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# Simple Compressibility Relation for Solids*

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Isothermal compression data derived from shock-wave and static-compression measurements on metals exhibit a nearly precise linear relation between the logarithm of the bulk modulus and the specific volume up to volume changes of 40%. As a result, solid isotherms can be accurately fitted or extrapolated in this range by means of two parameter functions of either a Birch or a modified Tait form.

## I. INTRODUCTION

The isothermal compression curve of metallic solids can be represented in a strikingly simple manner up to specific volume changes of 40% or up to pressures of nearly twice the normal bulk modulus. The observation is based on a more detailed treatment of static-compression measurements of some very soft metals (the alkalis) and isotherms calculated from shock Hugoniot data on a wide variety of metals.

The simple behavior of the isotherms of metals is evident when the logarithm of the isothermal bulk modulus $B$ is plotted against volume changes $\Delta V/V_0$ as shown in Fig. 1. The use of volume as the abscissa rather than pressure was suggested by the simple linear dependence previously found for the melting temperature.[1] Compared with the pressure $P_T(V)$, the log of the isothermal bulk modulus $B_T(V)$, which can be calculated from shock data with virtually the same accuracy as the pressure, is a more appropriate quantity to fit because of its relatively small variation over the large range of shock compression data. For this reason it is easier to recognize the advantages of a particular method of fitting compression data. Furthermore, a good fit to the volume dependence of the bulk modulus will correspond to an even better fit to the pressure along an isotherm (isothermal pressure). Thus, the nearly linear relation observed in Fig. 1 between $\log_{10} B$ and $\Delta V/V_0$ shows clearly that an extremely accurate two-parameter fit to isothermal pressures is possible over a range of 40% in volume changes.

The information for Fig. 1 was indirectly obtained from experimental data by special methods in both the cases of static- and dynamic-compression data. These methods are described in Sec. II. Various accurate ways of fitting the curves of Fig. 1 and comparisons with previous methods are made

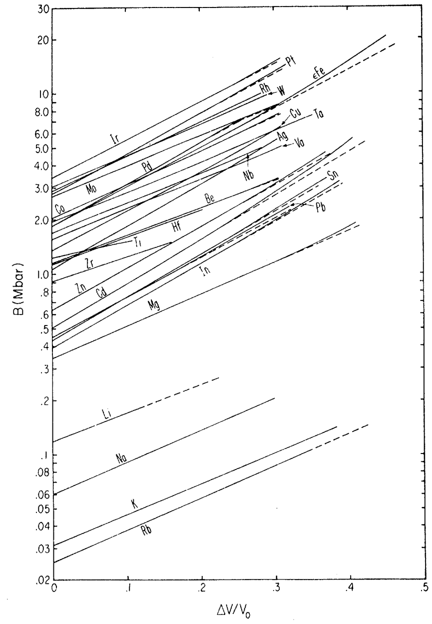

FIG. 1. Isothermal bulk modulus $B_T$ vs volume change of metals as calculated from shock-wave and static-compression data (see text).

in Sec. III. Finally, the applicability of this behavior to other types of solids is discussed in Sec. IV.

## II. DETERMINATION OF ISOTHERMAL BULK MODULUS FROM COMPRESSION DATA

The bulk of the data exhibited in Fig. 1 is derived from shock-velocity measurements which remains the only method of obtaining compressions in normal solids of 30% or more. These data have previously been shown to be in excellent agreement with static-compression data.[2] Figure 1 contains nearly all the available shock-wave results[3] for metals. In order to reduce the clutter of the graph, a few metals have been left out: Au, Ni, and Cr which are in the Fe group and Re which lies in the W group. Metals for which there is little or no data are pure Al, Mn, Ga, Tc, Ru, and Os plus some heavy elements. Shock data for a number of metals (Na, K, Rb, Hg, Te) lie entirely in the liquid phase, and are not included. In addition a number of metals, in particular the rare earths, the alkaline earths, and first transition elements below Ca and Se, exhibit phase changes at relatively low compressions. Their data have not been included because the range of compression in the low-pressure phases are too small to be of use here. Three metals having low-pressure phase transitions, Zr, Ti, and Hf, are included.

The 0-deg isotherms plotted in Fig. 1 are derived from shock-velocity data by standard methods.[4] Shock-velocity measurements on solids can nearly always be accurately fit by a linear relation between shock velocity $U_s$ and material velocity $U_p$; that is $U_s = C + SU_p$. The pressure and modulus along the Hugoniot, $P_H$ and $B_H$, are then

$$P_H = \rho_0 U_s U_p = \frac{B_0 x}{(1-sx)^2}\,, \qquad x \equiv \frac{\Delta V}{V_0}\,, \tag{1}$$

$$B_H \equiv -V\frac{dP_H}{dV} = B_0\,\frac{(1-x)(1+sz)}{(1-sx)^3}\,, \tag{2}$$

where $\rho_0$ and $B_0$ are the normal density and bulk modulus of the solid. Assuming that the solid obeys a Mie–Grüneisen equation of state and further that Grüneisen's $\gamma$ is related in one of several plausible ways to the shape of the 0-deg isotherm $P_K(V)$, the Hugoniot $P_H(V)$ then determines the 0-deg isotherm. Using standard theories, values of $B_K(V)$ were calculated for Mg as a typical example and compared with $B_H(V)$ as shown in Fig. 2. Nominal error bars in the experimental determination of $B_H(V)$ are also drawn to show that the differences between $B_K$ and $B_H$ become significant beyond 20% compression. The theory for $\gamma(V)$ most often chosen to derive equation-of-state

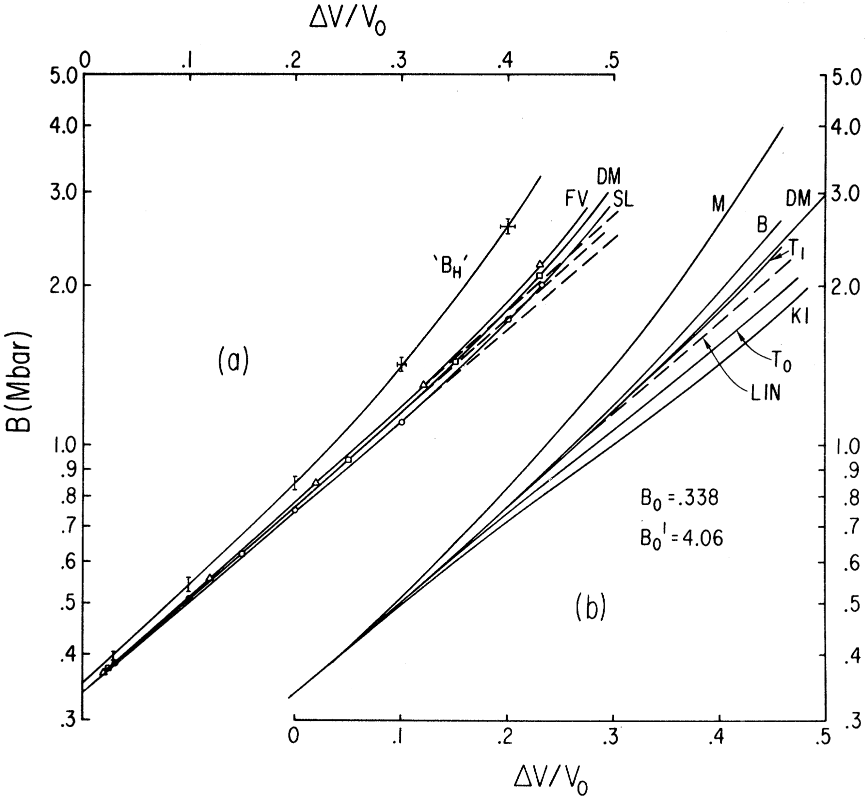

FIG. 2. Comparison of volume dependence of bulk modulus for Mg according to various theories. (a) Hugoniot modulus $B_H$ compared with bulk modulus on 0-deg isotherm calculated according to various theories (see text). Free-volume theory (FV), Dugdale–MacDonald theory (DM), and Slater-Landau theory (SL). (b) Comparison of DM bulk modulus with the Murnaghan (M), Birch (B), modified Tait ($T_1$), Tait ($T_0$), 2-parameter Keane ($K_1$), and the linear volume relation (see text).

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 (~ 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.*[5] 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.*[5] were plotted, run by run, on a large scale. Graphing accuracy was typically better than ±0.05% of the volume change at 45 kbar (about ±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 $B = -(\overline{V}/V_0)[\Delta P/(\Delta V/V_0)]$, where $\overline{V}/V_0$ 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 Murnahan equation[2] fit to the original data are excellent,[5] 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 Hugoniots.

## 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

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

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

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

can be derived from the standard Tait equation (5)[6]:

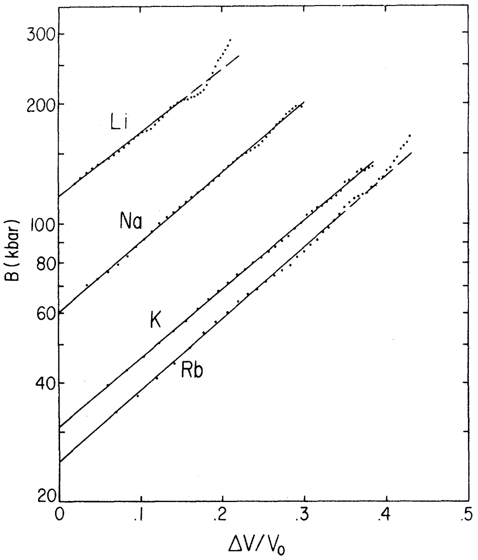

FIG. 3. Room-temperature isothermal bulk modulus vs volume change of the alkali metals from static-compression data—representative examples.

$$\alpha \Delta V/V_0 = \ln[1 + \alpha(P - P_0)/B_0] ,$$
$$P = P_0 + \frac{B_0}{\alpha} (e^{\alpha \Delta V/V_0} - 1) , \qquad (5)$$

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:

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

The bulk modulus derived from (6),

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

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[7]

$$P_T = \tfrac{3}{2} B_0 \eta^{5/3}(\eta^{2/3} - 1) [1 - \tfrac{3}{4} (4 - B_0')(\eta^{2/3} - 1)] ,$$
$$B_T = \frac{7\eta^{2/3} - 5}{3(\eta^{2/3} - 1)} P_T - \frac{B_0}{3} (4 - B_0')\eta^{2/3}(\eta^{2/3} - 1) , \qquad \text{Birch (B)}$$
$$B_T = B_0 \eta^{B_0'} , \qquad \text{Murnaghan (M)}$$
$$B_T = B_0[1 + \tfrac{3}{5} B_0' (\eta^{5/3} - 1)] , \qquad \text{Keane } (\mathrm{K}_1)$$

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[7] is actually a three-parameter equation of which the above $\mathrm{K}_1$ 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.[8] 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 attractive potential is reduced and $\gamma_G$ will decrease. This behavior seems to be characteristic of all metals. Thus to the extent that such force models are realistic for more complicated polyatomic solids, one may expect a similar type of behavior in their $\gamma_G$. However in the latter materials a quantitative estimate of the decrease is difficult.

There are two practical limitations to the use of these two-parameter fits for extrapolating low-pressure data on more complicated solids. The first is the frequent appearance of high-pressure phase transitions in polyatomic solids such as minerals which will limit the range of densities of a single solid phase by an unknown amount. The second is the necessity of accurately measuring the two parameters at low pressure. Unfortunately, ultrasonic measurements of $B_T'$ do not always agree among themselves or with shock-wave data. There remains, therefore, a strong need to improve the accuracy of ultrasonic measurements of $B_T'$ in order to obtain reliable extrapolations of solid-compression data.

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# Impurity Scattering in Polyvalent Metals

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The simplest successful approximation scheme for the calculation of scattering due to nonmagnetic impurities in metals, due to Blatt, has been applied to the cases of impurities in the polyvalent hosts Be, Mg, Zn, Cd, Al, In, Sn, and Pb, extending our previous work which was restricted to zinc. The results of this extended study are compared with available residual-resistivity data and, in the case of Cd, with some new experimental data. A new well-marked regularity has emerged from this extended study. If $Z$ and $Z_0$ denote the Periodic Table column numbers of impurity and host, respectively, it is found that for $Z < Z_0$ the model works very well, while for $Z > Z_0$ very little agreement with experiment is obtained. An interpretation of this behavior is proposed which offers a physical understanding of the *a priori* unexpected validity of the simple model for impurity scattering in metals.

## INTRODUCTION

In a previous publication[1] it was shown how the original Blatt model[2] of impurity scattering in monovalent noble-metal alloys could be extended to provide an interpretation of the residual resistivity of impurities in the divalent metal zinc. Because of metallurgical difficulties encountered in previous work[3,4] on zinc alloys, the experimental portion of Ref. 1 was restricted to impurities which displayed a $\sim 1$-at.% solubility. However, it was subsequently brought to our attention[5] that very reliable data also existed[6] for both Sn and In as impurities in zinc, even though the maximum solubility of these solutes is certainly very much less than 1 at.%. The present work was begun when calculation showed that, for these solutes, the Blatt model failed completely, despite the success encountered in Ref. 1 for the solutes Cu, Ag, Au, Cd, Hg, and Al. The distinc-