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Effect of volume on the isothermal bulk modulus of metallic solids

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Pseudopotential perturbation theory is used to calculate the variation of isothermal bulk modulus K of metals (valence $Z=1$ to 4) up to volume changes of 40%. A straight line is obtained from the plot of $\log_{10}K$ vs $\Delta V/V_0$ for all elemental solids. Results are compared with shock-wave and static-compression measurements.

I. INTRODUCTION

Recently, Grover *et al.*[1] have observed that the isothermal compression curves of metallic solids can be represented by a simple two-parameter relation of the form $\log K = \log K_0 + \alpha\,\Delta V/V_0$ for large number of solids whose experimental data from static-compression (alkali metals) and shock-wave (other metals) measurements are available. They have also shown that among the several two-parameter functions[2] commonly used to represent high-pressure compression data, the modified Tait equation and the Birch equation fit the experimental data well. These equations are obtained from thermodynamic considerations. In the present paper we present a method based on pseudopotential theory of metals[3] to relate the bulk modulus of a metal with its specific volume. The success of pseudopotential theory in calculating phonon spectra, elastic constants, band structures, and various other atomic and electronic properties of solids is well known.

We have calculated the bulk modulus at different specific volumes of solid using pseudopotential perturbation theory. The pseudopotential used here is a two-parameter (valence Z and core radius r_c) Ashcroft[4] empty-core type. It must be emphasized at the start that we should not expect too much quantitative agreement with the observed values in such calculations as the two parameters chosen here characterize the solid rather than being obtained by fitting them to some experimental values. Calculation of bulk modulus involves two derivatives of energy with respect to volume and thus it is a severe test to the theory. The variation of bulk modulus with volume becomes in a way the third derivative, and hence is a still more severe test for the theory. We present the basic formalism of the problem in Sec. II and apply it for finding out bulk modulus of solids at different specific volumes in Sec. III. Discussion follows in Sec. IV.

II. THEORY

We will not repeat here in detail all the derivations as they have been given elsewhere.[5] Consider a lattice consisting of N atoms and occupying a volume Ω. Atomic volume is defined in terms of the charge-density parameter r_s as $\Omega/N = Z\,\frac{1}{3}\pi r_s^3$, where Z is the valence of the atom. Following Singh and Young (Ref. 5) the total energy of the lattice per atom can be written (in a.u.)

$$\frac{E}{N} = E_{ex} + E_{\text{corr}} + \frac{1.105\,Z}{r_s^2} - \frac{0.896\,Z^{5/3}}{r_s} + \frac{\alpha Z^2 N}{\Omega} + \frac{N}{\Omega}\sum_{\vec{G}} \frac{G^2}{8\pi}\,|u(G)|^2\left(\frac{1}{\epsilon(G)} - 1\right). \tag{1}$$

The first term in Eq. (1) is the free-electron exchange interaction

$$E_{ex} = -0.458\,Z/r_s.$$

The second term is the Pines-Nozières[6] form of the the correlation energy

$$E_{\text{corr}} = (-0.0575 + 0.0155\ln r_s)Z.$$

The third term is the average kinetic energy of electrons and fourth and fifth terms have been obtained by adding three zeroth components of the electron-electron interaction, the ion-ion interaction and the electron interaction with the bare-ion array. It depends upon the form of pseudopotential chosen. In the present case $\alpha = 2\pi r_c^2$. The final term is the second-order term incorporating the usual self-energy correction. The sum is over all the reciprocal-lattice points $\vec{G}$. Thus, it also depends upon the form of pseudopotential as well as on the structure of the crystal. $\epsilon(G)$ is the Hartree dielectric screening function evaluated at the reciprocal-lattice points. We have taken it to be of the Lindhard[7] form

$$\epsilon(q, k_F) = 1.0 + \frac{1}{2\pi k_F \eta^2}\left(\frac{1-\eta^2}{2\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| + 1\right), \tag{2}$$

where $\eta = q/2k_F$ and k_F is the Fermi wave vector. $u(G)$ in Eq. (1) is the value of pseudopotential evaluated at the reciprocal-lattice point $\vec{G}$. We have taken it to be of Ashcroft empty-core type

$$u(q) = -(4\pi Z/q^2)\cos(q r_c). \tag{3}$$

Equation (1) corresponds to the identical equation

TABLE I. Parameters (in a.u.) used in Eq. (1).

Element	Valence	r_c	r_s
Li	1	1.13	2.88
Na	1	1.79	3.75
K	1	2.51	4.70
Rb	1	2.79	5.09
Cs	1	3.19	5.63
Be	2	0.58	1.91
Mg	2	1.23	2.33
Ca	2	1.87	2.80
Sr	2	2.13	3.07
Ba	2	2.55	3.53
Cd	2	1.83	2.62
Zn	2	1.40	2.37
Al	3	0.94	1.75
Tl	3	1.79	2.30
In	3	1.53	2.07
Pb	4	1.58	1.88
Sn	4	1.34	1.70

obtained by Ashcroft and Langreth[8] for the energy per atom of pure metals. The only difference is that they obtained α independently of r_c so as to fit the observed lattice constant while we have obtained it to be equal to $2\pi r_c^2$.

When this equation for energy per atom is differentiated twice with respect to volume we obtain an expression for the isothermal bulk modulus as follows:

$$K=-\frac{1}{6\pi Z r_s^2}\frac{d}{dr_s}\frac{E}{N}+\frac{1}{12\pi Z r_s}\frac{d^2}{dr_s^2}\frac{E}{N}. \tag{4}$$

At normal pressure the first derivative is zero and hence

$$K_0=\frac{1}{12\pi Z r_s}\frac{d^2}{dr_s^2}\frac{E}{N} \tag{5}$$

is the expression for bulk modulus at normal pressure.

III. RESULTS AND COMPARISON WITH EXPERIMENT

We identify each metal by its valence Z and core radius r_c. There is some choice[9] possible in the selection of r_c values and we have chosen them to be the Pauling radius of the corresponding metal (see Ref. 5 and also Meyer *et al.*[10]). Equation (1) expresses the energy per atom as a function of parameter r_s. For a given Z and r_c the equilibrium value of r_s is obtained by minimizing this expression in energy. The value of r_s thus obtained gives the atomic volume of the metal at normal pressure. These values of r_s along with other relevant data used in calculations for each metal are collected in Table I. Then r_s is varied from this equilibrium value such that the specific volume changes up to 40%. The isothermal bulk modulus is then calculated from Eqs. (1)–(4) for these values of r_s. Crystal structures used in these calculations are those given by Brewer[11] for the corresponding solid at the lowest temperature. The $\log_{10}K$ of each metal is plotted against $\Delta V/V_0$ as shown in Fig. 1. A straight line is obtained in each case. This fact is in agreement with the observation of Grover *et al.*[1] who arrived at the same conclusion after interpreting large amounts of experimental data from static-compression and shock-wave measurements. The intercepts of these curves with $\Delta V/V_0=0$ axis gives the isothermal bulk modulus ($\log_{10}K_0$) at normal pressure. Where ever possible the observed value of $\log_{10}K_0$ is given along with the curve in Fig. 1. The accuracy of these values is limited since numbers were "read" from Fig. 1 of Ref. 1. It is observed that there is a good agreement for these with experimental values in the case of metals with $Z=1$ and 2 and then there is a gradual failure of theory for higher valences.

IV. DISCUSSION

As pointed out in Sec. I. we should not expect too much agreement with the experimental values. We have characterized each element by two parameters and are trying to calculate every observed property of the solid on this basis. The present

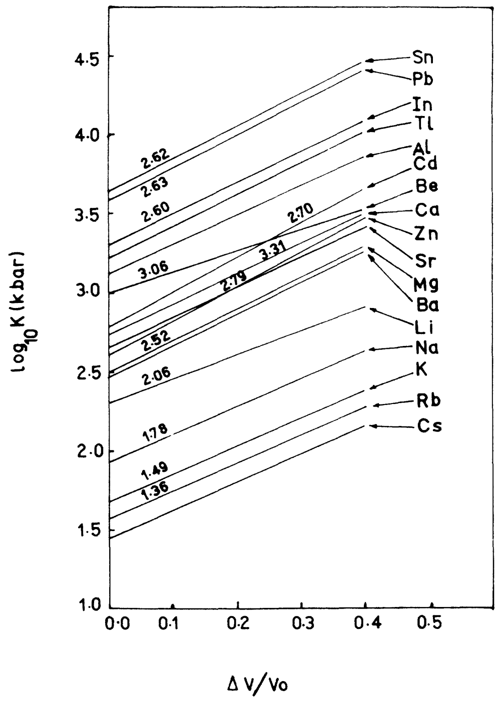

FIG. 1. $\log_{10}K$ (kbar) vs volume change for metals having valencies from 1 to 4 as calculated from Eqs. (1)–(4). Numbers shown along with the curves are the observed values of $\log_{10}K_0$ as read from Fig. 1 of Ref. 1.

calculations demonstrate two things very clearly. First, up to about 40% of volume change the plot of $\log_{10}K$ vs $\Delta V/V_0$ is a straight line for each of the solids studied as shown by Fig. 1. Second, it has been observed in all cases that at higher compressions (beyond 30%) the rate of increase of this curve is slightly faster than a linear rate. This observation is also in agreement with that of Grover *et al.*[1] A better quantitative agreement can be obtained if we choose α in Eq. (1) by fitting it to some experimentally observed property such as the lattice constant as has been done by Ashcroft and Langreth.[8] They found good agreement with experimental compressibilities for some of the elements. But as long as we restrict the number of independent parameters to be two, the choice of different pseudopotential will not alter the results too much.

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