CHAPTER 3

MEASUREMENT OF THE UNIAXIAL STRESS COMPONENT IN THE TUNGSTEN CARBIDE ANVIL CAMERA

The opposed-anvil configuration is most commonly used in the form of diamond anvil and tungsten carbide anvil cameras for x-ray diffraction studies of solids under high pressures. A uniaxial load is applied to pressurize the specimen. Because of the finite shear strength of solids, the pressure generated is quasi-hydrostatic when no pressure transmitter is used or when a solid pressure transmitter is used. The axial stress component is larger than the radial stress component. The difference between the axial and the radial stress components has been termed (49) the uniaxial stress component (USC). The quasi-hydrostatic pressure generated in an opposed-anvil set-up can be approximated to a superposition of a hydrostatic stress component and a USC. The presence of USC even in low shear strength materials, such as sodium chloride, has been detected experimentally (57). The stress anisotropy in the diamond-anvil set-up has been reported by Weaver et al. (47) and Kinsland and Bassett (50,51).
The presence of USC introduces a systematic error in the equation of state determined by high pressure x-ray diffraction methods. It was pointed out by Sato et al. (48) that the experimental bulk modulus of magnesium oxide was grossly overestimated when sodium chloride was used as a pressure marker. The effect of USC on the experimental equation of state was discussed in detail by Singh (58). It was shown (46) experimentally that the equation of state could be determined with precision by using epoxy as the pressure transmitter. To evaluate the performance of epoxy as a pressure transmitter, the uniaxial stress components in sodium chloride-epoxy, silicon-epoxy and magnesium oxide-epoxy mixtures have been measured.

3.1 Method of Estimating the USC

In the tungsten carbide anvil camera the sample is contained in a boron-epoxy gasket. The specimen occupies a very small region at the centre of the gasket. Typically, the diameter of the sample is ~ 0.3 mm while that of the gasket is ~ 3 mm. Hence, the load across the sample can be considered uniform.

At a given load, let the uniaxial and the hydrostatic components of stress be respectively $t$ and $p$. The lattice strain is given by,

$$
\varepsilon(hkl) = \varepsilon_p + \varepsilon_t (hkl)
$$
For a sample crystallizing in the cubic system,

\[ \xi(hkl) = \frac{a(hkl)}{a_0} - 1 \]

where \(a_0\) is the lattice parameter at atmospheric pressure and \(a(hkl)\) is the lattice parameter determined from the \((hkl)\) reflection at the applied load. It has been shown (49) that

\[ \xi(hkl) = \xi_p + s_{12}t + St \Gamma(hkl) \ldots \ldots (1) \]

where \(s_{ij}\) denotes the elastic compliances. Further,

\[ \Gamma(hkl) = \frac{h^2k^2 + k^2l^2 + l^2h^2}{(h^2 + k^2 + l^2)^2} \]

\[ S = s_{11} - s_{12} - \frac{1}{2}s_{44} \]

Eq. (1) indicates that a plot of \(\xi(hkl)\) against \(\Gamma(hkl)\) gives a straight line with slope \(St\). Therefore, the USC can be determined from the slope of the \(\xi(hkl)\) versus \(\Gamma(hkl)\) plot if \(S\) is known.

3.2 Experiments

The procedure described in Chapter 2 was followed for preparing the specimens. The samples (sodium chloride, silicon, magnesium oxide) mixed with epoxy resin in the
ratio 1:4 were filled in the central holes of the boron-epoxy gaskets and were pressurized in the tungsten carbide anvil camera (Chapter 2).

The x-ray diffraction patterns were recorded at different applied loads. These patterns were analysed to derive the strain $\varepsilon(hkl)$ on the several (hkl) planes and also to obtain the unit cell volume of the specimen. The pressure on sodium chloride at different applied loads were determined from the measured unit cell dimensions and the equation of state of sodium chloride (52). In the experiments with silicon and magnesium oxide, the pressures were determined following the calibration procedure discussed in Chapter 2. The experiments were repeated to collect a large number of data points.

At each pressure $p$, the observed values of $\varepsilon(hkl)$ were fitted to Eq. (1) by the method of least squares. The slopes of the $\varepsilon(hkl) - \Gamma(hkl)$ plot were obtained for sodium chloride-epoxy, silicon-epoxy and magnesium oxide-epoxy mixtures at different pressures.

3.3 USC in Sodium Chloride-Epoxy Mixture

In the case of sodium chloride, experiments were conducted with two types of epoxy. The first set of data shown in Fig. 20 was obtained with Scotch Household epoxy marketed by 3M Company of U S A. The second set of data
shown in Fig. 21 was obtained with Araldite marketed by CIBATUL Limited, India. The scatter in the data is typical of such plots. The large scatter in these experiments arises because to start with the accuracy of the lattice strain measurement in high pressure experiments is not very high, at best ± 0.0005, and the quantity plotted in Figs. 20 and 21 is the first derivative of strain (Eq. 1).

Further, it is seen that the slope of the $\epsilon(hkl) - \bar{n}(hkl)$ plot has both positive and negative values. The sign of $t$ is negative, since $t$ is compressive. The sign of the slope is thus determined by the sign of $S$; the slope should have a positive sign for a material having a negative value of $S$ and a negative sign for a material with a positive value of $S$. The values obtained experimentally have both positive and negative signs because of the experimental errors involved. However, the following analysis shows that the value of $t$ determined from these data has a right sign.

The USCs at different pressures were determined using the single crystal elastic constants of sodium chloride and their pressure derivatives (59). The values of $t$ were then fitted by the method of least squares to an equation of the type
Fig. 20. The slope of $\varepsilon(hkl)$ vs $f(hkl)$ line against pressure for NaCl-Scotch epoxy mixture.
NaCl-ARALDITE

Fig. 21. The slope of $\varepsilon(hkl)$ vs $\Gamma(hkl)$ line against pressure for NaCl-araldite mixture.
\[ t(p) = t(o) + p \, t'(p) \]

The results obtained with respectively Scotch epoxy and Araldite are:

\[ t(p) = -0.139 + 0.0021 \, p \quad \cdots \quad (2) \]
\[ t(p) = -0.112 + 0.010 \, p \quad \cdots \quad (3) \]

It is clearly seen from Eqs. (2) and (3) that the USC in sodium chloride when it is mixed with epoxy is nearly \(-0.1\) GPa and its pressure dependence is small.

The Eqs. (2) and (3) can be compared with that obtained in the case of pure sodium chloride (57), which is

\[ t(p) = -0.24 - 0.011 \, p. \]

It is evident that the USC is significantly smaller in sodium chloride-epoxy mixture than in pure sodium chloride.

3.4 USC in Silicon-Epoxy Mixture

In the case of silicon, the data points were obtained with Scotch epoxy. The data are shown in Fig. 22. The single crystal elastic constants of silicon and their pressure derivatives (60) were used to calculate \( S \) at various pressures. The slopes were converted to \( t \).
FIG. 22. SLOPE OF $\varepsilon(hkl)$ vs $\Gamma(hkl)$ LINE AS A FUNCTION OF PRESSURE FOR SILICON-SCOTCH EPOXY MIXTURE
Assuming a linear pressure dependence of $t$, the following relation was obtained:

$$t(p) = -0.7 - 0.07p$$

Thus the USC in silicon in a silicon-epoxy mixture is nearly $-0.7$ GPa. The USC, when silicon alone is compressed (57), is $-2.0$ GPa. It is seen that the USC is significantly reduced in the presence of epoxy.

3.5 **USC in Magnesium oxide-Epoxy Mixture**

In the case of magnesium oxide, the data points were obtained with Scotch epoxy. Fig. 23 shows these data as a function of pressure. Using the single crystal elastic constants of magnesium oxide and their pressure derivatives (61), an average value of $t$ was obtained as $-0.5$ GPa up to a pressure of about 8 GPa.

Kinsland and Bassett (51) studied the USC in pure magnesium oxide pressurized in a diamond-anvil camera. The diamond-anvil camera was modified to record the full diffraction ring. The USC was determined by a measurement of the ellipticity of the diffraction ring. A value of $-2.4$ GPa was obtained at 4 GPa for the USC in pure magnesium oxide.
Fig. 23. The slope of $\epsilon(hkl)$ vs $\sigma(hkl)$ line against pressure for MgO-Scotch epoxy mixture.
The present value of USC in magnesium oxide-epoxy mixture is -0.3 GPa around a pressure of 4 GPa. Thus it is clear that the USC is reduced significantly in the presence of epoxy.

### 3.6 Discussion

It must be noted that the results discussed so far were obtained with a specimen-epoxy ratio 1:4. The USC can be further reduced, at least in the cases where specimen can support large USC, by decreasing the specimen-epoxy ratio. This ratio, however, cannot be made too very small, because a low ratio will result in low intensity and also a low peak-to-background ratio in the x-ray diffraction patterns. The results of a number of experiments (46) indicate that a specimen-epoxy ratio of 1:4 or 1:5 is small enough to reduce the USC to an acceptable level, but not too small to render the quality of x-ray patterns unacceptable.

The use of epoxy as a pressure transmitting medium in the precise determination of the equation of state has been demonstrated in many cases (46). In these experiments the applied load was calibrated in terms of pressure at the centre of the gasket by making runs with sodium chloride—epoxy mixture. In subsequent runs with specimen-epoxy mixture the pressure is determined by making use of
the load-pressure relation determined in the calibration runs. The success of this method depends on the high degree of reproducibility of the load-pressure relation. This certainly appears possible if the experimental procedure described in Chapter 2 is strictly followed. It may appear advantageous to use a mixture of sodium chloride and specimen with epoxy as a pressure transmitting medium, because in such a case highly reproducible load-pressure relation is not essential. This is not found practicable for the following reason. If a reasonable ratio, say 1:4, of (specimen + sodium chloride) and epoxy is used, then the ratios of specimen-epoxy and sodium chloride-epoxy become small (1:8), and this results in poor quality of the x-ray diffraction patterns for both sodium chloride and the specimen.

The present study indicates that the use of epoxy as a pressure transmitting medium reduces the uniaxial stress component and makes the stress distribution nearly hydrostatic. It has been shown (46) that the equation of state of solids can be determined with precision by the use of epoxy as a pressure transmitting medium. However, truly hydrostatic pressure can be achieved only with a fluid pressure transmitting medium.