

For optical observation, the cassette is easily removed and the squeezer placed on the stage of a petrographic or metallurgical microscope, or in a spectrophotometer, without disturbing the sample.

ALIGNMENT PROCEDURES

Three different alignment procedures are needed—(1) anvil, (2) collimator, and (3) cassette alignment.

(1) Uniformity of pressure distribution and long life of the anvils depend largely on the anvil faces being strictly parallel. The alignment of the anvil faces is accomplished by a pair of rockers that have their axes of rotation at right angles to each other and in a plane perpendicular to the x-ray beam. Set screws at the ends of the rockers serve to provide translational motion and to lock the angular settings of the rockers. The alignment is tested in three ways—interference (Newton) rings with no sample, interference rings with a transparent sample under pressure employing monochromatic light (Fig. 3), and centering of high pressure phases in a sample such as silver iodide which undergoes several phase changes. Of these, the second is the most sensitive test of anvil alignment.

(2) The dark interference bands in Fig. 3 act as contours for the pressure distribution. They show that the maximum pressure as well as the lowest pressure gradient lies in the central portion of the sample area. This central portion, with a diameter approximately $\frac{1}{10}$ that of the whole sample area, is the most suitable for x-ray diffraction. It is important, therefore, that the collimator produce a beam approximately $\frac{1}{10}$ the diameter of the sample area, and that the collimator be securely positioned so that the beam passes through the center of the sample area.

In addition, the x-ray beam must be parallel to the axis of the piston assembly. This is assured by the collimator flange (part E), which has a flat surface that glides on the back of piston C. A very thin layer of modeling clay between these surfaces provides ample adhesion, while allowing necessary freedom for gliding adjustment. When the proper position is obtained, a small quantity of plastic cement is used to fasten the collimator securely.

The x-ray beam position within the sample area is tested by inserting a photographic film between the diamond anvils, applying enough pressure to produce an indentation by the anvil faces, and recording the x-ray beam photographically (Fig. 4).

(3) Since the geometry employed is essentially that of the Debye-Scherrer camera, it is important that the sample lie at the center of curvature of the film. Therefore, the cassette mount (parts G and H) is designed so that the cassette can be moved from side to side as well as front to back. Holes in the sides of the squeezer body make it possible to see the sample. Transparent plastic plates pinned to the cassette and having center of curvature marked on

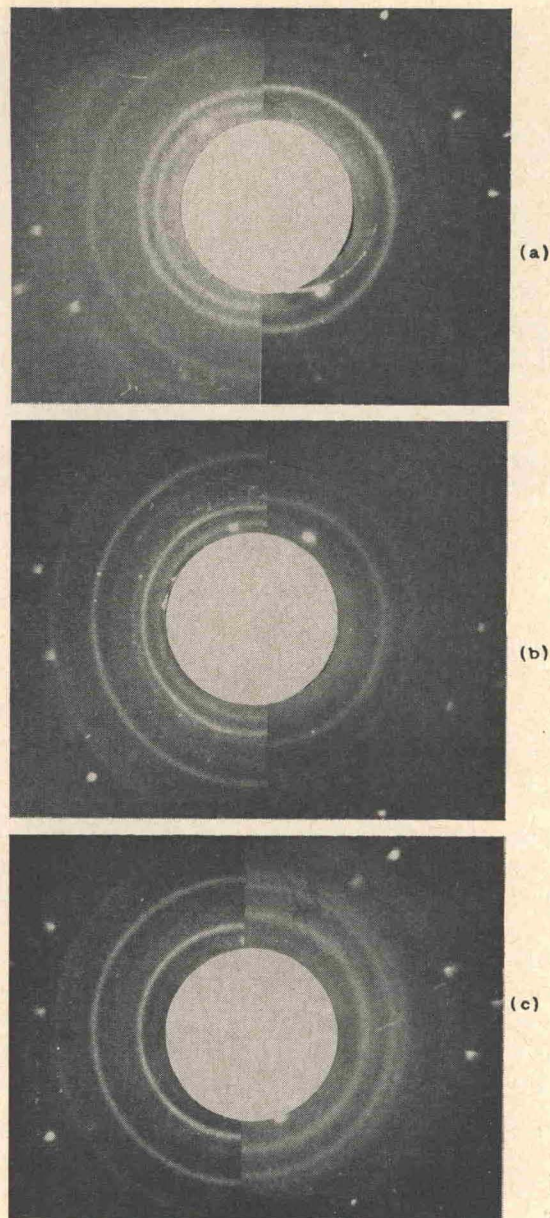


FIG. 5. X-ray diffraction photographs of the low pressure phase (left) and the high pressure phase (right) of (a) PbS, (b) PbSe, and (c) PbTe taken with filtered molybdenum radiation.

them can be used for aligning by direct sighting. Once the proper alignment is achieved, the adjustments can be locked. Subsequent removal of the cassette from the squeezer does not disturb the alignment. Holes in the film and the back of the cassette let the direct beam pass through to a lead stop outside of the assembly thus minimizing the effects of halation.

The design features outlined above allow the loading and unloading of film without disturbing the sample or any of the alignments. Also, the sample pressure can be changed without removing the sample, or the sample can be replaced without disturbing any of the alignments.

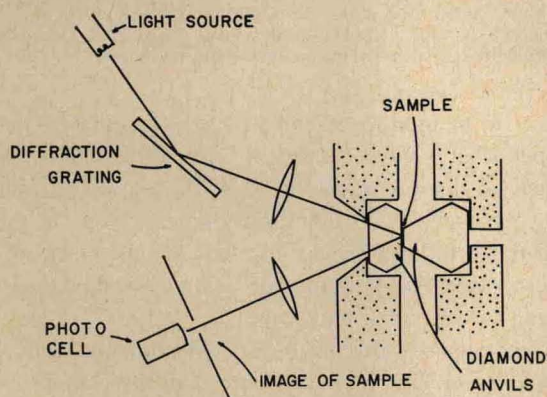


FIG. 6. Photomicrograph of iron under pressure in reflected light. The light area in the center is the high pressure phase.

EXPERIMENTAL PROCEDURES

Once the alignments described above have been achieved, the sample-to-film distance must be accurately determined before data are collected. This is calculated from a powder x-ray diffraction pattern of a known cubic solid placed between the diamond anvils and held at 1 bar pressure. By this means, the sample-to-film distance can be determined with an accuracy of $\pm 0.1\%$ or ± 0.05 mm when a 50 mm radius cassette is used. This determination is made before and after a series of high pressure runs in order to insure constancy of the camera geometry. It is reproducible within $\pm 0.1\%$.

The choice of collimator size depends on the objective of the experiment. For identification of phases, a 100 μ diam glass collimator has been used and gives satisfactory photographs with exposure times of 50 to 100 h. For precision measurements a 50 μ collimator is used. The precision obtained in lattice parameter measurements is $\pm 0.1\%$. With such a small collimator, a 200 to 300 h exposure is required.



SYSTEM FOR MEASURING REFLECTIVITY OF SAMPLES UNDER PRESSURE

FIG. 7. The arrangement used to make the photograph in Fig. 6.

Ilford 35 mm, double emulsion, no screen film has been used throughout our work. The photographic records have been measured by means of a standard Norelco comparator with a precision of $\pm 25 \mu$. In order to check the composite effect of elastic change in camera geometry during a run and film shrinkage, a thin platelet of polycrystalline sodium chloride was placed on the cassette side of the diamond in piston A and allowed to produce diffraction lines on the film along with the lines produced by the sample. Since no significant change in the sodium chloride pattern produced in this way has been observed from run to run, no correction for elastic deformation and film shrinkage is necessary.

PRESSURE CALIBRATION

The pressure to which a sample is subjected is measured by means of sodium chloride internal standard. The x-ray diffraction pattern of an intimate mechanical mixture of a sample with sodium chloride shows lines attributable to both substances. The lattice parameter calculated from the sodium chloride lines can then be used to determine the pressure, using the isothermal compressibility of sodium chloride. For this purpose we have used Decker's equation of state for sodium chloride.¹¹ At pressures below 200 kbar, Decker's equation of state agrees with Christian's shock compression data for sodium chloride,¹² within the 3% uncertainty claimed by Christian. Above 200 kbar, Decker's values agree with the shock data of Alder¹³ and Al'tshuler *et al.*¹⁴ within 5%. The agreement between Decker's equation of state and fixed calibration points is discussed by Jeffery *et al.*¹⁵

EXPERIMENTAL RESULTS

Identification of High Pressure Polymorphs of PbS, PbSe, and PbTe

Bridgman^{16,17} reported phase transformation in PbS, PbSe, and PbTe at 22.3, 42.5, and 40.3 kbar, respectively, at 25°C by means of volume determinations in a piston-cylinder device. All three of these compounds have the sodium chloride structure below their transformation pressures. The volume discontinuities found at these pressures are 2.0, 1.7, and 0.9%, respectively, unlike alkali halides, which undergo a volume change on the order of 10% as they transform from the sodium chloride structure to the

¹¹ D. L. Decker, *J. Appl. Phys.* **36**, 157 (1965).

¹² R. H. Christian, "The Equation of State of Alkali Halides at High Pressure," University of California Radiation Laboratory, Report 4900 (1957).

¹³ B. J. Alder, "Experiments with Strong Pressure Pulses" in *Solids Under Pressure*, W. Paul and D. M. Warschauer, Eds. (McGraw-Hill Book Company, Inc., New York, 1963), pp. 385-420.

¹⁴ L. V. Al'tshuler, L. V. Kuleshova, and M. N. Pavlovskii, *Zh. Eksperim. i Teor. Fiz.* **39**, 16 (1960) [English transl.: *Soviet Phys.—JETP* **12**, 10 (1961)].

¹⁵ R. N. Jeffery, J. D. Barnett, H. B. Vanfleet, and H. T. Hall, *J. Appl. Phys.* **37**, 3172 (1966).

¹⁶ P. W. Bridgman, *Am. Acad.* **70**, 285 (1935).

¹⁷ P. W. Bridgman, *Am. Acad.* **74**, 21 (1940).