

where p_i is the internal pressure generalized to include both the usual thermodynamic internal pressure $(\partial E/\partial v)_T$ and the cohesive energy density (p_i') given by the relation

$$p_i' = \epsilon_0/v_0, \quad (11)$$

where ϵ_0 is the cohesive energy at absolute zero. The internal pressure as used in this study is, therefore, defined by

$$p_i = (\partial E/\partial v)_T + \epsilon_0/v_0 = (a\beta_0)^{-1}. \quad (12)$$

The ratio of density (or specific volume) at pressure p to that at atmospheric pressure is found by combining Eqs. (12) and (8) with the definition of compressibility ($\beta = -d \ln v/dp$) to give the result

$$\rho_0/\rho = v/v_0 = (1 + p/p_i)^{-1/a}. \quad (13)$$

Usually $\epsilon_0/v_0 \gg (\partial E/\partial v)_T$; and, therefore, for evaluating this model, p_i is approximated by $p_i' = p_i$. This is similar to ignoring $\Delta v'$ as given by Eq. (3).

Equation (13) predicts that plots of $\log(v/v_0)$ against $\log(1 + p/p_i)$ should give straight lines of slope $-1/a = \epsilon_0\beta_0/v_0$. Before evaluating this prediction, it is of interest to relate the present derivation to the Grüneisen constant, as expressed by

$$\gamma = \alpha v_0/\beta C_v. \quad (14)$$

From Eqs. (14), (1), and (2), one can obtain

$$\gamma = 2\phi/3. \quad (15)$$

In the Grüneisen derivation γ is also given by

$$\gamma = -d \ln \nu_m/d \ln v, \quad (16)$$

where ν_m is the characteristic frequency of the vibrational modes of the solid. Since only vibrational energy is involved in H for thermal expansion of homonuclear solids (except near absolute zero and high temperatures where free electrons contribute appreciably to heat content), $\bar{T}$ should vary directly as ν_m , such that

$$\gamma = \frac{d \ln \nu_m}{d \ln v} = -\frac{d \ln \bar{T}_1}{d \ln v} - \frac{d \ln \phi}{d \ln v}, \quad (17)$$

which gives the result

$$a = 1 + 2\phi/3 = 1 + \gamma. \quad (18)$$

APPLICATIONS TO HOMONUCLEAR SOLIDS

Plots of $\log(v/v_0)$ against $\log(1 + p/p_i)$ were made for many metals, alloys, and other homonuclear solids where data were available. The majority of data gave straight line plots satisfying the linearity criterion with excellent precision. Two types of (expected) irregularities were noted and explained.

(1). In the alkali metals, for example, straight line plots were obtained only at high pressure, deviations from linearity being prominent at low pressures. The

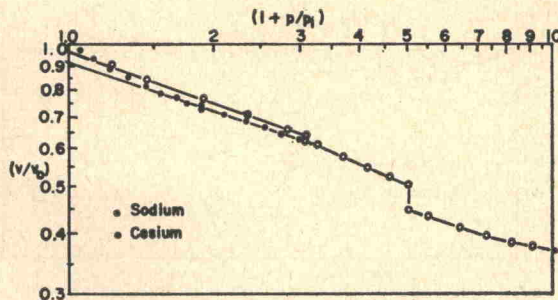


FIG. 1. Log-log plot for isothermal compression of sodium and cesium. Data from Ref. 6.

log-log plot for sodium (Fig. 1) deviated from linearity in the range $p < 12$ kbars, but was linear for $p > 12$ kbars. In this case the linear part of the curve extrapolates to zero pressure at about $v/v_0 = 0.92$ indicating a $\Delta v'/v$ contribution of about 0.08. All of the alkali metals are characterized by low cohesive energies and melting points, and have a significant contribution of thermodynamic defects according to Eq. (3). The energy required to form a hole should increase with pressure, however, according to the relation

$$w_0 = w_0^0 + pR^3,$$

where pR^3 is the extra work required to form a hole of volume R^3 at pressure p over that at $p=0$. Other homonuclear solids that exhibited nonlinear log-log plots were sulfur, tellurium, and some of the rare earths. Most of these have low melting points, and thus an appreciable $\Delta v'/v$ contribution at ambient conditions. Mercury, on the other hand, exhibited only a straight line log-log plot despite its very low melting point. In some cases gradual structure changes may also contribute to deviations from linear log-log plots.

(2). Sharp pressure-induced phase (or polymorphic) transitions caused first-order discontinuities in the log-log plots. Bismuth and cesium (Figs. 1, 5, and 6) are examples of this. The fact that the log-log plots are straight lines on either side of the transition is striking evidence for the validity of the present model.

A few examples of the log-log plots are given in Figs. 1-6. Table I, however, summarizes the information obtained from plots made for all homonuclear solids where data were available. The experimental $p(v)$ data

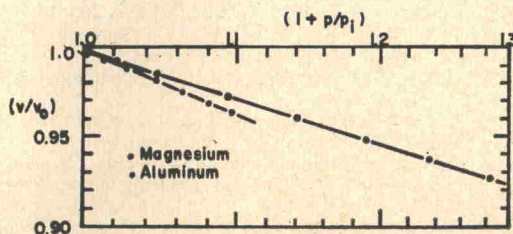


FIG. 2. Log-log plot for isothermal compression of magnesium and aluminum. Data from Ref. 6.

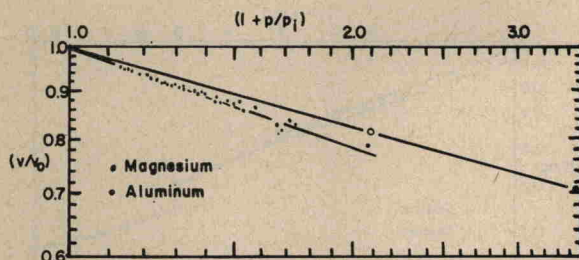


FIG. 3. Log-log plot for shock compression of magnesium and aluminum. Data from Refs. 8 and 9.

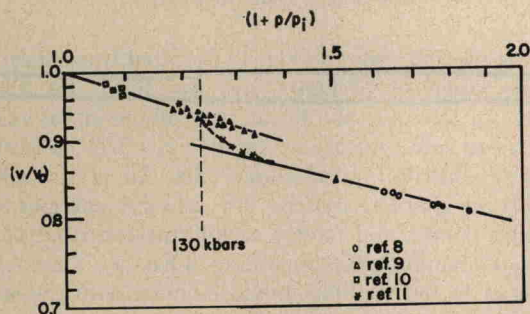


FIG. 4. Log-log plot for shock compression of iron. Data from Refs. 8, 9, 10, and 11.

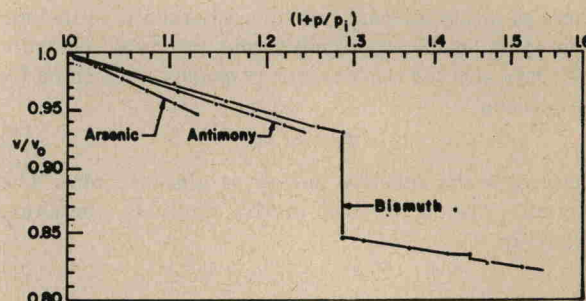


FIG. 5. Log-log plot for isothermal compression of arsenic, antimony, and bismuth. Data from Ref. 6.

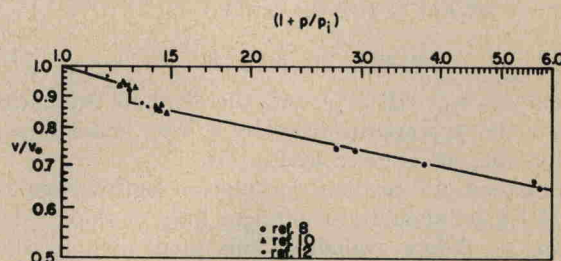


FIG. 6. Log-log plot for shock compression of bismuth. Data from Refs. 8, 10, and 12.

were taken from Bridgman⁶ (static pressure data), and from the brilliant work pioneered at Los Alamos using dynamic (shock) methods.⁷⁻¹⁵ Data for ϵ_0 were taken from Seitz¹⁶ and the Bureau of Standards.¹⁷

Values of a , found empirically from the slopes of the log-log plots of data obtained by the shock loading method, were an average of 15% higher than corresponding values for static compression, owing apparently to shock heating and other dissipative factors^{18,19}

⁶ P. W. Bridgman, *The Physics of High Pressures* (G. Bell and Sons, London, 1958); *Proc. Am. Acad. Arts Sci.* **74**, 21 (1940); **76**, 1, 9 (1945); **76**, 55, 71 (1949); **83**, 1 (1954); **84**, 131 (1957).

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⁸ M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid-State Phys.* **6**, 1 (1958).

⁹ S. Katz, D. R. Curran, and D. G. Doran, "Hugoniot Equation of State of Aluminum and Steel from Oblique Shock Measurement," Poulter Labs Tech. Report 025-57 (1957), Stanford Research Institute, Menlo Park, California.

¹⁰ D. S. Hughes, L. E. Gourley, and M. F. Gourley, *J. Appl. Phys.* **32**, 624 (1961).

¹¹ D. Bancroft, E. L. Peterson, and F. S. Minshall, *J. Appl. Phys.* **27**, 1207 (1956).

¹² R. E. Duff and F. S. Minshall, *Phys. Rev.* **108**, 1207 (1955).

¹³ J. M. Walsh and M. H. Rice, *J. Chem. Phys.* **26**, 818 (1957).

¹⁴ M. A. Cook, R. T. Keyes, and W. O. Ursenbach, *J. Appl. Phys.* **33**, 3413 (1962).

¹⁵ O. C. Trulson, D. E. Hudson, and F. H. Spedding, *J. Chem. Phys.* **35**, 1018 (1961).

¹⁶ F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., 1940).

¹⁷ U. S. Bureau of Standards, *Selected Values of Chemical Thermodynamic Properties* (U. S. Govt. Printing Office, Washington, D. C., 1952).

¹⁸ R. H. Wentorf, *Modern Very High Pressure Techniques* (Butterworths Scientific Publications, Ltd., London, 1962).

¹⁹ G. R. Fowles, "Shock Wave Compression of Quartz," Ph.D. thesis, Stanford University (October 1961).

that differentiate the shock process from the more common isothermal or adiabatic processes. The ratio of isothermal compressibility (β_T) to adiabatic compressibility (β_S) is found from thermodynamics to be

$$\beta_T/\beta_S = C_p/C_v. \quad (19)$$

Since C_p and C_v are nearly the same for solids, little difference should exist between isothermal and adiabatic compressibilities as compared to the larger difference between the isothermal and shock wave compressibilities. From Eq. (10) and the expected independence of p_i on the method used, one obtains

$$a_T\beta_{T0} = a_S\beta_{S0} = a_H\beta_{H0}. \quad (20)$$

Grüneisen Constants

A comparison of the γ 's obtained from the a 's and Eq. (18) with those obtained by more direct methods by Grüneisen,²⁰ Slater,²⁰ and Benedek²¹ are given in Table II. Included in this comparison are results computed from Eq. (15) using the data previously derived by the approximate method given in Ref. 1. The favorable comparison of results indicates that the present theory of a is satisfactory. The γ 's obtained from the ϕ 's and Eq. (15) are apparently not seriously in error either, which implies that the approximation used previously to calculate ϕ was reasonably reliable, but the method of relating ϕ to a , which involved the change of ϕ with density, was seriously in error.

²⁰ C. Kittel, *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1956).

²¹ G. B. Benedek, *Phys. Rev.* **114**, 467 (1959).