

be considered to depend on volume only, they give no contribution to the pure shear elastic constants.

Bardeen²⁰ and others^{19,21,22} have deduced pressure-volume relations for the alkali metals and compared the results with experimental *p-V* relations. Bardeen used Bridgman's²³ values of $\Delta V/V_0$ vs pressure for the alkali metals, making an extrapolation to 0°K of measurements made at 293°K. Since that time, compression measurements on the alkali metals have been made by Swenson¹³ at 4.2°K, and measurements on single crystals of sodium by the present author give values of the adiabatic bulk modulus and its pressure variation at room temperature more directly. The question arises then, which data to use in this interpretation.

Comparison of the results derived from Bridgman's compression data for sodium taken at 293°K and from Swenson's data taken at 4.2°K and shown in Tables I and II indicates that the initial bulk modulus increases about 15% in going from 293° to 4.2°, but that the initial values of dB/dP are essentially the same for the two temperatures. The low-temperature value of compressibility of sodium calculated from Swenson's data is about 15% above the 0°K value computed by Bardeen by theoretical extrapolation from the high temperature Bridgman data and displayed in Bardeen's Fig. 2.²⁰ Examination of the results obtained by Quimby and Siegel¹¹ for the adiabatic bulk modulus of sodium obtained over the range 80 to 210°K indicates an expected change of about 18% in going from 293°K to 4°K. However, their absolute values of B_s are out of line with those found by other investigators as shown in Table II.

We have chosen to apply the initial value of B_T derived from Swenson's low temperature data and our own value of dB_s/dP measured at room temperature on single crystals.

The bulk modulus B and its variation with volume $dB/d \ln \Omega$ may be written in terms of the cohesive energy per atom as follows:

$$\Omega_0 B = \Omega^2 \frac{\partial^2 E}{\partial \Omega^2} \Big|_{\Omega = \Omega_0},$$

$$\Omega_0 \frac{dB}{d \ln \Omega} = \Omega^2 \frac{\partial^2 E}{\partial \Omega^2} + \Omega^3 \frac{\partial^3 E}{\partial \Omega^3} \Big|_{\Omega = \Omega_0} \quad (6)$$

The cohesive energy per atom may be written as the sum of the energy of the lowest electronic state plus the average Fermi energy, i.e., $E_c = E_0 + E_F$. Following Fröhlich²¹ and Bardeen,²⁰ we take as an approximate expression for E_0 applicable to atomic volumes near the equilibrium volume;

$$E_0 = \frac{A}{(\Omega/\Omega_0)} - \frac{C}{(\Omega/\Omega_0)^3} \quad (7)$$

and for E_F we take the expression $E_F = B/(\Omega/\Omega_0)^{2/3}$. These expressions are only approximate in that they assume (1) that the values of the wave function near the boundaries of the atomic polyhedra do not differ appreciably from the free electron value, and (2) that the average effective mass of the electrons does not depend on the atomic volume for values near the equilibrium volume. The results given in this paper in the section concerned with volume variation of the shear elastic constants already indicates failure of these assumptions. Let us proceed with the approximate expressions, however, using experimental data to evaluate the constants A , B , and C , then to examine directly the effects of the failures of the assumptions by comparison of A , B , and C with the theoretically expected values. The experimental data used are:

1. The sum of the atomic heat of sublimation and the ionization potential.
2. The lattice parameter.
3. The bulk modulus.

All are to be taken at 0°K and evaluated at $P=0$. In order, these three conditions yield the following equations in terms of the constants A , B , and C of the equation of state,

$$E_c = \frac{A}{(\Omega/\Omega_0)} + \frac{B}{(\Omega/\Omega_0)^{2/3}} - \frac{C}{(\Omega/\Omega_0)^3} \quad (8)$$

$$10.04 \times 10^{-12} \text{ erg atom}^{-1} = A + B - C,$$

$$0 \text{ erg atom}^{-1} = -3A - 2B + C,$$

$$24.66 \times 10^{-12} \text{ erg atom}^{-1} = 18A + 10B - 4C.$$

Simultaneous solution of these yields:

$$A = 2.29 \times 10^{-12} \text{ erg atom}^{-1},$$

$$B = 5.46 \times 10^{-12} \text{ erg atom}^{-1},$$

$$C = 17.79 \times 10^{-12} \text{ erg atom}^{-1}.$$

The value of

$$\Omega \frac{dB}{d \ln \Omega} \Big|_{\Omega = \Omega_0},$$

predicted by these equations and called the "empirical" value is given by:

$$\Omega \frac{dB}{d \ln \Omega} \Big|_{\Omega = \Omega_0} = -4A - \frac{50}{27}B + \frac{16}{27}C$$

$$= -8.73 \times 10^{-12} \text{ erg atom}^{-1}.$$

Table III contains these values, and for comparison, a theoretical value for B from the free electron equation for the Fermi energy with $m^* = m$, and a theoretical value for C equalling the electrostatic energy of a uniform sphere with volume Ω of one electronic charge surrounding a positive ion, omitting the electrostatic self energy of the electron.²¹

¹¹ H. Fröhlich, Proc. Roy. Soc. (London) A158, 97 (1937).

²⁰ T. S. Kuhn and J. H. Van Vleck, Phys. Rev. 79, 382 (1950).

²³ P. W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 207 (1938).