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New Device for Obtaining X-Ray Diffraction Patterns from Substances Exposed to High Pressure

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A device is described for obtaining powder diffraction patterns of thin sheets pressed between opposing diamond pistons. The pressure, initially applied by a small auxiliary laboratory press, is clamped onto the sample by a lock-nut. The whole unit is designed to replace the sample mount of a standard x-ray diffraction unit. Sample patterns taken on two of the high pressure modifications of bismuth are exhibited.

EARLIER work in this laboratory[1–3] led to the development of a device for high-pressure x-ray diffraction studies to about 25 kilobars at room temperature. This device was a drilled 3-carat diamond pressure vessel in which miniature pistons were inserted. Because of the high background scattering from the diamond to the recording film, patterns could not be obtained for highly absorbing substances. Dilution of the sample was of no avail owing to the absorption by the diamond. The basic reason for

[1] A. W. Lawson and T. Y. Tang, Rev. Sci. Instr. **21**, 815 (1950).
[2] J. C. Jamieson, Z. Krist. **107**, 65 (1956).
[3] J. C. Jamieson, J. Geol. **65**, 334 (1957).

this behavior may be seen from an approximate calculation similar to that of Buerger[4] for estimating the optimum size of single crystals used in diffraction studies. For the intensity I of a diffracted beam corresponding to a sample of thickness t and absorption coefficient μ, contained within a material of thickness t_d and absorption coefficient μ_d, we have

$$I = kI_0 t^2 e^{-\mu t} e^{-\mu_d t_d}, \tag{1}$$

where $kt^2 I_0$ is the intensity of the diffracted beam in the absence of sample and diamond absorption, and k is a factor which allows for the geometry of the sample. For a cylindrical diamond with $t_d = 3$ mm, $e^{-\mu_d t_d} = 0.5$ for Mo K_α radiation if we neglect the variation of μ_d and t_d with strain. Buerger shows that a maximum in diffraction intensity occurs for $t = 2/\mu$. For this thickness,

$$I_{\max} = \frac{4I_0 k}{e^2 \mu^2} e^{-\mu_d t_d} = \frac{I_0 k}{4\mu^2}. \tag{2}$$

FIG. 1. High-pressure x-ray diffraction unit mounted on spectrometer.

Typical values of $I_{\max}(kI_0)^{-1}$ are 10^{-3} for NaCl, 10^{-5} for RbCl, and 10^{-7} for HgSe. With the geometry employed in the previous experiments, good patterns were obtained for RbCl by varying the effective t by dilution of the sample with zinc stearate, but none could be obtained for HgSe. Compensation for self-absorption by use of longer exposure times was useless because of the limiting effects of the background radiation from the diamond.

The purpose of this note is to describe a more satisfactory technique which avoids the difficulties arising from sample absorption and which gives a better signal to noise ratio.

The design chosen has been compounded from two sources: the simple squeezer of Griggs *et al.*[5] and the clamping scheme of Chester and Jones.[6] Both ideas have been heavily modified for the present work. The x-rays are diffracted by a flat specimen exposed to quasi-hydrostatic pressure generated by a diamond piston pressing the sample against a flat surface.

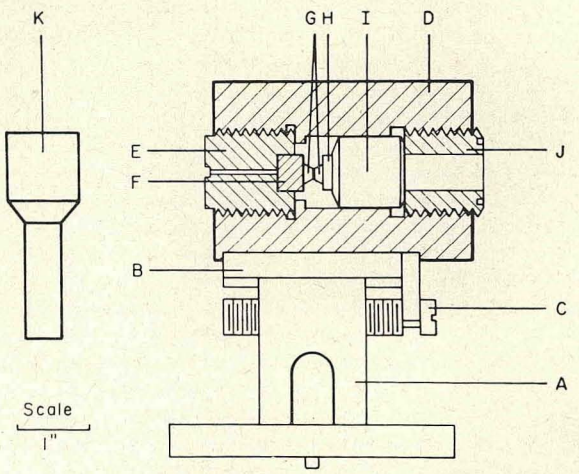

FIG. 2. Cross section of high-pressure x-ray diffraction unit.

The unit was designed to mount on a General Electric XRD-5, x-ray diffractometer using filtered Mo radiation although with suitable modification the unit could be used on any other x-ray diffractometer. The unit is shown in place (minus x-ray shields) on the XRD-5 in Fig. 1. It will be noted that it simply replaces the normal sample holder and the instrument is used in the usual fashion, a major advantage conferred by the clamping scheme. Also in Fig. 1 may be noted a device attached to the slit system of the XRD-5, to limit the height of the x-ray beam and lessen the amount of background scatter.

Figure 2 is a cross-section drawing of the new device. The upper cylindrical portion D is demountable from the base A to which it is securely attached by means of dowel pins (not shown) in the dovetail slide B, which is positioned horizontally in the x-ray beam by the micrometer screw C.

The cylinder D is a holder for the working parts of the apparatus and is machined from 1020 SAE steel. The threaded plug E contains the Carboloy insert F which supports the opposing diamond pistons G. Both F and G have been modified in later work as described below. The movable piston I contains the carboloy block H and is manufactured from 4140 steel, heat treated and drawn to 40 Rockwell C. This block in turn is held by the threaded plug J. Both J and E also are 4140 steel hardened and drawn to 40 Rockwell C. In use, E is advanced to its shoulder, then a small amount of sample trapped between the diamond faces. In an auxiliary press, the Solar piston K is used to advance I until the desired pressure is reached. I is clamped by the threaded plug, after which the stress applied by K is released. During this operation, only the portion of the apparatus contained by D is involved. After clamping, this portion is mounted on its base on the x-ray diffractometer. Pressure is estimated by measuring the area of the sample after exposure and knowing the applied stress.

[4] M. J. Buerger, *X-Ray Crystallography* (John Wiley & Sons, Inc., New York, 1942).
[5] Griggs, Fyfe, and Kennedy, Geol. Soc. Am. Bull. **66**, 1569 (1955).
[6] P. T. Chester and G. O. Jones, Phil. Mag. **44**, 1281 (1953).

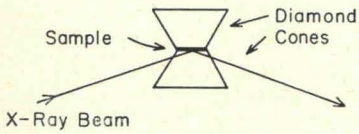

FIG. 3. Conical diamond pistons.

During initial testing, one of the pistons (Fig. 3), which contained a "knot"[7] broke at about 12 kilobars. It, and the carboloy insert F, were both replaced by an optically polished single crystal[8] sapphire flat which was successfully used in several studies ranging up to 35 kilobars before failure necessitated its replacement. At the same time, the other conical diamond was replaced with a diamond having natural facets on which was ground an optical flat normal to the diamond cubic axis of somewhat larger area ($\sim\frac{1}{4}$ in.^{2}) than the working face of the original cone. This replacement was made for fear of further breakage. Our present experience indicates that this change was probably unnecessary, and that the original design would have proved satisfactory if the diamond had been "knot" free.

The preparation of the sample depends on its mechanical properties. If the material is refractory powder, it is prepressed into a thin disk less than 0.002 in. thick. The area is kept less than $\frac{1}{4}$ the area of the diamond face so that some support for the stressed area of the diamond is gained. If the material is a soft metal such as the bismuth used in many of our test runs, it is pressed into a flat sheet, trimmed, repressed, etc. The resultant disks (again less than $\frac{1}{4}$ the area of the diamond face) are then mounted in the diamond press, brought to pressure and clamped in position. During this procedure, further flow occurs and, depending on the shear strength of the material and the pressure, the sample further decreases in thickness until the viscosity of the material and friction against the plattens prevents further appreciable flow within the time required to obtain a diffraction pattern. In the case of bismuth, this quasi-equilibrium thickness after exposure to 30 kilobars is only about 0.0004 in. Because of the enormous deformations produced in the sample by this history, it is reasonable to expect that a certain amount of preferred orientation will be produced in the sample. Furthermore, it is clear that a large pressure gradient will exist in the sample, although most of the gradient is presumably confined to a region corresponding to 3% of the radius near the periphery.[9] For both of these reasons, the intensities of the powder diffraction lines may be strongly affected, and caution must be exercised in their interpretation.

Several other phenomena occur as the result of the flow and pressure gradient. If a phase transformation to a new structure occurs as the result of the application of pressure, the transformation is never complete. Consequently, the diffraction pattern contains lines characteristic of both the high pressure and low pressure modifications. This effect is illustrated in Fig. 6, where the multiple structure of some of the lines arises from the coexistence of Bi I, Bi II, and Bi III. These transitions actually occur in the neighborhood of 28 000 bars.[10,11] Because the lines characteristic of the low-pressure modifications may be sorted out by successively taking pictures at higher and higher pressures, this effect is often helpful in indexing lines in the new structure.[12]

The effect of flow in producing preferred orientation is often ameliorated by recrystallization. This effect produces a selective change in the intensity of the diffracted peaks

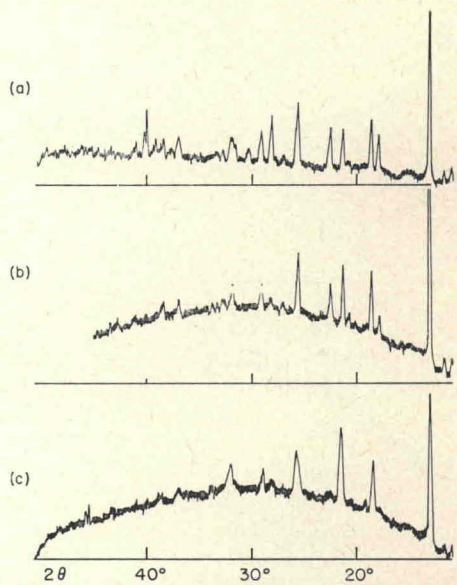

FIG. 4. Patterns of Bi under pressure. (a) Sample on sapphire diamond removed. (b) Bi I $P=0$ after pressure exposure. (c) Bi II $P=27\,000$ bars.

as a function of time. The distortion produced by remnant preferred orientation may be estimated by comparing the pattern obtained after a cycle of pressurization with a pattern obtained in the same material at zero pressure before any flow is induced. In this manner, one is able to circumvent some of the difficulties which otherwise arise in the interpretation of the patterns. In the case of Bi, a still further partial check was made[12] on the possibility of preferred orientation in the x-ray samples. Samples of pure Bi and Bi containing minor ($\sim$0.5%) amounts of Sn were extruded to flat disks in a squeezer device[5] at pressures above and below the Bi II-Bi III transformation. The disks were slid without deformation onto a moistened glass slide

[7] A "knot" is a crystalline defect in the diamond which makes grinding exceedingly difficult.

[8] It is necessary to back the sample with a single crystal to avoid interference by the diffraction pattern of the backing.

[9] P. W. Bridgman, Proc Am. Acad. Arts Sci. **71**, 387 (1937).

[10] P. W. Bridgman, Phys. Rev. **48**, 893 (1935).

[11] V. P. Butuzov, Soviet Phys.—Crystallography **2**, 533 (1957).

[12] A. W. Lawson and J. C. Jamieson. A detailed discussion of the Bi data obtained is to be submitted elsewhere.

and x-rayed in the spectrometer in the usual fashion. No trace of preferred orientation could be discerned in the patterns. However, the possibility of a very rapid recrystallization of Bi after exposure to pressure cannot definitely be ruled out.

Some of the phenomena discussed above are illustrated in Fig. 4, which clearly exhibits the nature of the background scattering from the diamond. This background has been materially reduced by slightly misaligning the sample in the spectrometer so that the amount of diamond bathed in the x-ray beam is minimized but the sample receives the peak intensity. The corresponding intensity of the Debye-Scherrer powder lines is strengthened markedly relative to the diamond background scatter owing to the small size of the sample. The error introduced by such "detuning" on the absolute values of the angles at which the diffraction intensities are a maximum may be elimi-

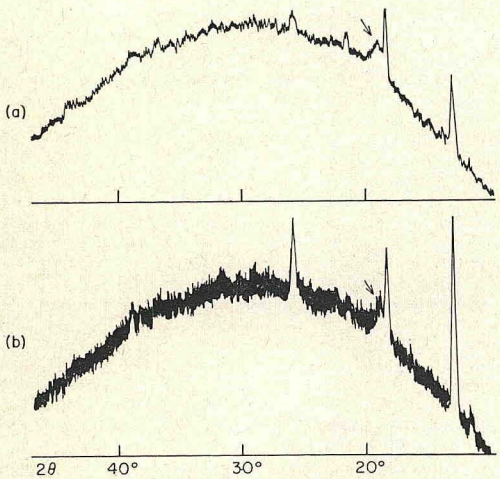

FIG. 5. Time effects in Bi under 35 000 bars pressure. (a) Initial pattern. (b) 20 hours later. [Different time constant setting than (a).]

nated by taking a calibration pattern at zero pressure with the diamond piston removed.

The patterns exhibited in Figs. 4, 5, and 6 are fairly convincing evidence that the technique is applicable to heavy materials at pressures up to 35 kilobars. The performance of the device on materials of lower absorption coefficients was also tested by studying the calcite transformations previously studied in the cylindrical diamond bomb.[2] The performance was comparable with that obtained with the older technique indicating that the present method is also applicable to materials of low atomic weight. One disadvantage of the spectrometer method which is not present

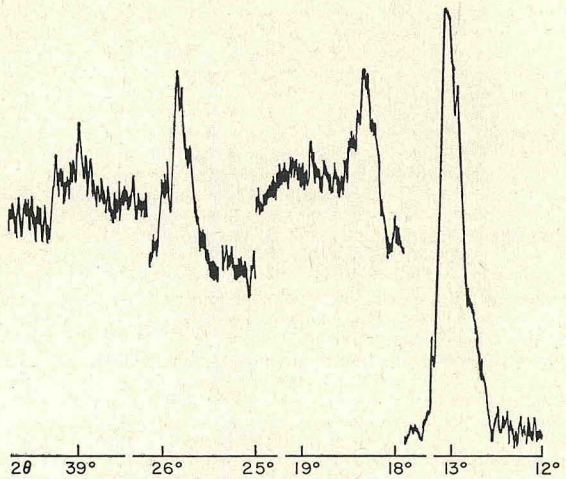

FIG. 6. Same sample as Fig. 5(b), slow scan, fast chart speed, showing multiple line structure. Some MoKα_1—Kα_2 splitting is also present.

in the older technique should be mentioned. Since the previous method used photographic detection, it was possible to discriminate visually between the Debye-Scherrer powder lines of the sample and the accidental Bragg spots diffracted by the diamond. The Geiger counter used as the detector on the XRD-5 provides no such discrimination and occasionally Bragg spots may interfere with pertinent parts of the diffraction pattern from the sample. This interference may be minimized by proper orientation of the diamond. In Figs. 5(a) and (b) the arrow indicates a partially detuned diamond Bragg reflection.

Although at the present time we have not extended our investigation to pressures above 35 kilobars, the possibility of doubling the available pressure range by returning to the original design involving two diamond pistons seems encouraging. The clamp design of Fig. 2 is adequate for a working stress of 200 kilobars. Howes and Tolansky[13] have reported cubic planes of diamonds withstanding stresses up to 140 kilobars before formation of pressure cracks. Weir[14] has employed a design similar to ours for infrared absorption studies, which operates consistently at 50 kilobars with occasional excursions to 70 kilobars.

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[13] V. R. Howes and S. Tolansky, Proc. Roy. Soc. (London) **A220**, 294 (1955).
[14] C. Weir (private communication).