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Apparatus for High-Pressure High-Temperature X-Ray Powder Diffraction Studies

P. J. Freud and C. B. Sclar*
Battelle Memorial Institute, Columbus Laboratories, Columbus, Ohio 43201

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A high-pressure high-temperature x-ray powder diffraction apparatus has been developed based on a modification of the belt apparatus, which is an internally heated compressible gasket device. The unique feature of this device is that the die-support ring assembly is fabricated in two parts which mate along a plane normal to the piston axis. The split-die design permits entry of the x-ray beam into the high-pressure volume and egress of both the diffracted rays and the undeviated beam through suitable grooves and fan-shaped slots ground in the mating surfaces. The high-pressure x-ray windows are either a beryllium ring with a wedge-shaped cross section or epoxy resin stops at the bore of the die. The high-pressure medium is "amorphous" boron, and the sample is in the form of a thin cylinder which is coaxial with the pistons and normal to the x-ray beam. The compressible gaskets between the pistons and the die are made of pyrophyllite, as they are in conventional devices, inasmuch as they are not part of the x-ray path. High sample temperatures are attained by resistance heating of carbon rods adjacent to the sample. Present limitations on pressure and temperature are 100 kilobars and 1000°C. High-intensity Mo K_α radiation is employed. The apparatus is portable and may be positioned on a conventional x-ray source.

INTRODUCTION

ONE of the potentially most promising areas of high-pressure research which is relatively unexplored is that of structural studies on crystalline solids at pressures in excess of 20 kilobars at sustained temperatures in excess of 300°C. Such studies could provide basic data on the equation-of-state, nonquenchable phase transitions, order–disorder phenomena, etc. of solids.

At present there are three basic designs being used for high-pressure x-ray diffraction measurements. The diamond cell[1–3] consists of a pair of diamonds in the configuration of Bridgman anvils and the x-ray beam is transmitted through the diamonds perpendicular to the anvil faces and the sample plane. Carbide Bridgman anvils are used for[4–6] x-ray diffraction measurements with the x-ray beam transmitted parallel to and between the anvil faces. The third design utilizes the tetrahedral high-pressure apparatus[7] to generate pressure and the x-ray beam is transmitted in and out of the high-pressure volume through the compressible gaskets. For high-pressure studies at elevated temperature the first two designs are restricted by the effect of external heating on the properties of the carbide or diamond anvils (less than 500°C). The tetrahedral device can be internally heated and is limited only by the combination of requirements fixed by the gasket material, i.e., low x-ray absorption, proper frictional qualities to effect a high-pressure seal, and high-temperature stability.

The apparatus described in this article utilizes a belt-type high-pressure cell[8] with a split die for entrance and egress of x rays from the high-pressure region. The essential feature of this design is the separation of the x-ray beam path from the compressible gasket region in an internally heated high-pressure high-temperature device. This permits the use of standard gasketing materials, such as pyrophyllite, to effect the pressure seal irrespective of their x-ray absorption characteristics. This design has been used to 1000°C and 100 kilobars.

APPARATUS

The high pressure is generated in a modified high-compression belt of the type developed by Bundy.[9] The high-pressure volume is 0.25 cm high by 0.5 cm in diameter, which is large enough for internal heating to over 1000°C. Fifty tons of ram force applied to the pistons produces over 100 kilobars internal pressure, so the whole assembly, 50-ton press, die, pistons, and binding rings, can be constructed with a total weight of less than 34 kg. The device, therefore, is portable and can be installed on an x-ray source. Figure 1 is a picture of the high-pressure apparatus aligned with the x-ray source, and Fig. 2 is a schematic representation of this assembly.

To provide entry for the x-ray beam and exit of both the diffracted rays and the undeviated beam, the die and the support ring assembly of the high-compression belt were fabricated in two halves which mate in a plane perpendicular to the piston axis. The entrance and exit ports are ground into the mating surfaces of the two halves (Fig. 3). The die halves (5 cm diam, 1.25 cm thick) are made of Carpenter–Hampton tool steel hardened to 60–62 R_c, and the binding rings (10 cm o.d., 5 cm i.d., 1.25 cm thick) are made of Vascojet 1000 hardened to 50 R_c. The die and binding ring halves fit together with 1° taper and 0.028 cm

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* Present address: Department of Geological Sciences, Lehigh University, Bethlehem, Pa.

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of interference. The faces are ground parallel. The die is made of tool steel to facilitate the grinding operations described below. A higher pressure range could probably be attained with the use of tungsten carbide.

An entrance–exit groove is ground across the mating surfaces of the two halves to a depth of 0.025 cm with a grinding wheel dressed to a 0.025 cm radius. The groove is centered on a diameter of the die and passes through the die center to within ±0.001 cm. A fan-shaped slot for diffracted rays is ground into the assembly on each side of the groove. The fan on one side of the groove covers the 2θ diffracted angles 5 to 30° and the fan on the other side covers 2θ angles 20 to 45°. This provides a range of measurable "*d*" values with Mo K_α radiation from 8.1 to 0.93 Å with overlap of the two slots from 1.37 to 2.04 Å. The fans have a vertical taper of 2°, which, at a film distance of 57.3 mm, gives an x-ray pattern 3 mm high. An initial flat region 0.025 cm deep is left in the fan for a distance of 1.25 cm from the bore center before the vertical taper is started. The flat region aids in effecting the pressure seal. The two halves are placed together and aligned by placing a 0.05 cm drill rod in the entrance and exit groove.

Two methods are used to prevent extrusion of the pressure medium into the slots and grooves. The first method employs epoxy resin to fill the slots and grooves to a distance of 0.5 cm from the periphery of the bore of the die. A clear epoxy loaded with 50–70% by weight of amorphous boron is suitable. An excess of the mixture is applied and then lapped parallel to the die face after curing. The epoxy–boron mixture has a linear absorption coefficient for Mo K_α x radiation of approximately 1.0 cm^{-1}, which results in an attenuation of intensity for the described configuration of 65%. When using the epoxy seal the internal temperature of the sample is limited to 500–600°C, since the temperature of the bore is approximately one-third the internal temperature and the epoxy begins to soften above 200°C.

The second method of sealing the pressure is by means of a beryllium ring with a wedge-shaped cross section. The bore is tapered where the two die halves mate so that the

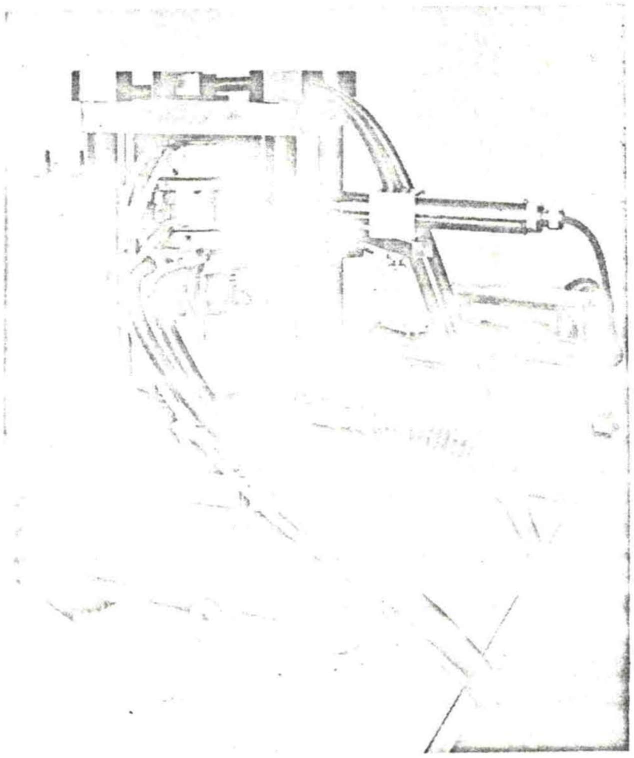

FIG. 1. Photograph of the high-pressure apparatus showing the press frame and hydraulic ram, the positioning table, the x-ray tube head (left), and the Geiger tube for aligning the press. The Debye–Scherrer camera is not in position so that one of the slots for the diffracted rays is shown. The scale is in centimeters.

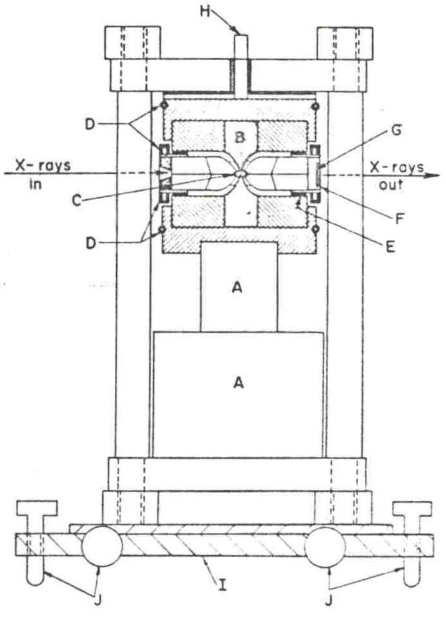

FIG. 2. Schematic drawing of the high-pressure apparatus. A—hydraulic 50-ton ram; B—WC pistons; C—die assembly; D—water cooling tubes; E—rubber shim to position die water-cooling tube; F—film cassette; G—x-ray film; H—insulated current lead; I—press positioning table; J—adjusting screws for vertical and horizontal positioning.

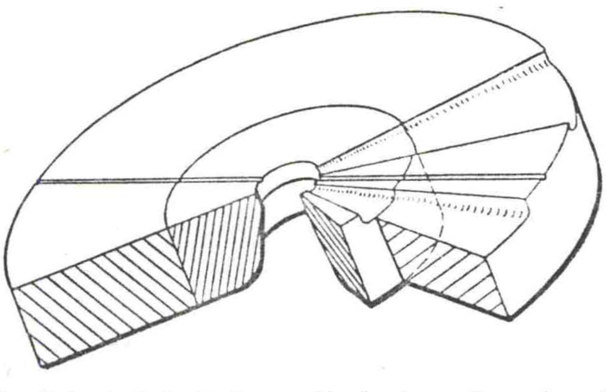

FIG. 3. One-half of split-die assembly showing mating surface with groove for entrance of x-ray beam and egress of undeviated beam and fan-shaped slots for egress of diffracted rays.

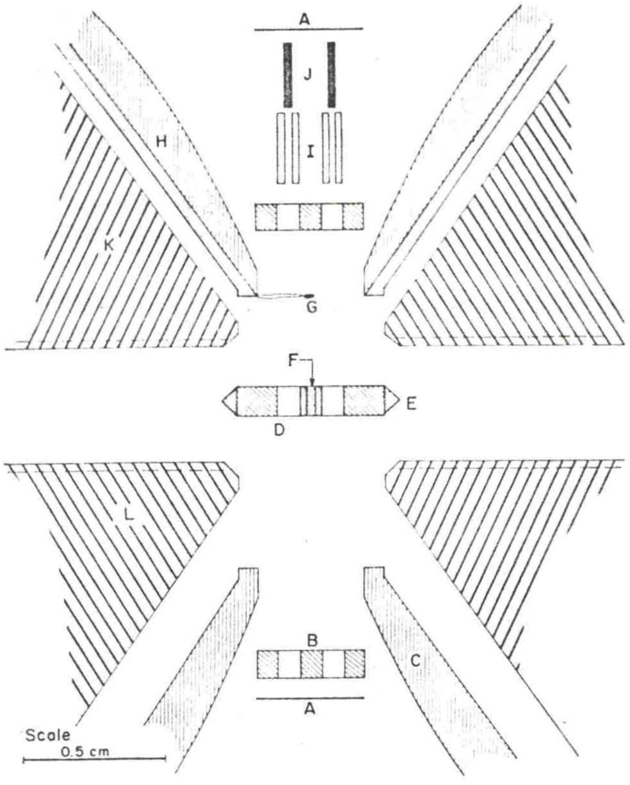

FIG. 4. Exploded view of internal components comprising the high-pressure volume of the apparatus. A—metal disk; B—baked pyrophyllite end pieces; C—pyrophyllite gasket; D—boron disk; E—Be ring pressure seal; F—sample; G—thermocouple junction; H—split pyrophyllite gasket; I—BN tubes; J—carbon heater rods; K—upper die half; L—lower die half.

Be ring fits in the taper and is supported by the die at all points except where the slots and fans have been removed. The ring and tapers on the die halves are shown in the cell assembly drawings (Figs. 4 and 5). At high internal pressures the ring is extruded slightly into the slot and fan regions but the ring seal has never failed by blowing out. The advantages of the Be ring seal are its low x-ray absorption coefficient (less than 10% loss) and high-temperature stability. Due to the slight flow of the ring, it is necessary to replace it after each run. Internal temperatures of 1000°C have been obtained with this method. Higher temperatures were not attempted since the steel die yields readily if the temperature of the die bore gets too high.

The medium surrounding the sample was a pressed amorphous boron pellet 0.51 cm diam by 0.1 cm thick. The sample is packed in a 0.03 cm hole drilled in the center of the pellet. Two carbon rods (0.038 cm diam) are placed in holes on either side of the sample hole and current is passed through the rods from piston to piston. To protect the carbon rods from the boron, they are sheathed with boron nitride tubes. A thermocouple junction of Chromel-Alumel or Pt/Pt-10% Rh is placed directly over the sample hole in the boron pellet. The temperature is therefore determined at a point less than 0.05 cm from the center of the compressed sample and less than 0.025 cm above the x-ray beam. The thermocouple is separated from the piston face by 0.075 cm of pyrophyllite.

PRESSURE MEASUREMENTS

Sample pressures are determined by calculating the change in the lattice parameter of NaCl which is intimately mixed with the sample under study. The equation of state of NaCl given by Decker[10–11] provides pressure calibration over the pressure–temperature range of 0–500 kilobars at 0–2000°C. An internal calibrant of this type is essential for accurate pressure–temperature studies. Decker's equation of state has been compared with other equations of state of NaCl by McWhan.[12] A problem involving recrystallization and grain growth of NaCl exists above 400°C. This results in spotty x-ray patterns that are difficult to read accurately. The problem can be minimized by diluting the NaCl with boron to separate the crystallites from each other.

X-RAY TECHNIQUES

The alignment of the x-ray beam through the die is accomplished by adjusting the press–die position relative to the fixed x-ray beam direction. Figure 1 shows the die in the press and the x-ray source facing the press. The entrance groove (0.05 cm diam circular cross section) is 5 cm long and provides the collimation. The press sits on an adjustable table which levels the press, moves it laterally, and rotates it about the x-ray entrance hole at the front of the die. The x-ray beam is observed by a phosphor painted on the die around the entrance hole. The

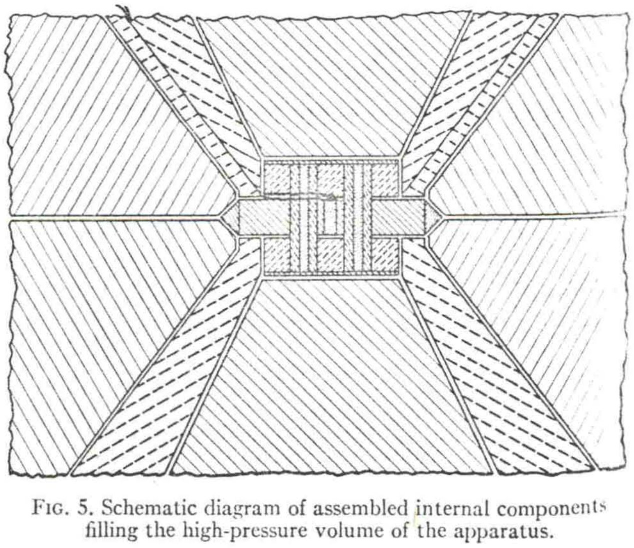

FIG. 5. Schematic diagram of assembled internal components filling the high-pressure volume of the apparatus.

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emerging undeviated beam is detected at the exit slit with a Geiger–Müller counter when alignment has been attained. Press movement relative to the x-ray source does not affect the alignment of the sample relative to the x ray beam since the dies, of which the sample is a part, do the collimating.

Powder diffraction patterns are recorded using standard x ray film and a Debye–Scherrer geometry. The film cassette consists of two coaxial semicircular cylinders between which the film is sandwiched with a rubber gasket. The inner cylinder has a 0.6 cm high slit around the circumference to allow x rays to reach the film. Aluminum foil is placed between the film and slit to provide a light seal. The film cassette is clamped to the o.d. of the die, as shown in Fig. 6. This locates the film on a precise 57.3±0.03 mm radius as measured from the die center. At full load, the o.d. of the die expands less than 0.02 mm making the o.d. a stable reference distance for the film position. The film cassette can be removed from the press after each exposure without disturbing the sample alignment because it is the sample position relative to the die which determines the alignment.

For lattice parameter measurements, the precision of the split-die device is comparable to that of Bridgman anvil x ray and tetrahedral x-ray devices (±0.2 to 0.4% depending on sample). Possible errors arise from film to die-center distance, sample positioning, and sample shifting. The film to die center is known to an accuracy of ±0.003 cm and the film is coaxial with the die center to that accuracy. In addition, the fan edges make sharp images on the film as is shown in Fig. 7. The angles of the fan edges relative to the x-ray beam are measured after they are ground to an accuracy of ±0.01° and thus can provide a precise determination of the center of the diffraction pattern and film shrinkage.

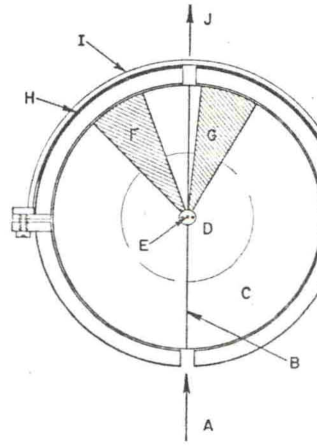

FIG. 6. Top view of mating surface of one-half of the split die. A—x-ray beam; B—beam entrance groove; C—die support ring; D—die; E—sample; F—20 to 45° diffraction slot; G—5 to 30° diffraction slot; H—x-ray film; I—film cassette; J—x-ray beam egress.

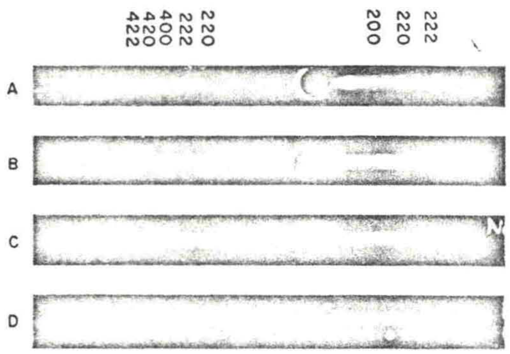

FIG. 7. X-ray powder diffraction patterns of NaCl under high pressure and temperature. A—14 kilobars, 25°C; B—53 kilobars, 25°C; C—70 kilobars, 600°C; D—60 kilobars, 800°C. Note the spotty patterns at high temperatures due to large grain size.

"Postmortem" microscopic examination of sample position indicates that shifts from center are less than 0.01 cm. The diffraction lines have a width which is proportional to the sample diameter inasmuch as the beam diameter is larger than the sample. Therefore, for precision measurements, the sample diameter is made as small as possible (less than 0.03 cm). Typical patterns of NaCl are illustrated in Fig. 7. Six lines are visible (200, 220, 222, 400, 420, 422) with the 220 and 222 lines appearing in both the 5–30 and 20–45° slots. The exposures were for 5–15 h using a Jarrell–Ash microfocus x-ray unit with Mo target (3 mA at 50 kV).

ADAPTATION FOR OTHER POSSIBLE USES

The split-die design might also be adapted for other kinds of studies. The apparatus is suited for high-pressure Mössbauer experimentation. The solid angle to the high-pressure region is large enough so that experiments with the absorber under high pressure are feasible. The high-temperature capability also makes the device unique for high pressure Mössbauer studies.

For high-pressure high-temperature optical studies, various windows could be cemented into the fan regions as was the epoxy for the x-ray application. Since the plain epoxy seal proves an effective pressure seal, a hard window material should be even more effective.