

in position of the maximum in the temperature-resistance curve for manganin at these very high pressures.

Of passing interest is the use of a manganin coil as a pressure gage in a non-hydrostatic environment by Montgomery, et al. (1963), and by Samara and Giardini (1964). Use of a manganin coil in non-hydrostatic media has been tried by others in the field but not extensively reported since the pressure coefficient is non-reproducible and the resistance is irreversible, at least on the sensitivity scale discussed above. Furthermore, the coefficient is drastically different from that measured using hydrostatic pressure. For qualitative interpolation between known pressure calibration points as used by these authors it has utility.

f. Gold-2.1 Percent Chrome Gage

As mentioned above, Darling and Newhall (1953) proposed the use of an Au-2.1 percent Cr alloy as an improvement to replace the manganin gage due to the improved temperature-resistance variation. Boren, Babb, and Scott (1965) and more recently Davis and Gordon (1967) have evaluated this gage in terms of its stability, reversibility, and general adaptability to use. They report a rather serious irreversible hysteresis loop, in no case being less than five bars wide according to Boren, et al. Davis and Gordon report a very serious resistance variation with temperature at high pressure even though a rather low variation is obtained at low pressure. Both authors report serious difficulty in stabilizing the resistance gage with appropriate seasoning techniques. Although significant stabilization occurs, it requires greater care and control than does manganin according to Davis and Gordon, and the final stability is much poorer than manganin. A further practical problem of making electrical connections to the gage wire is encountered as reported by Darling and Newhall. The improved resistance vs temperature characteristic gives improved response when changing pressure rapidly and gives added stability with respect to temperature at the lower pressures, but the material appears to have several rather serious drawbacks when considering its use as a secondary standard.

g. Conclusion

In the ever continuing search for better calibration and measuring techniques, several areas for future work appear significant.

1. It seems meaningful for the high-pressure community to specify and accept a particular specific manganin alloy and perhaps a manufacturer with appropriate specifications for general use as a pressure gage and also to specify a standard technique of winding and seasoning coils. If this were agreed upon, pressure calibration to within one percent could be assured without independent calibration of each gage.

2. To facilitate intercomparisons of gages as calibrated by independent workers, a two-point calibration should

be reported of the form:

$$P = A \left(\frac{\Delta R}{R} \right) + B \left(\frac{\Delta R}{R} \right)^2$$

for pressures less than 25 kbar.

3. As new alloys become available from the manufacturers of precision resistors, these alloys along with others not previously studied should be tested to see if improved resistance-temperature characteristics can be obtained consistent with other stability requirements and appropriate pressure coefficients.

4. Additional work needs to be carried out to increase the long-term stability of manganin coils. The use of coated manganin to prevent oxidation appears feasible and promising.

5. Additional data on manganin at higher pressures to increase our knowledge of the $R(T, P)$ function is significantly important for use of the gage at the higher pressures.

4.4. Other Pressure Gages

This section deals with additional properties of materials which vary continuously with pressure and therefore offer possible methods for pressure determination. All of them are capable of detecting phase transformations and hence, can utilize the fixed point pressure scale for pressure determination. The purpose of this section, however, is to discuss the continuous changes of these properties as a means of interpolating and extrapolating pressures.

a. Optical Absorption as a Pressure Gage

Many substances have absorption edges or bands within the visible, ultraviolet, or infrared which shift as a function of pressure. The direction and rate of shift vary greatly from material to material. However, there are some that shift rapidly across the visible spectrum and once calibrated provide remarkably sensitive and convenient methods for determining pressure.

Two types of instruments have been used for the study of absorption spectra of substances under pressure: (1) piston and cylinder with NaCl windows in the walls of the cylinder (Drickamer, 1961; Fitch, et al., 1957), and (2) diamond anvil press in which the diamond anvils serve as windows (Weir, et al., 1962). Drickamer has constructed two versions of the piston cylinder device. One has flat piston ends and a fairly large sample volume which can go up to 55 kbar. The other, which has tapered pistons with flats 0.090 inches in diameter, can achieve 200 kbar with occasional excursions to higher pressures. The pressure transmitting medium surrounding the sample is NaCl. Opaque masks of pipestone or aluminum are embedded in the NaCl along with the sample. Light enters and exits from the sample chamber through pressed NaCl plugs filling tapered holes in the cylinder wall.

In the diamond anvil press, a sample is squeezed

between flat diamond anvil faces which are mounted on the ends of pistons driven together by a lever and screw assembly. Axial holes in the pistons permit light to enter and leave the sample by way of the diamond anvils. In the piston-cylinder design, the whole high pressure unit is placed in the sample location of a spectrophotometer. In the case of the diamond press, the sample area can be imaged and photographed, or the image can be masked and small portions of it measured successively with a microspectrophotometer. An ungasketed sample within a diamond press sustains a large pressure gradient, thus the imaging and selection of portions of the image is necessary. With the use of a gasket, however, the diamond press can be placed directly in a spectrophotometer.

Drickamer (1963, 1965) and his coworkers have studied the effects of pressure on the absorption spectra of many substances. Many of these would be satisfactory for calibration for pressure determination; Lippincott and Duecker (1964) selected nickel dimethylglyoxime as a pressure gage in a study of pressure distribution in a diamond anvil high pressure cell. Zahner and Drickamer (1960) reported that the absorption maximum at $19,000\text{ cm}^{-1}$ for nickel dimethylglyoxime shifts toward lower frequencies with pressure with an initial slope of $-80\text{ cm}^{-1}/\text{kbar}$. The slope decreases with pressure and at 100 kbar, the frequency of the absorption band is approximately $13,000\text{ cm}^{-1}$. Thus, the absorption band of nickel dimethylglyoxime traverses most of the visible spectrum between 1 bar and 100 kbar.

Lippincott and Duecker using mixtures of nickel dimethylglyoxime with alkali halides in the diamond anvil press, were able to detect the effect of pressure on the absorption spectrum by three different methods. They observed a color change with pressure under a microscope in white light, they photographed the sample in monochromatic light of various frequencies thus identifying the portion of the sample at the pressure for which there is the maximum absorption for that frequency, and finally, they made step scans across the sample area by microscope spectrophotometer. They also used TlBr which has an absorption edge at $23,950\text{ cm}^{-1}$ and which according to Zahner and Drickamer (1959) shifts $-115\text{ cm}^{-1}/\text{kbar}$. This material is particularly suitable for the photographic technique since its absorption edge shows particularly well in a photograph.

Neither Zahner and Drickamer (1960, 1959) nor Lippincott and Duecker (1964) discuss precision or sources of error in their measurements. Zahner and Drickamer (1960), however, give a plot of experimental points having a spread of approximately 10 percent in pressure for three different runs. One gets the impression that if optical absorption is to be used seriously for pressure determination, the precision can be made much better than this. Since the optical absorption method is only a means of interpolation and extrapolation, the ac-

curacy of the method must depend upon the accuracy of the calibration of the standards.

The broadening of the absorption band in nickel dimethylglyoxime with increasing pressure may also be a serious source of error at higher pressures. Perhaps other substances would prove to be more suitable for higher pressures.

One of the chief advantages of this method is the rapidity with which it can give the pressure. One can make instantaneous observations of the color of the sample by microscope. Spectrophotometer measurements or photographic techniques take only minutes longer. Another advantage is that the method can give the pressure at a point in the sample even when a large gradient is present. Of all the methods of pressure determination described here, the optical absorption method is probably capable of determining pressure within the smallest volume of sample. An estimate of the lower limit of that volume is 50 cubic microns. By contrast, the smallest volume of sample under pressure for which an x-ray diffraction pattern has been obtained is of the order of 5,000 cubic microns.

The chief disadvantage of the absorption technique is that the samples which can be mixed with the pressure indicator without obscuring it are limited to those which are transparent and have refractive indices close to those of the pressure indicator.

b. Refractive Index as a Pressure Gage

Many aspects of the study of refractive index as a function of pressure are similar to those found in the study of sonic velocities as a function of pressure. This is true because refractive index is the normalized velocity of light. As in the case of sonic velocity measurements, refractive index can be calculated from the thickness of the sample and the time required for a signal to travel to the far side of a sample and back again. Also, as in sonic velocity measurements, the most precise way of measuring the travel time is by interferometry. Vedam and his coworkers (Vedam and Schmidt, 1966; Vedam, et al., 1966) have designed a liquid high pressure chamber with an alumina window which permits continuous observation of the interference between light reflected from the front and back faces of a block of sample hydrostatically compressed within the liquid medium. With this device, they have measured refractive indices for a number of materials up to 7 kbar. This technique is similar to the liquid systems used in the sonic velocity methods.

Bassett (unpublished) has attempted to measure refractive index as a function of pressure in a diamond anvil press by a method analogous to the one used by Katz and Ahrens (1963) for measuring sonic velocities. The time for the light to travel from the upper diamond-sample contact to the bottom one and back again is determined by interferometry using the same relationships as used in ultrasonic interferometry. The frequency and