

Figure 6 Proposed mechanism of crack formation.

keep in mind two experimental facts found by direct observation. One is that grown-in dislocations do not move; the second is that the slip line density is low near grain boundaries in comparison with the crystal bulk. That is, the pinning effect of impurity solutes on dislocation motion is extremely strong. From these observations it is inferred that crack formation in magnesium oxide occurs by the Stroh mechanism with impurity solutes or grown-in dislocations associated with impurity solutes acting as obstacles on which edge dislocations pile up. If the relation between moving dislocations and immobile grown-in dislocations satisfy the condition of crack formation given by the Cottrell model [5], cleavage fracture can occur under extension (Fig. 6).

In summary, fracture observation in bicrystal magnesium oxide indicates that fracture occurs not along the grain boundary, but in the bulk about 500 to 2000 Å from the boundary. This observation suggests a serious caveat associated with the interpretation of the chemical composition of so-called "grain-boundary" fractures, since these fractures may often be adjacent to, rather than at, the grain boundary.

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### High pressure X-ray studies of polymers. I. Calibration for the diamond-anvil cell in the range 0 to 15 kbar

The diamond-anvil pressure cell, first reported in 1959 [1], has been used to study materials at high pressures with a variety of methods, including optical observation [2], X-ray diffraction [2-8], absorption spectroscopy [9], and Raman scat-

tering [10]. The most serious drawback in using the diamond-anvil pressure cell is the measurement of the high pressure attained in the device. The usual method is to incorporate an NaCl standard with the sample and to make measurements of the lattice parameter using X-ray diffraction. The pressures can be determined through an equation of state [11]. Recently, a more convenient method has been reported by Piermarini and Block

using ruby fluorescence [12]. Both these methods are accurate at the ultrahigh pressures that can be achieved using the diamond-anvil pressure cell.

However, a variety of interesting phenomena is known to occur at comparatively low pressures for the case of polymeric materials. Crystallization of polyethylene at pressures of 3 to 5 kbar can give rise to unique morphologies, and it has been suggested that crystallization into a new crystal phase, not observed at room pressure [13–15], may be related to this. A reversible phase transition for the case of polytetrafluoroethylene has been reported at 7 kbar [16]. There are many other examples and, in fact, studies of polymers have been limited to pressures less than 15 kbar.

It would obviously be convenient to use the diamond cell to study these transitions, but neither the NaCl method nor the ruby fluorescence method provides sufficient accuracy at low pressures. When X-ray diffraction techniques are being used, the NaCl method is convenient but the changes in  $d$ -spacings at low pressures are too small to measure accurately. Molecular crystals, with weaker secondary bonds, have higher compressibilities than ionic crystals, and therefore would be more suitable pressure standards at low pressures. Two materials were considered, adamantane and hexamethylene tetramine (HMT). Adamantane would not be suitable, however, since a phase transition occurs at higher pressures [17]. No phase transition has been reported for the case of HMT [18], and the material is readily available in purified form. The compressibility of HMT has been reported as  $1.23 \times 10^{-11} \text{ cm}^2 \text{ dyn}^{-1}$ , approximately three times greater than the compressibility of NaCl. For these reasons, it was decided to compare the accuracy of the pressure determination using NaCl with the accuracy using HMT.

If a particular material is to be used as a pressure standard, it is necessary that the  $d$ -spacings be known for various pressures. For the case of NaCl, the change in  $d$  spacing at various pressures has been calculated by Dekker [11] from the equation of state. For the case of HMT, the equation of state has not been derived, but the pressure-volume relationship at 295° K for HMT has been investigated by Bridgeman [19]. Bridgeman measured the specific volume of HMT at different pressures up to 40 kbar. Unfortunately, his data in the low-

TABLE I

Pressure (dyn cm <sup>-2</sup> )	Volume (%)
$9.806 \times 10^5$	0.00
$1.718 \times 10^9$	1.54
$2.120 \times 10^9$	2.05
$2.885 \times 10^9$	2.64
$3.864 \times 10^9$	3.46
$4.835 \times 10^9$	4.25
$5.770 \times 10^9$	4.93
$6.862 \times 10^9$	5.67

1 kbar = 980.7 kg cm<sup>-2</sup> = 10<sup>9</sup> dyn cm<sup>-2</sup>.

pressure region of interest to us (0 to 15 kbar) are rather few and, in fact only three measurements could be used in this range: at 5, 10 and 15 kbar.

For this reason, Bridgeman's experiment was repeated by us using a dilatometer. Several measurements were made in the pressure range of greatest interest to us (0 to 7 kbar). These data are shown in Table I. In Fig. 1, the data are shown in graphical form combined with the three data points of Bridgeman.

According to Slater [20], at low pressures the pressure–volume relationship can be assumed to have the form:

$$\frac{V_0 - V}{V_0} = k_1 p - k_2 p^2 \quad (1)$$

where  $V_0$  is the initial volume.  $k_1$  and  $k_2$  are constants related to the thermal expansion coefficient of the material used, the compressibility, and the Grüneisen constant. A least-squares programme was used to obtain the best fit for the data, and the following values were obtained:  $k_1 = 9.77 \times 10^{-12} \text{ cm}^2 \text{ dyn}^{-1}$ ;  $k_2 = 2.16 \times 10^{-22} \text{ cm}^4 \text{ dyn}^{-2}$ . The best fit to the data is shown by the solid line in Fig. 1.

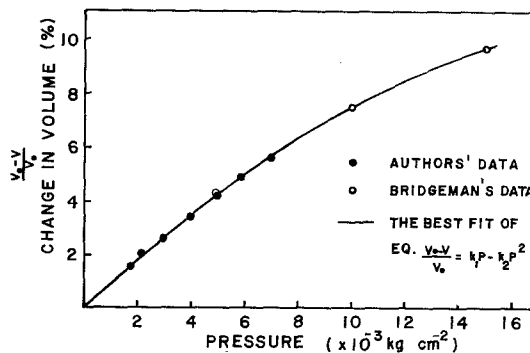


Figure 1 Volume–pressure relationship of hexamethylene tetramine at room temperature.

Since HMT has a cubic lattice, the  $d$ -spacings of any set of planes ( $hkl$ ) can be easily obtained from Equation 1 when  $k_1$  and  $k_2$  are known. As an example, the  $d$ -spacings of the (110) reflection (the most intense reflection) were calculated, and are shown in Table II. With the aid of Equation 2, HMT can be used as a pressure standard for the diamond cell.

TABLE II

Pressure (kg cm <sup>-2</sup> )	$d_{110}$ (Å)
1	4.9800
1 000	4.9644
2 000	4.9494
3 000	4.9350
4 000	4.9212
5 000	4.9080
6 000	4.8955
7 000	4.8837
8 000	4.8725
9 000	4.8620
10 000	4.8522
11 000	4.8430
12 000	4.8346
13 000	4.8268
14 000	4.8198
15 000	4.8135

1 kbar = 980.7 kg cm<sup>-2</sup> = 10<sup>9</sup> dyn cm<sup>-2</sup>.

HMT is a molecular crystal with a high melting point, and therefore can be used as a filler for most polymers. The advantage of this method is that the pressure on the HMT crystals embedded in the polymer matrix truly reflects the pressure on the polymer sample. Moreover, the HMT crystal-to-film distance is identical with the polymer-to-film distance. The constants of the best fit,  $k_1$  and  $k_2$ , are given by

$$k_1 = \frac{a_1}{1 + a_0}; \quad k_2 = \frac{a_2}{1 + a_0}$$

where  $a_1$  is approximately equal to the volume compressibility at zero pressure,  $a_0$  is related to the thermal expansion coefficient  $\alpha$  by  $a_0 = \int_0^T \alpha dT$ , and  $a_2$  is a measure of the change of compressibility with pressure. If we neglect  $a_0$ , small compared with unity in the above equations, we have

$$k_1 = a_1; \quad k_2 = a_2.$$

Using our data, we obtain a value for the compressibility of HMT of  $9.516 \times 10^{-12}$  cm<sup>2</sup> dyn<sup>-1</sup>.

The value for  $a_2$  provides a measure of the anharmonicity of thermal vibrations for HMT. Slater gives an approximation for the Grüneisen constant at zero pressure:

$$\gamma_0 = -\frac{2}{3} + \frac{a_2}{a_1^2 \left( \frac{1 + a_0 a_2}{a_1^2} \right)} \approx -\frac{2}{3} + \frac{a_2}{a_1^2}.$$

Using the values for  $k_1$  and  $k_2$  obtained, a value for  $\gamma_0$  of 1.597 was obtained. This is the first determination of  $\gamma_0$  for HMT reported.

At low pressures, the change in  $d$ -spacing is very small and so the principal source of error in the pressure determination is the measurement of HMT  $d$ -spacing from the X-ray film. Using film techniques, lattice parameters can be measured with an accuracy of 0.02 to 0.1% [21] on a routine basis, but the highest accuracy is normally obtained from only lines with the largest reflection angles ( $2\theta > 150^\circ$ ). In the case of the diamond cell, only lines with small Bragg angles can be studied ( $2\theta < 30^\circ$ ). For this reason, high accuracy would not be expected.

In addition, it is well known that different observers may choose different points as the position of the line [22]. Differences between the centre of blackening, the centre of intensity, and the peak intensity are appreciable. Moreover, specimen displacement and divergence of the primary beam will lead to systematic errors. Also, film shrinkage due to processing and ageing and absorption effects caused by the diamond anvil can be significant.

Since only the change in  $d$ -spacing is required in order to determine the pressure, a number of methods which eliminate the systematic errors can be used. Flack [16] has suggested recording the diffraction pattern from a sample under pressure and the pattern from a sample at room pressure on the same film. However, if it is required to record patterns at several different pressures, this is not a convenient method. It is more convenient to record each pattern separately, but to use the Debye-Scherrer ring diameters of the sample at room pressure to establish the film-to-specimen distance. In essence, this method achieves the same result as Flack's technique providing care is taken to minimize film-shrinkage differences.

The proportional change in  $d$ -spacing,  $\Delta d/d_0$ , which is used to determine the pressure, has some error  $\delta d/d_0$ . The error in pressure determination  $\delta p$  resulting from this will depend on the compressibility. If the compressibility of the pressure standard is  $C$ , then

$$\delta p = \frac{1}{C} \frac{\delta d}{d_0}$$

Now  $\delta d/d_0$  will be a function of angle. We can use the well-known relation

$$\frac{\delta d}{d_0} = \cot \theta \cdot \delta \theta$$

where  $\delta \theta$  arises from the error in ring-diameter measurement. If the ring diameter is  $D$  and the specimen-to-film distance is  $z$ , then

$$\tan 2\theta = \frac{D}{2z}$$

and

$$\delta \theta = \frac{1}{4} \sin 4\theta \left( \frac{\delta D}{D} + \frac{\delta z}{z} \right)$$

If  $z$  is determined using the known  $d$ -spacing for the pressure standard at room pressure,

$$\frac{\Delta z}{z} = \frac{\delta D'}{D'}$$

where  $D'$  is the measured ring diameter at room pressure. Since the error of measurement for  $D$  and  $D'$  is the same,  $\Delta z/z = \delta D'/D' = \delta D/D$ . Collecting these terms, we find

$$\delta p = \frac{1}{2} \frac{1}{C} \cot \theta \sin 4\theta \frac{\delta D}{D},$$

and this equation can be used to compare NaCl and HMT in their effectiveness as pressure standards at low pressures.

As an example, we consider two assumed working pressures, 3 and 5 kbar. In order to make a good comparison, it is convenient to assume measurements are made at the same Bragg angle  $2\theta$ . If we use the (220) reflection for NaCl ( $2\theta = 20.6^\circ$ ) and the (222) reflection for HMT ( $2\theta = 20.2^\circ$ ), this condition is approximately true. We can assume a specimen-to-film distance of 8 cm and a proportional error in the measurement of the diameter of 0.1%. The resulting errors are shown in Table III.

TABLE III

Pressure standard	% error at 3 kbar	% error at 5 kbar
NaCl	44	27
HMT	20	12

From these calculations, it is clear that NaCl should not be used as a pressure standard at pressures less than 5 kbar. The errors involved in the case of HMT are large, but certainly acceptable in this range. It should also be noted that the specimen-to-film distance assumed (8 cm) is quite large. Smaller distances are often used, since this reduces the exposure time; for example, Flack used to film-to-specimen distance of 3 cm. If this practice is carried out, it is likely that the errors could be even higher than indicated by Table III.

A careful error analysis for the ruby fluorescence method was not carried out. Piermarini and Block [12] suggest that the pressure dependence of the  $R_1$  ruby fluorescence line at 6942 Å is linear (0.365 Å kbar) at 25°C. The shift in wave number is  $-0.77 \pm 0.03 \text{ cm}^{-1} \text{ kbar}^{-1}$ . However, different measurements at the same pressure can give a spread in wave number of  $\pm 2 \text{ cm}^{-1}$ , and a report by Forman *et al.* [23] gives a standard deviation of 1.5 kbar. For comparison with the X-ray results, it is clear that the errors at 3 and 5 kbar would be 50 and 30%, respectively; this is slightly more inaccurate than the NaCl method. We suggest that the ruby fluorescence method should also not be used for pressures less than 5 kbar.

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