Reprinted from Journal of Applied Physics, Vol. 34, No. 8 2330–2336, August 1963

Printed in U. S. A.

Compressibility of Solids and Liquids at High Pressures

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(Received 30 November 1962)

An equation for compressibility (identical in form to the Tait equation) derived previously from the virial theorem and the Fermi–Thomas atomic model is modified on the assumption that one of its parameters ($a\beta_0$) is reciprocally related to the *internal pressure* when the *cohesive energy density* is assumed to be an essential part of the internal pressure. Pressure–volume data for about fifty homonuclear solids, two alloy systems, twenty ionic compounds, and five secondary bonded liquids are analyzed and the model found to fit with surprising accuracy when due consideration is given to pressure-induced phase or polymorphic changes and thermodynamic "holes" (most important near, and above, the melting point) that may contribute appreciably to specific volume. Data from static and shock methods of compression are considered and the differences noted. The model is apparently applicable to the compression of homonuclear solids and liquids, if indeed not all condensed materials in general.

INTRODUCTION

By application of the virial theorem and the Fermi–Thomas model, the following equations were derived[1] for thermal expansion and compressibility of homonuclear solids:

$$\alpha/3=\alpha'=C_v/2\bar{T}_1, \tag{1}$$

$$\beta=9R(M/\rho)^{\frac{2}{3}}N^{\frac{1}{3}}/4\bar{T}, \tag{2}$$

where α = bulk thermal-expansion coefficient, α' = linear thermal-expansion coefficient, β = compressibility, $\bar{T}$ = average effective kinetic energy, $\bar{T}_1$ = average kinetic energy in the valence orbital, C_v = heat capacity, R = bond distance, ρ = density, M = atomic weight, and N = Avogadro's number. The basic idea was simply that the Fermi–Thomas (or particle in a box) model, which implies a definite relationship between the average kinetic energy and the density $[\bar{T}=f(\rho)]$, could be used to describe changes in solids. Thus, in treating thermal expansion the energy

$$H=\int_0^T C_v dT$$

was considered to lower the average kinetic energy by H. Since the total energy E is negative, a positive energy H decreases $|E|$. The virial theorem was used to relate $\bar{T}$ and E. For compressibility, on the other hand, the work of compression should increase $\bar{T}$ by $-(\frac{3}{2})RFN$, where F is the average force applied on each of the bonds.

The theory was considered to explain only the contribution to density changes from lattice parameter changes, and did not include those changes attributed to thermodynamic defects. For example, the contribu-

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* Present address: Corning Glass Works, Corning, New York. This article comprises part of the dissertation submitted by Leo A. Rogers to the Graduate School, University of Utah in partial fulfillment of the requirements for the Doctor of Philosophy degree, June 1962.

[1] M. A. Cook, Discussions Faraday Soc. **22**, 203 (1956); "Properties of Solids," Bulletin No. 53, University of Utah, September 1951; J. Appl. Phys. **30**, 725 (1959); *The Science of High Explosives* (Reinhold Publishing Corporation, New York, 1958), Chap. 9.

tion to the volume ($\Delta v'$) from Schottky-type defects according to Mott and Gurney[2] is given approximately by

$$\Delta v' = R^3 N \gamma B e^{-w_0/kT} \tag{3}$$

(see Ref. 2 for definition of constants γ, B, and w_0). For solids $\Delta v'$ should become appreciable only at temperatures approaching the melting point. It may be neglected at room temperature in solids having high cohesive energies and melting points.

The kinetic energy of the valence orbital $[T_1 = f(\rho_1)]$ was assumed to be given approximately by the Fermi–Thomas equation

$$\bar{T}_1 = (h^2/2m)(3\rho_1/8\pi)^{\frac{2}{3}}, \tag{4}$$

where h = Planck's constant, m = electron mass, and ρ_1 was assumed to vary directly as the density of the atom. For all the other electrons, the kinetic energy $\bar{T}_i = f(\rho_i)$ ($\bar{T}_i$ the kinetic energy of the ith electron) was assumed to obey this "particle in a box" equation, or in other words, the ρ_i's being determined by the Fermi–Thomas "orbital size" equation. However, the ρ_i's were not all considered to change in the same proportion as energy H was added to or taken from the system. In thermal expansion the only appreciable change considered was that in the valence electrons, since electrons in filled bands would not be excited thermally. In compression, on the other hand, the kinetic energy was assumed to change in proportion to the "surface area" of the orbital computed on the basis of spherical charge distributions and the ratio $\bar{T}_i/\bar{T}_1$. Thus, all orbitals were considered to contribute to the "hardness" of an atom in proportion to $\bar{T}_1/\bar{T}_i$. This crude approximation proved inaccurate in describing the distribution of the applied force among the (Z) electron orbitals. That is, it led to values of effective average kinetic energy as a function (ϕ) of the kinetic energy of the valence orbital ($\bar{T} = \phi \bar{T}_1$) sometimes considerably in error based on the variance between calculated and experimental compressibilities. It may still be assumed, however, if the Fermi–Thomas model applies, that changes in the $\bar{T}_i$'s for compression of the atom are all related to the kinetic energy of the valence orbital, such that $\bar{T} = f(\rho)$ and also $\phi = g(\rho)$. This assumption alone permits integration of the last term or pressure coefficient of compressibility in the equation

$$\beta = \beta_0 + \int_0^p \frac{d\beta}{dp} dp. \tag{5}$$

Differentiation of Eq. (2) with $N^{\frac{1}{3}} R (m/\rho)^{\frac{1}{3}}$ replaced by a constant times the specific volume (v) gives the result

$$\frac{d\beta}{dp} = \beta \left[\frac{d \ln v}{dp} - \frac{d \ln \bar{T}}{dp} \right] = -\beta^2 \left[1 - \frac{d \ln T_1}{d \ln v} - \frac{d \ln \phi}{d \ln v} \right]. \tag{6}$$

Based on Eq. (4) the term $-d \ln \bar{T}_1 / d \ln v$ becomes just $\frac{2}{3}$. Then with the additional assumption that $\bar{T}_i \neq f(v)$ for $i \geqslant 2$, one obtains $-d \ln \phi / d \ln v = b = \frac{2}{3}(1 - 1/\phi)$. This was the basis for the original derivation of $a = (5/3) + b$. However, this assumption is clearly in error, and the theory for a should thus be modified. For example, $\bar{T}$ should vary as θ_D, the Debye characteristic temperature, and, therefore, $-d \ln \bar{T} / d \ln v = \gamma$, the Grüneisen constant. Thus while the previous derivation of b gives $b \leqslant \frac{2}{3}$, the result should instead be $\gamma - \frac{2}{3}$, or about 1.3. Therefore, we shall here replace the questionable assumption about the constant value of ϕ by the alternate assumption $\bar{T} = f(v)$, such that from Eq. (4) one obtains $\phi = g(v)$ which leads to the result that b is a constant. Equation (6) then becomes

$$d\beta/dp = -\beta^2 (1 + \tfrac{2}{3} + b) = -a\beta^2, \tag{7}$$

where $a = (5/3) + b$. Combining Eqs. (5) and (7) and integrating successively by parts one obtains

$$\beta = \beta_0 \sum_{i=0}^{\infty} (-a\beta_0 p)^i = \beta_0 / (1 + a\beta_0 p). \tag{8}$$

[More simply, differentiate Eq. (8) to get Eq. (7).] We shall, however, use an alternate method described below to evaluate a from which b is obtained. Equation (8) has the same form of the Tait equation

$$\beta = C/(L + p), \tag{9}$$

and would be identical to it if the constants C and L were defined by a^{-1} and $(a\beta_0)^{-1}$, respectively.

The original model was intended to apply without the use of empirical constants by providing theoretically computed values of a. Unfortunately, the theory for a proved inadequate giving theoretical values in the range $1.8 < a < 2.3$, while actual values required to give the correct β's fell in the range $1.8 < a < 6$. Moreover, the required a's averaged about 3.0 which is greater than the upper limit of a permitted by the theoretical approximation in Ref. 1. It is the purpose of this article to modify the theoretical basis for a and to show that the improved model provides a reliable model for the high pressure compressibility of solids, if indeed not all condensed materials in general.

MODIFIED THEORY OF "a"

The proposed modification of the theory of a is based on the fact that Eq. (8) is of the form of the successful Tait equation, and that the L in the Tait equation has already been interpreted (although somewhat intuitively) as an internal pressure.[3–5] Thus, it is here postulated that for homonuclear solids

$$L = (a\beta_0)^{-1} = p_i, \tag{10}$$

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[2] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1953), p. 31.

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