50-kilobar gasketed diamond anvil cell for single-crystal x-ray diffractometer use with the crystal structure of Sb up to 26 kilobars as a test problem[*]

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A single-crystal gasketed diamond anvil cell of a new design for use on a diffractometer is described. It has achieved hydrostatic pressures of 50 kilobars as determined from the ruby fluorescence shift. The design combines several advantages. Nearly half the area of the Ewald sphere is available without having to remount the crystal. For reflecting planes nearly parallel to the diamond anvil faces, all reflections in the angular range $\sim4^\circ \leq \theta \leq 85^\circ$ can be observed. Alignment of the diamonds, as well as loading and alignment of the sample crystals, is very simple and quick. The diffractometer geometry allows accurate measurements of weak reflections as well as accurate determinations of the x-ray absorption corrections for the cell. The materials of construction are nontoxic except for one diamond mount, a small beryllium cylinder situated so that it is never touched, scraped, or rubbed. As a test problem, the z parameter of antimony has been found to increase linearly from $z=0.23357$ at 1 bar to $z=0.2380\pm0.0005$ at 26 kilobars.

I. INTRODUCTION

This paper describes a single-crystal gasketed diamond anvil cell of a new design for use on a diffractometer. An excellent review of the relative advantages of diffractometer and film methods for high-pressure single-crystal x-ray structure determinations is contained in a recent article by Merrill and Bassett[1] and will not be repeated here. In that article the authors presented a very different diamond anvil cell design for diffractometer use. Other diamond anvil cells for use on precession cameras have been presented by Weir, Piermarini, and Block,[2] and by Fourme.[3]

The motivation for the present design was a desire to study the variation of the A-7 structures of As, Sb, and Bi with pressure. The space group is $R\bar{3}m$. There are three quantities to be determined: the lattice parameters a and c (hexagonal axes), and the atom position parameter z. Accurate determinations of a and c are not difficult, because only measurements of the Bragg angle θ are required. Determinations of z are quite difficult because accurate measurements of x-ray intensities are required. Absorption of x rays by the high-pressure cell can be on the order of 30–60% and is path dependent owing to the complicated shapes of the diamonds and other components of the cell. The set of $(00.l)$ reflections (hexagonal axes) up to the 21st or 24th order or higher provides a sensitive determination of z even if absorption corrections are fairly crude. When this cell was being designed, it was known that crystals could be prepared in the shape of small flakes whose faces are parallel to the (00.1) plane. Thus, the crystals naturally align themselves in the diamond anvil cell with their (00.1) planes parallel to the diamond faces. To make maximum use of the $(00.l)$ reflections, the x-ray path is through one of the diamonds in the geometry shown in Fig. 1. By designing supports for diamond (A) to minimize x-ray absorption, all $(00.l)$ reflections with a Bragg angle θ up to 85° can be observed. Diffractometer geometry also allows accurate determinations of the absorption corrections for the cell by comparing 1-bar intensities from the crystal in the cell with the known 1-bar intensities.

Orientation of the crystals about the [00.1] axis was expected to be difficult to control as the delicate samples were put in the cell. For this reason the framework holding the diamonds was made as open as possible.

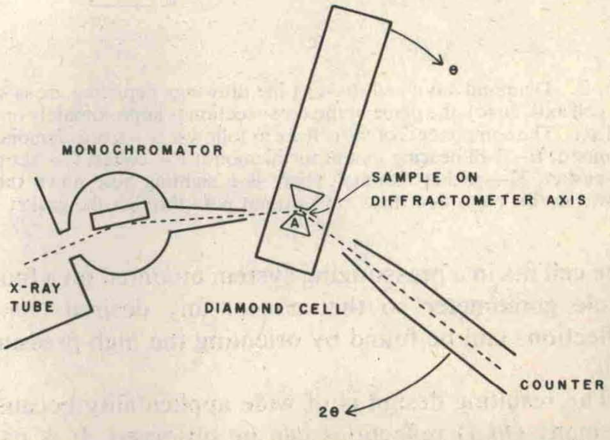
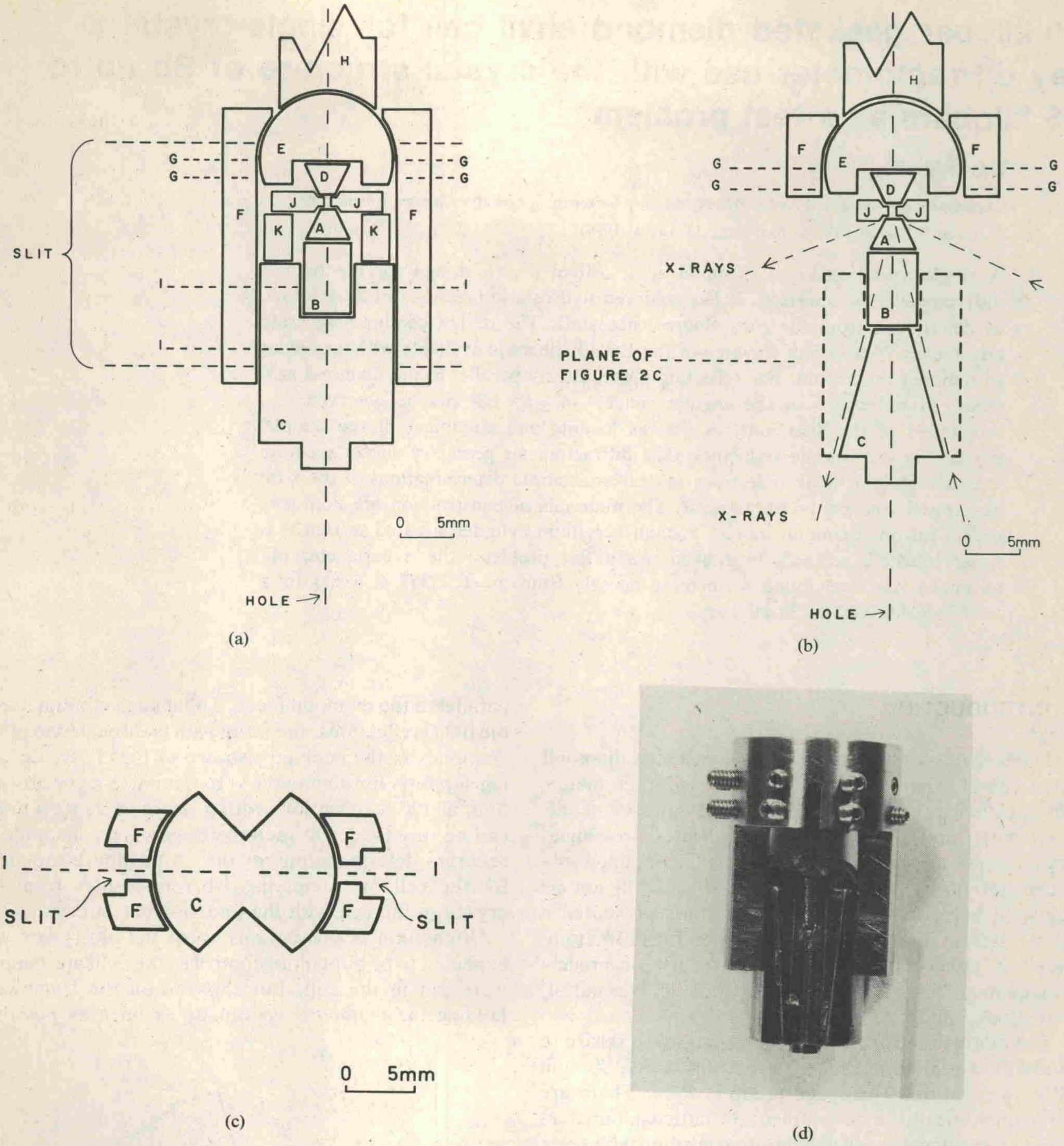


FIG. 1. Schematic diagram of the diffractometer geometry utilized in the design of the high-pressure cell. Monochromatized x rays are sent into the sample and diffracted back out through one diamond (A). The scattering plane is in the plane of the paper. Each component of the system is denoted by the same letter in all the figures.



(a)

(b)

(c)

(d)

FIG. 2. Diamond anvil cell. (a–c) Line drawings depicting cross-sectional views of the cell. In (a) and (b) the plane of the drawing is through the cell axis. In (c), the plane of the cross section is approximately one-third of the way up from the bottom of (a) and (b) and is perpendicular to the cell axis. The components of the cell are as follows: A—fixed diamond; B—beryllium cylinder; C—cutaway stainless steel cylinder; D—adjustable diamond; E—ball-bearing mount for diamond; F—collar; G—set screws; H—thrust rod, actually part of the external lever system; I—bolts; J—gasket; K—gasket mounts. There is a sighting hole down the axis of the cell. Possible x-ray paths in the plane of the paper are also shown in (b). Note that the x rays do not pass through the gasket. (d) A photograph of the assembled cell without the gasket.

The cell fits in a pressurizing system mounted on a four-circle goniometer so that almost any desired $(hk.l)$ reflections can be found by orienting the high-pressure cell.

The resulting design is of wide applicability because so many $(hk.l)$ reflections can be observed. It is particularly well suited to the study of structures in which only one of the atom position parameters x, y, or z varies. This cell is primarily useful for providing much more accurate crystallographic data once the lattice parameters and space group are at least approximately known.

II. DESIGN

Each component will be designated by the same letter in all the figures. The diamond anvil cell, excluding the lever system to apply force to the diamonds, is shown in Fig. 2. One diamond (A) is rigidly mounted on a beryllium cylinder (B), which in turn is set in a stainless steel cylinder (C). The cylinder (C) is cut away as much as possible to provide maximum access to the cell for the incident and diffracted x-ray beams. The other diamond (D) is mounted with its face near the center of a hollowed ball bearing (E).[4] The ball bearing can be rotated to align the diamonds, then held rigidly in place in the collar (F) by sixteen set screws (G). The ball bearing (E) fits in a spherically hollowed seat at the top of the collar (F) as shown in Figs. 2(a) and (b). Much of the collar is also cut away, and it slips tightly over the cylinder (C) when force is applied to the ball bearing (E) by the thrust rod (H), which is part of the external lever system. The collar (F) is kept from rotating about any axis with respect to the cylinder (C) by the bolts (I). These also prevent the lower portion of the collar (F), as shown in Fig. 2(a), from spreading when the force is applied.

The diamond anvils (A and D) were obtained from the Dubbledee Corp. and are affixed to their respective mounts (B and E) by Devcon R-205 5-min epoxy cement. This cement surrounds the diamonds, but it is not between them and their mounts. The diamonds are the same size, and their edges are aligned while the epoxy sets by observing their positions through a hole down the axis of the cell. The faces of the diamonds are aligned parallel by observing the interference fringes while tightening the set screws (G). As the set screws (G) are tightened, the ball bearing (E) rotates slightly. By tightening the set screws (G) in the proper succession, the diamonds (A and B) can be quickly aligned so that only the center maximum of the interference pattern is visible.

After the diamonds are aligned, the gasket (J) is glued with Duco cement to the gasket supports (K) such that the hole in the gasket is centered on the diamond faces. Sometimes the gasket is glued to the face of the diamond (A) as well with a very thin film of Zipbond cyanoacrylic contact cement. This procedure ensures that the sample will not slip under the gasket as the high-pressure fluid is added and seems useful in sealing the fluid at relatively low pressures (<5 kilobars). This cement is not necessary for sealing at higher pressures, and may even be detrimental because the thin film of cement seems the most likely place for the system to rupture.

Gaskets of several materials and thicknesses are used. In all cases, the hole in the gasket is spark-cut to have a diameter of 0.05 cm, which is about half the diameter of the diamond anvil face. The gaskets are highly polished to minimize the force required to seal the high pressure fluid. The gaskets ranged in thickness from 0.005 to 0.025 cm. Such thin gaskets can be used because the sample crystals are etched to thin flakes approximately 0.001 cm thick. Thin gaskets have the advantage of allowing observation of more low index (*hkl*) reflections. Gaskets 0.005 cm thick allow observation of reflections with θ as low as 4°. However, higher pressures can be achieved for a given force on the diamonds with thicker gaskets.

Pd gaskets 0.005 cm thick tend to rupture at about 20 kilobars. Monel gaskets 0.010 cm thick tend to rupture between 30 and 40 kilobars. Inconel 750X gaskets ranging in thickness between 0.010 and 0.025 cm do not usually rupture below 50 kilobars. The Inconel gaskets were annealed. The softness of the metal allowed higher pressures as force was first applied, while the work hardening as the gasket deformed apparently helped prevent rupture.

The lever system which applies force to the diamonds is shown in Fig. 3. The high-pressure cell of Fig. 2 is denoted by L here. The cell (L) fits into the yoke (M). The thrust rod (H), level arms (N), and push bar (Q) are connected to each other and to the yoke (M) by the pivot rods (P) as shown in Fig. 3. Pressure is applied by turning the ¼-20 bolt (S) to compress the spring (R). The force F on the thrust rod (H) is related to the force F_Q of spring (R) on the push bar (Q) by

$$|F| = |F_Q/2| \cot\psi .$$

In practice, the maximum force $F_Q(\max)$ on the push bar

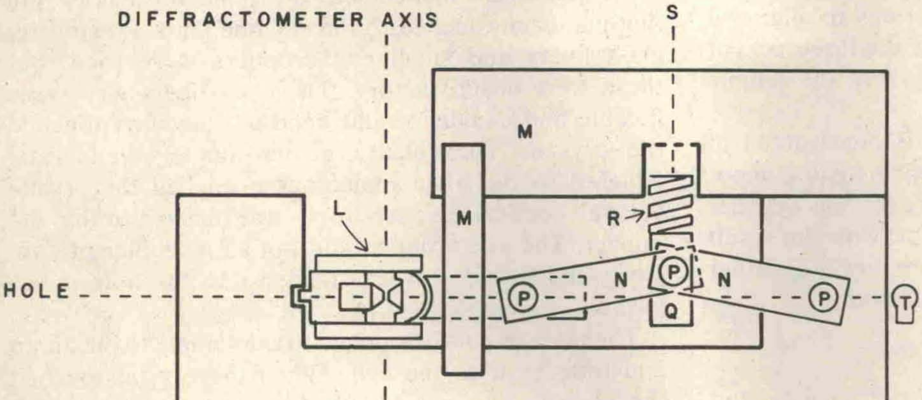


FIG. 3. Pressurizing lever system. The cell of Fig. 2 is denoted by L in this figure. Other components are H—thrust rod; M—yoke; N—lever arms; P—pivot rods; Q—push bar; R—spring; S—bolt; T—light bulb. When the bolt (S) is turned, the levers (N) transmit force to the cell via the thrust rod (H). The levers (N) are at an angle ψ with respect to the cell axis. When the bolt (S) is released, the thrust rod (H) retracts far enough to allow easy removal of the cell (L).

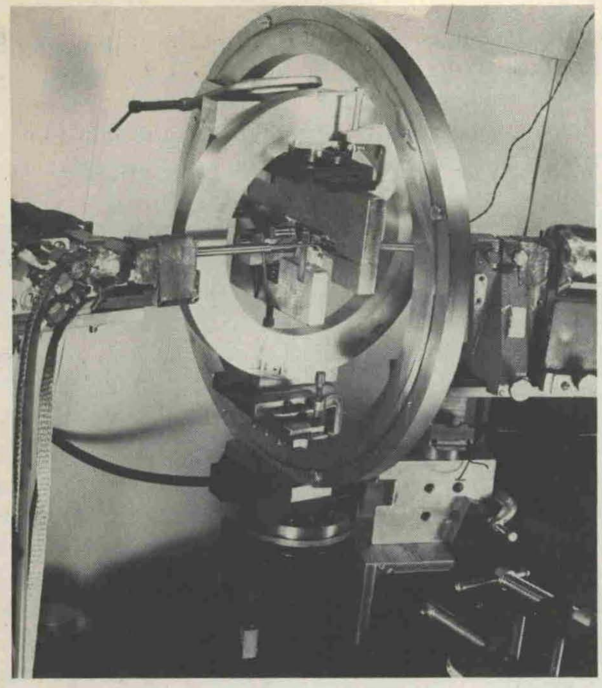


FIG. 4. High-pressure cell mounted on a four-circle goniometer. The system is based upon a spectrometer built by Compton (see Ref. 5). Part of this instrument can be seen in the lower portion of the photograph. Two circles are most prominent in the photograph. The smaller circle, the axis of which is along the cell axis, provides the ϕ orientation; the larger circle provides the χ orientation. The spectrometer axis provides the ω orientation for the crystal and the 2θ orientation for the counter. The x-ray tube, monochromator housing, and collimator can be seen on the left; the scintillation counter is on the right. The C-clamps ensure stability about certain key points. The cord goes to the light (T).

(Q) is on the order of 1000 N and $\psi \approx 10°$; thus $|F| \approx 10|F_Q/2| \approx 5000$ N. If the diamond faces are 1 mm square the maximum pressure attainable is of the order of 50 kilobars. All of the components of the lever system have holes or slits in them so that there is a light path from the light bulb (T), down the axis of the cell (L), and through the left end of the yoke, as indicated.

As shown in Fig. 4, the yoke (M) is mounted on a four-circle goniometer. The entire high-pressure apparatus can be translated in the x, y, and z directions to align the sample so that it is centered on each of the three axes of the goniometer ω, χ, and ϕ, which govern the sample orientation.

Most of the high-pressure system is constructed of Stainless Steel 304. The only potentially toxic component is the beryllium cylinder (B). However, this cylinder is not near moving parts of the system, with the result that it is never scraped or rubbed. Moreover, it is rather difficult to touch with the fingers accidentally.

III. PRESSURE DETERMINATION

The light path down the axis of the cell, as indicated in Figs. 2(a), 2(b), and 3, allows use of the ruby R-line fluorescence to determine the pressure in the cell.[6–8] The bulb (T) in Fig. 3 is replaced with a Coherent Radiation model CR-3 1 W argon-ion laser, which excites the ruby R-line fluorescence. The laser is necessary for sending enough light down the long, narrow path to the sample. The wavelength shift is measured with a Spex model 1700 Czerny–Turner spectrometer. Second-order spectra were used and positions of the lines could be determined within an error ranging from ±0.15 to ±0.3 Å, depending on the slit width and the stability of the scanning motor speed.

The ruby fluorescence has been used primarily to test the pressure capability of the cell. The antimony data discussed below were collected by using the known compressibility of antimony along the a and c directions, because the equipment for measuring the ruby fluorescence shift was not available at the time the data were taken.

IV. SAMPLE LOADING

Just before loading the sample, a thin film of high-viscosity Dow-Corning silicone fluid was placed on the face of the anvil (A) near the center of the gasket hole. This film served to hold the samples in place as the high-pressure fluid was added. The high-pressure fluid, which is the standard 1 part ethanol to 4 parts methanol by volume,[9] actually softened the silicone slowly. Nonetheless, the crystals did not move once pressure was applied. They sometimes shifted their orientations a few degrees when the pressure was changed, but almost always kept their orientation with respect to the cell at constant pressure. At pressures up to 50 kilobars, the silicone fluid did not become so viscous that the samples were damaged by shear forces generated in this fluid as the pressure was changed. No broadening of the x-ray reflections from Sb or of the ruby fluorescence lines could be detected. It should be mentioned that, while x-ray intensity measurements on Sb were carried out only up to 26 kilobars, the strong (00.9) (hexagonal axes) reflection was scanned for one very small Sb crystal subjected to pressures up to about 55 kilobars. Because Sb single crystals are easily ruined, it seems safe to conclude that no significant shear stresses were ever present in the silicone fluid.

Samples were loaded into the cell with a brass pin that had been touched to the silicone fluid. Previously, glass fibers and small eye droppers were tried, but these were unsatisfactory. The glass fibers were very flexible and usually would bend as they first touched the crystal. The release of tension as the crystal adhered to the fiber sometimes propelled the crystal several centimeters, where it was destroyed by the impact. The eye droppers did not allow sufficient control while the crystal was loaded into the hole in the gasket.

The pin was gently touched to the sample to pick it up and transfer it to the cell. When the crystal touched the silicone film on the anvil face, it usually stayed in place. The crystal could easily be centered in the hole of the gasket and rotated by pushing it gently with a clean brass pin. This entire process was observed under a 60× binocular microscope. No damage was done to the crystal by this procedure. In this manner, the crystals could be aligned with respect to the cell to within 5° of the desired orientation by the methods described below.

The alignment of the sample within the cell could be determined in two ways. The first was to mount the stainless steel cylinder (C) before a back-reflection Laue camera such that the x-ray beam was along the cylinder axis. The resulting Laue photograph contained single-crystal patterns due to the sample and the diamond (A), and often a powder pattern due to the gasket. The pattern due to the sample could easily be distinguished from the others, and the alignment could be determined by standard Laue techniques. The Laue spots also provided a check on the quality of the sample crystal. The final alignment of the crystal was done with the four-circle goniometer shown in Fig. 4.

The orientation could also be determined directly with the sample crystal in the cell in place on the four-circle goniometer. The counter was set with a wide window at the position of a low index reflection. The position of the crystal was then varied by moving the three circles ω, χ, and ϕ governing the crystal orientation until the reflection was found. Large increment (~10°) about the two circles visible in Fig. 4 were possible; thus the procedure was fairly rapid. Of course, this is the only alignment procedure possible for phases produced at high pressure.

V. TEST PROBLEM: VARIATION OF THE ANTIMONY CRYSTAL STRUCTURE WITH PRESSURE

A. Sample preparation

An antimony ingot of 99.9999% purity was obtained from the Cominco Co. This was in the form of a single crystal which contained a large low-strain region with a mosaic half-width of 0.2°. From this region sheets measuring approximately 2 × 0.5 × 0.05 cm, with the principal plane parallel to the (00.1) crystallographic plane, were cut with either an acid string saw or a spark-cutter.

The sample preparation was completed while viewed with a 60× binocular microscope. Each of the sheets of Sb was etched in a solution (SOL1) of 50 parts HCl, 5 parts HNO_3 and 100 parts H_2O by volume. This solution dissolved the sheet into approximately twenty small flakes with the same relative crystallographic orientation as the original sheet. At this stage of preparation, these flakes measured approximately 0.06 × 0.06 × 0.007 cm and contained numerous etch pits approximately 0.001 cm in depth. A second solution (SOL2) containing 50 parts HCl, 160 parts HNO_3, and 100 parts H_2O by volume served as a chemical polish for the samples. Sometimes the crystals became coated with an undetermined antimony compound which was a product of the polishing reaction with SOL2. When this happened, small amounts of SOL1 were added until the coating dissolved. The samples quickly became highly polished as SOL2 acted upon them. However, when the crystals were rinsed with distilled water, they appeared to develop minute etch pits which caused them to have a pearly appearance under 60× magnification. The final samples were approximately disks with a diameter of 0.025 cm and a thickness of 0.001 cm, or thin flakes of other shapes but of comparable dimensions.

B. Data collection

The data collection system consisted of a Picker scintillation counter and NIM bin electronics, including an Ortec model 486 amplifier/single-channel analyzer, Ortec 449-2 ratemeter, Mech-Tronics model 715 dual scaler/timer, and Mech-Tronics model 1200 Teletype printing system.

The x-ray generator produced x-ray currents stable to 0.5%. Power to the x-ray generator was provided by a voltage stabilizer. Long-term drifts as high as 2% were observed, however. These were presumably due to changes in the line voltage.

The radiation was Mo K_α monochromatized by a flat pyrolytic graphite monochromator mounted between the x-ray tube and sample. The single-channel analyzer removed the $\lambda/2$, $\lambda/3$, and $\lambda/4$ wavelengths passed by the monochromator. The monochromator greatly reduced the background due to scattering from the diamonds and made possible accurate measurements of weak reflections such as the (00.21) and (00.24) at 1 bar. The diamonds could easily be aligned so that no diamond reflection interfered with a reflection from the Sb crystals. Data was taken with the moving counter–moving crystal method.

To observe drifts in the counting rate due to line voltage drifts, the beam was monitored for each reflection with a counter and monochromator over one of the other ports of the x-ray tube. In addition, several reflections were periodically scanned for changes in intensity during each run. Each ($hk.l$) intensity was normalized to a fixed monitor counting rate to correct for this drift.

For the preliminary experiments at 15 and 26 kilobars, only the ($00.l$) intensities were measured. Each ($00.l$) peak was scanned slowly to obtain good counting statistics. The profile of each peak was recorded on a chart recorder to detect any deformation of the crystal while it was under pressure. In practice, the only time the crystals ever became deformed was while the pressure was being increased. When this happened, the sample was discarded.

The ($00.l$) intensities with $3 \leq l \leq 24$ provide a sensitive determination of z. In fact, determinations of z based on only carefully measured ($00.l$) intensities should not be much less accurate than those based on a much more complete set of x-ray intensities. This appears to be the case. The 1-bar values of z for Sb and As determined by Morosin and Schirber[10,11] at room temperature with several hundred reflections do not differ greatly from the values of z found from only ($00.l$) reflections by Barrett, Cucka, and Haefner[12] for Sb and by Schiferl and Barrett[13] for As. The respective values are compared in Table I. It can be seen that the

TABLE I. Comparison of values of the atom position parameter z of As and Sb obtained with only (00.l) reflections to values obtained with several hundred ($hk.l$) reflections.

Element	z	Error	Method	Reference
Sb	0.23349	±0.00031	(00.l) only	12
Sb	0.23357	±0.00006	many ($hk.l$)	10
As	0.22707	±0.00005	(00.l) only	13
As	0.22728	±0.00007	many ($hk.l$)	11

z values based on only the (00.l) reflections are quite accurate. Further high-pressure work, in which about 30 reflections were used to determine z, was done at 7 and 13 kilobars.

The principal difficulty in the data analysis is correcting for the x-ray absorption of the sample and the components of the high-pressure cell. Absorption of x rays by the cell can be on the order of 50% and is path dependent owing to the complicated shapes of the diamonds and other components of the cell. Accurate determinations of the absorption corrections for the cell and crystal together were made empirically. The ($hk.l$) intensities from the Sb sample in the cell were measured at 1 bar. These were compared to the known intensities to determine absorption correction factors along the various x-ray paths in the cell. Because absorption by the Sb samples is not negligible despite their small sizes, absorption correction factors were redetermined for each new sample crystal. The corrections become less reliable as the pressure is increased. The Bragg angle θ for the higher index reflections can be shifted by several degrees at pressures of the order of 30 kilobars and higher. In addition, the crystal seems to shift position slightly each time the pressure is changed. Thus the path travelled by the x rays through the cell is somewhat different at high pressure. Finally, the absorption by the crystal changes as its density increases. The use of many orders of various ($hk.l$) reflections minimizes the effect of errors in the absorption corrections on determinations of z.

The integrated intensity I_0 of each reflection was taken as $I_0 = I_t - Q$, where I_t is the total integrated intensity and Q is the background count, computed from measurements of background on both sides of the reflection, for the same angular range of integration. Each observed intensity I_0 was corrected by the empirical absorption correction factor and by the appropriate Lorentz and polarization factors. For high index reflections, where the Mo K_α doublet was resolved, separate Lorentz and polarization factors were applied to the K_{α_1} and K_{α_2} lines.

The parameter z, thermal parameters β_{11} and β_{33}, and the reliability factor R given by

$$R = \Big[\sum_r w_r(F_{\text{obs}}{}^2 - F_{\text{cal}}{}^2)^2\Big]^{1/2}\Big[\sum_r w_r(F_{\text{obs}}{}^2)^2\Big]^{-1/2},$$

where F_{obs} and F_{cal} are the observed and calculated structure amplitudes and w_r is the weight given to the rth reflection, were calculated at each pressure. The weight w_r given each reflection was $w_r = 1/(I_t + Q)$. To estimate the error in z, these calculations were repeated with all reflections given unit weight.

The relativistic Hartree–Fock x-ray scattering factors of Doyle and Turner[14] were used with the relativistic anomalous scattering factors of Cromer and Liberman.[15] Refinement of the crystal structure based on $|F|^2$ was performed with program 36E7118 by J. Gvildys from the Argonne National Laboratory Applied Mathematics Division.[16]

C. Results

The atom position parameter z as a function of pressure p is shown in Fig. 5. The present work contributes the values of z above 3 kilobars. These values were obtained with weights w_r as discussed above. The error bars represent the difference between the z values obtained with each reflection given weight w_r and those obtained when unit weights were used. This is only a tentative estimate of the error in z. The reliability factors were $R = 2.5\%$ at 15 kilobars and $R = 4.3\%$ at 26 kilobars, using only 00.l reflections; and $R = 6.8\%$ at 7 kilobars and $R = 5.3\%$ at 13 kilobars, using about 30 other reflections.

Also plotted are the values of z obtained at 1 bar and 3 kilobars by Morosin and Schirber[10] and at 1 bar and room temperature by Barrett, Cucka, and Haefner.[12] The three sets of data are in excellent agreement. The apparatus used by Morosin and Schirber[10] is of a very

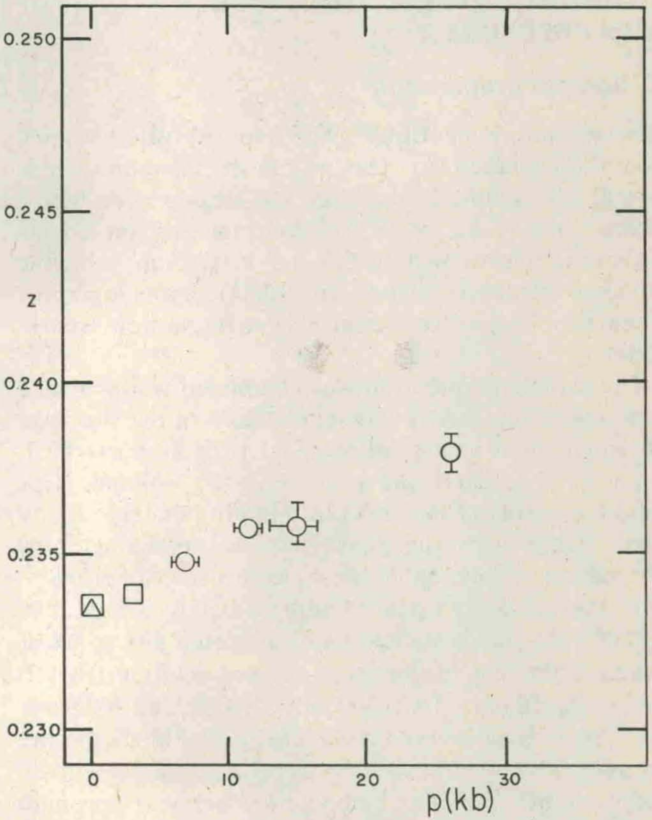


FIG. 5. Atom position parameter z as a function of pressure p. The value shown by a triangle is from Ref. 12. The values shown by squares are from Ref. 10. The circles denote the present work. The absence of an error bar indicates that it is too small to be indicated on the plot.

different design, and their value of z is based on approximately 30 reflections. Thus, it is quite remarkable that the agreement between the present results and theirs is so close. The agreement is all the more pleasing in view of the fact that very few complete structure determinations of any type have been done at high pressure.

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[1] L. Merrill and W. A. Bassett, Rev. Sci. Instrum. **45,** 290 (1974).

[2] C. E. Weir, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **40,** 1133 (1969).

[3] R. Fourme, J. Appl. Crystallogr. **1,** 23 (1968).

[4] A slightly different ball mount was independently developed earlier by Barnett, Block, and Piermarini (see Ref. 6).

[5] A. H. Compton, Rev. Sci. Instrum. **2,** 365 (1931).

[6] J. D. Barnett, S. Block, and G. J. Piermarini, Rev. Sci. Instrum. **44,** 1 (1973).

[7] R. A. Forman, G. J. Piermarini, J. D. Barnett, and S. Block, Science **176,** 284 (1972).

[8] G. J. Piermarini (private communication).

[9] G. J. Piermarini, S. Block, and J. D. Barnett, J. Appl. Phys. **44,** 5377 (1973).

[10] B. Morosin and J. E. Schirber, Phys. Lett. A **30,** 512 (1969).

[11] B. Morosin and J. E. Schirber, Solid State Commun. **10,** 249 (1972).

[12] C. S. Barrett, P. Cucka, and K. Haefner, Acta Crystallogr. **16,** 451 (1963).

[13] D. Schiferl and C. S. Barrett, J. Appl. Crystallogr. **2,** 30 (1969).

[14] P. A. Doyle and P. S. Turner, Acta Crystallogr. **A24,** 390 (1968).

[15] D. T. Cromer and D. Liberman, J. Chem. Phys. **53,** 1891 (1970).

[16] M. H. Mueller (private communication).

[17] W. A. Bassett, T. Takahashi, and P. W. Stook, Rev. Sci. Instrum. **38,** 37 (1967).