

Albuerno and Drickamer, 1965). Of these, the one which has been used the most is NaCl (Jamieson and Lawson, 1962; Bassett, et al., 1967; Jeffery, et al., 1966; McWhan, 1967). NaCl has several properties which make it desirable as an internal standard.

1. It is cubic.

2. It has a high compressibility resulting in a more sensitive standard than the other materials which have been used.

3. It flows plastically thus providing a pressure transmitting medium.

4. It is not as heavy an absorber as some of the other materials and therefore can be used in larger abundances.

5. It has no phase changes up to 300 kbar. (Johnson, 1966; and Bassett, et al., 1968).

6. It is ionic and so the principal terms in lattice energy are easily treated theoretically.

7. There is a great deal of experimental data on NaCl.

The tetrahedral high pressure x-ray diffraction apparatus has been used for volume determinations at simultaneous high pressure and high temperature (Snyder, 1967). The temperature was measured by thermocouple, the volume by x-ray diffraction, and the pressure was calculated by means of Decker's equation of state for NaCl (Decker, 1966). A disadvantage in the use of NaCl for pressure determination at high temperatures is the tendency for recrystallization to take place resulting in large single crystals which cause spotty diffraction lines and Laue spots that reduce the accuracy of the diffraction measurements. This seems to become a serious problem only at temperatures above 300 °C.

McWhan (1964) discusses two sources of error in his high pressure x-ray method employing a gasketed sample between Bridgman anvils with an x-ray beam traversing the space between the anvils and producing a diffraction pattern on a photographic film. The first of these is line measurement, the second is physical. Using a cylindrical film of diameter 114.6 mm with the sample at the center, he reports that he is able to measure the diffraction angle  $\theta$  to  $\pm 0.01^\circ$ . His overall average error in  $d$ -spacing due to reading is approximately 0.1 percent.

He breaks the physical sources of error down into five categories: (1) film shrinkage, (2) effective camera diameter, (3) absorption, (4) sample eccentricity, and (5) pressure distribution. The use of a printed scale on the film helps minimize error due to film shrinkage. Careful machining should result in an error less than 0.01 percent due to camera diameter. Dilution of the sample can reduce the source of error due to absorption to the range, 0.1 percent to 0.3 percent. Error due to eccentricity can be kept to 0.1 percent in  $d$ -spacing by very careful positioning of the sample at the center of the anvil faces. Pressure gradient which is considerable in an opposed anvil device can lead to line broadening of from  $0.04^\circ$  to  $0.1^\circ \theta$  at 150 kbar. Taken together,

these errors result in a minimum absolute error in  $d$ -spacing of about 0.5 percent.

McWhan estimates that by using a Guinier focusing geometry which eliminates absorption as a source of error, he is able to reduce his error to 0.2 percent. However, an advantage which the Debye-Scherrer geometry has over the Guinier geometry is the camera symmetry which allows measurement of both sides of a diffraction line, thus providing a means of checking sample centering for each determination. McWhan concludes that with a correction curve and careful work the minimum realistic error in  $d$ -spacing, hence lattice parameter, that can be obtained with molybdenum radiation in the Debye-Scherrer geometry is 0.1 percent and in the Guinier geometry is 0.07 percent. For a given equation of state for NaCl, an error of 0.1 percent in lattice parameter leads to an error of 2 percent in pressure at 100 kbar.

Mao, et al. (1967) discuss four sources of error in their high pressure cell in which a sample is placed between two opposed diamond anvils, and an x-ray beam passes perpendicular to the anvil faces and produces a diffraction pattern on a cylindrical film of 100 mm diameter (Bassett, et al., 1967). These are: (1) reading error, (2) change in film dimension, (3) change in sample-to-film distance, and (4) change in x-ray wavelength due to change in monochromator orientation. Repeated readings of the same pattern show a standard deviation of 0.03 percent for  $d$ -spacings. Sources (2), (3), and (4) taken together result in a standard deviation of 0.15 percent for  $d$ -spacings. The sample-to-film distance is calculated from the diffraction data of a sample of known lattice parameter at one bar pressure between the anvil faces. Since the same errors are involved in the sample-to-film distance determination as in the high pressure lattice parameter determinations, these errors are cancelled out as long as they are constant. By placing a polycrystalline platelet of NaCl or MgO on the film side of the back diamond anvil, it is possible to mark the film with a known diffraction pattern even while the sample is under pressure. In this way, corrections can be made for changes in both film and camera dimensions. Since this external polycrystalline sample is able to clearly resolve  $\text{MoK}_{\alpha 1}$  and  $\text{MoK}_{\alpha 2}$ , it provides a means for determining the spectrum of radiation being used. All photographs for which a monochromator was used show that the radiation was pure  $\text{K}_{\alpha 1}$ . Therefore, variation of wavelength, (4) may be eliminated as a source of error. Absorption is not considered to be a serious source of error because of the very thin (5 microns) tabular shape of the sample. Line broadening indicates a pressure range of approximately 10 kbar in the x-ray beam at 150 kbar. However, if the diffraction lines are always read at the center, the pressure distribution does not introduce a serious error.

Since sample-to-film distance is determined in such a way as to cancel errors and a means for correcting for film shrinkage is used, the accuracy is probably approxi-



mately equal to the precision. Thus, the diamond anvil cell can be expected to produce data with a minimum error of 0.15 percent in average  $d$ -spacing or lattice parameter and 3 percent in pressure at 100 kbar for a given equation of state of NaCl.

One of the principal advantages discussed by Jeffery, et al. (1966) of the tetrahedral press over opposed anvil designs is the homogeneity and hydrostaticity of pressure throughout the sample. This permits a pressure resolution of 0.5 kbar or better. They estimate their precisions for lattice parameter measurements to be approximately 0.1 percent or less than 2 kbar when pressure is determined by means of an NaCl compression curve up to 100 kbar. In repeat runs of actual measurements of pressure phase transformations in Bi and Ba using the NaCl internal standard, they found errors between 1 percent and 2 percent in pressure thus confirming their estimates of the precision of their technique.

In conclusion, three analyses of instrumental error in the application of x-ray diffraction to the measurement of pressure by means of an equation of state for NaCl have been reviewed. They were found to be in remarkably good agreement on the sources and magnitude of error for such diverse geometries. It should be remembered, however, that in each analysis the equation of state of NaCl was assumed to be correct and so it was not considered as a source of error.

#### c. Neutron Diffraction

Although very little work in high pressure neutron diffraction has been undertaken, the technique clearly has some advantages over high pressure x-ray diffraction (Bennion, et al., 1966; Brugger, et al., 1967; Smith, et al., 1966). One is able to detect ordering of the magnetic spins, since scattering is by the nucleus and the scattering powers differ from those for x-ray diffraction and scattering powers are not dependent on scattering angle. Bennion, et al. (1966) and Brugger, et al. (1967) report that by means of a piston and cylinder high pressure vessel and a fixed angle of time-of-flight detector they were able to achieve an accuracy of  $0.0002 \text{ \AA}$  (0.1% to 0.2% of their  $d$ -values), a capability comparable to that of x-ray diffraction, and to resolve peaks to  $0.020 \text{ \AA}$  apart, a resolution far superior to that of x-ray diffraction. They have used NaCl as an internal pressure standard in the same manner that it has been used in high pressure x-ray diffraction. With their accuracy, the use of an internal standard is as satisfactory as it is in the x-ray techniques. The accuracy reported by Smith, et al. (1966) is also 0.1 percent to 0.2 percent for the more conventional goniometric measurements and should also permit reliable use of an internal pressure standard.

#### d. Sonic Velocity Measurements

In the preceding sections, we considered two types of techniques, dilatometry and diffraction, which yield

data on molar volume as a function of pressure and temperature. Sonic velocities, however, yield data from which we may calculate the first derivative of volume with respect to pressure (compressibility) or the reciprocal of compressibility (bulk modulus). When sonic velocities are measured over a range of pressures, the first and second derivatives of bulk modulus may be calculated. The pressure range over which sonic velocity measurements can be made with reasonable accuracy is limited by the need for hydrostatic conditions. As a result, most measurements have been made in the one bar to 10 kbar range. However, equations of state based on measurements of bulk modulus and its derivatives at low pressure can be used to predict  $P(V)$  along an isotherm to much higher pressures with fairly good accuracy (Anderson, 1966).

Frequencies for making sonic velocity measurements are chosen so that wavelengths are smaller than sample thicknesses. Thus, ultrasonic frequencies in the range of tens of megacycles per second are used.

Ultrasonic velocities in solids are usually measured by cementing a quartz crystal transducer to a block of the material being studied and applying an electric signal of the desired frequency to the quartz. In turn, the quartz produces sound waves of the same frequency which traverse the sample and are reflected from the far surface. The travel time for a pulse of sound can be measured by picking up the reflected pulse with the same transducer. The more bounces the pulse makes within the sample, the greater the effective path length and the greater the accuracy. Lazarus (1949) made ultrasonic measurements by this technique up to 10 kbar by placing the sample and transducer in a hydrostatic fluid medium inside a high pressure vessel.

The accuracy of ultrasonic measurements has further improved with the use of phase comparison or interferometry for measuring the travel time of the sound through the sample (McSkimin, 1950).

In both of the methods described above, longitudinal or transverse waves may be produced in the sample by the choice of  $x$  or  $y$  cut quartz crystals cemented either directly to the specimen or with a buffer rod of quartz or fused silica between the quartz driver and the specimen. By various combinations of longitudinal and transverse waves with different orientations of a single crystal of sample, it is then possible to obtain the various second order elastic constants for the sample.

McSkimin and Andreatch (1964) further refined the techniques for ultrasonic velocity measurements by designing a device in which they can place the sample under a uniaxial stress while sonic velocities are being measured. This is done by squeezing a cube of sample between two very flat stainless steel surfaces, and at the same time bouncing sound waves between two of the exposed surfaces of the sample cube.

In addition to the hydrostatic and intentionally stressed systems described so far, measurements have been made in a solid system up to forty kbar using