Of the possibilities presented in (2) for RPF_4 we prefer the dynamic model of an equatorially substituted trigonal bipyramid on the basis of analogy to PF_5. It has been shown recently[18] that $Sb(C_6H_5)_5$ is a tetragonal pyramid in the solid state. However, packing factors in the solid state could easily lead to distortion of a trigonal bipyramid.[19]

Our observations indicate that the more electropositive groups always are found at equatorial positions. Hydrogen atoms or alkyl groups may tend to be equatorial because the phosphorus bonding orbitals in this plane have maximum s character.[20] Alternatively, the stereochemical results may be generalized by stating that the more electronegative ligands tend to go to axial positions where the bonds are more ionic. There is, of course, the possibility that large steric repulsions may lead to stereochemistries that do not fit these generalizations; this would be most likely in an X_2PF_3 species.

It is further suggested that intramolecular exchange processes are quite common in trigonal bipyramid structures. It is significant that spectroscopic equivalence of ligands is found for $Fe(CO)_5$[21] in C^{13} n.m.r. and for PF_5,[22] RPF_4, AsF_5,[23] and SOF_4[24] in F^{19} n.m.r. We plan to test this hypothesis by a general n.m.r. study of MX_5 and MX_4Y structures. Ease of intramolecular exchange may well account for the indicated absence of isomers in the large number of substituted phosphorus fluorides that we have examined.

Experimental

The preparation of the phosphoranes has been described previously.[1] The volatile derivatives were purified by distillation. To minimize any intermolecular fluorine exchange process, the alkyl and aryl phosphoranes were distilled from sodium fluoride, and in many cases a small amount of sodium fluoride was added to the n.m.r. tubes to remove possible traces of hydrogen fluoride. Transfer of all volatile reagents was effected in a vacuum system.

Apparatus—The F^{19} n.m.r. spectra were obtained on a Varian high resolution spectrometer Model V4300 and associated magnet at 56.4 Mc. Calibration of spectra was effected by superposition of an audiofrequency on the sweep field to produce side band peaks. The external reference was trifluoroacetic acid.

(18) P. J. Wheatley, *Proc. Chem. Soc.*, 251 (1962).

(19) The dipole moments of $P(C_6H_5)_5$, $As(C_6H_5)_5$, and $Sb(C_6H_5)_5$ in solution are about 1 D.[18] Non-zero values could be due to a field induced moment.

(20) In $[(CH_3)_3N]_2AlH_3$, the hydrogen atoms attached to the aluminum atom are at the equatorial positions of a trigonal bipyramid: R. W. Parry, personal communication.

(21) (a) F. A. Cotton, A. Danti, J. S. Waugh, and R. W. Fessenden, *J. Chem. Phys.*, **29**, 1427 (1958); (b) R. Bramley, B. N. Figgis, and R. S. Nyholm, *Trans. Faraday Soc.*, **58**, 1893 (1962).

(22) H. W. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(23) E. L. Muetterties and W. D. Phillips, *J. Am. Chem. Soc.*, **81**, 1084 (1959).

(24) F. B. Dudley, J. N. Shoolery, and G. H. Cady, *ibid.*, **78**, 568 (1956).

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Some High Pressure Studies on Ytterbium[1a]

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Pressure, temperature, volume, resistance, and X-ray diffraction measurements have made it possible to establish a partial *P–T* phase diagram for metallic ytterbium. An electronic transition, previously indicated as occurring at 60 kb., 25°, has been shown to occur at 39.5 kb., 25°. This transition pressure is lowered by increasing temperature, $\Delta P/\Delta T$ being -19.1 bars/deg., and is accompanied by a change in volume of -0.65 cm.^{3}/mole simultaneously with a change in crystal structure from FCC to BCC. This is the first time a pressure-induced transition from a close-packed to a non-close-packed structure has been observed. Heat absorption at the transition is 89 cal./mole. A number of second-order transitions were discovered. Of particular interest are transitions in bond type from *P–T* regions in which directional bonds predominate to *P–T* regions in which metallic bonding predominates.

Introduction

In 1954 Bridgman published data showing the change in electrical resistance of Yb as a function of pressure as measured in his opposed anvil apparatus.[2] He reported a discontinuity occurring at 60 kb. where the resistance, after having increased by a factor of about 12, suddenly decreased by a factor of about 15. Bridgman's resistance *vs.* pressure curve is reproduced as curve A in Fig. 1. Curve B, which shows the Yb resistance discontinuity occurring at 39.5 kb., represents results obtained in this study.

Bridgman also measured the compressibility of Yb which he reported in table form.[2] These data are given in graph form in Fig. 2 along with the compressibility data from this work.

Electrical Resistance Measurements

The Yb used was purchased from Nuclear Corporation of America, Research Chemicals Division, Burbank, California. Purity was indicated as being 99% nominal with tantalum and oxygen as the principal

(1) (a) Research supported by the National Science Foundation and the Alfred P. Sloan Foundation; (b) Alfred P. Sloan Research Fellow.

(2) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **83**, 1 (1954).

foreign elements. Strips of material approximately 0.005 in. thick by 0.025 in. wide were cut from Yb sheet for use in the resistance measurements. Small pieces of 0.005 in. sheet were prepared by compressing bits of Yb between flat anvils in a hydraulic press. This could readily be accomplished because Yb is rather soft. A 0.030-in. diameter hole was drilled along the axis of a 0.188-in. diameter by 0.100-in. long AgCl cylinder to receive the Yb strip. The surface of this hole was coated with a film of molybdenum disulfide–silicone suspension (Molykote M-88, manufactured by the Alpha-Molykote Corp., Stamford, Connecticut). This film prevents chemical reaction between the Yb and AgCl which would otherwise take place. Resistance measurements were then made in an identical fashion with that described below under calibration procedure.

Our resistance measurements were made in the tetrahedral press[3] and "Belt"[4] type apparatus. The Yb resistance discontinuity commenced at 39.5 kb. in both devices. Pressure gradients are much less severe in these apparatus than in Bridgman anvils, and the pressure obtained is not influenced by small variations in sample and cell geometry. These factors may have been responsible for the high value of the pressure obtained by Bridgman for the Yb transition.

The pressure we have assigned for the electrical resistance transition in Yb is based on a pressure calibration for the tetrahedral press utilizing electrical resistance transitions in Bi (25.3 kb.), Tl (37 kb.), and Ba (59 kb.). These pressure calibration points are currently being used by most workers in the field (former values used for Tl and Ba were 45 and 80 kb., respectively). Since there may yet be some future revision of the pressure scale and since all workers in the field are not following the same calibration procedures, we set forth below the details of the calibration of the tetrahedral press for this work.

Calibration Procedure

Tungsten carbide anvils with 12% cobalt binder were used. The triangular faces of the anvils had lengths of 0.750 in., and the sloping shoulders of the anvils made angles of 144.7° with the triangular face. The height from circular base to triangular face was $1^3/_8$ in. An alloy steel binding ring surrounded each anvil. The tetrahedral press used in these experiments utilized hydraulic rams with 8-in. diameter pistons which generated a maximum thrust of 200 tons each at 8000 p.s.i. oil pressure. At anvil closure, the rams advanced approximately 2 in., thus leaving an oil "cushion" of approximately 100 in.^{3} volume behind each ram piston. This press was equipped with an Anvil Guide Device[5] that automatically advanced all four anvils simultaneously and symmetrically toward the center of the tetrahedron as oil pressure was applied.

The tetrahedral cell was machined from "grade A lava" (pyrophyllite) obtained from the Tennessee Lava Corporation, Chattanooga, Tennessee. Solid pyrophyllite tetrahedra 1.000 in. on edge were first made (refer to Fig. 3). A central slab 0.100 in. thick then was cut from the tetrahedron with twin, pen-nib, slitting saws 0.006 in. thick. The faces of the central slab were parallel to two opposite edges of the tetrahedron. A 0.188-in. diameter sample hole then was drilled through the center of the slab perpendicular to the faces. A silver chloride cylinder 0.100 in. long and 0.188 in. in diameter (to fit the above sample hole) was prepared with a small axial hole to receive an approximately 0.020-in. diameter calibration wire of Bi, Tl, Ba, or other material. The calibration wire was connected to annealed silver disks, 0.005 in. thick by $^1/_8$ in. diameter located at the ends of the silver chloride cylinder. Electrical connection to the silver disks was made with 0.005-in. thick by 0.25-in. wide nickel connecting

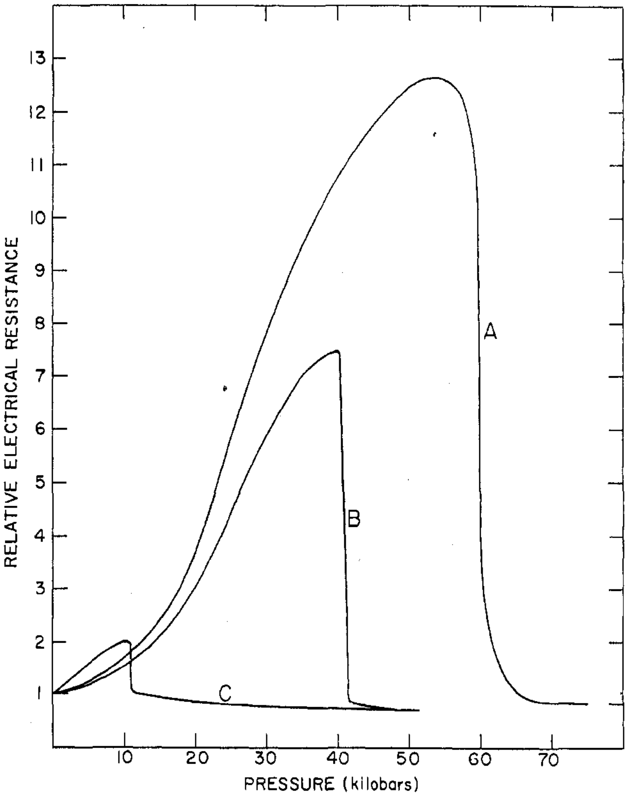

Fig. 1.—Electrical resistance *vs.* pressure for Yb: A, Bridgman's data; B, this research; C, unloading (hysteresis curve).

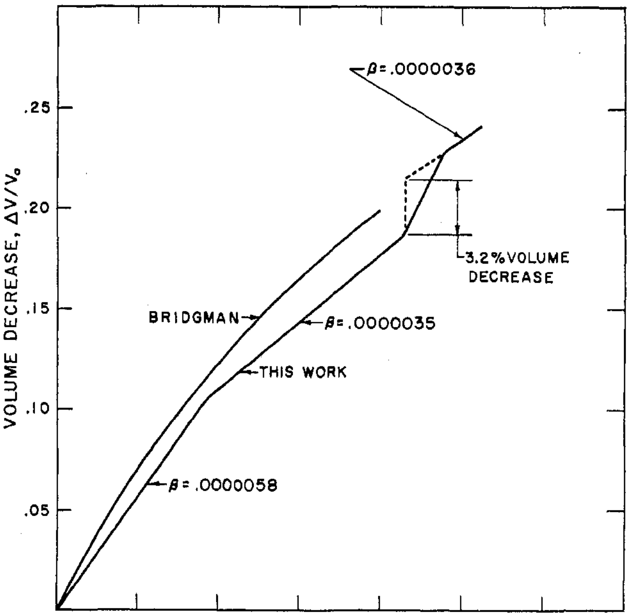

Fig. 2.—Comparison of Bridgman compressibility data for Yb with compressibility data from this study.

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(3) H. T. Hall, *Rev. Sci. Instr.*, **29**, 267 (1958).
(4) H. T. Hall, *ibid.*, **31**, 125 (1960).
(5) H. T. Hall, *ibid.*, **33**, 1278 (1962).

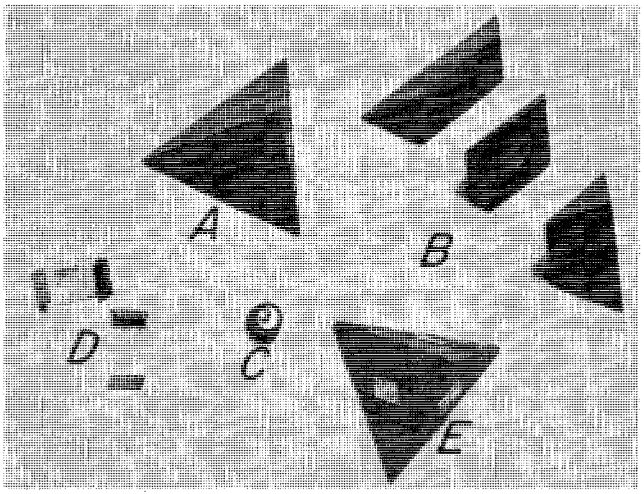

Fig. 3.—Components of tetrahedral cell: A, solid lava tetrahedron; B, central slab (with hole) and end pieces; C, silver chloride cylinder containing calibration wire connected to silver end disks; D, metal connecting tabs; E, assembled tetrahedral cell.

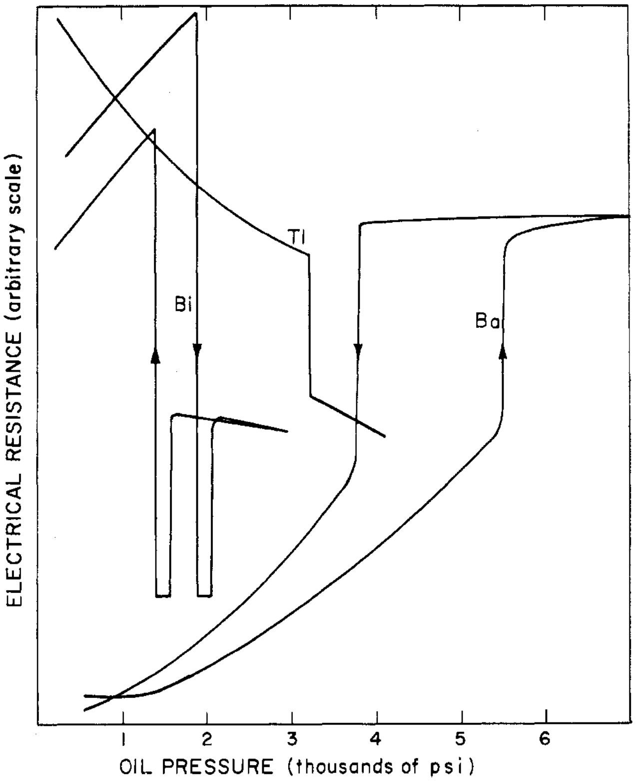

Fig. 4.—Relative electrical resistance of Bi, Tl, and Ba *vs.* ram oil pressure for tetrahedral press as used in this research.

tabs which in turn made electrical contact with the anvils. The assembled cell was held together with Borden Company's "Elmer's Glue All" used sparingly and judiciously. The external surface of the completed cell was painted liberally with a thin paste of rouge (Fe_2O_3, red iron oxide) suspended in ethyl alcohol to produce a coating about 0.010 in. thick. The assembly then was dried in an oven at 90–100° for 2 hr. and kept in a desiccator until used.

Resistance readings were taken with a Kelvin double bridge connected to the appropriate anvils. Readings in the vicinity of transitions were taken at 10 p.s.i. oil pressure intervals. Oil pressure was measured by a 12-in., 0–10,000 p.s.i. precision Heise Bourdon tube gage. About 0.5 hr. was taken to pass through the vicinity of a Bi, Tl, or Ba transition in order to ensure that equilibrium conditions were approached. Several separate runs were made on each calibration material. The oil pressures required to obtain the transition in all runs were found to not vary from each other by more than 1%. The oil pressure required to obtain the transition was taken at the mid-point of the best straight line that could be drawn (by eye) through the steep portion of the transition. Resistance curves for the calibrating metals are shown in Fig. 4. Hysteretic phenomena, mainly in the pyrophyllite, and, to a lesser extent, in the calibrating metal itself, are responsible for the disparity between ascending and descending curves. In general, measurements are always made with increasing increments of pressure, and the pressure calibration graph (Fig. 5) shown for the tetrahedral press and cell assembly used in these experiments is valid for increasing pressure only.

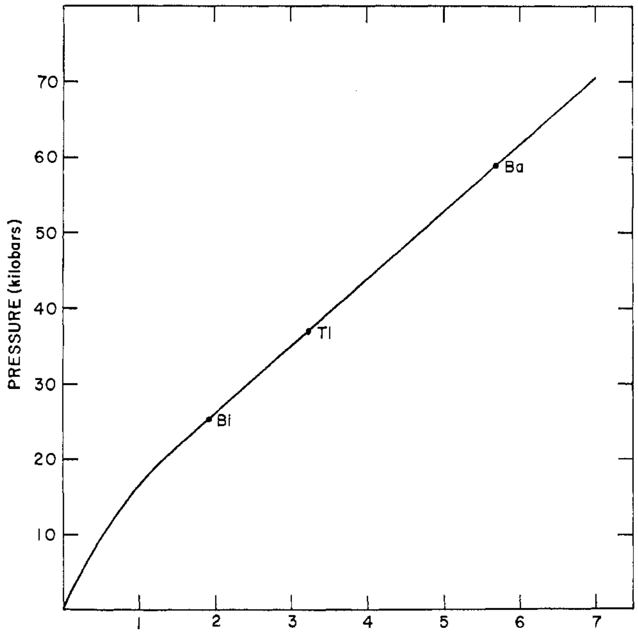

Fig. 5.—Pressure calibration curve for tetrahedral press and cell assembly used in this research.

The 0.188-in. diameter by 0.100-in. long cylindrical space (0.00276 in.^{3}) occupied by the silver chloride and its axial pressure sensing wire was the "working volume" of the tetrahedral cell used in these experiments. This was 2.34% of the initial (1 in. on edge) tetrahedral volume and 5.55% of the volume of a tetrahedron formed by the completely closed anvils (0.75 in. on edge). Because the working volume was only a small percentage of the total tetrahedron volume, the average pressure exerted on the surface of a specimen, initially filling this volume at 1 bar, would be given by the calibration curve of Fig. 5, even though the compressibility of the specimen may have differed widely from that of the silver chloride used to fill this space during calibration. In the cell arrangement just described, a rather uniform pressure is distributed over the sample surface and distortion of the sample is small.

In the above cell arrangement, material occupying the working volume is heated indirectly by passing an electrical current through thin metal or graphite-cloth strips occupying positions akin to those of the metal connecting tabs shown in Fig. 3. If the sample is electrically conducting or disposed to react with the heating strip, a thin sheet of isolating material is interposed between the heater and the ends of the sample. If the sample is a poor thermal conductor, it usually is desirable to encase it in a good thermal conductor to facilitate heat transfer to the sample from the strip heaters. It is desirable to utilize heating strips with relatively high electrical resistance in order to reduce the current density at the juncture of anvil and heating tab. High local heating, caused by high current densities in this region, causes cracking and breaking of the carbide anvils.

Although the pressure calibration is carried out at room temperature, the same calibration is utilized when the sample is subjected to high temperature at high pressure. This is necessary because a satisfactory procedure has not yet been devised for establishing a pressure calibration at high temperature. Reasonable estimates, however, indicate that pressure changes due to temperatures as high as 1500° in a sample cell such as that described above probably can be neglected when compared to other uncertainties.

Rate Studies on 40 kb. Transition

The initial resistance experiments showed the transition responsible for the large drop in electrical resistance to be quite sluggish. Consequently more than 30 individual tetrahedron samples were prepared and run to determine the minimum pressure at which the transition would begin and the effect of "overpressing" on the rate of transition. Because of the sluggishness of the transition, some experiments were of more than 20 hr. duration.

The minimum pressure required for onset of the transition was best determined by recording Yb resistance from the output of a Kiethley Instruments Model 503 milliohmeter. As the transition was approached, oil pressure was increased in 10 p.s.i. increments. At each pressure, resistance was recorded for a 10-min. period. The pressure at which the recorder gave the first indication of a resistance drop after the 10-min. period was taken as the minimum pressure, P_m, required for onset of the transition. This pressure was found to be 39.5 kb.

The effect of overpressure on the rate of the transition was explored by increasing the pressure to about $0.90P_m$, followed by rapidly increasing pressure to $1.05P_m$, $1.10P_m$, $1.15P_m$, etc. The pressure then was held constant while the change in electrical resistance was recorded. Making the assumption that the fraction of Yb converted to the high pressure form was proportional to the fractional change in resistance, it was possible to obtain linear plots on a log time *vs.* pressure scale with fraction converted as parameter.

The series of straight lines obtained converged at time = 6.5×10^6 min. and P = 35.7 kb. At 1 min. time the % conversion lines intersected the pressure axis as follows: 10%, 43.0 kb.; 50%, 44.0 kb.; 60%, 44.1 kb.; 75%, 44.8 kb.; 90%, 45.5 kb.; 95%, 46.3 kb.; 98%, 47.4 kb. We have not been able to attach any physical meaning to the common intersection of the lines. The fact that overpressure increases the rate of the transition indicates that the activated state probably occupies less volume than the initial state. At 1 bar, 1 g.-atom of Yb occupies a volume of 24.8 cm.^{3}. At the transition pressure the untransformed material occupies a volume of 20.1 cm.^{3}/mole while the transformed Yb occupies a volume of 19.5 cm.^{3}/mole. Reaction rate theory indicates that the slope of the above straight lines should be of the order of $\Delta V^*/RT$ where ΔV^* is the experimental volume of activation, R is the molar gas constant, and T is the temperature. Use of the expression gives $\Delta V^* = -31$ cm.^{3}/mole for the 10% conversion line and -17 cm.^{3}/mole for the 98% conversion line. Again, these values seem to escape physical interpretation.

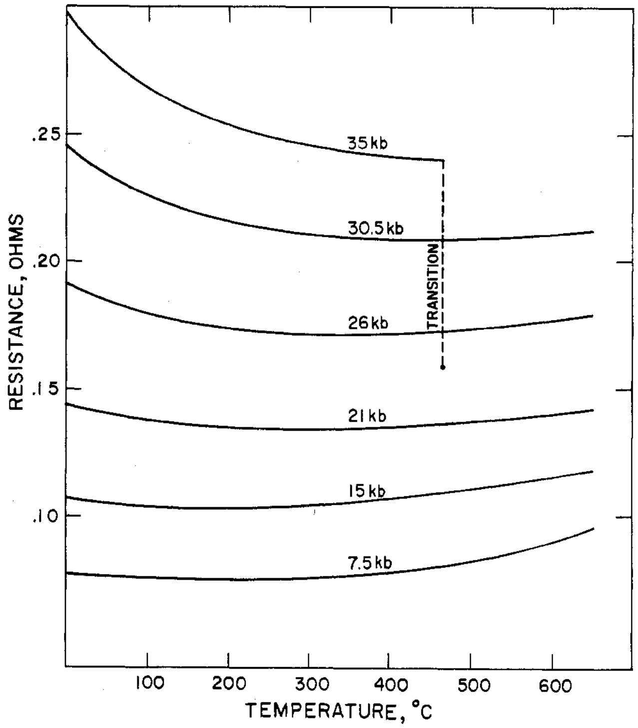

Fig. 6.—Electrical resistance of Yb as a function of temperature with pressure as a parameter.

Effect of Temperature on Electrical Resistance

If, with pressure as parameter, the electrical resistance of Yb as a function of temperature is measured, the curves shown in Fig. 6 are obtained. At 1 bar, the electrical resistance remains relatively constant near room temperature, but then develops a strong positive temperature coefficient at higher temperature. As pressure is increased, the resistance begins to show a decrease with increasing temperature followed by increasing resistance. The initial negative temperature coefficient becomes more and more pronounced as the pressure becomes higher. The abrupt electrical discontinuity that occurs at 39.5 kb. at room temperature is shifted to lower pressures with increasing temperature. Also, with increasing temperature the change in resistance at the transition decreases until it vanishes at about 1000°. The slope of the transition line, $\Delta P/\Delta T$, is -19.1 bars/deg. Compressibility measurements, to be discussed later, give $\Delta V = -0.65$ cm.^{3}/g.-atom. These data, coupled with the Clapeyron equation, indicate a latent heat absorption for the transition of 89 cal./g.-atom at 39.5 kb., 25°. The negative temperature coefficient of electrical resistance indicates, of course, that under the pressure and temperature conditions where this prevails Yb is a semiconductor. Consequently, in these regions the bonding between atoms tends to be directional (covalent) in character. On the other hand, bonding tends to be nondirectional (metallic) in character in the positive temperature coefficient regions.

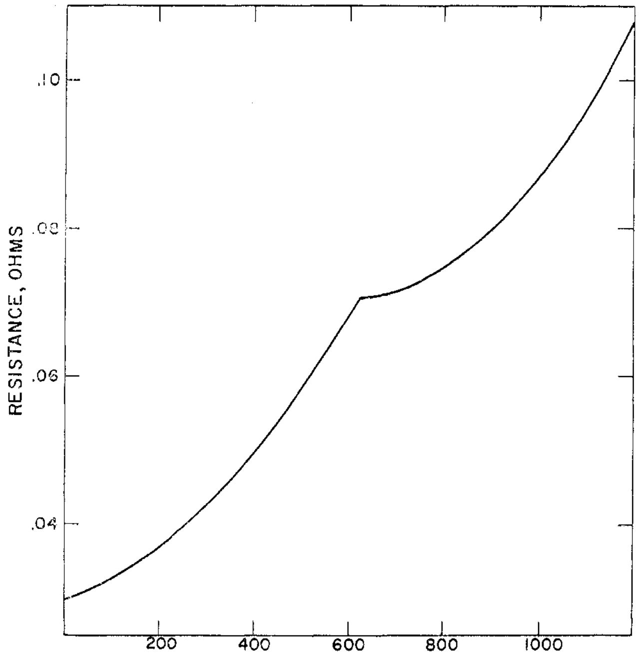

Fig. 7.—Electrical resistance of Yb as a function of temperature at pressures of 40–70 kb.

Observation of the electrical resistance curve of Fig. 1 suggests that a "second order" transformation occurs in the vicinity of 18 kb., where upward curvature is changing over to downward curvature. Confirmation that the change in curvature corresponds to a transition is available from compressibility measurements wherein a change in compressibility is noted at the same pressure as that required to reverse the curvature in the electrical resistance measurements.

At pressures above the 39.5-kb. transition, electrical resistance measurements as a function of temperature reveal still another transition occurring at about 625°. This is shown in Fig. 7. Pressures to 70 kb. have a negligible effect on shifting this transition temperature. Figure 7 also reveals that, over the range covered, the Yb bonding is metallic in character above the 39.5-kb. transition.

Hysteresis

Of all the metallic materials for which we have determined the pressure effect on electrical resistance, Yb displays the greatest room temperature hysteretic effects. Curve C of Fig. 1 shows the electrical resistance measured as hydraulic ram thrust is reduced on a specimen in the tetrahedral press. Of course, a portion of the hysteresis (approximately 35%) is due to the confining strength of the pyrophyllite. The remaining hysteresis, however, is due to the intrinsic sluggishness of the reverse Yb transition. We have found higher temperatures to decrease considerably the amount of hysteresis. Also, as would be expected because of the reduced hysteresis, the relative resistance rise on passing through the reverse transition is greater at high temperatures. It is quite possible that the high pressure phase would transform at such a slow rate if kept at low temperatures that it could be "captured" for study at 1 bar pressure.

Pressure–Volume Measurements on Yb

A double-ended simple piston and cylinder apparatus was used to determine the volume of Yb as a function of pressure at room temperature.[2] The tungsten carbide pistons and chamber contained 6% cobalt binder; the piston diameter was 0.375 in. Piston and cylinder were both lubricated by a 0.0002-in. thick coat of molybdenum disulfide, silicone bonded paint (Molykote M-88). Clearance between coated piston and cylinder was 0.0002 in. The only seal provided was a "dished," 0.005-in. thick by 0.375-in. diameter disk of nickel (punched from cold-rolled, unannealed strip) placed against the tip of each piston. As the pistons pushed these disks against the sample, the disks flattened. Therefore the edges of the disks were forced tightly against the cylinder wall. This simple seal prevented extrusion of Bi or Yb between piston and cylinder. An Elmes 300-ton hobbing press with 12-in. diameter ram provided thrust for driving the carbide pistons.

Sufficient sample was weighed out to form a cylinder about $^3/_8$ in. long when compressed into the chamber. To check the operation of the apparatus, four runs were made on bismuth metal. An Ames dial gage, readable to 0.00001 in., was used to measure the decrease in distance between the upper and lower platens of the press as a function of hydraulic oil pressure. Readings were taken at 5 p.s.i. intervals in the vicinity of phase transitions and at intervals of 10 p.s.i. elsewhere. Measurements were made with both increasing and decreasing pressure. A "blank" run was made with substitution of a tungsten carbide cylinder 0.375 in. in diameter by $^3/_8$ in. long for the bismuth. Everything else remained unchanged. Deflections measured in the blank run were subtracted from corresponding deflections obtained for bismuth. This procedure corrected for compression of the pistons, backing blocks, etc. A small additional correction for compression of the blank and a correction for expansion of the carbide cylinder also were made. These corrections were of opposite sign and were almost identical in magnitude.

Typical curves resulting from the above procedure are given in Fig. 8 (curves A and B). Curve A was obtained with increasing oil pressure; curve B with decreasing. The difference in the curves is attributed to friction between the carbide pistons and cylinder, the solid sample and the cylinder, and to friction in the hydraulic ram. With increasing oil pressure, friction hinders the advance of the pistons, thus requiring a higher oil pressure to produce a given pressure within the sample than would be required in a hypothetical, frictionless system. When oil pressure is decreased, friction hinders retraction of the pistons, thereby causing the pressure within the sample to be higher than in a frictionless system.

These opposite effects are of approximately the same magnitude. Therefore, the correct curve would lie midway between the ascending and descending curves. The correct curve is obtained by a rectilinear superposition of the ascending curve over the descending curve so as to obtain the best possible correspondence. (The upper, rounding part of the descending curve is ignored since this is a "backlash" region in which frictional forces are reversing direction.) An average curve then is drawn through the superimposed curves. The coordinates of the average curve then are shifted one-half the amount initially required to superimpose the ascending over the descending curve. The resultant curve is shown as curve C in Fig. 8, and represents the true compression of bismuth. Compressibilities are calculated from curve C by first shifting the scale to zero, where the curve intersects the Y axis. Then, at a given pressure, the corresponding deflection is read from the Y axis. This deflection when divided by the initial length (0.372 in.) of the Bi cylinder gives the compressibility, $\Delta V/V_0$.

The four bismuth compressibility runs agreed with each other within ±1% and also agreed within ±1% with results previously given by Bridgman[6] over the range to 40 kb. Our experiments gave an average value of 25.3 ± 0.3 kb. for the Bi I–II transition.

Ytterbium was run in an identical manner with that used for Bi. However, the procedure used to correct for friction in the case of Bi could not be used for Yb because of the large, intrinsic hysteresis previously mentioned in the resistance measurements. As an approximation, we have assumed that the correction used for Bi would be approximately correct for Yb since the runs were identical except for substitution of Yb for Bi. With this assumption, the curves of Fig. 9 represent the true compression of Yb and show the extent of the intrinsic hysteresis in this material. Calculation of compressibility from these curves would be carried out in the same manner as described for Bi.

Portions 1, 2, T, and 3 of the ascending curve correspond to 1′, 2′, T′, and 3′, respectively, on the descending curve. Sections T and T′ are thought to correspond to the 39.5-kb. resistance transition.

The actual piston load required to traverse T ran from about 40 kb. through 53 kb. These pressures lie in the upper useful range of this apparatus and considerable breakage was experienced. Because of this problem and because of the importance of minimizing the plastic flow of the carbide pistons occurring at this pressure level, only 15 min. was utilized in passing from 40 to 53 kb. (The same amount of time was used in decreasing the pressure through this region in order to avoid the breakage that often occurs when unloading occurs too rapidly.) It is quite likely that the transition T would take place over a more limited pressure range if additional time could be allowed in passing through this region. Also, T′ undoubtedly could be sharpened by releasing pressure more slowly (10 min. was taken to pass through this region). Maximum pressure, followed by unloading without breakage, was achieved in three runs. They all gave essentially the same results as shown in Fig. 9.

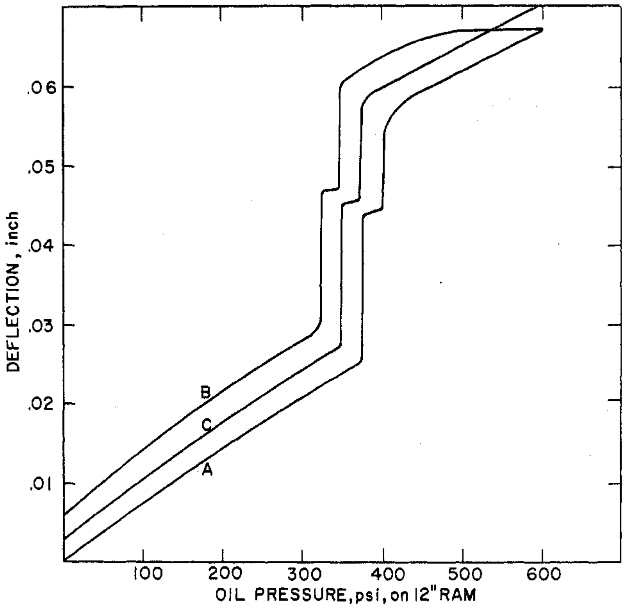

Fig. 8.—Fully corrected deflections for compression and decompression of Bi cylinder (0.375-in. diameter by 0.372 in. long) in double-ended, piston-cylinder apparatus (curves A and B). Center curve C has been corrected for friction.

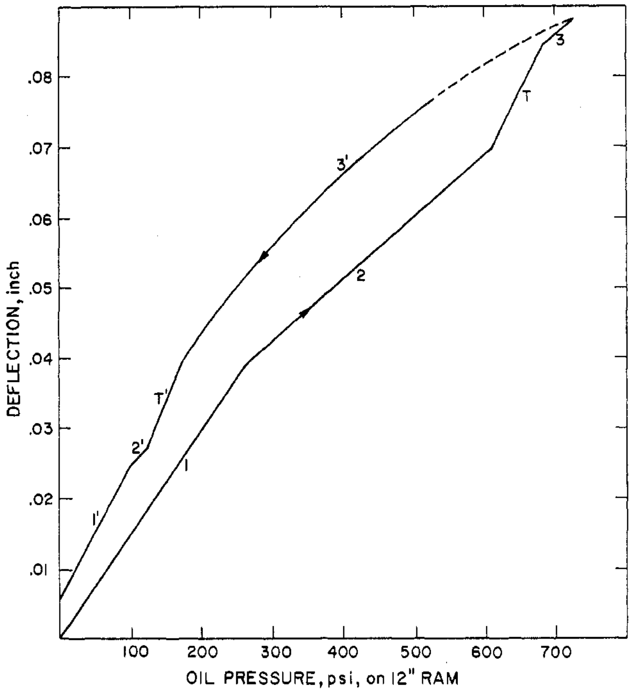

Fig. 9.—Compression and decompression of Yb (corrected for friction by the same amount as used for the bismuth runs).

Ytterbium Phase Diagram

Results obtained from the above experiments make it possible to delineate some features of a phase diagram for Yb. This is shown in Fig. 10. High pressure X-ray diffraction experiments (performed in this Laboratory; to be described elsewhere) have disclosed that

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(6) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **74**, 425 (1942).

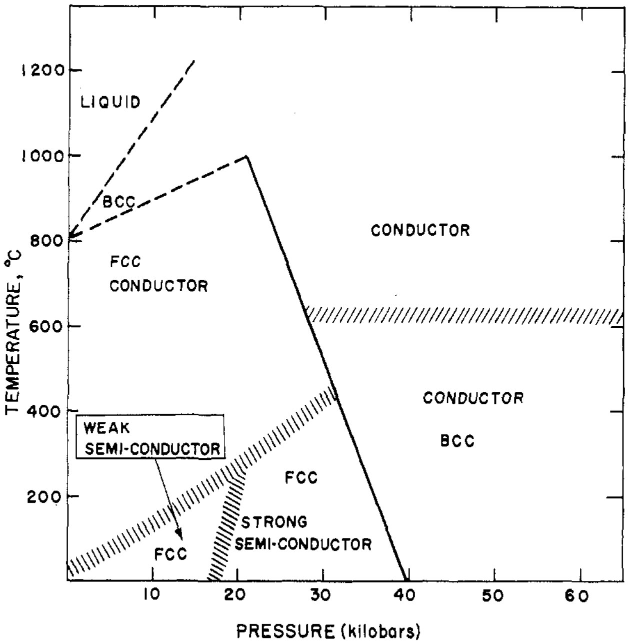

Fig. 10.—Partial pressure–temperature phase diagram for Yb.

the new phase appearing at the 39.5 kb., 25° transition has a body centered cubic structure. The original phase was face centered cubic. Electrical resistance measurements were made simultaneously with the X-ray diffraction measurements and unequivocally established the identity of the resistance transition with the phase transition. From Fig. 2 we note that Yb undergoes a macroscopic volume decrease of about 3.2% at this point. This, coupled with the change from FCC to BCC structure, means that an individual, spherical Yb atom shrinks in volume by 11.1% on passing through this transition. This volume decrease probably is associated with an electronic transition; namely, the promotion of a 4f electron to the conduction band. The atomic radius of the FCC modification at 39.5 kb. and 25° is 1.82 Å. (unit cell dimension is 5.12 Å.). The atomic radius of the BCC modification at 39.5 kb. and 25° is 1.75 Å. (unit cell dimension is 4.02 Å.). It is of interest to note that the 1 kb., 25° radius of Yb (1.940 Å.; valence +2) is anomalously large when compared with the radii of adjacent rare earths.[7] However, the 39.5 kb., 25°, BCC modification of Yb fits right on the rare earth radius *vs.* atomic number curve, making it a "normal," +3 valent, rare earth metal.

Europium is a rare earth with an anomalously large radius and a valence near +2. Consequently, high pressure studies on this element may be expected to give results similar to those for Yb. Cerium, which shows some of the anomalies of Yb, has been studied extensively at high pressure.[8] Cerium undergoes an electronic FCC to FCC transition at 7600 kb., undergoing about a 13% decrease in volume. High pressure X-ray diffraction studies conducted in our Laboratory confirm the experimental results of Lawson and Tang[9] that the crystal structure is face centered cubic both before and after this volume discontinuity. The pressure required to obtain the electronic transition in Ce decreases with decreasing temperature until the transition begins to take place at 1 bar when the temperature is lowered to −170°. In contrast to this, the electronic transition occurring in Yb requires a higher pressure as temperature is decreased (see Fig. 10).

If the Yb transition had been a FCC–FCC transition, as in the case for Ce, the individual Yb atoms would have only had to decrease in volume by 3.2% (same as macroscopic volume change). However, the FCC–BCC transition requires an 11.1% decrease in the size of the individual atoms, as already has been indicated. A pressure-induced transition of this type (close-packed to non-close-packed structure) has never before been observed.

The pressure induced BCC phase of Yb may be continuous with the temperature induced (798°, 1 bar) BCC structure. However, we have not as yet been able to establish with certainty the boundary between FCC and BCC phases in the 1–20,000 bar pressure range. For the present we have shown this boundary as a dashed line slanting upward from 798° at 1 bar to about 1000° at 20 kb. The melting line, likewise, has not yet been definitely determined.

Second order transition boundaries are shown in Fig. 10 as shaded bands.

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(7) See, for example, K. A. Gschneidner, Chapter 14 in "The Rare Earths," F. H. Spedding and A. H. Daane, Ed., John Wiley and Sons, New York, N. Y., 1961, p. 206, Fig. 14.7.

(8) For summaries of the results, see ref. 7, pp. 194–198 and 199–201.

(9) A. W. Lawson and T.-Y. Tang, *Phys. Rev.*, **76**, 301 (1949).