6. Compressibility (Bulk Modulus)

The compressibility, which is the reciprocal of the bulk modulus, has been measured more extensively than has any other elastic property. Over 90% of the values listed in Tables IV and V are based on the extensive work of Bridgman. Bridgman's data were carried to quite high pressures (especially for his day), which were sufficient to determine the pressure dependence of the compressibility. Bridgman's early work was conveniently summarized as analytical fits of the experimental data, usually of the form

$$\Delta V/V = aP + bP^2 \tag{6.1}$$

where $\Delta V/V$ is the compression for a given pressure P (in kg/cm^2), and a and b are constants fitted to the experimental data. The isothermal compressibility at zero pressure is given by a, and the pressure dependence of the compressibility is given by b. Bridgman's later data, however, were not fitted to an expression such as Eq. (6.1); instead, the $\Delta V/V$ values were tabulated for a number of convenient pressures.

All of the data given by Bridgman are relative to the compressibility of iron, which he measured absolutely. In the late 1930's and early 1940's he redetermined the compressibility of iron[14–16] and found that the older values were incorrect, especially the value of the b term in Eq. (6.1). Unfortunately, considerable confusion has arisen regarding the redetermination, and therefore an attempt will be made here to clarify the situation.

In 1940 Bridgman[14] published a paper in which he noted that the absolute compressibility of iron previously used was incorrect. He expressed the revised data for iron in terms of $\Delta l/l$ rather than $\Delta V/V$:

$$\Delta l/l = -1.942 \times 10^{-7} P + 0.23 \times 10^{-12} P^2. \tag{6.2}$$

Slater,[17] who had derived an expression for the Grüneisen constant (see Section 28) based only on the a and b constants of Eq. (6.1), needed to know the revised values of a and b. Therefore, from the data given by Bridgman,[14] Slater[17] found that

$$-a_{\text{new}} = -a_{\text{old}} + 0.04 \times 10^{-7}, \tag{6.3a}$$

and

$$b_{\text{new}} = b_{\text{old}} - 1.30 \times 10^{-12}. \tag{6.3b}$$

In 1946 Bridgman[15] reviewed the recent developments in the high-pressure field. Therein, he gave the revised compressibility for iron as

$$\Delta V/V = -5.826 \times 10^{-7} P + 0.80 \times 10^{-12} P^2, \tag{6.4}$$

and furthermore he pointed out that the data published prior to 1940 must be corrected by using the following relations:

$$-a_{\text{new}} = -a_{\text{old}} + 0.033 \times 10^{-7}, \tag{6.5a}$$

and

$$b_{\text{new}} = b_{\text{old}} - 1.56 \times 10^{-12} - (0.022 \times 10^{-7}) a_{\text{old}}. \tag{6.5b}$$

A comparison of Eqs. (6.3a) and (6.3b) with Eqs. (6.5a) and (6.5b) reveals that the value suggested by Slater for correcting the a parameter is almost the same as that given by Bridgman, but that the corrections for the b parameter are quite different. Since Bridgman's and Slater's corrections are based on the same measurements, it is difficult to see why this discrepancy arose. Neither Bridgman's articles[14,15] nor his book[16] give further clues which might shed some light on this discrepancy. Perhaps Bridgman found another error in his measurements before 1940 which he did not discuss. In any event, since only Bridgman had intimate knowledge of his experimental techniques, it is felt that his values for correcting a_{old} and b_{old} are probably correct. Fortunately, almost all of the data Bridgman obtained for the pure elements prior to 1940 were redetermined. The only exceptions are boron, red phosphorus, vanadium, chromium, nickel, and hafnium. For these six elements Eqs. (6.5a) and (6.5b) were used to convert a_{old} and b_{old} into a_{new} and b_{new}.

It is also unfortunate that Bridgman's book,[18] which was reprinted in 1949, contains a tabulation of the *old* a and b values for a large number of elements, but no remark was made to warn the reader that they, especially the b values, are incorrect. Examination of the literature indicates that most authors are not aware of this.

For the above reasons and because almost all the compressibility data published by Bridgman after 1940 are available only in tabular form, and not as analytical fits,[19] all of Bridgman's data for the elements have been reduced to an equation of the form

$$\Delta V/V = aP + bP^2 + cP^2 + \cdots \tag{6.6}$$

by the method of least squares. In most instances only the first two terms of Eq. (6.6) were necessary to obtain a satisfactory fit. The elements which required more than two terms to fit the experimental data are,

[14] P. W. Bridgman, *Phys. Rev.* **57**, 235 (1940).
[15] P. W. Bridgman, *Rev. Mod. Phys.* **18**, 23 (1946).
[16] P. W. Bridgman, "Physics of High Pressure," pp. 416–417. Bell, London, 1949.
[17] J. C. Slater, *Phys. Rev.* **57**, 744 (1940).

[18] P. W. Bridgman, "Physics of High Pressure." Bell, London, 1949.
[19] J. J. Gilvarry fitted Bridgman's data for Li, Na, Al, K, Mn, Rb, Mo, Cs, Ta, and Au to an equation of the form of Eq. 6.6. In some instances more terms containing powers higher than P^2 were required (*J. Chem. Phys.* **23**, 1925 (1955)).