (5)<sup>6</sup>:

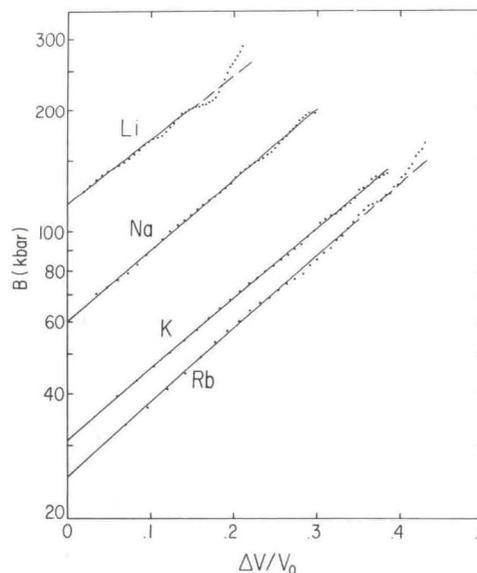


FIG. 3. Room-temperature isothermal bulk modulus vs volume change of the alkali metals from static-compression data—representative examples.

$$\alpha \Delta V/V_0 = \ln[1 + \alpha(P - P_0)/B_0], \quad (5)$$

$$P = P_0 + \frac{B_0}{\alpha} (e^{\alpha \Delta V/V_0} - 1),$$

for an isotherm starting at pressure  $P_0$  with an initial bulk modulus of  $B_0$ . A plot of Eq. (4), however, shows  $\ln B_T$  to be increasing somewhat less than linearly at the higher compressions where the shock isotherms increases more quickly than a linear rate. Moreover, at still higher compressions Eq. (4) is qualitatively unrealistic since it predicts that  $B_T$  goes through a maximum and decreases to zero at infinite compression. However, a further modification of the Tait equation (5) is satisfactory in these regards:

$$P = P_0 + \frac{B_0}{\alpha + 1} \left( \frac{V_0}{V} e^{\alpha \Delta V/V_0} - 1 \right). \quad (6)$$

The bulk modulus derived from (6),

$$B_T = B_0 \frac{\alpha + V_0/V}{\alpha + 1} e^{\alpha \Delta V/V_0} (T_1), \quad (7)$$

is seen in Fig. (2b) to accurately represent the DM curve to  $\Delta V/V_0 \sim 0.4$ . This means that the simple expression (6) for the isothermal pressure will fit shock calculations to very high accuracy.

For comparison Fig. (2b) also shows calculations for a number of other two-parameter formulas commonly used to represent high-pressure compression data. In order to compare the accuracies with which various formulas can be extrapolated to high pressure, all functions are started with the same initial values and slopes appropriate to Mg. The various functions are<sup>7</sup>

$$P_T = \frac{3}{2} B_0 \eta^{5/3} (\eta^{2/3} - 1) [1 - \frac{3}{4} (4 - B_0') (\eta^{2/3} - 1)],$$

$$B_T = \frac{7\eta^{2/3} - 5}{3(\eta^{2/3} - 1)} P_T - \frac{B_0}{3} (4 - B_0') \eta^{2/3} (\eta^{2/3} - 1),$$

Birch (B)

$$B_T = B_0 \eta^{B_0'}, \quad \text{Murnaghan (M)}$$

$$B_T = B_0 [1 + \frac{3}{5} B_0' (\eta^{5/3} - 1)], \quad \text{Keane (K}_1\text{)}$$

where  $\eta = V_0/V$ . There are extensions of each of these equations involving additional parameters which could be used to fit the isothermal data with greater precision but the additional parameters can never be measured with sufficient accuracy at low pressures to be useful in extrapolations. The Keane formula discussed by Anderson<sup>7</sup> is actually a three-parameter equation of which the above  $K_1$  equation is a special case corresponding to an ideal-gas behavior at infinite compression.

The superiority of both the modified Tait and Birch fits to the Mg isotherm is evident. The two-parameter Murnaghan equation is actually a much better fit to the uncorrected Hugoniot,  $B_H(V)$ , a

fact that has been noted on previous occasions and mistakenly thought to justify its use for extrapolating isotherms to high pressure. The differences between the Birch and modified  $T_1$  fit to the Mg isotherm are also seen to be within the uncertainties of the experimental data and the thermal corrections to the Hugoniot. This is also true for all the other metals shown in Fig. 1. Although it is therefore not possible to detect a strong preference for either of these forms in the experimental data, the modified Tait, Eqs. (6) and (7) are the simpler functions.

On the other hand the Birch equation is derived systematically from the theory of finite strain in which the pressure is expanded in powers of an Eulerian-strain variable  $x \equiv (V_0/V)^{2/3} - 1$ . It was long ago recognized that coefficient of the second power of  $x$  was generally small for metals. The excellence of the bulk-modulus fits reported here indicates that the coefficient of the  $x^3$  term is also small and confirms the indication that the Eulerian-strain expansion for the pressure has a large radius of convergence.

#### IV. APPLICATIONS

The nearly linear dependence of the log of the bulk modulus on volume appears to be as universal in metals as the linear velocity relations found in the shock-wave data. It is interesting to speculate on the possibility that  $\ln B_T$  is linear in volume for a single phase of any solid. In the case of metals the linear volume dependence is apparently the result of a linear shock-velocity relation combined with thermal corrections represented by a Grüneisen  $\gamma_G$  which decreases with volume. The method used here for calculating  $\gamma$  and its volume dependence is well based in theory and is in approximate agreement with experimental data on metals.<sup>8</sup> However, for polyatomic solids both this theory and experimental data are inadequate. Nevertheless, for more complicated solids, the decrease of  $\gamma_G$  with compression may be expected according to the following more qualitative arguments.

The intermolecular forces which govern the compressibility of a solid and also its thermal pressure are believed in all cases to be composed of weak long-range attractive forces plus short-range repulsive forces. It is readily shown that for a simple power-law intermolecular potential  $r^{-n}$ ,  $\gamma_G = \frac{1}{6}(n+2)$ . However when a second attractive potential is added to the repulsive power law, it effectively cuts off the repulsion at a finite radius. The effect is the same as increasing the exponent  $n$  or  $\gamma_G$  above the value characteristic of the repulsive part of the potential. Therefore as one compresses the solid, the effect of the attrac-