

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  $\epsilon_0$  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  $\gamma$  is also given by

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

where  $\nu_m$  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  $\nu_m$ , 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

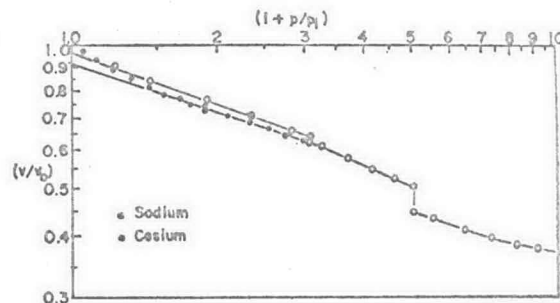


Fig. 1. Log-log plot for isothermal compression of sodium and cesium. Data from Ref. 6.

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

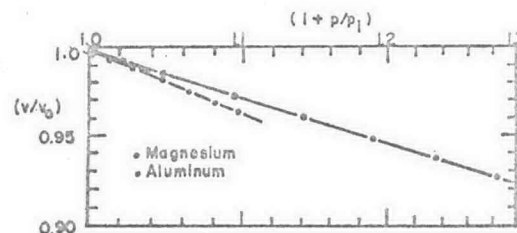


Fig. 2. Log-log plot for isothermal compression of magnesium and aluminum. Data from Ref. 6.