

AN X-RAY DIFFRACTION TECHNIQUE FOR THE
STUDY OF HIGH-PRESSURE PHASE CHANGES IN IRON ALLOYS

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ABSTRACT

Static high-pressure x-ray diffraction experiments on metals and alloys are the only means available for simultaneously determining: (a) the structures of martensitic phases formed at high pressure, (b) the fraction of the sample which these phases represent, (c) the pressures at which they begin to form, and (d) the pressures at which the high-pressure phases begin to return to the original crystallographic structure. While employing a combination of existing techniques, the present investigation developed modifications in the experimental procedures as well as improvements in the diffraction recording technique. It was found that the body-centered-cubic to hexagonal close-packed martensitic transformation in pure iron occurs at 70 kilobars rather than at the 130 kilobars reported by previous high-pressure x-ray investigations¹⁻⁵, and agrees more closely with values of 80 and 50 kbar recently determined by electrical resistivity⁶⁻⁷. In addition, some common interpretation difficulties, concerning primarily pressure determination and phase fraction estimation are discussed.

INTRODUCTION

High-pressure x-ray diffraction studies are used principally to detect any phase change that may be occurring at high-pressure and to determine the crystallographic structure of phases involved.

High-pressure studies are also of interest because they give a qualitative measure of the relative stability of phases which could not otherwise be studied because the phases do not coexist at ambient pressure. These high-pressure studies add a third dimension to the standard temperature-composition equilibrium diagrams, thus permitting a more complete understanding of the nature of the equilibrium between phases. Of course, in the study of martensitic transformation, the diagrams are metastable equilibrium diagrams because of the nonequilibrium nature of the martensitic transformation.

The application of high pressure to induce phase changes in metals has been carried out for the past several decades. But it is only within the past 10 years that the use of x-ray diffraction at pressures above 30 kilobars (kbar) has enabled investigators to determine the nature of the change taking place and the crystal structure of the resulting phase^{1-5,8-9}.

Measurements using x-ray diffraction are capable of determining the structure of the phases present, the fraction of the sample that they represent, the pressure at which the new phases begin to form, and the pressure at which they begin to return to the original structure. The three other techniques used to study high-pressure transformations under static or incrementally increased pressurization conditions are electrical resistivity, volume change, and Mossbauer spectroscopy. Although all three of these techniques are capable of determining transition pressures, none is capable of determining the structure of the phases and the fraction of the sample that has transformed.

EXPERIMENTAL TECHNIQUE

By incorporating improvements into existing techniques for obtaining and interpreting high-pressure x-ray diffraction patterns, the experimental program described in the present paper makes it possible to more closely monitor phase changes

as a function of pressure. This improved method includes modified beam collimation, sample mounting and diamond alignment procedures and the use of a high-speed, high-contrast Polaroid film to significantly reduce exposure times and errors due to cassette placement and film shrinkage.

Sample Preparation

High-purity commercial iron powder and vacuum-melted iron alloys were used throughout this study. Filings from the iron alloys were annealed in evacuated Vycor capsules at 1900°F. Thin sheets of some of the alloys were produced by "pack-rolling"¹⁰ to thicknesses ranging from 0.002 to 0.006 inch. The problem in using samples produced by this method is the preferred orientation or texture present in the thin sheets even after annealing. The resulting difficulties in diffraction-pattern interpretation will be discussed later.

Equipment and Procedure

A schematic drawing of the commercially available high-pressure x-ray camera¹¹ used to obtain the high-pressure x-ray diffraction patterns is shown in Figure 1. The unit consists essentially of a cylinder inside which a piston is free to move. A flat-faced piston diamond is attached to one end of the piston, and a similar anvil diamond is attached to a demountable anvil assembly that is held in place by a backing plate during operation. The diameter of the anvil diamond face, 0.040 inch, is approximately twice that of the piston diamond. The sample is placed between the two diamond surfaces. Pressure is applied to the sample using a known gas pressure on the back surface of the piston assembly. The gas is fed through a high-pressure gas line and pressure regulator attached to a tank of dry nitrogen. The high ratio - approximately 10,000 to 1 - of the surface area of the back of the piston assembly to that of the piston diamond face made it possible to generate the high pressures required to induce transformations in the specimen.

X-rays leaving the source are collimated using a tube having restricted openings at either end. The opening at the x-ray source-end is approximately 0.02 inch, while that at the sample end is about 0.01 inch. During the course of this study it was found that better beam definition could be achieved and spurious x-ray lines on the pattern could be eliminated by placing a 0.015-inch-thick piece of lead containing a pinhole approximately 0.008 inch in diameter over the sample end of the collimator.

It was also found that alignment of the x-ray beam relative to the center of both the piston and anvil diamonds was important. Since pressure gradients increase with distance from the center of the diamond faces, the x-ray beam should pass as close to the center of the diamond faces as possible. Alignment can be determined by placing a sheet of standard x-ray film wrapped in aluminum foil between the diamond faces, applying a force of about 2 lb, and turning on the x-ray beam for less than a second⁵. This procedure produces an image of the outside edges of both diamond faces superimposed on the image of the beam. Measurements showed that the piston diamond diameter was 0.022 inch, the anvil diamond 0.040 inch, and the beam diameter 0.012 inch where it passed through the sample.

Since the chances of developing destructive fracture in the diamonds at high loads are greatly increased if the piston and anvil diamond faces are not strictly parallel, one should determine the extent of non-parallelism before beginning the high-pressure experiments. Interference microscopy can be used for this purpose, and Figure 2 is an interference photomicrograph of the high-pressure surface of a piston diamond taken at 170X. In this case, the diamond surface was misaligned by 1.7 degrees relative to a plane perpendicular to the axis of the piston assembly.

Two problems encountered in diffraction-pattern interpretation are "nonsample" diffraction lines and low diffraction line intensity. Nonsample diffraction lines are caused by lead between the anvils getting into the path of the x-ray beam. Low diffraction line intensity is due to extrusion, at high pressure, of copper from behind the face of either diamond into the path of either the main x-ray beam or the diffracted x-rays. The copper which is used to fasten the diamonds to their assemblies, can be easily removed with a long needle or razor blade.

An opening in the anvil assembly having a 20 angle of 45° (Figure 1) permits the recording of diffraction lines from lattice planes having spacings less than 1 \AA when molybdenum $K\alpha$ radiation is used. The diffraction patterns were recorded on Polaroid Type 57-3000 speed sheet film at a specimen-to-film distance of about 4 cm. The film was held in a Polaroid XR7-Land Diffraction Cassette (#57-1) which has a fluorescent intensification screen. The use of this combination of film and cassette permitted patterns to be recorded in periods ranging from 3-15 hr, whereas standard wet film required exposures ranging from 20-50 hr under the same test conditions. Figure 3 shows the difference between diffraction patterns recorded on the Polaroid film and on a high-contrast, high-speed wet x-ray film. These patterns are of an annealed iron powder sample obtained at ambient pressure. Although the wet film gives an obviously sharper and higher contrast pattern, the difference in exposure times, 8 and 44 hours respectively, is large enough to make the use of the wet film undesirable except for circumstances justifying the long exposure time. The advantage of much shorter exposure time combined with the absence of shrinkage correction, ease of handling, and avoidance of cassette movement during a series of high-pressure x-ray diffraction exposures led to the exclusive use of the Polaroid film.

During the course of these experiments, it was found that the manner in which the sample is placed between the two diamonds and the material used to prevent the sample from extruding from between the diamond surfaces at high pressure were important. Figure 4 shows the sequence used to place a sample in the high-pressure x-ray camera. The procedure for mounting powder samples consisted of taping a piece of 0.03 inch-thick sheet lead over the anvil diamond (4a) and placing both the piston and anvil assemblies together with about 5 lb of force (4b). The cavity thus formed had a thin portion of lead covering the anvil diamond face. The center of this thin portion was removed with a needle, and the cavity was filled with the sample powder (4c). The sample was then compacted at light loads between the piston and anvil diamonds (4d). Thus, a uniform sample, surrounded by a thin gasket of lead and excess sample, was obtained.

Application

Phase-pressure information was obtained by taking a series of diffraction patterns as follows: for ambient and increasing pressures at 10 or 20 kbar increments up to a nominal pressure of 80 kbar; and for decreasing pressures, again at 10 or 20 kbar increments, down to ambient pressure. Transformation pressures and percentages of phases present were noted as a function of nominal pressure. The diffraction patterns were then measured and interplanar spacings calculated. The actual pressures were arrived at by substituting our experimentally determined lattice parameters into the equation developed by Mao et al.⁴. As an example of the type of information obtained by these procedures, Figure 5 shows four of a series of twelve x-ray diffraction patterns obtained from iron at various pressures. These patterns and results are typical of the two "pressure-phase" determinations which were made on iron. The actual pressure appears in kbar next to each pattern. The arrows indicate increasing or decreasing pressure. The numbered vertical lines running between the patterns indicate the approximate positions of the lines which are identified in the table below the patterns. The lines for the face-centered-cubic (γ) phase are included only for comparative purposes. No fcc material was detected in this sample. It can be seen that at 70 kbar the sample contains a very small amount of the hcp phase (line 3). Prior to reaching this pressure, no hcp was detected. As Figure 5 shows, after the pressure was decreased to 10 kbar, only a small amount of hcp remained. All of the hcp present at high pressure had transformed to bcc before ambient pressure was reached. Using a series of twelve diffraction patterns, it was possible to determine that the bcc-to-hcp transition began at 70 ± 10 kbar and that the reverse transition, hcp-to-bcc, began at 27 ± 10 kbar.

Problems of Interpretation

There are two problems of major concern in the use of opposed-anvil high-pressure x-ray techniques in the study of high-pressure martensitic transformations:

(1) the existence of a pressure gradient from the center to the edge of the sample, and (2) the combination of factors affecting determination of the fraction of the sample that has transformed.

In considering the first of these problems, we find that there are actually two consequences: (a) variation in pressure across the irradiated portion of the sample, and (b) the difficulty of determining the pressure at any given point in the sample.

Myers et al¹² found that the variations in pressure across the center 75% of the sample become negligible when the sample diameter-to-thickness ratio is greater than 20:1. This ratio, together with an x-ray beam diameter less than one-half the sample size, can eliminate most of the pressure variation across the irradiated portion of the sample.

Given the existence of a pressure gradient, it is not possible to calculate the pressure at a given point in the irradiated portion of the sample on the basis of applied gas pressure and the ratio of the area of the piston assembly to that of the piston diamond. The value arrived at on this basis will necessarily be lower than the actual value. However, by using known variations of the bcc iron lattice parameter with pressure⁴ as an internal calibrant, it was found that all pressures could be determined within a one sigma error of 10 kbar. This error is small in comparison with the 50 to 130 kbar range of the previously reported transformation pressure for iron^{1-5,7}. Most of the 10 kbar error was introduced during diffraction pattern measurement.

For work with metals having a cubic crystal structure for which lattice parameter-pressure information is not available, an accurate estimate of the change in lattice parameter with pressure can be obtained from volume-pressure data such as those presented by Bridgman¹³. An alternate method of determining pressure is to mix into the sample a material, such as NaCl, whose pressure-lattice parameter characteristics are well known²⁻⁵.

The second of the two major problems in high-pressure x-ray diffraction work stems from the difficulties involved in estimating the percentage of each particular phase. Since the percentage of each phase is estimated on the basis of relative diffraction line intensity and the structure factor, any factors, in particular preferred orientation and line overlap, that interfere with the correct determination of line intensity will also lead to an incorrect estimate. Preferred orientation is usually present in cold-rolled metals even after annealing. Annealed powdered metals often develop a preferred orientation during deformation during the compaction at low pressures. This preferred orientation is usually not as severe as that found in cold-rolled and annealed foils.

Diffraction line overlap is shown in Figure 6, which is a schematic representation of interplanar spacing for the three structures of iron. As this figure illustrates, the different structures of a metal can give diffraction lines at the same points on the diffraction pattern. Overlapping lines occur at about 2.05 Å, 1.26 Å, and 1.08 Å. Because of these overlapping lines, only a few of the diffraction lines can be used in the estimation of phase percent. A minor point illustrated in the figure is that the (100), (102), and (200) lines of the hexagonal close-packed structure are only weakly diffracting planes.

SUMMARY

To sum up, the existing techniques for the use of a commercially available opposed-anvil high pressure x-ray diffraction unit in the study of high-pressure transformations in iron alloys were modified to permit one to more closely monitor these phase changes as a function of pressure. Modifications affected specifically: beam collimation, beam and diamond alignment, and mounting procedures. The use of Polaroid film to record the diffraction patterns was introduced.

Methods of minimizing pressure-determination difficulties associated with the existence of the pressure gradient across the irradiated portion of the sample were described. The procedure for using diffraction lines to determine phase fractions was discussed.

Employing the modified techniques, it was demonstrated that the transformation of bcc iron to the hcp phase occurs at 70 kbar.

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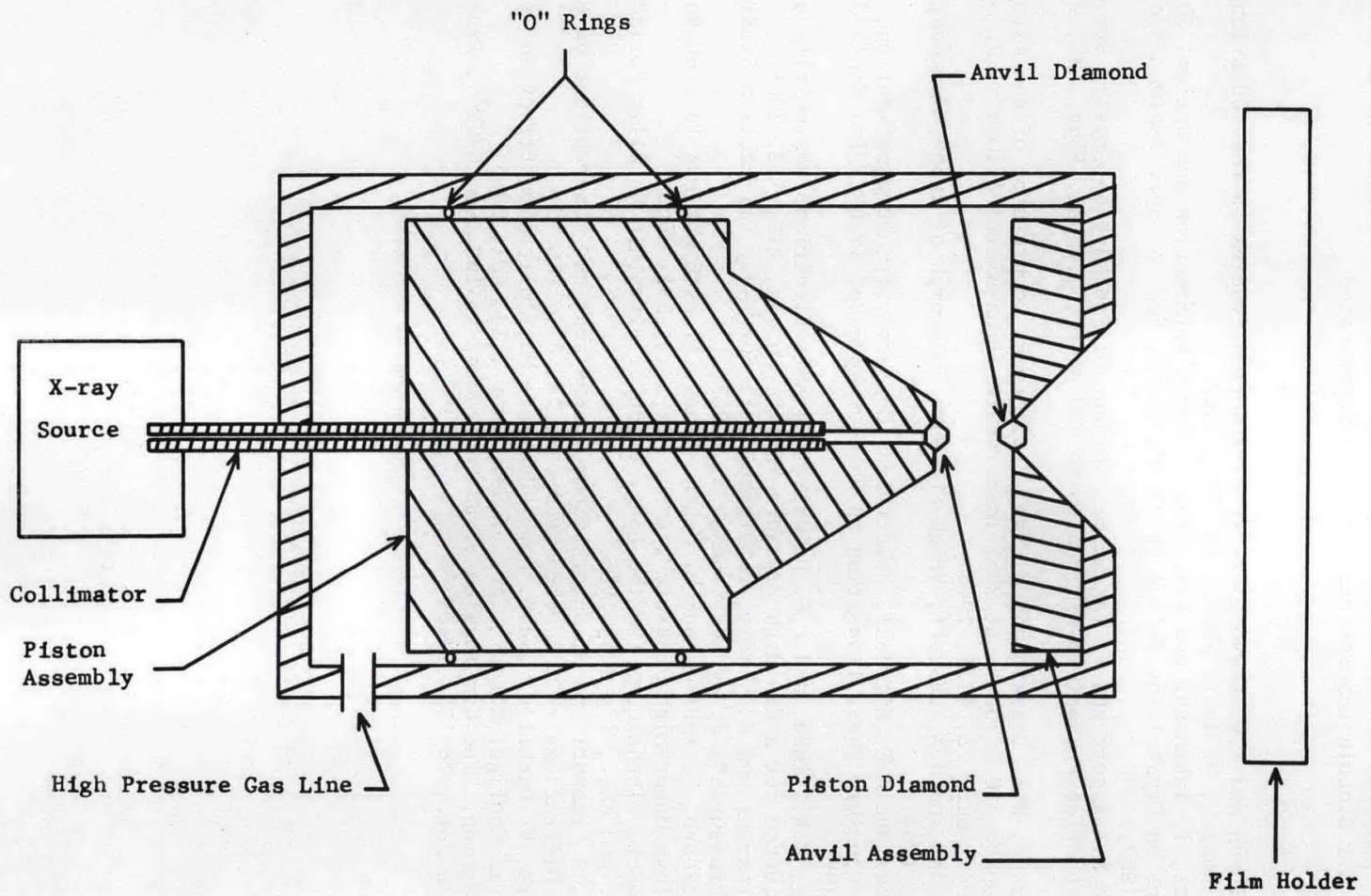
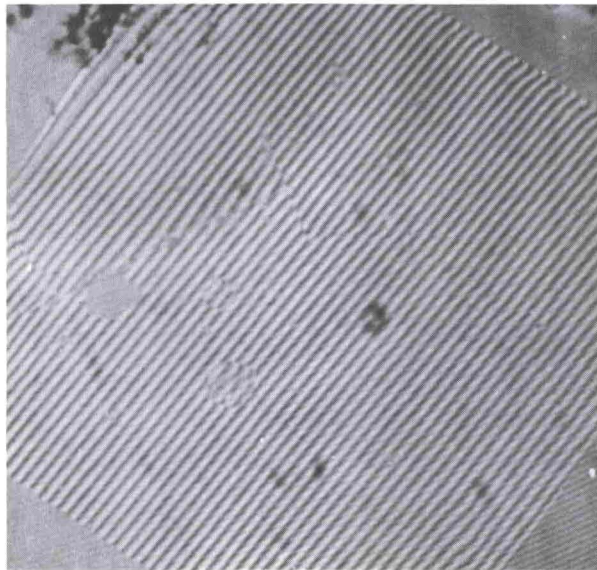


Figure 1. Schematic drawing of high-pressure x-ray diffraction camera.



170X

Figure 2. Interference photomicrograph showing misalignment of the high-pressure surface of the piston diamond.

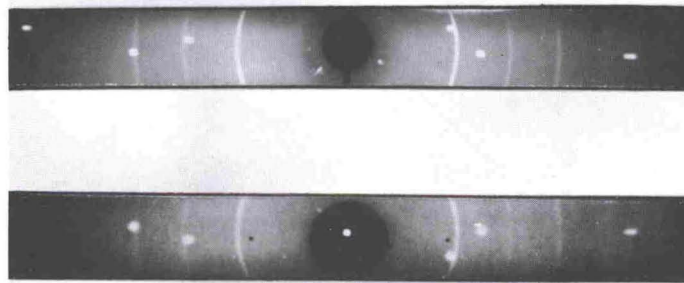


Figure 3. Diffraction patterns obtained from a powdered iron sample at ambient pressure. Upper pattern is a 44-hr exposure on high-contrast, high-speed wet x-ray film. Lower pattern is an 8-hr exposure on Polaroid Type 57-3000 speed film.

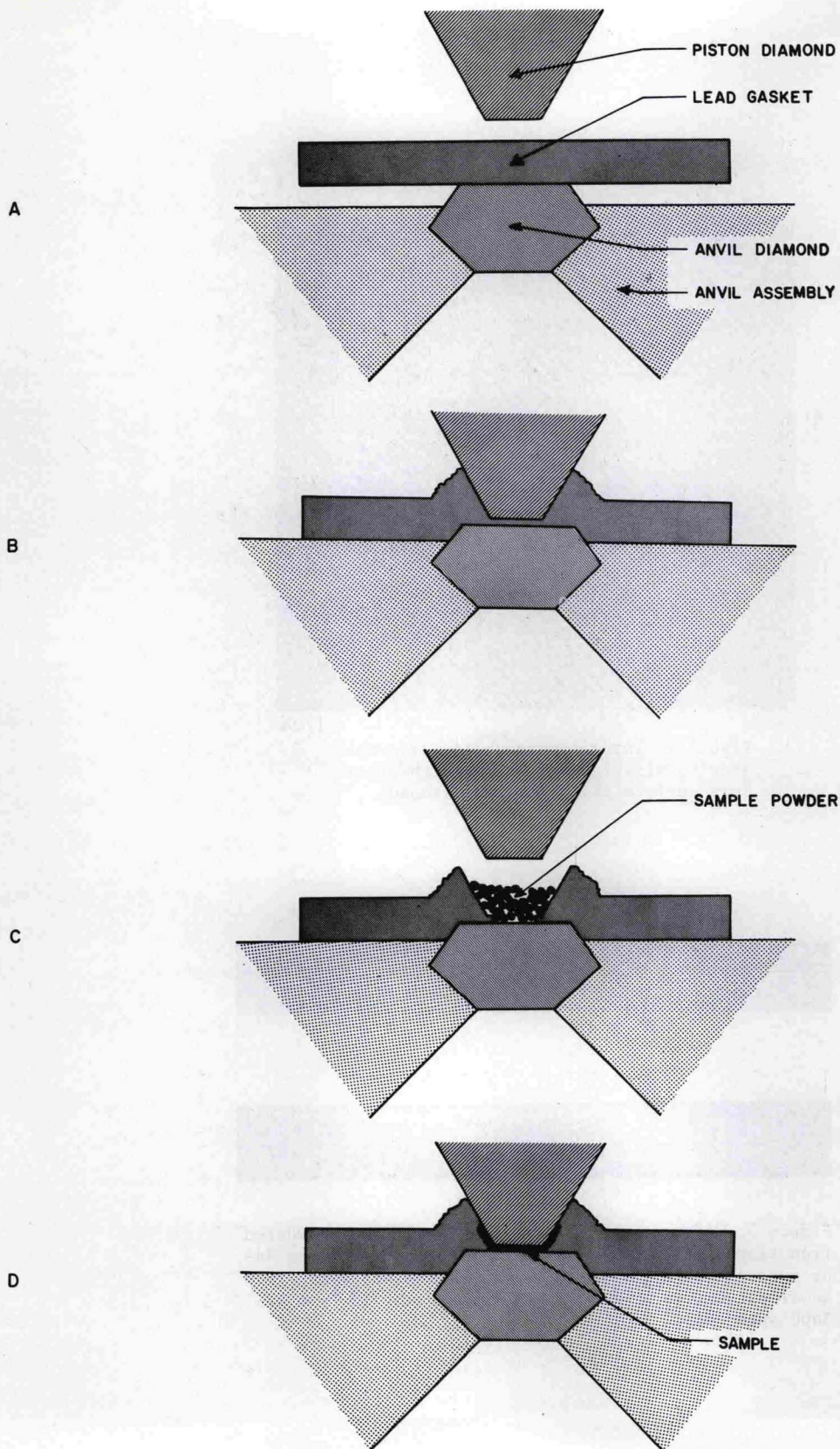
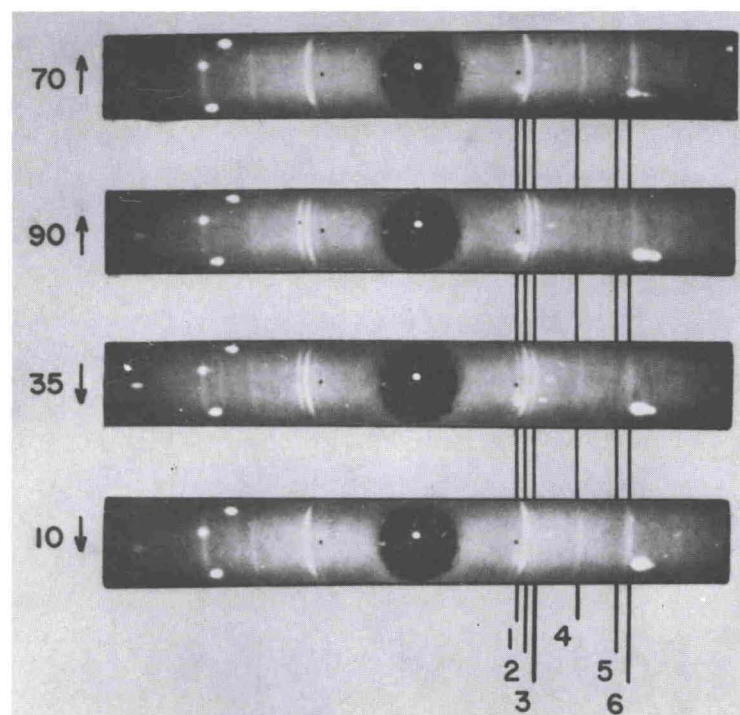


Figure 4. Series of schematic drawings showing procedures used to mount powder sample between the diamond surfaces.



LINE	INTERPLANAR SPACING, Å	PHASE AND INDICES
1	2.17	$\epsilon_{(100)}$
2	2.04	$\alpha_{(110)}$ $\epsilon_{(002)}$ $\gamma_{(111)}$
3	1.92	$\epsilon_{(101)}$
4	1.43	$\alpha_{(200)}$
5	1.25	$\epsilon_{(110)}$ $\gamma_{(220)}$
6	1.17	$\alpha_{(211)}$

Figure 5. High-pressure x-ray diffraction patterns of iron, with diffraction lines identified. Pressure in kbar is shown to the left of each pattern. Arrows pointing up show that the pressure was raised to that level; arrows pointing down show that the pressure was lowered to that level.

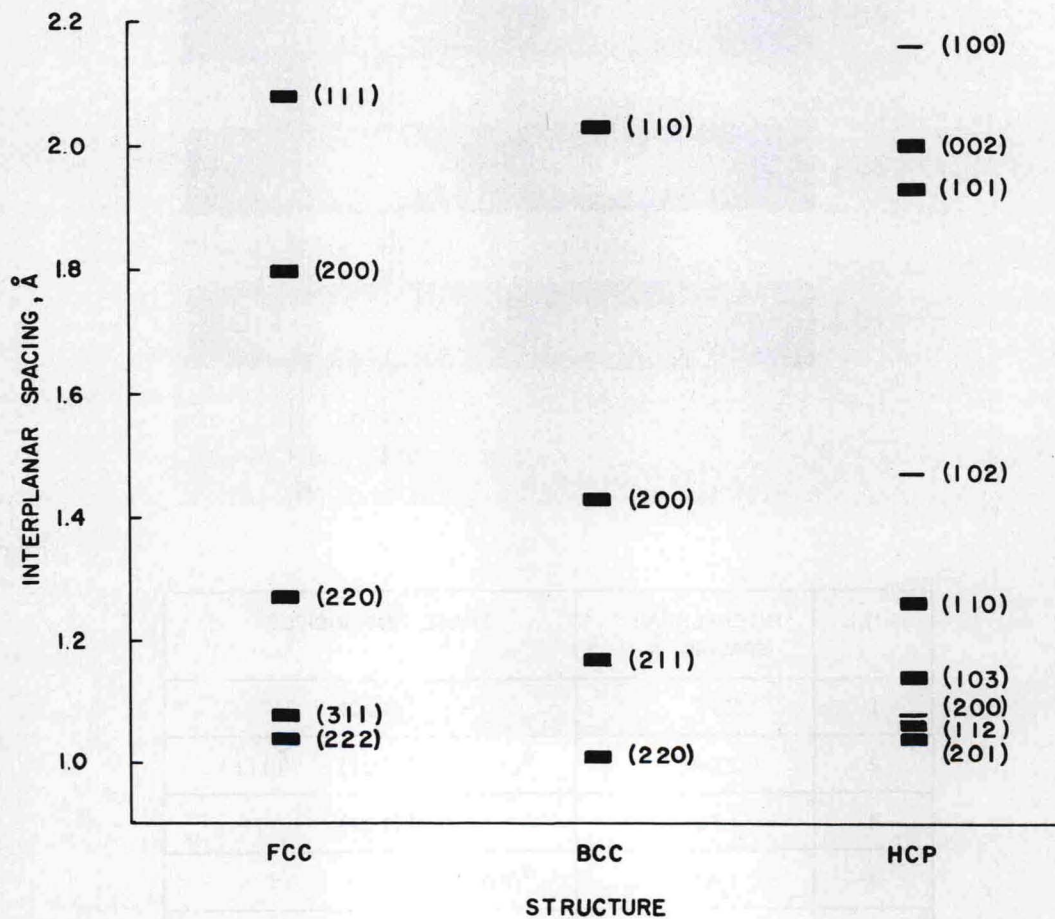


Figure 6. Schematic representation of the diffraction patterns given by three phases of iron, showing the limited number of diffraction lines where overlap does not occur.