PROBLEM OF A METHOD OF X-RAY ANALYSIS FOR SUBSTANCES UNDER HIGH PRESSURE

II. APPARATUS FOR THE PRODUCTION OF POWDER PATTERNS UNDER PRESSURES UP TO 18,000 kg/cm² *

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The design of a new apparatus is discussed for the X-ray analysis of polycrystalline substances under high pressures

The majority of effects which take place under h pressures are reversible. X-ray diffraction terns of crystalline solids under direct pressure of considerable interest in finding out what urs in solids under compression. Such investitions provide direct information regarding the nges in crystal lattice parameters, the nature of se transformations etc. etc. It also helps to rify our ideas regarding the mechanism of the pressibility of solids and other mechanisms conted with the behaviour of a crystal lattice under ssure. However, despite the considerable scienc value of X-ray studies at high pressures only inute number of works have been carried out in s field, due to experimental difficulties.

Papers [1-7] describe a number of designs for h pressure equipment for X-ray analysis, but not e of them pretends to provide a complete solution the problem of obtaining X-ray diffraction patns from any crystalline substance in a sufficiently le range of pressures.

In the X-ray apparatus which we will here desbe a beryllium high pressure vessel of original ape was used, and it was designed so that it ld be rigidly fixed. There is also a special stem of adjustment and a system for checking the ray chamber [8] in the apparatus. The aperture the beryllium chamber can be adjusted to different sizes depending on the optimum depth of the st specimens. The design provides for rotation of the specimen under pressure. The apparatus is comparatively simple in construction and it permits assessment of the pressure level inside the chamber in a comparatively narrow range of pressures; it is transportable and the film can be recharged without relieving the pressure.

General description of the apparatus. The general appearance and details of the apparatus are shown in Figs. 1, 2 and 3. It consists of steel plates, *1*, *4* and *16*, joined together by three columns, *2*. Between plates, *4* and *16* there are supports, *9* and *14*, which are made of steel 45KhNMFA. Between these columns in its turn is the high pressure chamber, *24*, which is usually made of beryllium (the space between the supports in our experiments was 1.5-2 mm). The components between plates, *4* and *16*, are attached to one another by means of the upper screws of column, *2*. The magazine, *10*, with X-ray film, *13*, is attached to the conical surface of the lower support, *9*, together with ring, *20*, which holds the film against the casing of the cassette and is also used for disposing the filters. The magazine is tapered to 6°. There are hollows with a taper of 30° in the supports for the beryllium chamber. Figs. 1 and 2 show the arrangement of the collimator with diaphragm, trap, bushings with fluorescent screen and protective lead glass, which are usual for Debye cameras.

Dynamometer, *3*, with watch-type indicator and graduations of 0.002 mm is placed between plates, *1* and *4*. It is used to measure the force transmitted to the specimen through the system of upper and lower pistons and the medium between

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them. The medium which transmits the pressure (lithium), *19*, fills part of the channels of supports, *9*, and, *14*, and the inside space of the beryllium chamber, *24*. It is compressed by the pistons in the upper and lower supports by means of screw, *17*, and also the lower screws in column, *2*. In this way

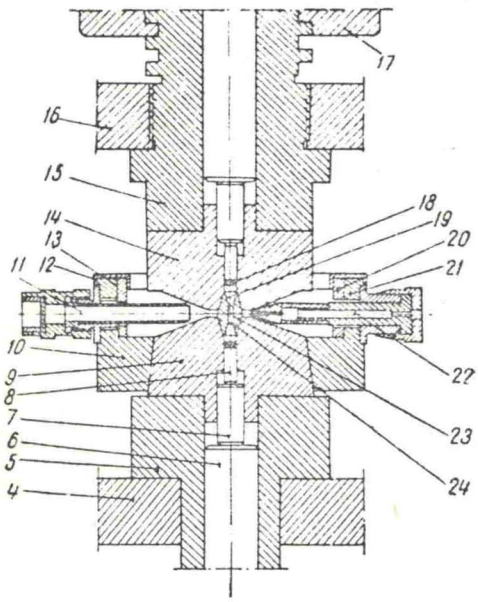

FIG. 1. Diagram of high pressure X-ray chamber.

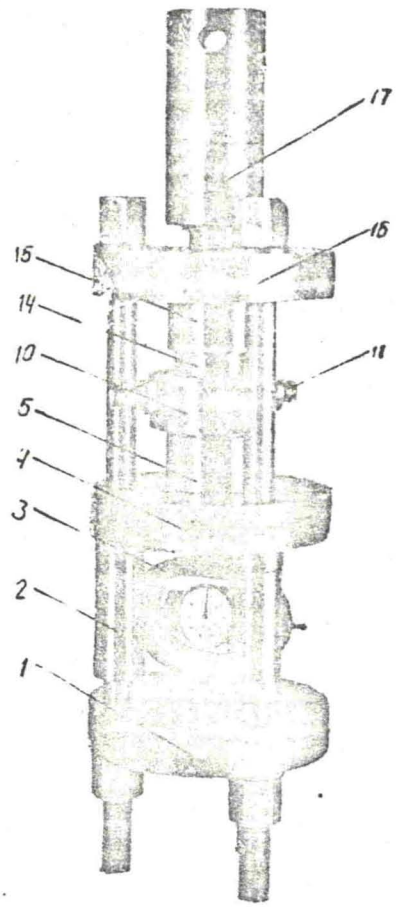

FIG. 2. General view of a high pressure apparatus.

the pressure created in the channels of the upper and lower supports is transmitted to beryllium chamber, *24*, and specimen, *23*.

The creation of pressure does not require very considerable force. In our experiments a pressure of up to 10,000 kg/cm² was easily created in the apparatus, which was on the supporting table of the X-ray tube. The position of the specimen inside the beryllium chamber was checked by means of the fluorescent screen. The maximum pressure created in the apparatus was 18,000 kg/cm². Piston, *8*, and the piston in the upper chamber corresponding to it were made of steel R18 with subsequent quenching to Rockwell hardness of 62. Paraffin wax, *18*, was used for packing, in the form of 2-3 mm high cylinders.

High pressure vessel. The experiments showed that the degree of purity, grain size, previous deformation and nature of the heat treatment of beryllium all affect the level of the working pressure in the apparatus, the quality of diffraction patterns obtained and the life of the high pressure vessel, i.e. the beryllium chamber. Home-produced beryllium was used for the high pressure vessel.

We observed the following order in manufacturing the beryllium chamber. First of all the chamber was made in the shape indicated in Figs. 1 and 3, height 12 mm, internal diameter 1 mm, external diameter 7 mm, internal taper 30°. The optimum taper figure was found experimentally as a result of a series of experiments with chambers of different geometrical dimensions. Then the inner and outer tapers were carefully ground, and the cylindrical inside of the chamber. After this it was filled with lithium, placed in the apparatus and a pressure of 10-12,000 kg/cm² was created. The pressure was raised and lowered 2-3 times. Then the surface finish of the chamber was further improved and it was given a heat treatment to produce a coarse crystalline structure in the beryllium. It was placed in zirconium crucibles in a quartz tube in which a vacuum of 2×10^{-5} mm

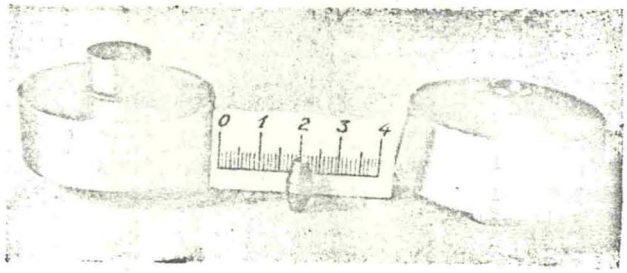

FIG. 3. Upper and lower supports and beryllium chamber.

was created. It was held at a temperature of 1050°C for 3 hr and cooled smoothly down to room temperature in the course of 16 hr.

An X-ray diffraction pattern of the beryllium chamber after it had been aged under pressure is shown in Fig. 4 (upper picture). The pattern taken after heat treatment is shown in the same figure. A chamber produced in this way was repeatedly used at pressures up to 12,000 kg/cm², with only trivial deformation. The beryllium grain remained virtually unaltered up to pressure of 6-7,000 kg/cm².

Pressure calibration of the apparatus. The following measures were adopted to reduce friction in the apparatus. The inner surface of the beryllium chamber and the channels of the supports were very well surface-finished. Pistons, *7* and *8*, of the lower support and the corresponding pistons of the upper one had a clearance of 0.06-0.09 mm in the channels. Paraffin wax was used as the packing material. The packings here and in the tapers of the supports (beryllium-support) worked very well during tests up to 18,000 kg/cm².

As can be seen from Fig. 1, as regards the system of transmitting force to the centre of the chamber, the apparatus is symmetrical around a plane perpendicular to the drawing and passing through the centre of the beryllium chamber and the collimator. It therefore made no difference to which piston, *6*, or the corresponding upper one, the force which was used to create the pressure in the apparatus was applied. This was checked experimentally and it was found that the pressure difference at the top and bottom of the beryllium chamber was the same with any force applied to piston *6* or the corresponding upper one.

The apparatus was calibrated in the usual kind of machine with compression and tension using a reference dynamometer type DS-3. From the forces determined on reference dynamometer DS-3, which was at the top of the apparatus, and dynamometer, *3*, the pressure round the top and bottom of the beryllium chamber was calculated. To calculate the pressure the areas had to be calculated from precise measurements of the diameters of the corresponding openings in the supports. The pressure in the centre of the beryllium chamber was determined as half the sum of these pressures. Graduation was carried out separately for each chamber and for each substance tested.

The accuracy of the pressure measurement in the apparatus was determined from a considerable number of experimentsin calibration, and it was found to be 2 per cent of the measured pressure value (up to 10,000 kg/cm²). Pressure changes of 0.06 mm³ could be observed on the indicator of dynamometer *3* as the pressure rose.

X-ray diffraction camera. The X-ray diffraction camera was very carefully adjusted both in the course of manufacture and in assembly. The following requirements had to be very carefully satisfied.

a) The interior surface of magazine, *10*, should have the exact shape of a cylinder and the taper of the cassette should precisely correspond with that of support, *9*. The axes of the cylindical surface and the taper of the magazine must coincide with the axis of both supports and the beryllium chamber, *24*, (maximum permissible deviation is 0.015 mm).

b) The collimator axis must form an angle of 90° to the axis of the cylindrical surface of the magazine and it must be in the centre of the split in ring, *20*.

An ordinary microscope with magnification 25 was used to adjust the X-ray camera and to check its accuracy. Its focal length was 50 mm and the eyepiece was fitted with a micrometer (graduations of 0.05 mm). Adjustment was made by means of a

quartz hair 0.04 mm thick and a wire of metallic aluminium 0.23 mm in diameter. Besides the microscope adjustement of the camera, X-ray photographs were also made of the aluminium wire. After the relevant parameters had been measured on the X-ray patterns the necessary corrections were made to the adjustment of the camera or components were replaced as required.

A further check was made on the camera by making X-ray patterns of the same wire, but made of aluminium whose lattice constant was known exactly. The lattice parameter of the aluminium was calculated from the X-ray pattern line with indices (333) for CuK_{α_1} and CuK_{α_2} radiation. The photography was carried out by the asymmetric method.

To find the effective radius of the camera diffraction patterns were taken with the specimen fixed but with the sections of the film moved first to the left and then to the right of the beam. The following was obtained for the aluminium lattice parameter at 25°C: $a = 4.04143 \pm 0.00003$ kX (this is in very good agreement with Iyevin'sh and Ozol's data [9], 4.04145 ± 0.00002 kX).

In the diaphragm of the collimator there was a cylindrical aperture 0.3 mm in diameter. The diameter of the magazine was 68.4 mm. As the magazine, *10*, is based on the taper of the lower support, expansion of the support under pressure had to be checked. It was found that the diameter expanded by not more than 0.005 mm at a pressure of 11,000 kg/cm² and for this reason, in operation the magazine was fixed to the support after the desired pressure had been reached.

X-ray diffraction patterns obtained with and without rotation* of the test specimens under pressure are completely satisfactory. The results of experiments carried out on this apparatus are given in the next article.

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* In our apparatus the specimen was rotated under pressure by rotating the axis of the apparatus through a small angle every few moments in time. In this way the position of the magazine in respect of the beam was kept unchanged.

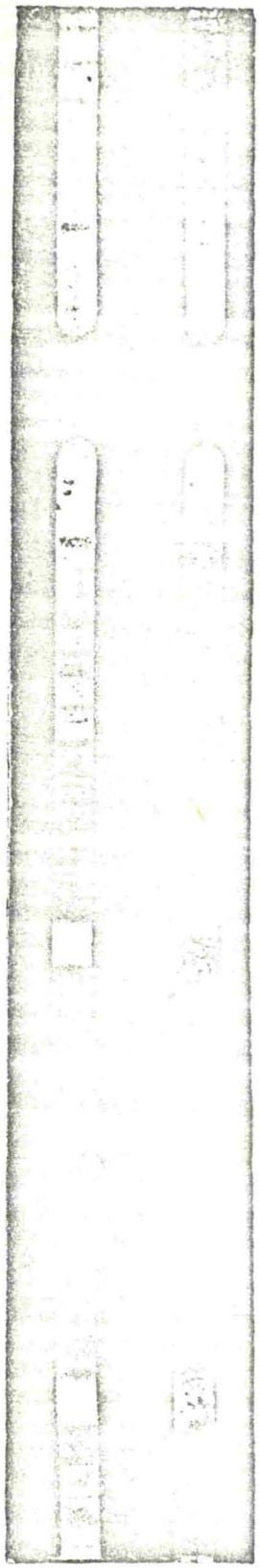

FIG. 4. X-ray pattern of beryllium chamber.

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2. A.W. Lawson a 20, 763 (1949).
3. A.W. Lawson a 21, 815 (1950).
4. L.F. Vereshcha *Dokl. Akad. Na*
5. L.F. Vereshcha V.V. Yevdokim 3, 90 (1958).
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