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Deviatoric stress: a nuisance or a gold mine?

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Abstract

Both synchrotron radiation and deviatoric stress were once considered to be nuisances. Now synchrotron radiation is one of the most important tools available to scientists of all disciplines and deviatoric stress is one of the most useful aspects of x-ray diffraction at extreme conditions. Samples in high-pressure devices are under true hydrostatic pressure only when surrounded by a fluid, thus limiting true hydrostatic pressure studies at ambient temperatures to pressures below about 11 GPa. Elevated temperature is able to extend this limit but has rarely been used for this purpose. Instead, noble gases have been used as pressure media as their solids are especially soft. Deviatoric stress and resultant anisotropic elastic strain in solid samples and solid media have led to many subtle errors in determinations of elastic properties and crystal structures, especially in the days before it was realized that they could be measured and were potentially a valuable source of information. In recent years, measuring anisotropic elastic strain by x-ray diffraction has provided new insights into materials strength, elastic properties, crystal structures, mechanisms of phase transitions, slip systems, lattice preferred orientation, and, of course, ways to make corrections when deviatoric stress is indeed a nuisance.

1. Introduction

When I was a post-doc at Brookhaven National Laboratory from 1958 to 1961, I used to explore the site of the Alternating Gradient Synchrotron. It was under construction, and I often visited it after the workmen went home for the day. The amount of shielding was impressive. The synchrotron required massive amounts of power to keep the particle beam in the ring as well as the massive amounts of shielding. I was told it was old battleship decking and had to be used because of the extraordinary amount of electromagnetic radiation emitted by the charged-particle beam as it was bent by the magnets. There seemed to be no appreciation for this kind of radiation. In other words, it was considered a nuisance. It was only in 1978, when I moved to Cornell University, that I began to learn of the multitude of uses that could be made of this kind of radiation.

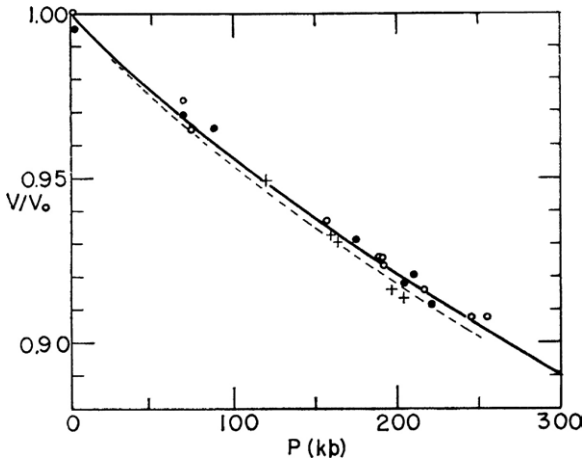

Figure 1. Isothermal compression measurements of three spinel phases of $(Fe, Mg)_2SiO_4$ with NaCl as pressure medium (Mao *et al* 1969). Open circles are data collected on Fe_2SiO_4. Pluses are data collected on $Fe_{1.8}Mg_{0.2}SiO_4$. Closed circles are data collected on $Fe_{1.6}Mg_{0.4}SiO_4$. The solid line is a least-squares fit to a Birch–Murnaghan equation for Fe_2SiO_4 and $Fe_{1.6}Mg_{0.4}SiO_4$. The dashed line is a least-squares fit to a Birch–Murnaghan equation for $Fe_{1.8}Mg_{0.2}SiO_4$.

2. Deviatoric stress: a nuisance

Back in the 1960s Taro Takahashi and I along with our graduate student, Dave Mao, had a similar experience when we first started using the diamond anvil cell to measure compressibilities of minerals (Mao *et al* 1969, 1974). People like Murnaghan and Birch (Birch 1947) had developed equations to describe the compression behaviour of solids. According to their equations, a plot of volume versus pressure should bow downward. But many of our plots failed to bow downward and some actually bowed upward, as in our early measurement of compression of γ-$(Fe, Mg)_2SiO_4$ (figure 1). In virtually all of our measurements our data did not conform well to the equations. Not everything we did back then showed great wisdom, but at least we were smart enough to conclude that the source of the discrepancy probably lay with us and not with the likes of Murnaghan and Birch, and so we forced their equations onto our data and found that if we made the curve dark enough it looked as if the data fit. It did not take us too long to figure out the cause of the discrepancy, and, yes, it did reside with us. Apparently, the diamonds were causing deviatoric stress in our samples, resulting in anisotropic distortion. Because our x-ray beam entered through one diamond anvil and exited through the other, thus passing along the direction of maximum stress, our diffraction patterns were not recording the full range of d-spacings for a given set of hkl, but were in fact recording some of the largest d-spacings of the distorted crystallites in our polycrystalline sample. In other words, calculating volume based on these d-spacings did not yield data representative of the molar volume under hydrostatic conditions. Even a 'soft' pressure medium like NaCl did not make the effect go away. This was especially true if there was too little pressure medium, and bridging occurred as sample grains contacted each other.

3. Fluid medium: a solution

At least we knew the source of the trouble. What to do about it? Obviously, using a fluid pressure medium rather than a 'soft' solid medium seemed appropriate. At that time liquid

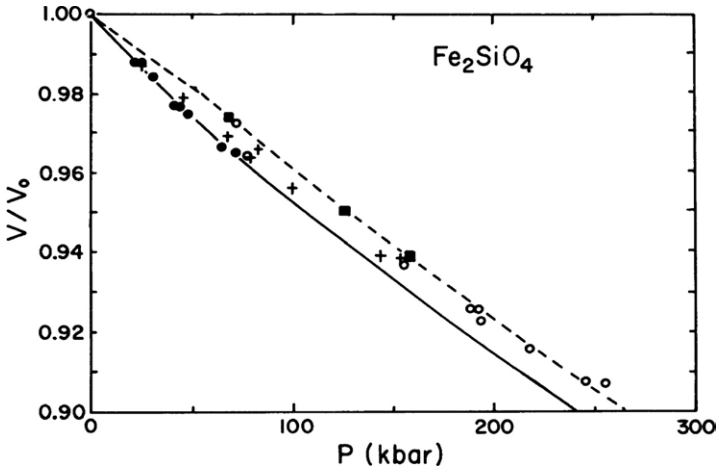

Figure 2. Isothermal compression measurements of the spinel phase of Fe_2SiO_4. Open circles are data collected under ungasketed, non-hydrostatic conditions using NaCl as pressure medium and as calibrant from Mao *et al* (1969). Squares are data collected under ungasketed, non-hydrostatic conditions using NaCl as pressure medium and as calibrant (Wilburn and Bassett 1976). Pluses are data collected under gasketed conditions using NaCl as pressure medium and calibrant (Wilburn and Bassett 1978). Closed circles are data collected under gasketed, hydrostatic conditions using a methanol–ethanol mixture as pressure medium and NaCl as pressure calibrant (Wilburn and Bassett 1978). The solid curve is a least-squares fit to a Birch–Murnaghan equation. The dashed line is an interpretation based on the data of Kinsland and Bassett (1976).

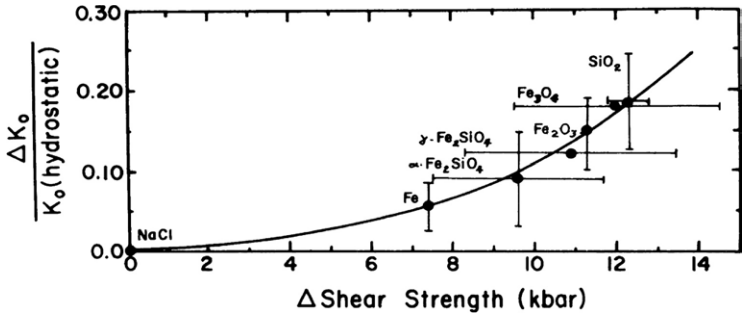

Figure 3. Discrepancy in bulk modulus between non-hydrostatic and hydrostatic measurements plotted as a function of contrast in shear strength between sample and pressure medium from Wilburn and Bassett (1978).

media had been used for single crystal studies by Van Valkenburg and others (Van Valkenburg *et al* 1971, Piermarini *et al* 1973), but to my knowledge no one had used liquid media with powdered samples. Wilburn and I did just that and made a comparison between our earlier measurements in NaCl and those made in an ethanol–methanol mixture (Wilburn and Bassett 1978). The difference was dramatic (figure 2). The discrepancy caused by this effect was zero at 1 bar pressure, increased with increasing pressure, but then levelled, thus leading to the upward bowing effect. As can be seen in figure 2, all of the high-pressure points showed larger molar volumes than in the runs using a fluid medium. Wilburn and I made compression measurements on a number of samples and plotted the normalized discrepancies in bulk modulus versus the shear strengths of the samples and their pressure media and observed a strong correlation (figure 3).

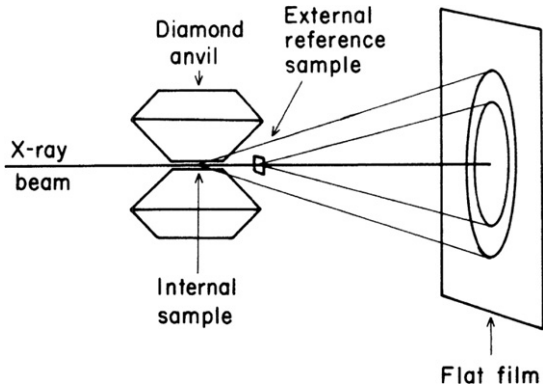

Figure 4. Diagram of the cross-axis, more recently known as radial-diffraction, geometry used by Kinsland and Bassett (1977) to record diffraction rings made elliptical by anisotropic elastic strain in the sample. The external reference sample produced rings that could be used to determine sample-to-film distance and to make corrections for ellipticity caused by tilt of the film.

4. Radial diffraction, analysing deviatoric elastic strain

At about that same time Gary Kinsland, Scott Weaver, and I had the idea of directing the x-ray beam through a sample perpendicular to the compression axis (Kinsland and Bassett 1976). If we were failing to see the smallest d-spacings by directing the x-ray beam along the compression axis, why not direct it perpendicular to the compression axis (figure 4)? Of course this meant designing a new type of diamond cell, which we called the XP cell for cross-axis press (figure 5). When we tried it out on a sample with no pressure medium, we were rewarded with elliptical diffraction rings and realized the great benefit of being able to measure the full range of d-spacings simultaneously. Our observation not only verified our suspicions about the source of errors in our compression measurements but also provided a means for determining the range of elastic deformation in the individual sample grains. Figure 6 shows the relationship between lattice spacings and diffraction rings. We interpreted the limit of elastic strain as a measure of the strength of the sample when it was subjected to uniaxial stress (Kinsland and Bassett 1977). This, in turn, we could measure as a function of pressure. Although the details of this interpretation were questioned by Meade and Jeanloz (1988), the new geometry converted the effect of deviatoric stress on x-ray diffraction measurements from a nuisance to a potential source of information not just about strength but about other properties as well.

Kinsland measured the diffraction patterns using projection equipment designed for reading photographs of particles in cloud chambers and bubble chambers. He reduced the data using a very early computer. I would like to clarify a point about our method of reading the patterns, a point that I think has been misunderstood by some who used a similar geometry. In our method, no gasket was used and so the x-ray beam traversed the entire sample from low pressure to high pressure and back to low pressure. At that time we had no experience with the use of beryllium or boron-epoxy as a gasket material, and in fact did not want to disturb the distribution of elastic strain in our sample, and so we devised a method for reading the patterns rather than trying to eliminate the low-pressure portion of our sample. Our diffraction patterns consisted of lines made broad by the range of elastic strain in the sample traversed by the x-ray beam. These lines had sharp outer edges as represented diagrammatically in figure 7. This allowed us to identify the portion of a line produced by the smallest interlayer spacing for a given *hkl* and to distinguish it from the portion of the line produced by the largest interlayer

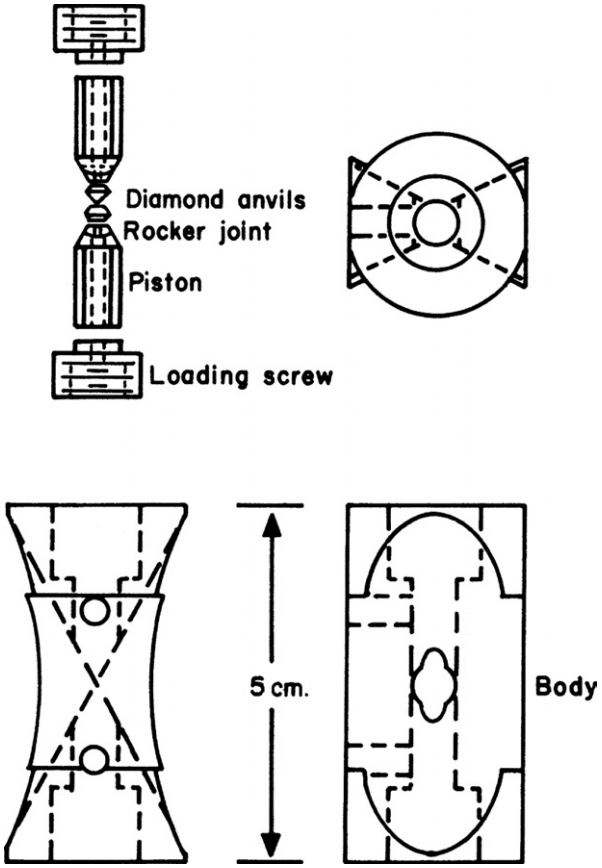

Figure 5. XP type of diamond-anvil cell used by Kinsland and Bassett (1977) to measure anisotropic elastic strain. Screws were used to mechanically apply load.

spacing for a given *hkl*. Our procedure was to measure the outer edge (largest 2θ) and subtract half of the width of a diffraction line produced at 1 bar pressure, which we called the 'natural' line width. There was never any doubt in our minds that this yielded information about the part of the sample subjected to the highest stress and therefore having the largest elastic strain. We interpreted this to be the portion of the sample at the highest pressure and almost certainly at the centre of the sample area between the diamond anvils if the diamonds were well aligned. Even today, given a choice between doing it this way or using a gasket, I would have no hesitation about trusting the results from either.

5. Interpreting deviatoric elastic strain

Kinsland and Bassett (1977) plotted the strain parallel to the compression axis versus the strain perpendicular to the compression axis. Any discrepancy between the two strains shows up as a departure from a 45° line in such a plot. Figure 8 shows just such a departure in the plot for MgO. We then considered this discrepancy as representing the maximum elastic deformation before yielding, and from it we calculated the maximum strength. As the sample was further squeezed, the pressure increased, making it possible for us to plot uniaxial stress as a function of pressure (figure 9). We interpreted this as representing strength as a function of pressure. A

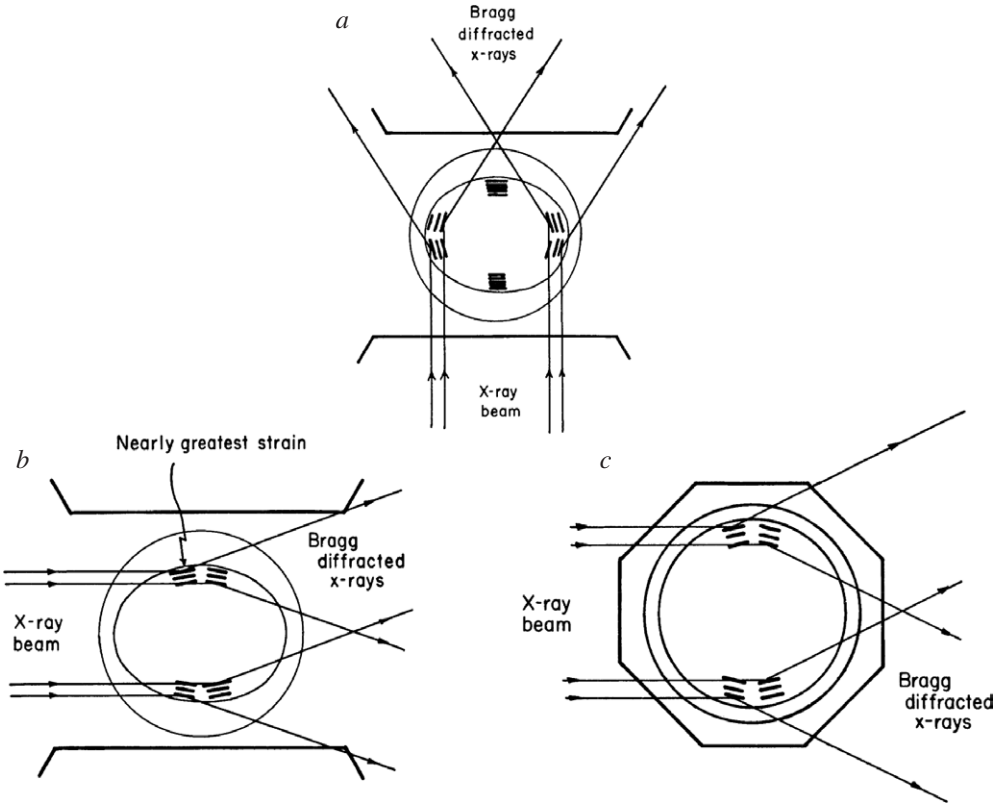

Figure 6. Diagrams showing the interaction of the x-ray beam with the d-spacings in a polycrystalline sample under deviatoric stress. (a) X-ray beam parallel to the load axis. (b) X-ray beam perpendicular to the load axis Bragg reflected by planes nearly perpendicular to the load axis. (c) X-ray beam perpendicular to the load axis Bragg reflected by planes parallel to the load axis. Sections of the d-spacing ellipsoid are included for reference.

comparison between the behaviour of MgO and that of NaCl showed MgO to be significantly stronger than NaCl as expected. We also measured a sample of pyrope garnet and were surprised by the extreme departure from a 45° line (figure 10), so much so that we did not have the nerve to publish the results. Since then we have learned that others have made similar observations on garnets (Sinogeikin *et al* 1997, Kavner *et al* 2000).

Several years later, Wu and Bassett (1993) revisited measurement of deviatoric stress. We applied a new method developed by Weidner *et al* (1992) in which the anisotropic response of polycrystalline gold to deviatoric stress was compared to results using the method developed by Kinsland and Bassett (1976). We also provided a more detailed analysis of deviatoric stress in the diamond anvil cell.

6. Deformation of the diamond anvils

Kinsland and I observed another very interesting consequence of our cross-axis geometry. We were using a conventional x-ray tube without a monochromator, hence the x-ray spectrum contained a broad white Bremsstrahlung component in addition to the monochromatic characteristic radiation we used for recording the diffraction rings. All of our early diffraction

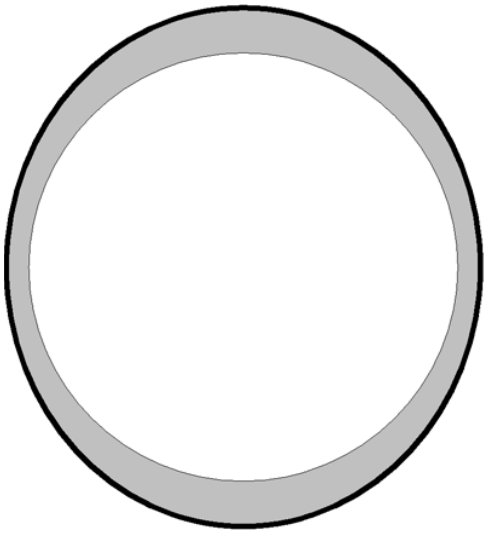

Figure 7. Diagrammatic representation of a diffraction ring from a highly strained sample. The x-ray beam traverses the full range of strain from edge to centre of the sample and is therefore broad. The outer edge of the diffraction ring is produced by the most highly strained portion of the sample at its centre since the d-spacings are smallest there. The outer edge is darkened in the diagram to indicate that it is well defined in most diffraction rings because the sample thickness is greater in the centre.

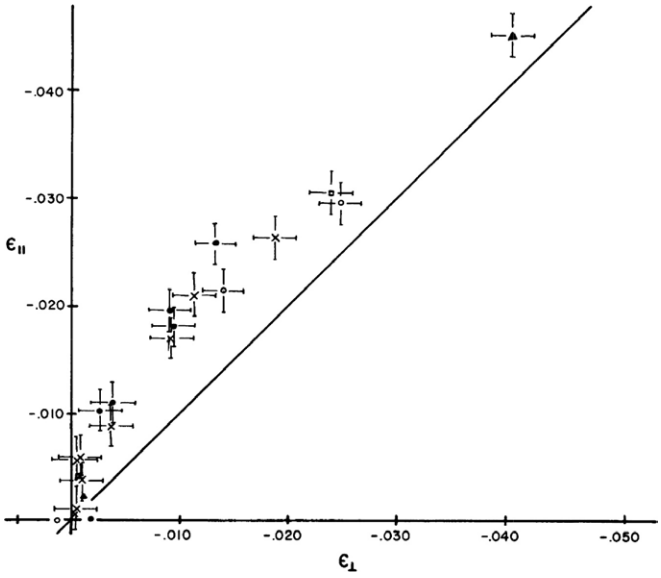

Figure 8. Strain parallel to the load axis, $\varepsilon_{\parallel}$, versus strain perpendicular to the load axis, $\varepsilon_{\perp}$. The solid line represents $\varepsilon_{\parallel} = \varepsilon_{\perp}$. The pluses are data collected on MgO using diffraction rings produced by lattice planes 200 and 220 (Kinsland 1974).

patterns made with this type of x-ray source contained Laue spots produced by the diamond anvils. What was so interesting about the Laue spots produced by our device is that each spot was elongated and had the shape of a 'C' (figure 11). Could these be telling us something about

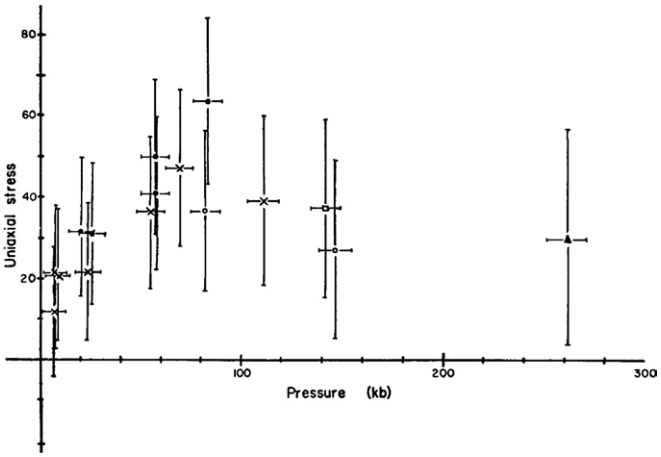

Figure 9. Uniaxial stress calculated from elastic strain versus pressure for MgO 200 reflections (Kinsland 1974). This was interpreted as indicating the strength of MgO as a function of pressure.

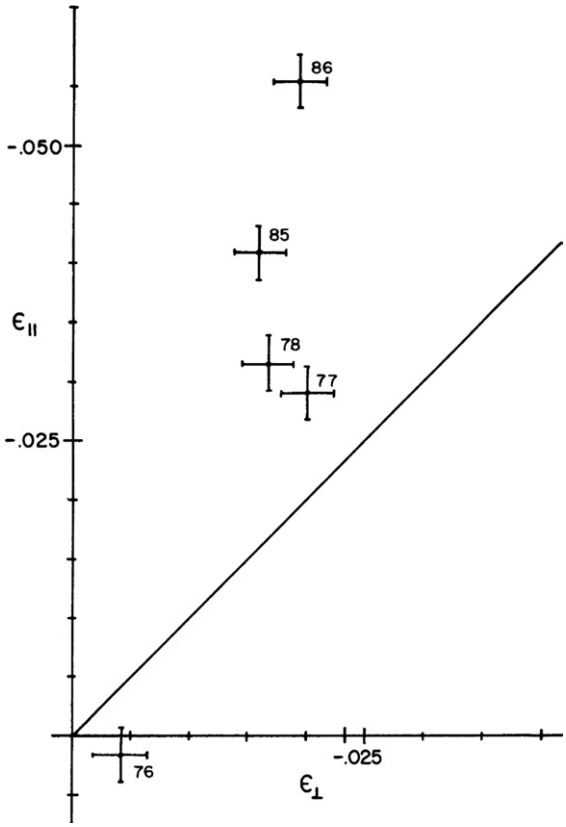

Figure 10. Strain parallel to the load axis, $\varepsilon_{\parallel}$, versus strain perpendicular to the load axis, $\varepsilon_{\perp}$. The solid line represents $\varepsilon_{\parallel} = \varepsilon_{\perp}$. The pluses are data collected on pyrope garnet using diffraction rings produced by lattice planes 400 (Kinsland 1974).

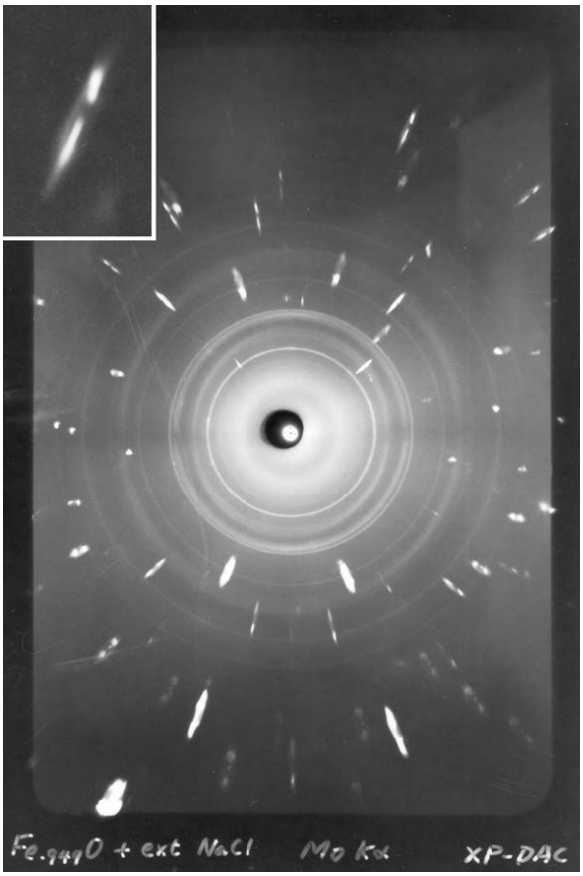

Figure 11. X-ray diffraction pattern collected on flat film. Rings are produced by wustite under stress and by external NaCl at 1 bar pressure. Ellipticity of the wustite rings is best observed by looking at the space between the pair of rings third from the centre. Lengthened Laue spots are produced by reflection of bremsstrahlung radiation from the distorted diamond lattice as the diamond anvils are cupped around the sample. Inset: enlarged 'C'-shaped Laue spot from upper right corner. The radius of curvature of the distorted diamond lattice in the anvil face was calculated from the length of the spot and is only a few millimetres.

the lattice distortion in each diamond? If so, might it be possible to determine the nature and amount of such distortion? We first reported this phenomenon in 1974 (Bassett and Takahashi 1974). We reasoned that the two ends of each 'C' (figure 9) were coming from the diamond near the edges of the 0.5 mm anvil face, i.e., where the pressure was lowest, and that the centre of each 'C' came from near the centre of the anvil face where the pressure was highest. If true, it should be possible to measure the size of each 'C' and with a little trigonometry determine the radius of curvature of the anvil face. To our surprise, we calculated a radius of curvature of only a few millimetres. We had chosen diamonds to serve as our anvils because they are hard and unyielding. Thus a radius of curvature of millimetres seemed counterintuitive. Nonetheless, the evidence was there and it may be valuable for you who use diamond anvil cells to keep in mind that the anvils can indeed distort dramatically to accommodate the geometry of the sample you have placed between them. For instance, interference rings in transparent samples as well as variations in light transmission through coloured samples indicated cupping of the anvil faces.

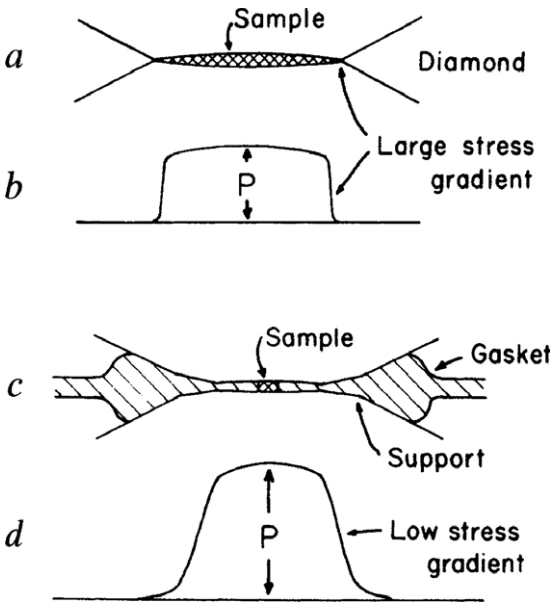

Figure 12. Diamond anvil distortion and its effect on pressure distribution. (a), (b) Unbevelled anvils; (c), (d) bevelled anvils (Mao and Bell 1978).

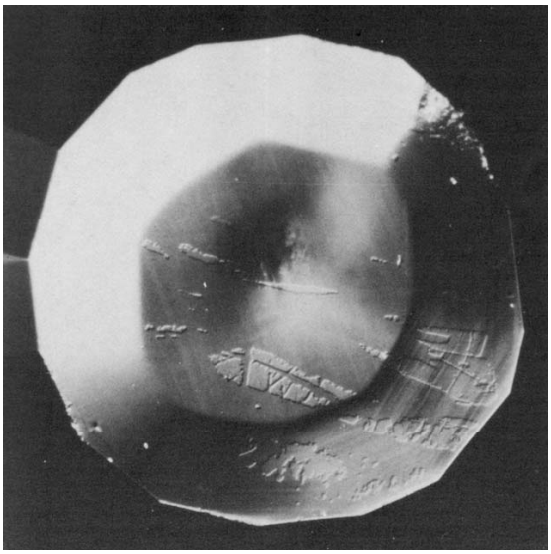

Figure 13. Permanent depression resulting from plastic deformation in the face of a diamond anvil subjected to 1.7 Mbar (Mao and Bell 1978).

Realization that cupping of the anvil faces occurred helped us to understand that a very large portion of our sample was at high pressure as recognized by Mao and Bell (1978) and shown in figure 12. This, in turn, helped explain why the elliptical diffraction rings we observed had such dark and well defined outer edges. In other words, there was very little low-pressure sample, i.e. sample that the beryllium gasket would have eliminated. When the pressure was decreased and the sample removed, the Laue spots returned to small, nearly circular spots, indicating that the distortion had been entirely elastic. It was only later that Mao and Bell (1978) observed permanent cupping of diamond anvil faces (figure 13).

7. Deviatoric stress: a gold mine

Since our early experiments there have been many studies of the effects of deviatoric stress and other forms of stress inhomogeneity on diffraction data such as the elegant determination of elastic moduli of iron at core pressures (Singh *et al* 1998). These studies are shedding new light on elastic and rheological properties of materials. These properties are of particular interest to members of the earth sciences, as they can provide valuable information for modelling the dynamics of Earth's interior as well as the interiors of other planets. Although many of these studies have been made using diamond anvil cells, many others have been made in large-volume presses. All have contributed to a better understanding of materials at high pressures and temperatures. I am happy that we had a chance to be involved in the very early stages of the development of a technique that has come to be such an important source of information.

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