Final Report

ULTRAHIGH PRESSURE, HIGH TEMPERATURE X-RAY DIFFRACTION APPARATUS

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In accordance with the original research proposal, a tetrahedral-anvil, high-pressure apparatus has been designed and constructed with the necessary modifications and adaptations to allow X-ray diffractometry analysis of samples while they are subjected to pressures to 100,000 Kb. The construction phase of the work has been completed, and the preliminary testing of the completed system has been carried out. No refinements have yet been made to indicate the accuracy or limits of operation of the apparatus, but no major difficulties have arisen. Preparatory to taking reliable data the following work is in progress: (a) pressure calibration,. (b) X-ray system alignment, (c) optimization of X-ray intensity and resolution, and (d) study of sample geometry and construction.

A high-current, low-voltage internal heating system has been built into the apparatus, and exploratory investigations have been made to check the adaptability of the system to temperature. Due to the delays incident to construction, initial testing with temperature has not been started but will be initiated within a few weeks.

The complete system, as shown in Fig. 1, includes the tetrahedral-anvil press itself, the control console, the X-ray counting systems, and the X-ray high-voltage generator (not shown). Two photos of the press itself are shown in Figs. 2 and 3. These photos were taken in the direction shown by arrows (2) and (3) in Fig. 1. Some of the finer details of the X-ray detectors and slit system, the X-ray tube mount, and the scanning carriage and track are shown in close-up photographs in Figs. 4, 5, and 6. These photographs were taken in directions (4), (5), and (6) as indicated in Figs. 2 and 3. A study of these photographs in connection with the schematic drawing discussed below will aid in correlating the three-dimensional geometry of the tetrahedral press and the X-ray diffraction geometry.

The tetrahedral-anvil press was machined to an accuracy consistent with the precision of an X-ray diffractometer. This accuracy was necessary since the diffractometer is an integral part of the press. All of the geometry critical to the X-ray analysis lies in a plane which contains the axes of two of the tetrahedral rams. A sectional drawing of such a plane is shown in Fig. 7. This plane contains the scanning tracks (not shown in section), the sample, the X-ray tube target, the axis of one of the tie bars, and the compressible gasket which forms between the two tetrahedral anvils whose axes are not in this plane. The two rams not shown and the other tie bars never pass through this plane.

The X-ray tube is mounted in a cylindrical cross-axis hole in one of the hydraulic rams as indicated. This ram is referred to as the X-ray tube ram. When the X-ray tube is excited, an X-ray beam passes through a collimator along the axis of this ram and emerges through a small hole in the center of the carboloy piston, The hole in the piston face is plugged with beryllium to prevent excessive extrusion of the material of the pressure cell down the collimator. The details of this construction and geometry are indicated in an enlarged drawing (Fig. 8) of the sample region. The tetrahedral sample chamber is made of solid LiH to reduce X-ray absorption. These tetrahedra are formed by pressing polycrystalline LiH in an appropriate die. The size of the individual crystals of LiH is approximately .030" in average dimension. This large crystal size reduces the X-ray absorption and also the chance of proper orientation for X-ray diffraction from LiH near the sample which would be recorded as a peak by the counters. After striking the sample, the diffracted X-rays pass out of the pressure chamber through the thin gasket and are detected by scintillation counters mounted on a motor-driven, geared carriage. The width of the diffracted X-ray beam entering the counter is restricted by the anvils, whose axes are not in the plane of Fig, 7, between which the gasket is formed. The thickness of this gasket can be seen in Fig. 8 in the region labeled B. Region B is symmetrically equivalent to the region labeled A where the X-rays actually pass, but shows the gasket in cross section, The carriage moves along the high-precision circular track in order to scan the 2θ angles characteristic of X-ray diffraction. The diffracted X-ray signal is inherently small due to the absorption and small solid angle. To improve the detectability, the background count is reduced by use of a pulse height selector in the electronic system.

As can be seen in the photographs, three separate and distinct detection systems are utilized, each with an independent counter, carriage, track, and electronic system. Each of the scanning tracks lies in a plane similar to the plane of Fig. 7. Each of these planes passes through the axis of the X-ray tube ram and the axis of one of the other three rams. The X-rays detected by each individual counter pass through the same sample but leave the tetrahedral sample chamber through a different gasket. Although X-rays are being scattered from the material of the pressure chamber all along the path of the direct beam, the detector slit system only views the small region around the sample, thus eliminating a large percentage of the spurious scattered X-rays. This slit system also requires the sample to be near the center of the tetrahedron as indicated in Fig. 8. The proper alignment of these slits, which is necessary to insure meaningful measurements, is one of the major problems of the X-ray geometry. This problem is enhanced since the

tracks themselves are attached to the tie bars of the tetrahedral press and expand slightly as pressure is applied to the sample. Angular measurements of X-ray peak location as measured by the counter are measurable to 0. 02°, but due to lack of accurate information on sample position under pressure, the limits of accuracy of meaningful data perhaps will not be this good. Since only relative measurements are needed, this problem may not be too critical. Studies of the accuracy and reproducibility are now under way in regard to this problem.

To indicate the operation and capabilities of the instrumentation, X-ray diffraction patterns obtained in the preliminary testing from a sample of KCl at various oil pressures are shown in Fig. 9. No attempt has been made to relate the oil pressure to sample pressure in this discussion since this involves the pressure calibration of the press using LiH with this particular sample geometry. This series of patterns (shown in Fig. 9) was taken to check the feasibility of detecting phase changes and determining crystal structure of a high-pressure modification. The well-known KCl volume transition reported by Bridgman at approximately 20 Kb is indicated here. The X-ray lines of the high-pressure phase are indexed to a CsCl-type structure and the Miller indices are indicated for the new phase by an asterisk. This transition is known to be very "sluggish" in its behavior and is very evident as one observes the disappearance of the lines of the low-pressure structure and the appearance of the lines of the high-pressure structure as pressure is increased.

How much of this "sluggishness" is due to rate reaction or lack of adequate pressure transmission is still an unanswered question. These patterns are given here only as an indication of the quality of the obtainable patterns and the versatility of the instrumentation. This series of patterns was taken over a period of several hours, each pattern requiring approximately 20 minutes to record. If longer recording time were used, higher quality patterns could be obtained due to improvement in counting statistics. Molybdenum radiation was used, as will generally be the case, and no filter was used in order to preserve intensity. The identification of the β lines is easily made by momentarily inserting a filter in front of the detector. The a and β lines of the diffraction pattern are indexed separately.

Quantitative measurements taken from a more careful scanning of the intense peak in the two patterns yields a change in volume consistent with Bridgman's compressibility data to an accuracy of a few per cent, even though no corrections were applied to the data. The crystal structure of the high-pressure modification is definitely CsCl-type, as can be easily seen, and is consistent with the volume change.

The feasibility of compressibility measurements can also be seen from the slight, but clearly discernible change in position of the lines as a function of pressure. Quantitative measurements without corrections agreed with Bridgman to within a few per cent. The question of accuracy is of prime importance in compressibility measurements since an X-ray measurement measures a linear dimension and, therefore, must be three times as precise as a volume measurement in order to yield the same accuracy in the compressibility.

Although several refinements in technique and calibration are yet to be made, the general operation of the apparatus is very encouraging. The advantage of instantaneous observation of structural change gives a tremendous versatility and insight into the behavior of the test materials.

During the progress of this research, three graduate students have carried out work as part of their degree requirements- -Mr. Gordon Bethers, who completed a master's degree in August 1961, Mr. Roy Bennion as a master's candidate, and Mr. Leo Merrill as a Ph.D. candidate.

Respectfully submitted,

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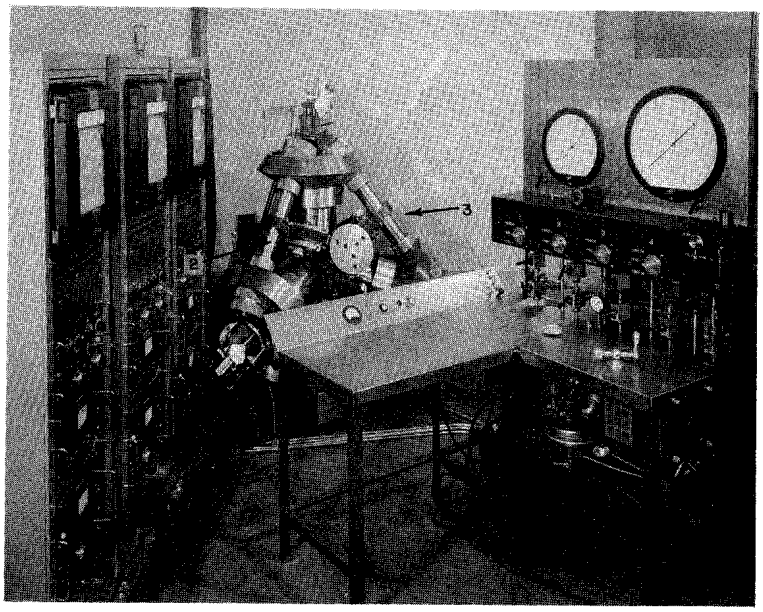

FIG. 1 COMPLETE TETRAHEDRAL-ANVIL HIGH PRESSURE, HIGH TEMPERATURE X-RAY DIFFRACTION APPARATUS

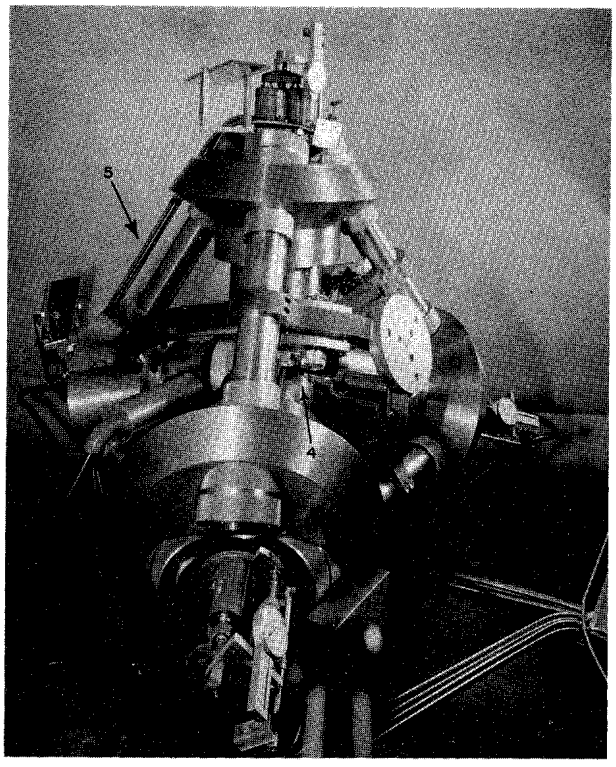

FIG. 2 TETRAHEDRAL-ANVIL PRESS (VIEW 1)

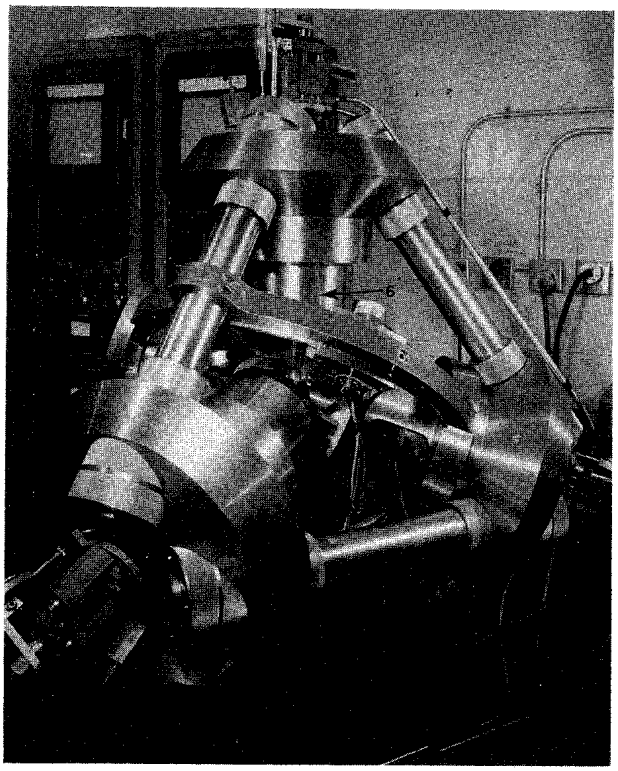

FIG. 3 TETRAHEDRAL-ANVIL PRESS (VIEW 2)

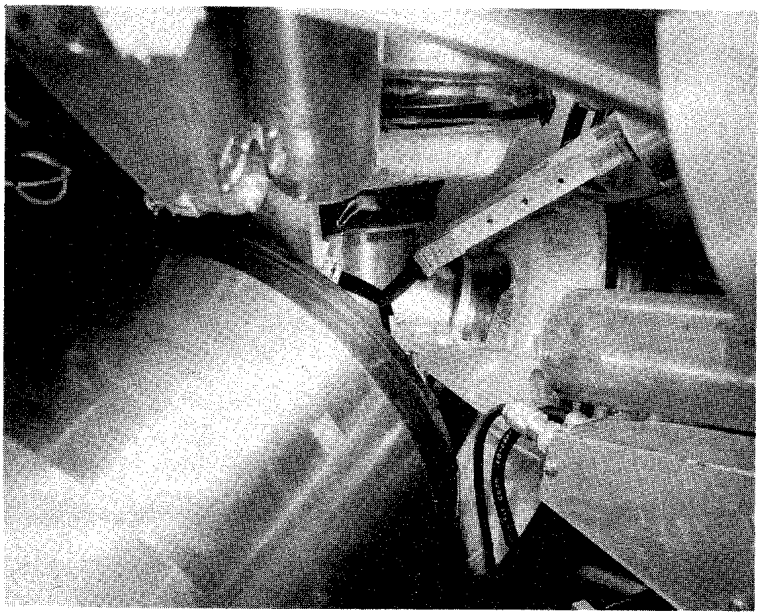

FIG. 4 COUNTER AND SLIT SYSTEM DETAIL

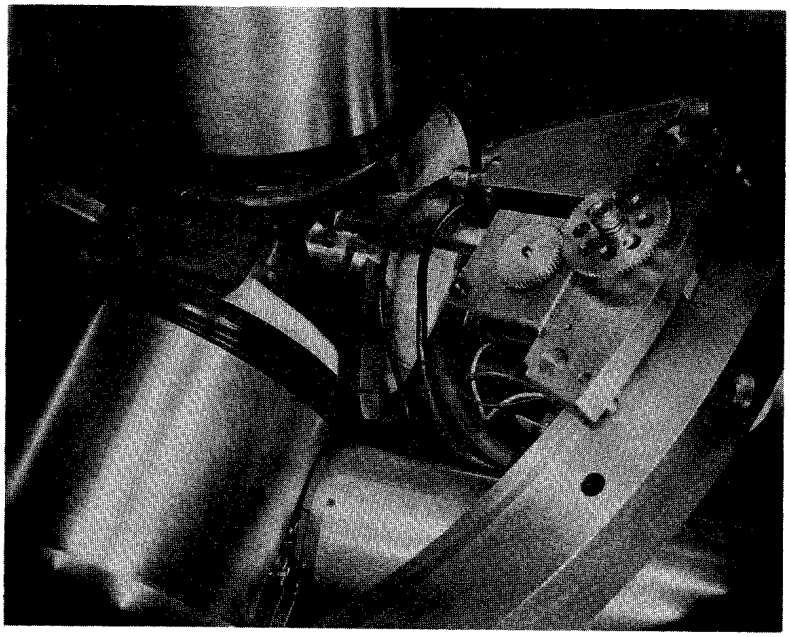

FIG. 5 X-RAY TUBE AND GEARED CARRIAGE DETAIL

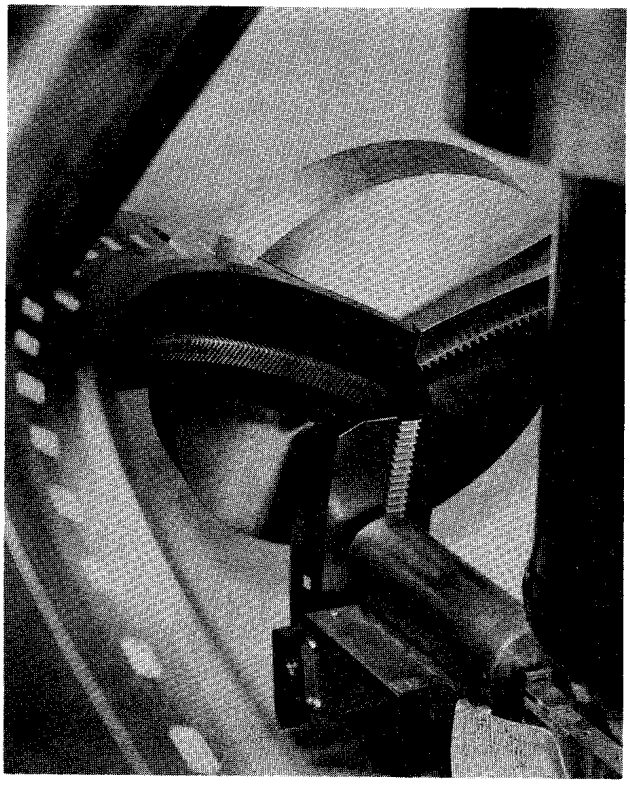

FIG. 6 SCANNING TRACK DETAIL

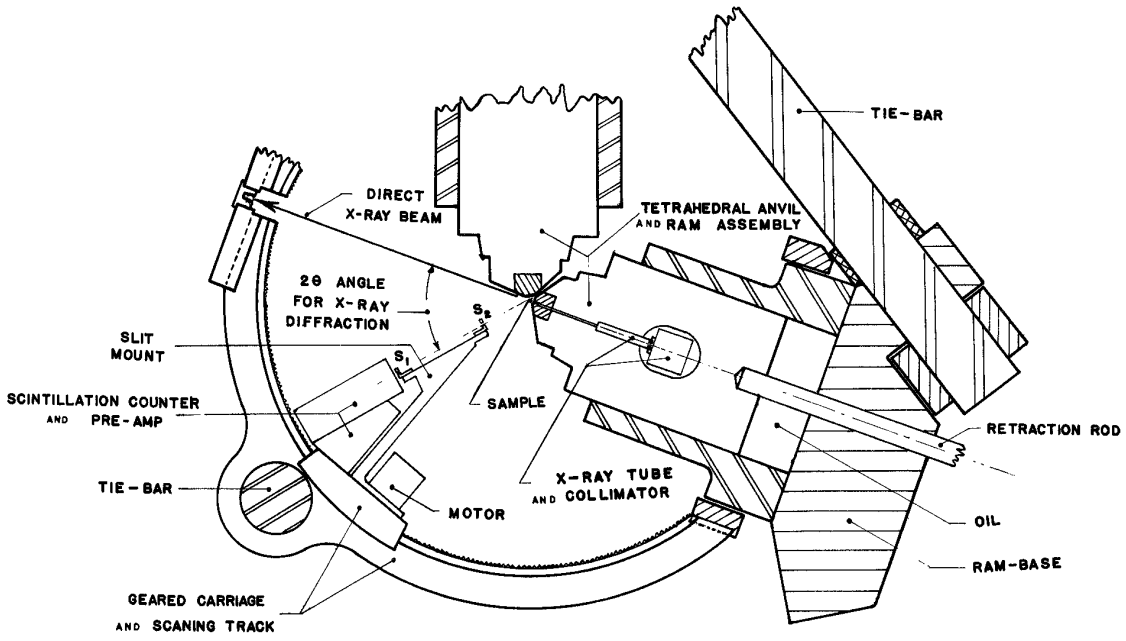

FIG. 7 RELATIONSHIP OF X-RAY GEOMETRY TO TETRAHEDRAL-ANVIL PRESS GEOMETRY

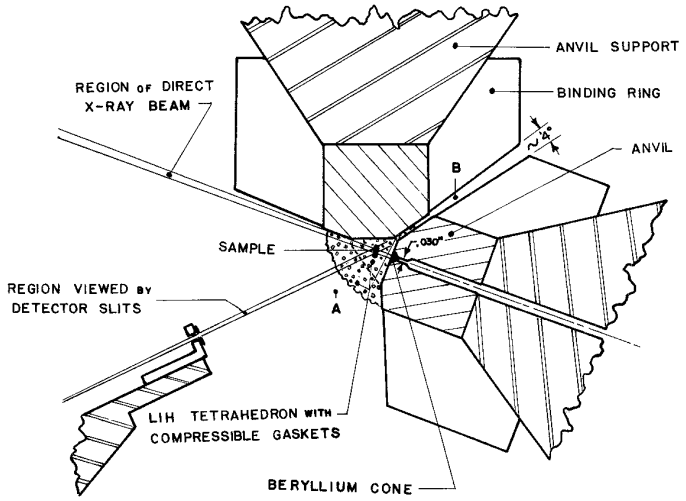

FIG. 8 SAMPLE CHAMBER DETAIL

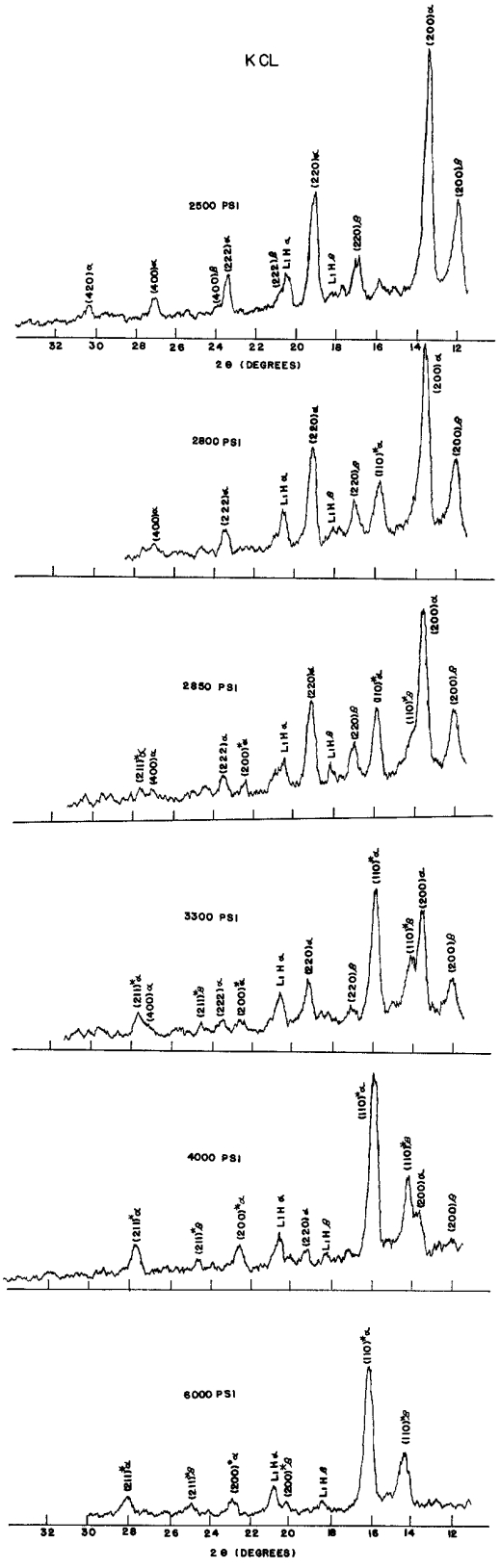

FIG. 9 X-RAY DIFFRACTION ANALYSIS OF THE POLYMORPHIC PHASE TRANSITION IN KCL AT APPROXIMATELY 20 KB