DETERMINATION OF INTERATOMIC DISTANCES OF SOLIDS UNDER PRESSURE

I. Compressibility of Barium and Strontium

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We have developed a simple method of determining compressibility by x-ray diffraction patterns obtained at pressures up to 15,000 kg/cm^2. The error in the determined values of the compressibility of strontium and barium did not exceed 3%.

The determined values were compared with those obtained by Bridgman [1], who used linear compressibility.

It is well known that some properties of metals depend greatly on the interatomic distances. This dependence is found, for example, in the case of electrical, galvanomagnetic, and magnetic properties (displacement of the Curie and Neil points under the effect of pressure [2,3]). Consequently, knowledge of the correct values of interatomic distances and their variation with pressure are of utmost importance for the understanding of processes occurring in metals. In the majority of cases, the variation of interatomic distances under the effect of pressure is determined by measurements of compressibility under pressure.

Measurements of volume compressibility under high hydrostatic pressure are usually made either by the "movable piston" method or by determining the linear compressibility, from which volume compressibility is calculated.

In both cases, it is necessary to make numerous corrections of the results by accounting for the deformation of the compression chamber, pistons, and compression gaskets, and the compressibility of the pressure-transferring medium and other parts of the apparatus.

If the relative change of the length of the sample is measured with an instrument with a sliding contact, it is necessary to make corrections for the variation of the electrical resistance of the standard wire with pressure, for the unevenness of its cross section along its length, etc.

The conversion factor by which the measured linear compressibility is transformed into volume compressibility must be corrected; this factor cannot be equal exactly to 3, even in the case of substances with cubical symmetry, because the compressibility may be different in different directions due to the presence of a binding substance between the crystals of the sample.

The compressibility of the intercrystalline substances and of the microspaces between the crystals of the sample cannot be determined by this method; they become part of the total compressibility of the substance. Therefore, it seems of interest to compare the data obtained by this method with those obtained by the x-ray diffraction method.

The x-ray diffraction method of determining the relative change of the volume by the change of the lattice parameters of the substance is free of these defects.
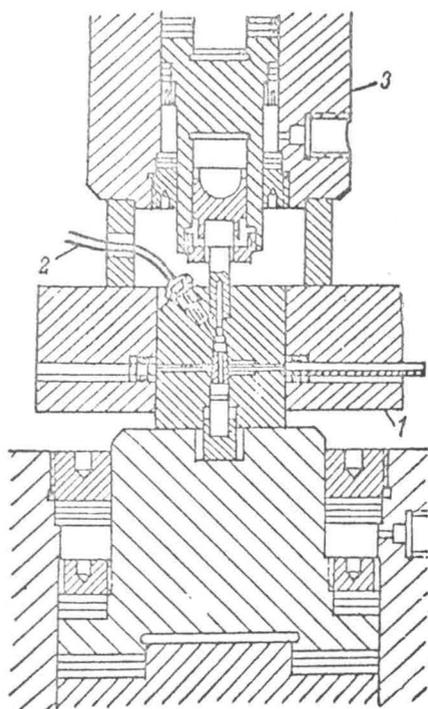
Fig. 1. High-pressure chamber for x-ray diffraction (1); with a manganin manometer (2); in the multiplier (3).

Cohn [4] was the first to propose the application of x-ray diffraction to the investigation of substances under pressure, in 1933. In 1939, Jacobs [5] determined the compressibility of two metals by this method. His apparatus made it possible to obtain a rather complete diffraction pattern of the metal, but the pressure range was narrow (up to 4500 kg/cm^2), the apparatus was cumbersome, and its operation was complicated [6].

Lawson and Riley [7], working with beryllium containers, succeeded in increasing the hydrostatic pressure up to 10,000 kg per cm^2. Unfortunately, in this case the quality of the x-ray diffraction patterns deteriorated due to the presence of a strong background and of wide dark beryllium bands. Lawson et al. [7, 8] later increased the pressure limit even more by using diamond chambers. However, in this case the pressure in the sample, essentially nonhydrostatic, had to be calculated by taking friction into account. The fact that the pressure is not well defined, and is not hydrostatic, renders this method unsuitable for determining the effect of pressure on compressibility, although it is quite convenient for the investigation of polymorphic transformations.

We investigated two metals: strontium and barium. We chose these metals because they are highly compressible and, consequently, considerable displacement of diffraction lines under the effect of pressure could be expected. Furthermore, these metals give sufficiently clear diffraction patterns when photographed in beryllium pressure chambers.
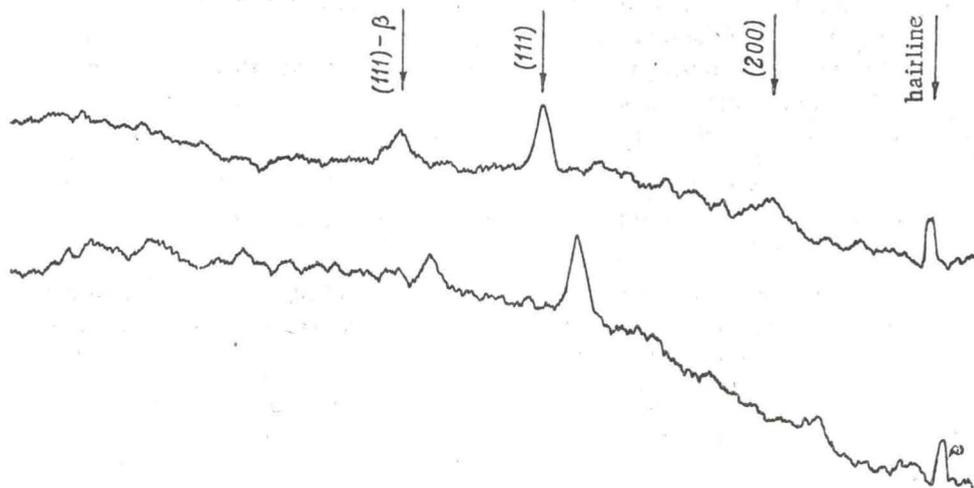

Fig. 2. Photogram of two strontium patterns obtained without pressure (upper curve), and under a pressure of 11,400 kg/cm^2 (lower curve).

Compression chambers of special construction were used for determining the compressibility of each of these metals by x-ray diffraction.

In the case of strontium, we used a compression chamber described earlier [9]. The chamber and its support are represented in Fig. 1; in this apparatus, benzine was used as the pressure-transference medium and the pressure was measured with a manganin manometer. The sample was placed in a conical beryllium container which was pressed into a steel chamber with a slit for the passage of diffracted rays. The cone-shaped chamber was, in turn, pressed into a massive steel support. The casette with the film was introduced in a special slot in the support.
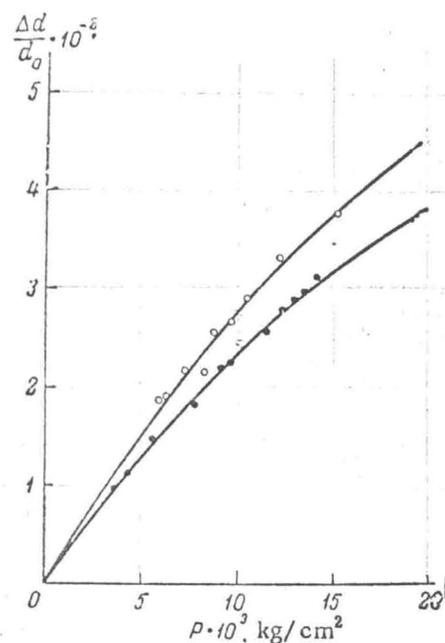
$$\frac{\Delta d}{d_0} \cdot 10^{-3}$$

$P \cdot 10^3$, kg/cm^2

Fig. 3. Variation of the relative change of interplanar distance with pressure for strontium (lower curve) and barium (upper curve).

This arrangement allowed us to get two photographs on one film — before and after the application of pressure.

The pressure was transmitted by benzine and measured by the change of resistance of the manganin manometer.

We investigated metallic strontium of relatively low purity; it contained 3% FeO, 2% CrO, and 0.003% Cu. The samples were thin wires drawn in baths filled with water-free vacuum oil. The bath was fixed in a special box filled with pure argon. The sample was introduced into the beryllium container while in the argon box. As a result of these precautions, the diffraction patterns were free from strontium oxide and hydroxide lines.

The x rays used were obtained with a copper anticathode; the exposure was 15-20 hours.

Our apparatus is not free of defects. The main defect has been pointed out by many investigators using beryllium pressure chambers. It consists in the fact that one can see on the photograph only a limited number of lines belonging to the sample (essentially obtained with a small angle θ) on the background of dark bands corresponding to the beryllium container. We obtained only three face lines corresponding to the strontium sample: the (111) line, the same line from β-radiation, and the (200) line.

Figure 2 represents the photogram of one of the patterns. The upper curve corresponds to atmospheric pressure, the lower to a pressure P = 11,400 kg/cm^2. Three peaks corresponding to the diffraction line on the x-ray photograph can be seen on both curves. Two peaks are displaced relative to each other. The last, undisplaced peak — a hair line — was made mechanically for reference.

We performed about 50 experiments with strontium at different pressures up to 15,000 kg/cm^2. The pressure was measured with the manganin manometer, which was graduated by comparison with a free-piston manometer.

The pressure was determined with a precision of 100 kg/cm^2. In a number of experiments, the pressure in the chamber dropped 1000-2000 kg/cm^2 during the exposure. This leads to an uncertainty in the corresponding values of compressibility, and, consequently, to the necessity for corrections.

Absolute measurements of lattice parameters by the face lines is imprecise. However, we were interested only in relative measurements of the lattice parameters; these were made by measuring the displacement of the lines corresponding to the sample before and after the application of pressure.

The fact that, in our apparatus, both x-ray photographs are obtained on the same film allowed us to eliminate the corrections due to absorption by the sample and curling of the film during processing.

Figure 3 represents the variation of the relative change of the interplanar distance as a function of pressure for strontium and barium. The experimental points were obtained by averaging the values for all indices, which is quite legitimate in the case of cubic crystals.

The barium metal investigated contained the following impurities: 0.01% Fe, 0.0023% Zn, 0.004% Cr, 0.004% Pb, 0.0001% Cu, and 0.00018% Cd.

The samples were obtained by the same method used for strontium. For barium we used a chamber designed by one of the authors (Fig. 4). In this case, the beryllium container plays the role of a cone-shaped piston in the pressure chamber. As the result of forward motion, the beryllium piston fits tightly into the channel of the chamber due to the developed force of friction. The dimensions of the pressure chamber were decreased to a minimum, which allowed the creation of pressure with a screw piston hand pump. When the pressure was established, the press with the chamber was fixed on the bench of a standard x-ray apparatus of the URS-70 type (Fig. 5). The
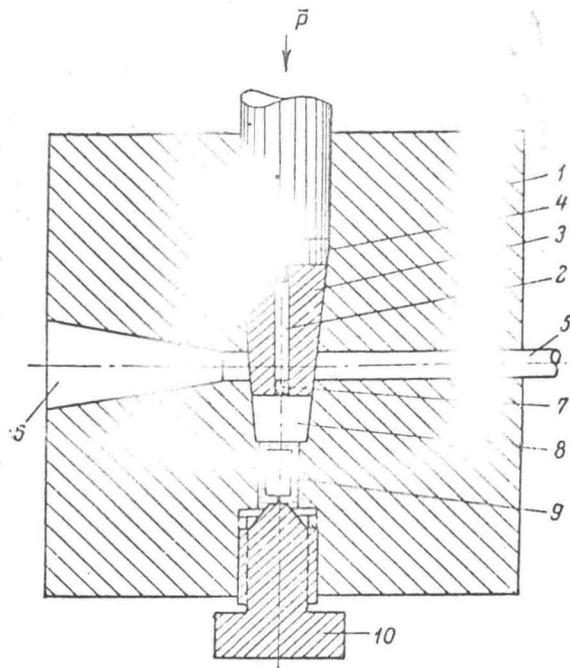
Fig. 4. High-pressure chamber for x-ray diffraction in which the beryllium container (3) plays the role of the conical piston. The sample (2) is placed in the channel made in the beryllium container; the upper part of the channel is closed by the conical compressor (4); the lower part of the channel is closed with a lithium stopper (7). The x-rays pass through the diaphragm (5), and through the sample. The diffracted rays pass through the slit (6). The empty part of the chamber is filled with benzine (8); the pressure is determined by the change of the electrical resistance of the manganin manometer (9), fixed on the electrode (10).

cylindrical casette of special construction, which was 114 mm in diameter, allowed us to obtain 4 photographs on the same film. In the case of barium, we used x-rays obtained with a molybdenum anticathode. The exposure time was 7-8 hours. Up to 9 lines were visible on the x-ray diffraction pattern of the sample in the beryllium container. The photogram of one of the films is represented in Fig. 6. The lower curve is relative to the sample under a pressure of 10,000 kg/cm². One can clearly see the displacement of this curve with respect to the upper curve, which corresponds to the sample not subjected to pressure. The extreme left, undisplaced peak corresponds to the hair line made for reference.

Knowing the relative change of the interplanar distance with pressure, one can deduce the relative change of volume with pressure. In the range of pressures investigated, this relationship can be expressed by the following equation:

$$-\frac{\Delta V}{V_0} = aP + bP^2.$$

By the method of least squares we obtained the following values of the constants for strontium:

$$a = 81.0 \cdot 10^{-7} \pm 1.4; \quad b = -101.1 \cdot 10^{-12} \pm 3.4.$$

Calculations on the basis of the face lines when the diameter of the compression chamber is relatively small (80 mm) leads to considerable errors; however, by smoothing the curves, one can obtain for $\Delta V/V_0 = f(P)$ much more precise values.
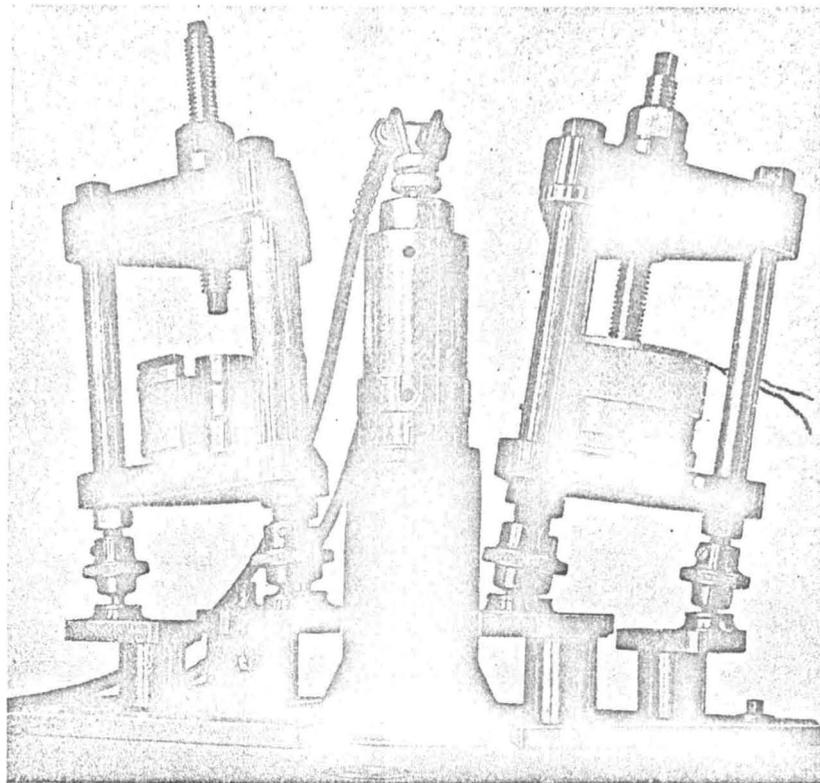
Fig. 5. Two hand presses together with the high-pressure chambers for x-raying, and with the casettes fixed on the bench of the URS-70 x-ray apparatus.
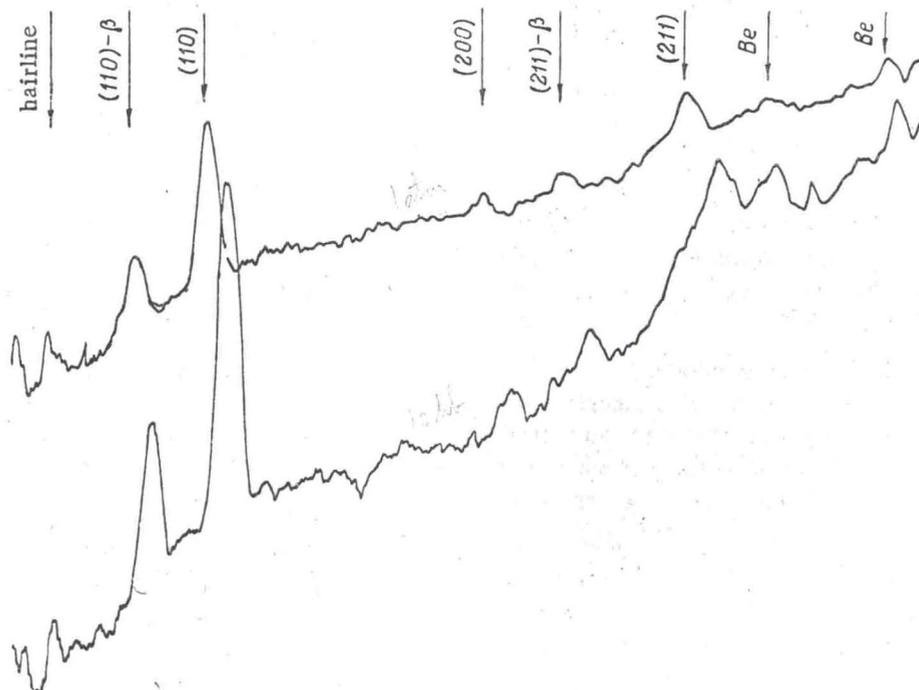

Fig. 6. Photogram of the x-ray diffraction patterns corresponding, respectively, to barium under a pressure of 10,000 kg/cm^2 (lower curve) and barium not subjected to pressure.
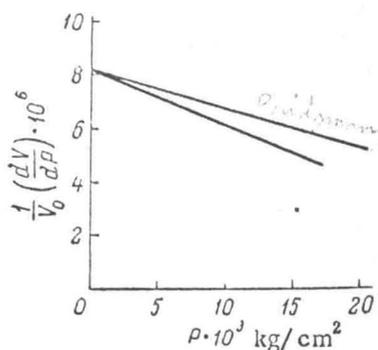
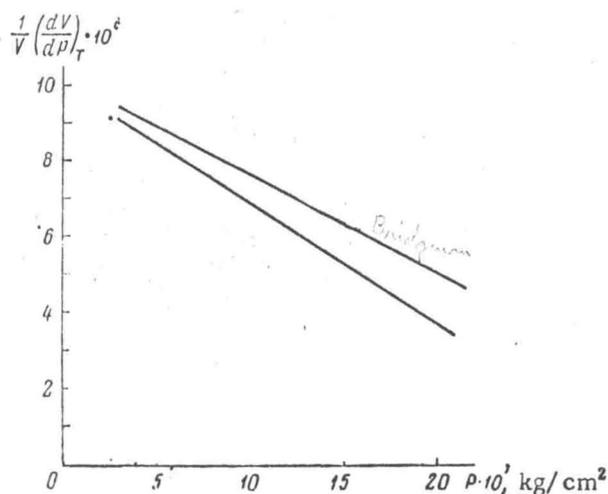Fig. 7. Compressibility of strontium as a function of pressure. The upper curve was obtained by Bridgman.

Fig. 8. Compressibility of barium as a function of pressure. The upper curve was obtained by Bridgman.

For strontium, Bridgman gives the following value:

$$-\frac{\Delta V}{V_0} = 81.84 \cdot 10^{-7} P - 70.92 \cdot 10^{-12} P^2.$$

For barium we found, by the x-ray diffraction method, the following values:

$$a = 100 \cdot 10^{-7} \pm 4.4; \quad b = -155.5 \cdot 10^{-12} \pm 9.0.$$

By the method of linear compressibility, one finds for barium the following expression:

$$-\frac{\Delta V}{V_0} = 101.87 \cdot 10^{-7} P - 127.42 \cdot 10^{-12} P^2.$$

The compressibility can be expressed by the following relationship:

$$\frac{1}{V_0}\frac{dV}{dP} = a + 2b.$$

The large difference in the values of the constant b in the two cases leads to a considerable divergence of the compressibility curves drawn on the basis of data obtained by us and by Bridgman, as shown in Figs. 7 and 8. The difference in the values of compressibility obtained by the two different methods exceeds the experimental error, which is about 3%.

Jacobs [5] has previously obtained an analogous result for copper and aluminum. The difference in the values of compressibility exceeding the experimental error is explained by Jacobs as follows: when the "movable piston" or linear-compressibility method is used, an unavoidable error is introduced in the results due to the fact that the microspaces and the intercrystalline substance are not taken into account; this error is not eliminated even when the sample is compressed previous to the experiment.

The pressure at which this fact ceases to affect the compressibility is not known, and it would be logical to assume that the higher the compressibility, the smaller this pressure will be. For barium, however, which is one of the most compressible metals, the effect of microspaces is still noticeable at a pressure of 15,000 kg/cm². On the other hand, the increase of the divergence of the curves in Figs. 7 and 8 with pressure can be explained by the fact that the corrections introduced in the results in the case of the method of linear compressibility, which are usually either calculated with the formulas of the theory of elasticity, or determined experimentally, are insufficient to some degree in this case.

It must be noted that the experiments for the determination of compressibility by the x-ray diffraction method are relatively simple, and do not require complicated equipment.

The use of an ion diffractometer will make it possible to obtain more precise results with a much shorter exposure.

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