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ULTRA-HIGH-PRESSURE, HIGH-TEMPERATURE APPARATUS: THE “BELT”

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Ultra-High-Pressure, High-Temperature Apparatus: the "Belt"

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Equipment is described for maintaining pressures of 100 000 atmos at temperatures in excess of 2000*C for long periods of time. The equipment makes use of conical Carboloy pistons that push into each end of a specially shaped Carboloy chamber. Both chamber and pistons receive lateral support from stressed binding rings. Axial motion of the conical pistons in and out of the chamber is accomplished (while still maintaining a pressure seal) by the use of a specially shaped sandwich gasket made up of naturally occurring pyrophyllite and a steel cone. The arrangement gives a multistaging effect in a single stage. Pyrophyllite in addition to its use in the gasket is also used as pressure transmitting medium, thermal insulation, and electrical insulation. The sample is heated by passage of an electric current through a metal or graphite tube. Methods of pressure and temperature calibration as well as construction details are discussed.

In the "belt," an ultra-high-pressure, high-temperature apparatus, materials can be subjected to pressures of 100 000 atmos at temperatures in excess of 2000°C. These conditions can be simultaneously maintained for hours.

Diagrams and photographs of the apparatus are shown in Figs. 1-4.

The functions of the various parts are as follows (see Fig. 1): Two conical Carboloy pistons (1) push into each side of a specially shaped Carboloy chamber (2). Pressure is transmitted to the sample contained in the metal tube (3) by pyrophyllite (wonderstone) (4), a hydrous aluminum silicate. The pyrophyllite also serves as thermal and electrical insulation. The sample is heated by passage of electricity through the metal tube (3). Current enters this tube from the pistons via the steel rings (5) and the metal disks (6). The short pyrophyllite cylinders (7) provide thermal insulation at the ends of the sample tube (3). A sandwich gasket composed of pyrophyllite (8), (10), and steel (9) maintains the pressure in the chamber. Hardened steel binding rings (11) and (12), which are strained near their elastic limits by forced-on tapered fits, greatly strengthen the chamber (2). Binding rings (13) and (14) do the same for the conical pistons. Soft steel safety rings (15) and (16) offer protection from flying fragments when binding rings break.

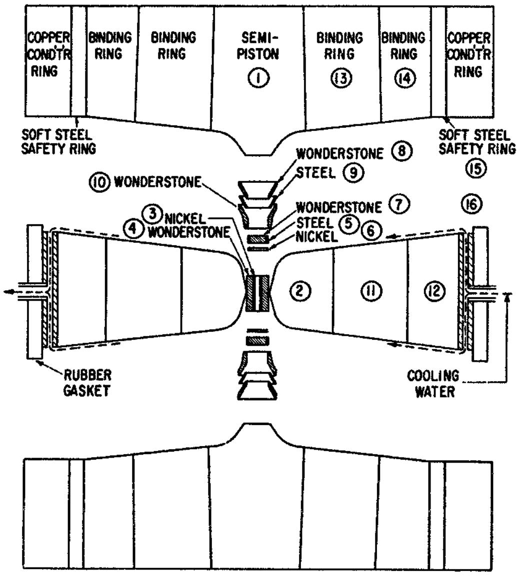

FIG. 1. The "belt": high-temperature, high-pressure apparatus. "Exploded" assembly.

The chamber (2) and binding rings 11 and 12, form a toroidal "belt" around the sample, hence the name of this apparatus. The equipment is water cooled as shown.

In March of 1952, P. W. Bridgman[1] described an ingenious single-stage apparatus for producing pressures to 100 000 kg/cm^2 (1 kg/cm^2 = 0.9678 atmos). The apparatus (see Fig. 5, 1) consisted of two Carboloy "anvils" A and B held in compression by steel binding rings C and D. The anvil faces are ½ in. in diam and slope away at a 4 deg angle. The sample to be compressed is a disk 0.407 in. in diam and 0.010 in. thick. The sample is contained by a "pipestone" gasket 0.500 in. o.d., 0.407 in. i.d. and 0.010 in. thick. "Pipestone" or Catlinite is a red indurated clay from the upper Missouri region. it is found at Pipestone National Monument, a part of the Sioux Indian Reservation in Minnesota. As the name implies, the Indians carve smoking pipes from the material.

Pipestone, in thin sections, has the property of becoming very strong in a direction transverse to the direction of compression. Under

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[1] P. W. Bridgman, Proc. Roy. Soc. (London) A203, 1 (1950) and Proc. Am. Acad. Arts and Sci. 81, 165 (1952).

compression, the submicron-size grit of the pipestone "bites" into the Carboloy, giving very high frictional resistance to relative Carboloy-pipestone motion.

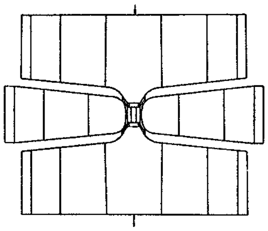

FIG. 2. The "belt", ultra-high-pressure, high-temperature assembly.

P. W. Bridgman has measured the electrical resistance of most of the metals to 100 000 kg/cm^2 (taking pressure as force over area) by folding a ribbon of the metal between two silver chloride disks as shown in cross section b of Fig. 5, I. Silver chloride has about the same compressibility as pipestone. In addition, it has a very low coefficient of internal friction, making it the best solid pressure-transmitting medium known at the present time. All materials ordinarily liquid become solid at or before 30 000 atmos at room temperature.

The sample in Bridgman's equipment is very small and of course cannot be heated to high temperature. A larger sample could be obtained at a sacrifice in ultimate pressure by making recesses in the anvils as shown in Fig. 5, II. Bridgman experimented with such anvils but found that the recesses seriously weakened the Carboloy.

An early improvement in Bridgman's apparatus by F. P. Bundy[2] is shown in Fig. 6(a). This pair of recessed anvils (called the "saucer") has provision for heating a small sample at the center and permits a substantial increase over Bridgman's working volume. The smoothly contoured recess keeps stress concentrations low and in addition tends to force the gasket material (a) inward when the anvils come together. Additional recesses (c) are filled with fired Al_2O_3 or MgO for thermal insulation. A heating spool of graphite (d) holds the sample in a small cavity (f). A ring of Al_2O_3 or MgO (e) fills the notch in the heating spool. The sample is heated by passing current through the heating spool. Bundy, following the suggestion of L. Navias of this Laboratory, found that pyrophyllite[3], a hydrous aluminum silicate, could be used in place of pipestone for the gasket. It is obtained more easily, is less expensive, and is a more uniform material than pipestone.

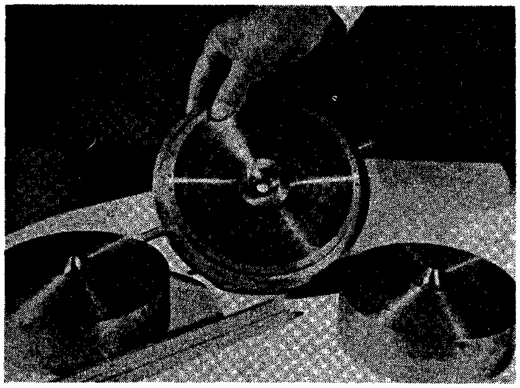

FIG. 3. Photograph of apparatus.

Bundy found about 0.030 in. to be the maximum gasket thickness that could be used at the anvil shoulders (the part of the anvils that touch if brought together without gasket and sample). Thicker gaskets tend to crumble and break out, with resultant loss in pressure. Of course, the thickest gasket possible should be used, since the thicker the gasket, the larger the sample that can be accommodated. This device performs very satisfactorily to temperatures of about 2500°C and pressures somewhat over 35 000 atmos. At this pressure, the gasket thickness at the shoulders decreases to a limiting value in the neighborhood of 0.002 to 0.004 in. Additional press load cannot bring the anvils closer together, and hence a limiting pressure is reached.

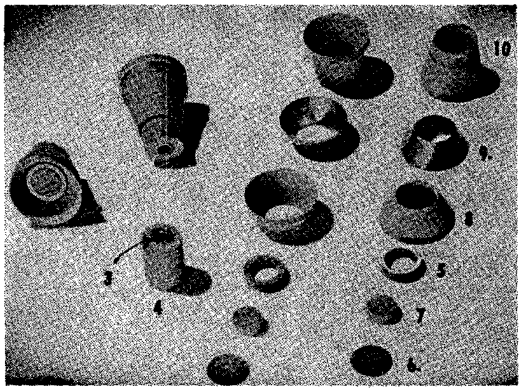

FIG. 4. Chamber parts.

The desire to increase the sample size and pressure over that obtainable in Bundy's apparatus led the author to the development of the "belt." Three ideas give the belt its high performance. They are listed in the following sections.

1. The Conical Piston, Gasket, and Chamber

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[2] Of this Laboratory (unpublished work).

[3] Available as "Lava, Grade A" from American Lava Corporation, Chattanooga 5, Tennessee.

If a gasket were arranged at an angle less than 90° to the direction of compression, (as is gasket (3) of Fig. 7) the thickness along the line of compression could be increased to s=t/cosÈ. The stroke therefore would be correspondingly increased. Here s is the distance between the arrows b-b (Fig. 7) and t is the limiting thickness of 0.030 in. The thickness perpendicular to the frictional surface (distance between arrows a-a in Fig. 7) is still t. The force acting perpendicular to the contact area between the gasket and the Carboloy is reduced by cosÈ over the case where the gasket is perpendicular to the direction of compression. Therefore, the friction between the gasket and the Carboloy will be reduced by cosÈ. Now, the smaller the angle È is made, the larger s becomes. The limit on the smallness of È is set by the frictional forces along the gasket-Carboloy interface. When they become too small, the gasket will be blown out by the pressure. The design of Fig. 7 with È=45° gave pressures over 33 000 atmos in samples twice as thick as were possible in the "saucer."

A conical piston has much greater strength than the usual cylindrical piston of high-pressure equipment. In addition, accurate alignment of conical piston and chamber in the apparatus of Fig. 7 is not necessary, and a slight "cocking" will not break the piston.

2. Double Ending

If the part of the apparatus below line S of Fig. 7 is eliminated and the part of the apparatus above S is rotated 180° around the line S, a "double-ended" apparatus evolves. Double ending increases the symmetry, thus eliminating some stress concentration points. Also, the sample size is more than doubled. Removal of contents after a run is accomplished easily by ramming the material out of the chamber.

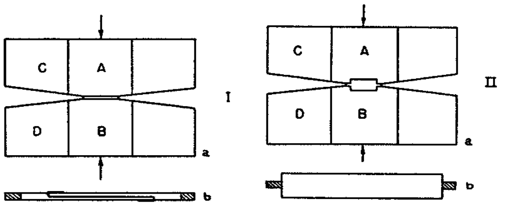


Fig. 5. I, P. W. Bridgman's "anvil" apparatus for producing pressures to 100 000 kg/cm²; II, modification of Bridgman's apparatus.

3. The "Sandwich Gasket"

The "sandwich gasket" will increase the stroke and hence the sample size and ultimate pressure of any system utilizing stone gaskets. The author first tested this idea in Bundy's "saucer." The thickness of the gasket at the shoulders of the anvils can be more than doubled by inserting a thin metal disk between two gaskets as shown in Fig. 6(B). This increases the sample thickness by 0.040 in. (0.010-in.-thick steel disk+0.030-in. additional lava stone). In operation, each thickness of stone crushes to its limiting thickness of 0.002 to 0.004 in. The steel disk, as does the stone, becomes extremely strong transverse to the direction of compression.

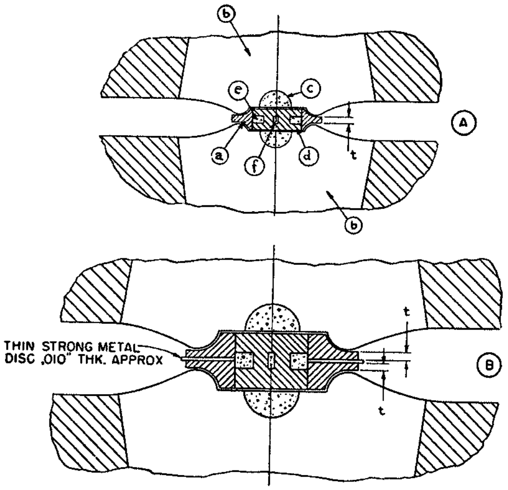
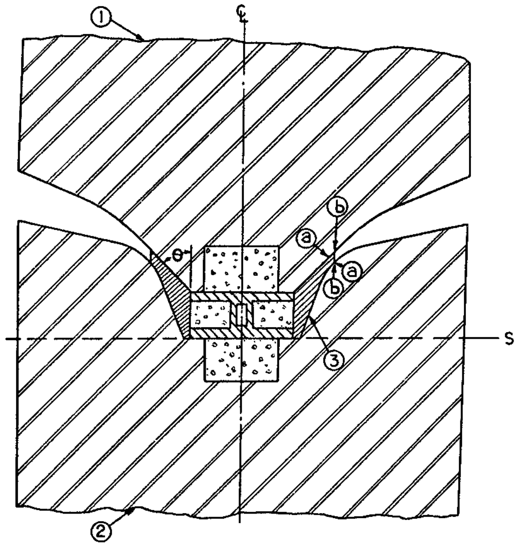


Fig. 6. A, Francis P. Bundy's "saucer" anvils; B, "sandwich" gasket.



HIGH–PRESSURE, HIGH-TEMPERATURE REACTION CELL

Fig. 7. High-pressure, high-temperature apparatus with conical piston, gasket, and chamber.

Pressures of 47 000 atmos, as measured by a Manganin wire gauge[4] were obtained with this

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[4] P. W. Bridgman, The Physics of High Pressure (G. Bell and Sons, London, 1949), p. 72.

arrangement. By using still another metal and lava disk, sample thickness was increased another 0.040 in., and a pressure of 51 000 atmos was obtained.

The available stroke of the "belt" apparatus is 0.23 in., compared with 0.026 in. for the "saucer." The chamber size is large enough to permit using thermal insulation as part of each sample instead of recessing it in the anvils as was done in the apparatus of Figs. 6 and 7. The recessed insulation is undesirable on two counts: (1) The recess weakens the anvils, thus lowering the ultimate pressure attainable and shortening apparatus life, and (2) the recessed insulation spalls and must be replaced frequently.

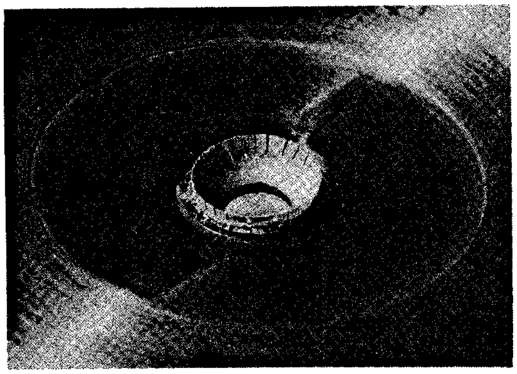

FIG. 8. Gasket after high-pressure run.

In the "belt," the center of the assembly, where the sample is located, sustains more load than the outer regions. An indication of this is given by the picture of Fig. 8. This shows a gasket after a run at high pressure. The pyrophyllite gasket is darkest where it has been compressed the most. Calculation of the average projected area over which the press load is applied to obtain known pressures (from known transition points) within the cell gives a circle of diameter about 0.40 in. The total projected area of the gasket is enclosed by a circle 0.600 in. diam.

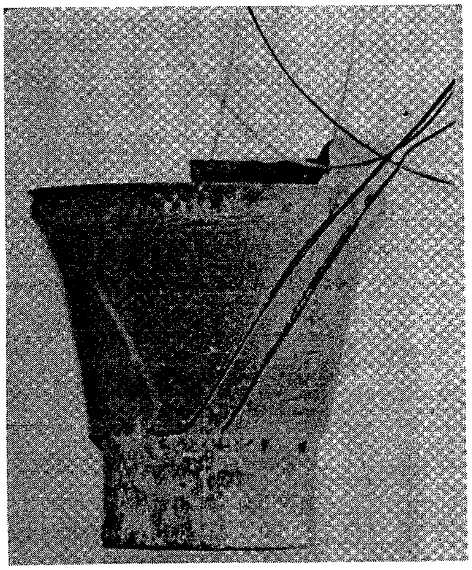

FIG. 9. Thermocouple wires emerging from gasket assembly.

The gradual drop of pressure along the gasket probably occurs in the following idealized manner: The outermost shell of the gasket has only the atmosphere for outside support, but has some support from above and below due to friction. The outermost shell then gives some support to the back of the next shell, which can give even greater support to the next inner shell because of increased support at its back, and so on. The 30-deg "conical gasket" allows some slippage between gasket and metal; the outer shells slip more than the inner shells, so that the inner shells become more highly compressed. The gradual drop of pressure along the gasket provides a gradually decreasing support to the conical piston. This gives a multistaging effect. (Multistaging is building one piece of pressure apparatus inside another. Theoretically, tremendous pressures could be developed in this manner if the very difficult technical problems could be solved.)

The chamber (2) of Fig. 1 also obtains a multistaging effect because the thrust of the conical pistons develops a compression component in the chamber parallel to the centerline of the system.

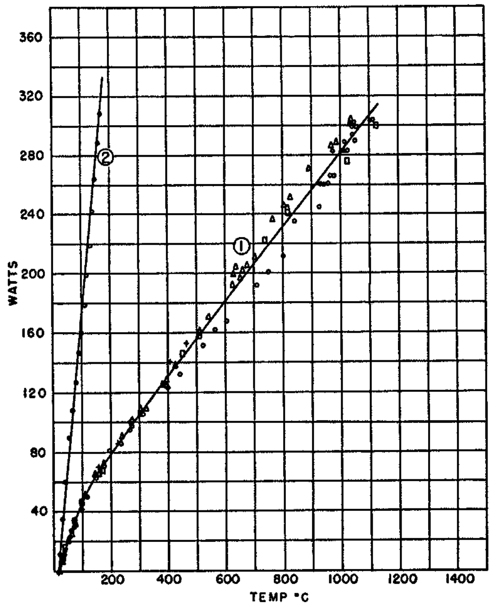

FIG. 10. Temperature *vs* watts input for "belt". (1) center of heating tube; (2) temperature at $r=0.200$ in., $z=0$ in. (center of symmetry = origin).

TEMPERATURE CALIBRATION OF THE "BELT"

The temperature obtained inside the sample tube for a given wattage input depends on the thermal conductivity of the material in the tube. The thermal conductivity of the heating tube and the end disks will also affect the temperature. It is possible to measure the temperature inside the tube with a thermocouple. A very tiny junction is placed at the desired point and the leads brought out through tiny holes and slots in the pyrophyllite. The wires placed in slots are covered over with pyrophyllite powder worked into place with a dental spatula. Figure 9, a picture of an assembly after a run, gives an idea of how this is done.

As a guide, a temperature calibration is given in Fig. 10 for the case of a nickel tube filled with pyrophyllite. The end disk was also nickel. All stone components were pyrophyllite except the end insulation (7 of Fig. 1) which was pipestone. Chromel and Alumel thermocouple wire of 0.005 in. diam with Formex insulation was used in the temperature calibration.

In Fig. 10, Curve (1) gives the temperature measured by thermocouples located at the middle of the heating tube as a function of watts input. Curve (2) gives the temperature at r=0.200 in., z=0 in. (using cylindrical coordinates for the system with the center of symmetry as origin).

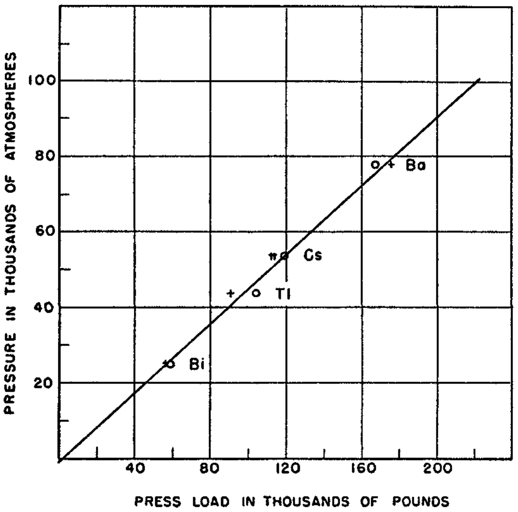

FIG. 11. Pressure calibration of the "belt."

Moderate pressures of 2000 to 10 000 atmos were used in making the temperature calibrations. Prior to the temperature calibration by thermocouple, the watts input required to melt lithium and potassium carbonates had been used to obtain an idea of the temperature. These points fell within the bounds of the thermocouple curve. More recently, "Thermocolor" paint[5], which changes color at fixed temperatures, has been used to check the thermocouple calibration. The agreement is good. Curve (1) of Fig. 10 probably gives the temperature at the center of the tube to 5% at the higher temperatures. Accuracy will be better at the lower temperatures. Thermocolor paint indicates that the temperature at the ends of the heating tube is near 900ºC when the temperature at the center is near 1000ºC. Homogeneity of temperature probably could be obtained by slightly increasing the thickness of the end insulation.

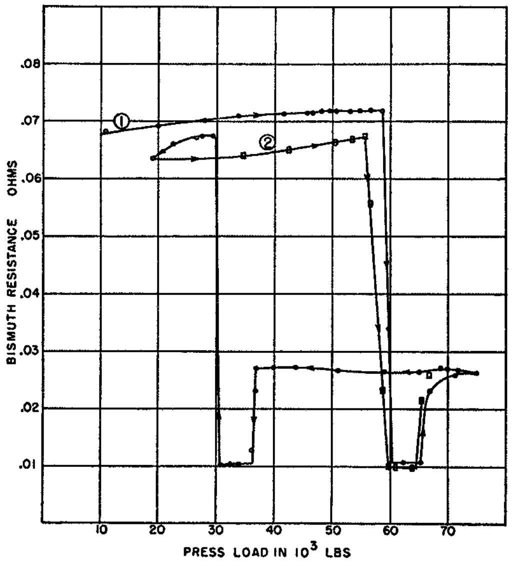

FIG. 12. Bismuth transition at 24 800 atmos.

PRESSURE CALIBRATION OF "BELT"

The press load required to produce a given pressure in the sample chamber of the "belt" has been determined with the aid of phase transitions. Five were used: the sharp changes in electrical resistance of bismuth, thallium, cesium, and barium[6] at 24 800, 43 500, 53 200, and 77 400 atmos, respectively, and the growth of a new dense silica at 35 000 atmos[7]. The calibration for Carboloy pistons and chamber is shown in Fig. 11. Each of the transitions is discussed below.

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[5] Made by Badische Anilin und Soda Fabrik, Ludwigshafen am. Rhein. Available from Bryson Oil Company, Harriman, Tennessee.

[6] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, (4), 165 (1952).

[7] L. Coes, Science 118, 131 (1953).

BISMUTH TRANSITION

A cylinder of silver chloride the same diameter and length as the heating tube was put in the lava in place of the heating tube. A bismuth wire about 0.025 in. in diam was placed in a 0.030-in.-diam hole drilled down the axis of the silver chloride. The bismuth wire made contact at each end with the nickel end disks. Resistance was measured with a Kelvin double bridge.

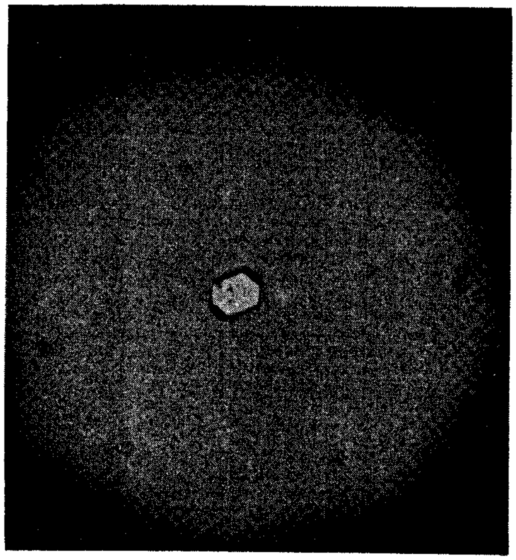

Fig. 13. Dense silica crystal.

Figure 12 shows the resistance change with loading (1), unloading, and reloading (2).

The sharp decrease in resistance is due to the Bi I-Bi II transistion occurring at 24 800 atmos. The less spectacular rise in resistance following the large drop is due to Bi II-Bi III at 26 200 atmos. A large hysteresis is noted on reducing the press load. Bridgman observed this same type of phenomenon in his "anvil" work. When the press load is increased a second time, the Bi I-Bi II transition occurs at about 10% lower press loading than on the initial loading.

DENSE SILICA FORMATION

The author has studied the formation of a new, dense, crystalline form of silica from solutions of waterglass. Near 650°C there is a sharply defined press load (71 000 lb for the "belt") below which quartz crystals grow from the waterglass. Above this sharply defined press load, only dense silica grows. A change of 3% in press load will shift the equilibrium one way or the other. Changing the temperature between 550° and 750°C does not appreciably affect the transition pressure. Five minutes of growing time is sufficient to produce myriads of dense silica crystals up to 500 ì across. This is interesting in view of Coes' reported 15 hr required to grow 40-ì crystals from sodium silicate in diammonium hydrogen phosphate. A photomicrograph of a dense silica crystal is shown in Fig. 13.

Coes gives the dense silica transition pressure as 35 000 ± 2000 atmos. This pressure is based on an extrapolation of the Bi I-Bi II transition pressure.

THALLIUM TRANSITION

The thallium transition at 43 500 atmos was detected by the change in electrical resistance in the same fashion as the bismuth transition. A plot of resistance vs press load is shown in Fig. 14. Hysteresis is present as with bismuth. Observe also that the transition occurs at about 10% lower press load on the second loading.

CESIUM TRANSITION

This transition gives a well-defined "pip" at 53 200 atmos (see Fig. 15). Curve (1) is the first cycle (compaction). Curve (2) is the second cycle and gives the usual lower press loading to obtain the transition.

The difficulties encountered in handling the extremely reactive metal cesium were overcome in the following way: A thin-walled glass vessel

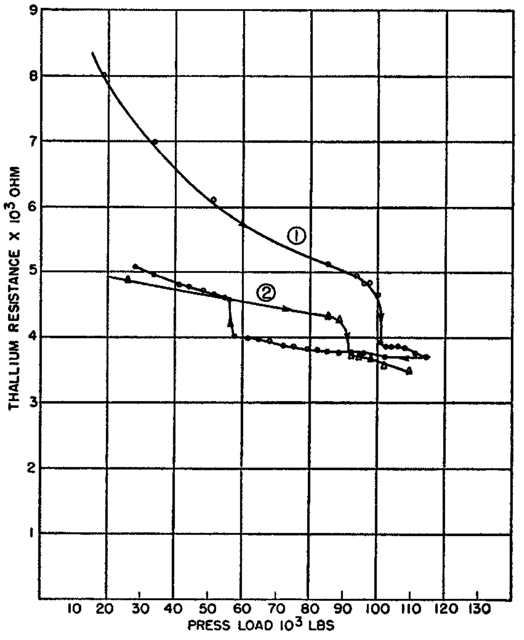

Fig. 14. Thallium transition at 43 500 atmos.

containing cesium in vacuum was broken under mineral oil. The mineral oil was at a temperature near 40ºC, so that the cesium, which melts at 28.5ºC, would be liquid. Thin-walled glass capillaries, 0.050 in. o.d. and about 10 in. long, were prepared. A little mineral oil was drawn into a capillary tube with a suction bulb and then, immediately behind the oil, the cesium was drawn in. When the tube was almost filled, a little mineral oil was drawn in behind the cesium. In this manner, the cesium was prevented from coming in contact with the atmosphere. A 0.400-in.-long section was then cut from the capillary, after daubing petroleum jelly where the cuts were to be made. The cut was made with sidecutting pliers.

The capillary containing the cesium then was inserted in a hole in the AgCl in the same manner as was the bismuth wire. The ends of the capillary were kept covered with petroleum jelly. Tiny copper "thumb-tacks" were inserted in each end of the capillary to make contact with the cesium. The heads of the tacks make contact with the metal end disks.

BARIUM TRANSITION

A barium wire was used in the same manner as was the bismuth wire. The barium must be protected from oxidation by a coat of petroleum jelly. The transition is shown in Fig. 16.

The upper pressure limit for steel chambers and pistons is around 45 000 atmos. Carboloy must be used above this pressure.

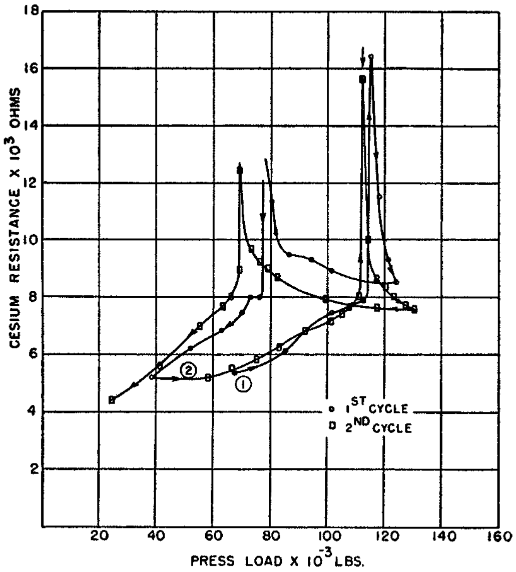

FIG. 15. Cesium transition at 53 200 atmos.

LIFE OF EQUIPMENT

The tapered pistons and chamber of the "belt" are subjected to the highest stresses. The life of these parts will depend on the pressures used and the number of loadings and unloadings. Experience to date shows that conical, tool-steel pistons (Rockwell hardness C-60) begin to crack after about 100 runs at 45 000 atmos and 1000ºC. Some of the runs lasted 5 to 6 hr, but the average run was 1/2 hr. The pistons can be used for about 25 additional runs after cracks appear. At 45 000 atmos and 1000ºC, the chamber when made of tool steel (Rockwell hardness C-60) begins to crack after about 40 runs. Again, some of the runs were 5 to 6 hr, but most of them averaged 1/2 hr. After the first cracks appear, an additional 10 to 20 runs can be made. At 50 000 atmos and 1000ºC, a Carboloy chamber shows its first fine crack after about 40 runs. It maintains pressure for approximately 35 additional runs. Enough runs have not been made with Carboloy tapered pistons at this pressure to determine their lifetime. At 100 runs, they seem as good as new.

Considering other workers' experience (10 to 20 runs) with equipment operating at these pressures and only at room temperature[8], the "belt's" lifetime is excellent. At this writing, experience at 100 000 atmos in the "belt" is limited. Runs have been made at 100 000 atmos with temperatures in excess of 3000ºC (temperature based on a linear extrapolation of the graph of Fig. 10). Lava, which at 1 atmos melts near 1300-1400ºC, withstands this temperature at high pressure.

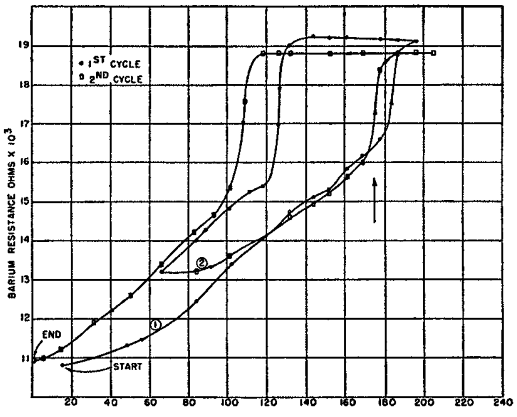

FIG. 16. Barium transition at 77 400 atmos.

MODE OF CRACKING IN CONICAL PISTONS AND CHAMBER

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[8] Reference 3, p. 396.

Cracks first appear on the surface of the cone of the steel pistons lying in a plane through the centerline. Later, the crack may spiral to the base of the cone, ending in a crack lying in a plane perpendicular to the centerline.

The chamber (of steel or Carboloy) cracks first on the inside surface in lines lying in planes through the centerline of the system. Later, a single crack perpendicular to these appears. This crack eventually splits the ring in two.

REMARKS

The development of the apparatus described here has opened a thermodynamic region heretofore inaccessible. It is possible to place several lead wires in the sample in addition to thermocouple leads so that properties such as the electrical resistance of a substance at ultra-high pressure and high-temperature can be measured. Studies of melting points, phase transitions, crystal growth, rock and mineral formation, and a host of other phenomena can be made. This new experimental region will be of particular interest to geologists since 100 000 atmos correspond to a depth of about 240 miles in the earth.

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[*] Tracy's Hall's Present address: Brigham Young University, Provo, Utah.

[†] Publication of the material had to be delayed because of a U.S. Government secrecy order.