Reports

Pressure Distribution Measurements in Fixed-Anvil High-Pressure Cells

Abstract. *Absorption spectra of selected microsections of materials with pressure-sensitive absorption bands mounted in diamond-anvil high-pressure cells were determined. The shift in the absorption peak, combined with data obtained at uniform pressure, permits calculation of the pressure of the microsection selected. Examples of a parabolic decrease in pressure from the center to the edge of the diamond anvil are demonstrated by contour diagrams.*

The nature and magnitude of the pressure distribution within high-pressure cells has been a matter of concern since the beginning of high-pressure research. Bridgman (*1*) has given a qualitative description of the factors leading to an uneven pressure distribution; in particular, he was concerned with the concavitation of the piston (after several applications of pressure) due to the nonuniform pressure distribution. Nevertheless, because of his inability to measure this pressure distribution, he did not arrive at any consistent pattern with the many materials tested. Consequently, it was necessary to neglect the pressure variation across the anvil so that the pressures reported by Bridgman are "mean applied pressures."

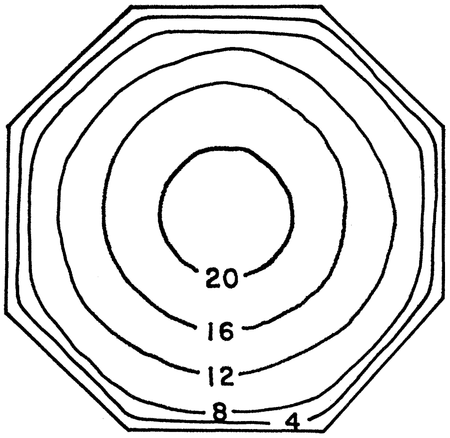

Fig. 1. Pressure contours for sample of nickel dimethylglyoxime in NaCl (1:3) at applied pressure of 10 kb.

The introduction of less deformable anvils, such as pyrophyllite and diamond, should presumably lead to a less complicated pressure distribution than that observed by Bridgman. There have been attempts to assess the pressure variation in opposed anvil high-pressure cells. Roy *et al.* (*2*) have observed the location (that is, distance from the center) of the Bi(I-II) transition at 25.4 kb for various applied pressures. The somewhat limited data indicate such an increase in pressure from the edge to the center that the maximum pressure at the center is about 2.5 times the applied pressure. Christiansen *et al.* (*3*) compressed silica glass in a similar type of pressure cell, and used the densification of the glass to evaluate the pressure distribution. The resulting pressure distribution is different from that reported by Roy *et al.*, being lower in the center than at the edge. Deaton and Graf (*4*), using the Bi(I-II) transition, have compared the pressures at center, edge, and face of a tetrahedral anvil high-pressure cell. While the pressure at the face and center were within a few percent of each other, pressures nearer the edge were only 70 percent of the value at the center.

A number of attempts have been made to evaluate mathematically the pressure distribution under rigid Bridgman type anvils (*5, 6*). These derivations arrive at a relation of the form,

$$P = P_o \cdot G(r) \cdot \exp(2f/h)(r_o - r)$$

where f is the coefficient of friction, h the distance between the anvils, P the pressure at radius r, and $G(r)$ a function of r or unity. Jackson and Waxman (*6*) have discussed the expected pressure distribution for elastic as well as plastic materials with different arrangements of anvil and sample. For plastic materials a pressure increase toward the center is predicted along with a rather abrupt (and presumably objectionable) pressure rise near the center.

Thus, a need for more precise measurement of the magnitude and especially the shape of the pressure distribution in high-pressure cells is indicated before very reliable state and spectroscopic data can be obtained. The fact that materials reacting in the diamond high-pressure cell (*7*) can now be observed with conventional optical microscopes has made it possible to observe large pressure gradients across the face of the diamond anvils as judged by phase changes and color changes. In order to make accurate spectroscopic measurements on materials, it is indeed desirable first to evaluate this pressure gradient.

A microscope spectrophotometer (*8*) was built to facilitate measurements of the spectrum of selected areas (as small as 10^{-7} cm^2) of the sample compressed between fixed diamond anvils with an area of 10^{-2} to 10^{-3} cm^2. Therefore, with a material which has an absorption band whose peak position is known as a function of pressure, it is possible to make as many as 10^4 pressure determinations across the surface of a sample at a given applied pressure. While very smooth pressure profiles could be obtained by taking measurements at linear intervals of 10^{-3} cm, we chose to take data at intervals of 7×10^{-3} cm to save

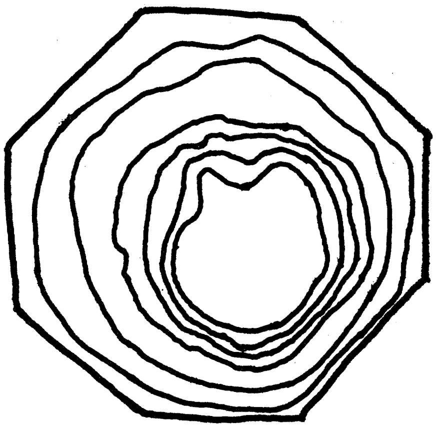

Fig. 2. Pressure contours in sample of pure thallium bromide at 20 kb; lines at 2, 6, 15, 24, 33, and 37 kb.

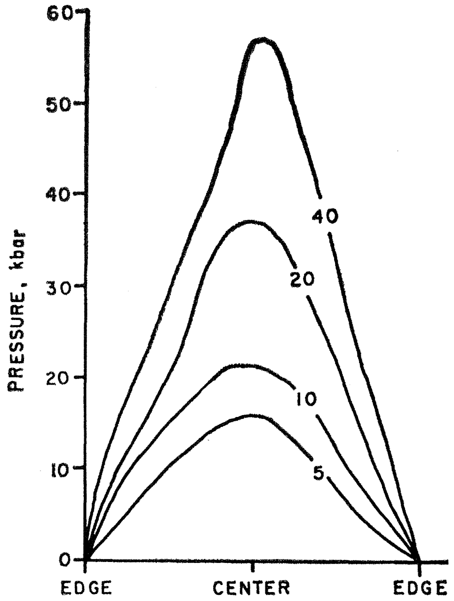

Fig. 3. Pressure gradient for nickel dimethylglyoxime in KBr (1:2) at specified applied pressure in kilobars.

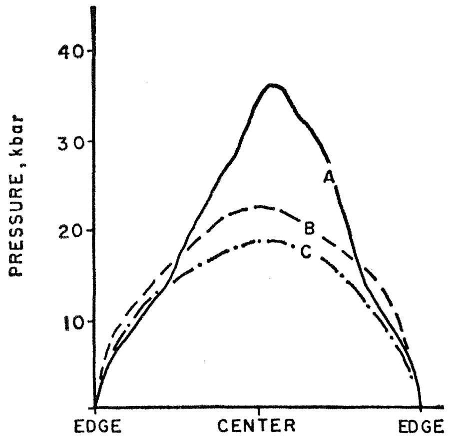

Fig. 4. Pressure gradient of nickel dimethylglyoxime in NaCl at concentrations of (*A*) 1:5, (*B*) 1:3, (*C*) 1:2 by weight. All data at applied pressure of 10 kb.

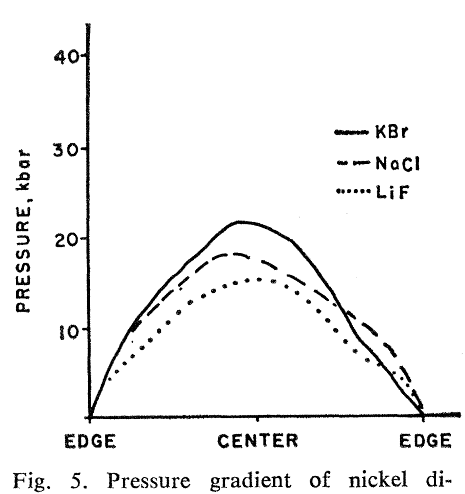

Fig. 5. Pressure gradient of nickel dimethylglyoxime diluted with two parts by weight of different alkali halides.

time and still get data of reasonable quality.

Nickel dimethylglyoxime has a pressure-sensitive absorption band at 19,000 cm^{-1} and the position of the peak as a function of pressure has been reported by Zahner and Drickamer (*9*). A repetition of this work with the average applied pressure of the diamond high-pressure cell is in excellent agreement with their results. On the basis of these data a linear shift of −80 cm^{-1}/kb is used to convert the observed peak position of the spectrum to a pressure measurement. Figure 1 gives a typical determination of pressure contours over the surface of the octagonally cut diamond.

A photographic technique may be applied to materials which have an absorption edge which shifts with pressure, such as thallium bromide. Zahner and Drickamer (*10*) have also reported the position of the absorption edge of this material as a function of pressure, a shift of −115 cm^{-1}/kb being indicated. A sample of TlBr in the diamond cell at a given pressure may be photographed with monochromatic radiation. Photographs taken as the wavelength of the radiation is increased by increments (corresponding to a pressure decrease) may be used to determine pressure contours directly, as shown in Fig. 2.

The technique of Roy *et al.* (*2*), that is, following the position of a phase transition as a function of applied pressure, may also be used for those materials which form two phases with different properties of the spectrum, such as mercuric iodide.

Since the diagrams of the pressure distribution were found to be symmetrical about the center, we simplified our procedure to the measurement of pressures along a diameter of the diamond cell and arrived at radial pressure-gradient profiles. The effect of applied pressure on the shape and magnitude of the gradient is given in Fig. 3. Thus a parabolic curve is obtained at all pressures.

The quality of the spectroscopic data with nickel dimethylglyoxime was improved by dilution with an alkali halide. The effect of the diluent concentration is given in Fig. 4. The pressure gradient also depends greatly on the alkali used, as shown in Fig. 5. In general, the pressure gradient decreases with the compressibility of the diluent. Indications are that the method may be developed so that determinations of compressibility can be made.

By exact alignment of the diamonds a uniform pressure gradient may be obtained (*7*). Figure 6 gives the pressure contour of a nonuniform pressure distribution. A summation of the pressure-area products for each terrace led to a calculated pressure of 11.9 kb compared with an applied pressure of 12.0 kb.

However, the calculated pressures do not always agree so well, especially in the case of very compressible materials, such as KBr, at high pressures. This may in part be due to the occasional formation of "material streams" during the extrusion of the sample from the cell on initial compression. The subsequent fissure formation within the sample results in a lower effective contact area and hence in a steeper pressure gradient. The effect of diluent concentration may be partially explained on this basis.

The relation of the compressibility of the material to the observed pressure gradient may be extended to other materials. Since NaCl and TlBr have similar compressibilities, we might compare the pressure gradients obtained on thallium bromide by the photographic method to those obtained with nickel dimethylglyoxime highly diluted with NaCl. We find that the magnitude and shape of the two pressure gradients agree within the experimental error.

In summary, it is possible to measure the pressure distribution within transparent high-pressure cells by use of a material with a pressure-sensitive absorption band. The pressure, *P*, at a distance *r* from the center of the cell

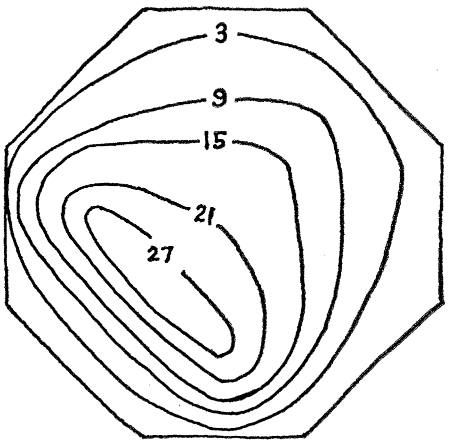

Fig. 6. Nonuniform pressure contours of nickel dimethylglyoxime in KBr (1:5) at applied pressure of 12 kb.

may, as a first approximation, be expressed by the equation

$$P = P_m\left[1 - \left(\frac{r}{r_0}\right)^2\right]$$

where r_0 is the radius of the anvil surface and P_m is the pressure at the center of the cell.

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Twilight Phenomena Caused by the Eruption of Agung Volcano

Abstract. *Increase in twilight glow and in the dust stripes in the twilight arch have been observed from several places in the northern hemisphere from the fall of 1963 until now. Measurements of the twilight brightness indicate a considerable increase of dustiness in the stratosphere; this turbidity may be due to drifting ashes from the eruption of Agung volcano on Bali.*

Since the early fall of 1963, very intense twilight glows have been observed in the United States (*1, 2*) and in Europe (*3*). Many observers assumed they were caused by ashes ejected into the stratosphere during the eruption of Agung volcano on Bali Island (9°S, 114°E) on 17 March 1963. In the Southern Hemisphere, strong sunset afterglows were noticed soon after the eruption (*4*). A considerable reduction of star and solar radiation by about 0.4 stellar magnitudes at 5000 Å was measured over Australia and South Africa (*4*), and a bright disc of white light was seen around the daytime sun (*5*).

The twilight glow observed in the Northern Hemisphere appears when the sun is depressed about 5 deg below the horizon (about 30 minutes after sunset) as a purple-colored disc, of lateral size about 40 deg, centered above the position of the sun. This disc is much more purple than the normal disc at this time. Shortly afterward, the purple glow contracts toward the horizon, with a relatively sharp upper border parallel to the horizon; the color is deep crimson, like the faint stripes of color that usually appear along the horizon (*6*). Crepuscular rays, caused by distant clouds casting a bluish shadow in the dust layer, increase the spectacular appearance of the twilight glows. The crimson glow fades very low at the horizon at a sun depression of about 9 deg.

Apart from this general change of twilight, fine ripple cloud formations (dust lenses) have been observed occasionally from sunset until the sun is depressed to about 6 deg in the lower part of the twilight arch. The lenses are usually about 0.3 deg by 3 deg wide, and are arranged with some regularity, sometimes slightly inclined to the horizon; they are similar to noctilucent clouds, being of whitish-silvery tone. Such clouds have often been observed after strong volcanic eruptions and are called "ultra cirri." Their first appearance as isolated wisps may have been as early as 25 September 1963 over Colorado (*7*); Mitchell (*2*) observed them on two clear evenings in late October in Washington, D.C. I observed similar phenomena at Weissenau, south of Stuttgart, on the evening of 17 November, the morning and evening of 20 November, and in the evening of 25 November. Since then, I have not seen these wisps, the observations being partly hampered by fog and by considerable haziness near the ground. But the twilight clouds were again observed from Feldberg Observatory, Black Forest, on 8 and 9 December by Schreiber (*3*). During the same periods, color pictures clearly showing the dust stripes were taken in southern England by F. Ludlam.

From the relation between the maximum elevation angle and the solar depression presented in Fig. 1, I estimate that the dust "lenses" were at an altitude of 20 to 25 km. Similar clouds of unknown origin observed occasionally from November 1961 to January

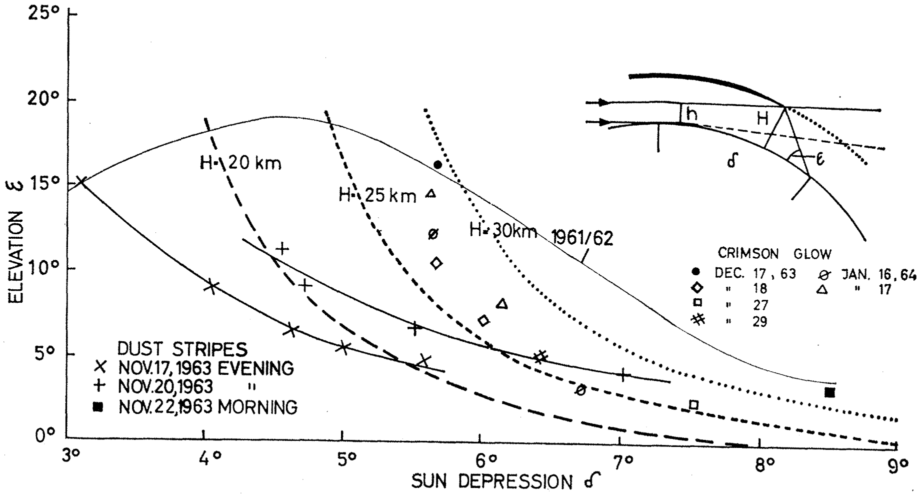

Fig. 1. Twilight dust stripes (ultra cirri) and crimson glow, maximum elevation, ϵ, versus sun depression, δ. Dust stripes observed in November 1963 at Weissenau and during the winter of 1961–62. Dotted lines: maximum elevation of the visibility of dust clouds at an altitude of 20, 25, and 30 km (H) if the minimum height (h) for solar illumination is 10 km. According to observers of noctilucent clouds, h may be even larger than 10 km for the faint dust stripes but may be smaller for crimson glows as revealed by the appearance of crepuscular rays.