

Bridgman anvils (Katz and Ahrens, 1963). In this apparatus, an x cut quartz crystal is attached to the back of one anvil and a y cut quartz crystal is attached to the back of the other. This makes it possible to introduce either longitudinal or transverse waves through an anvil and into the sample by activating one or the other.

An important result of ultrasonic work is the determination of isothermal bulk modulus, B_T , and its pressure derivatives, B'_T , B''_T :

$$B_T = -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{1}{\beta} \quad (25)$$

where β is the isothermal volume compressibility. Since in acoustical measurements there is insufficient time during compression for dissipation of heat, the values which can be derived directly from the measurements are the adiabatic bulk modulus B_s and its pressure derivatives B'_s and B''_s :

$$B_s = -V \left(\frac{\partial P}{\partial V} \right)_S \quad (26)$$

The relationship between the adiabatic and isothermal bulk moduli is given by:

$$B_s = B_T (1 + \alpha\gamma T) \quad (27)$$

where α is the volume coefficient of thermal expansion and γ is the Gruneisen ratio.

For a cubic crystal at zero pressure the adiabatic bulk modulus is derived from the adiabatic elastic moduli by:

$$B_s(0) = \frac{c_{11} + 2c_{12}}{3} \quad (28)$$

where c_{11} and c_{12} are the elastic moduli oriented parallel and perpendicular respectively to the applied normal stresses and (0) indicates zero pressure.

The elastic moduli of a crystal may be derived from the velocities of longitudinal and transverse acoustic waves propagating through the crystal in different directions. These relationships for a cubic crystal are given in table 16.

The first pressure derivative of the bulk modulus can be determined from two types of sonic velocity measurements, (1) the variation of elastic moduli as a function of pressure in a hydrostatic system (Anderson, 1966) and (2) the third order elastic moduli calculated from acoustic velocities in a uniaxially stressed sample (Thurston, 1967; McSkimin and Andreatch, 1964). The relationship of the first pressure derivative of bulk modulus to the third order elastic moduli for a cubic ($m3m$) substance at zero pressure is given by:

$$B'_s(0) = -\frac{1}{9B_s(0)} (c_{111} + 6c_{112} + 2c_{123}) \quad (29)$$

Fourteen different combinations of stress, propagation, and vibration directions are necessary to acquire enough data to calculate the third order elastic constants. McSkimin and Andreatch (1964) give the equations relating the velocities to the third order elastic constants.

TABLE 16. Relationship of elastic moduli to acoustic wave velocities in cubic crystals

| Velocities | Propagation direction | Vibration direction | Mode |
|------------|-----------------------|---------------------|-------|
| V_1 | (001) | (001) | Long |
| V_2 | (001) | (110) | Trans |
| V_3 | (110) | (110) | Long |
| V_4 | (110) | (001) | Trans |
| V_5 | (110) | (110) | Trans |

Elastic moduli

$$\begin{aligned} c_{11} &= \rho V_1^2 \\ c_{11} &= \rho(V_5^2 + V_3^2 - V_4^2) \\ c_{12} &= \rho(V_1^2 - 2V_3^2) \\ c_{12} &= \rho(V_3^2 - V_5^2 - V_4^2) \\ c_{44} &= \rho V_2^2 \\ c_{44} &= \rho V_4^2 \end{aligned}$$

The conversion from B'_s to B'_T is given by:

$$\begin{aligned} B'_T(0) &= B'_s(0) + T\alpha\gamma \left(\frac{B_T(0)}{B_s(0)} \right) \\ & \left[1 - \frac{2}{\alpha B_T(0)} \left(\frac{\partial B_T(0)}{\partial T} \right) - 2B'_s(0) \right] + \left[T\alpha\gamma \left(\frac{B_T(0)}{B_s(0)} \right) \right]^2 \\ & \left[B'_s(0) - 1 - \frac{1}{\alpha^2} \cdot \left(\frac{\partial \alpha}{\partial T} \right)_P \right] \quad (30) \end{aligned}$$

The second pressure derivative of bulk modulus can be calculated from the fourth order elastic moduli. For a cubic ($m3m$) substance at zero pressure the relationship is given by:

$$\begin{aligned} B''_s(0) &= [-2c_{11} - 15B_s(0) - 9B_s(0)B'_s(0) \\ & + c_{1111} + 8c_{1112} + 6c_{1122} + 12c_{1123}] / 27B_s^2(0) \quad (31) \end{aligned}$$

The authors know of no experimental determinations of the fourth order elastic constants, and the conversion of adiabatic values to isothermal ones has not been worked out.

Anderson (1966) in a discussion of precision of ultrasonic velocity measurements estimates that the change of velocity with pressure in a hydrostatic system can be known to at least four significant figures provided the pressure also can be measured to four figures. This can be realized in measurements employing a dead weight loader for a primary pressure standard. He concludes that B_s can be measured to five figures, B'_s to three and possibly four figures, and B''_s to two and possibly three figures.

McSkimin and Andreatch (1964) estimate that their measurements of velocities as a function of stress have a possible error of five parts in 10^5 . The third order elastic constants which are utilized in the calculation of B'_s have errors which would result in an error of approximately 2 percent in the B'_s .

By substituting any combination of equations in table 16 into the equation for the adiabatic bulk modulus of a cubic substance, we obtain:

$$B_s(0)/\rho = v_p^2 - 4/3(v_s^2) \quad (32)$$

where v_p is the velocity of longitudinal waves and v_s is the velocity of transverse waves. This equation is also valid for a perfectly isotropic substance (Katz and Ahrens, 1963). Thus the ratio of bulk modulus to density may be found directly from the longitudinal and transverse sonic velocities in either a properly oriented single cubic crystal or a polycrystalline sample (which is essentially isotropic if the wavelength is long compared with the crystallite size.) Anderson and Schreiber (1965) have determined the bulk modulus and other elastic constants of MgO from sonic velocities in a polycrystalline sample under hydrostatic pressure up to 4 kbar. Katz and Ahrens (1963) have made velocity measurements on polycrystalline KCl and CaCO₃ between Bridgman anvils at pressures up to 40 kbar.

Pressure as a function of the ratio of bulk modulus to density at a given temperature is easily found from an equation of state. Thus, it is possible to find the pressure of a sample from its sonic velocities when its equation of state is known.

The high sensitivity of ultrasonic measurements suggests a possible secondary pressure gage in hydrostatic systems. Heydemann (1967b) has studied the feasibility of such a gage and proposes the use of fused quartz as the gage material. Indications are that such a gage would be more repeatable, more accurate, and more convenient than the manganin gage. In solid systems, a technique such as that employed by Katz and Ahrens (1963) is potentially useful as a means for determining pressure. Some advantages which it has to offer are: (1) sonic waves do not require special materials as windows or plugs for access to the sample; the source can be attached to the outer surface of a pressure chamber or anvil as in the apparatus of Katz and Ahrens, and (2) it is possible that in a carefully designed system the use of various geometries could yield information on the anisotropic strain within the sample. On the other hand, it has some disadvantages which make it generally less attractive than other methods. These are: (1) the sample must be homogeneous thus not allowing an intimate mixture of a sample with a calibrant as in high pressure x-ray diffraction, (2) the sample must be contained between two very parallel faces and the distances between the faces must be well known, and (3) lack of hydrostaticity may introduce a serious error in the calculations.

Studies indicating the potential use of ultrasonic meas-

urements to characterize liquid media to 50 kbar have been made by Heydemann and Houck (1968).

4.3. Resistance Gage

Secondary pressure gages based upon interpolation and extrapolation methods can be constructed using any physical parameter which varies monotonically with pressure. Criteria for selection of a particular phenomenon in preference to others are convenience, simplicity, reliability, and sensitivity. The resistance gage based upon the change of electrical resistance of a given length of metallic wire offers a very convenient and straightforward measurement consistent with a relatively high degree of reliability and sensitivity.

The possible use of such a gage for hydrostatic-pressure systems was first realized by Lisell (1903), who had measured the change of resistance with pressure for several metals. For most metals the very small change, a few parts per million for a pressure change of one bar, requires a very accurate measurement of the resistance. Earlier Palmer (1898) and later Bridgman (1909b) used the resistance of liquid mercury in a glass capillary, since for liquid mercury the change in resistance with pressure is almost two orders of magnitude greater than for most solid metals. Lisell proposed the use of manganin wire and when Bridgman (1911a) extended his measurements to pressures above the freezing pressure of mercury at room temperature, he adopted manganin as a resistance gage and studied its properties sufficiently to develop a secondary standard as reproducible and as sensitive as his primary free-piston gage in its stage of development at that time. Based upon continued development by Bridgman (1940a, b; 1946) and by Michels and Lenssen (1934) and careful studies by Adams, Goranson, and Gibson (1937) the manganin resistance gage became the accepted secondary gage for use in hydrostatic systems.

With significant increases in the precision, reliability, and range of the primary free-piston gage, re-evaluations of the resistance gage have been made (Newhall, 1962). The increased precision in both the primary and the resistance gages indicated limitation of the gages as discussed below. The significant considerations in selecting a suitable material for a resistance gage and the inherent advantages of this gage in contrast to other interpolation devices will be discussed before presenting the recent developments.

a. Requirements of an Acceptable Resistance Gage

One can enumerate those properties of a metal which would be desirable for use as a resistance gage: (1) high sensitivity of resistance to pressure, (2) low sensitivity of resistance to temperature, (3) a high degree of reproducibility from gage to gage (i.e., low sensitivity to chemical composition and manufacturing techniques), (4) a stable value of resistance with time or past history, (5) linear or nearly linear response with pressure, (6) high