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High Pressure Electrical Resistance Cell, and Calibration Points above 100 Kilobars*

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A high pressure electrical cell is described consisting of tapered Carboloy pistons supported by a pyrophyllite pellet. The pistons are heavily work hardened. A calibration is obtained based on the barium transition at 59 kb, the bismuth transition at 90 kb, and an extrapolation of Bridgman's data. The pressure range is to 500 kb under favorable circumstances. New fixed points include a discontinuous rise in resistance of lead at 161 kb, a discontinuous rise in resistance of barium at 147 kb, a discontinuous rise in the resistance of rubidium at 193 kb, a maximum in the resistance of calcium at 370–75 kb, and a maximum in the resistance of rubidium at 425 kb. In addition, there is a discontinuous rise in resistance of iron at 133 kb which is consistent with the shock wave pressure point found at 131 kb and 37°C.

AN apparatus has been developed which permits the measurement of electrical resistance to pressures as high as 500 kb.

A number of previous investigators have measured the effect of pressure on electrical resistance. The most accurate measurements in the high pressure range to date have been those of Bridgman[1,2] in his 30 000 kg/cm^2 apparatus, using pentane as a pressure transmitting fluid. His data have been used for calibration in this work.

To extend the pressure range, Bridgman[3] used Carboloy pistons in the form of truncated cones 1 in. in diameter with a $\frac{1}{2}$-in. diameter flat. The pressure transmitting medium was silver chloride. With this apparatus he reached an apparent pressure of 100 000 kg/cm^2. There seems, however, to be a discrepancy in the pressure scales in the high pressure region as indicated by differences in the transition pressures of thallium, barium, and cesium obtained for resistance measurements and from p-v measurements.

Jura *et al.*[4] recently modified Bridgman's design by introducing a tighter press fit for the jackets surrounding the pistons. Pressures in the 400 kb range have been reported.

Bundy[5,6] has used the General Electric "belt" apparatus[7] to obtain the phase diagrams for bismuth and rubidium from electrical resistance measurements. He observed the VI–VIII transition in bismuth which is used as a calibration point in this work.

DESIGN OF CELL

Figure 1 shows a schematic diagram of the resistance cell. The grade 55A Carboloy insert is pressed into a Crucible La Belle HT steel jacket and ground for a tight slip fit on the Carboloy pistons which are 0.875 in. in diameter and $1\frac{1}{4}$ in. long. They are pressed into A1S1 4140 steel jackets. The pistons were ground with an 18° taper, leaving a flat 0.090 in. in diameter. One piston is ground 0.004 in. undersize to permit it to be insulated from the cell using 0.001-in. thick mica.

Grade 999 Carboloy pistons are always used for the moving piston, and generally for the stationary piston. (Grade 883 is occasionally used in this latter service, as discussed below.)

A pellet of the appropriate size and shape to give a center thickness of 0.012 in. is machined from pyrophyllite. This material was also used to seal the sample and silver chloride in the center (see Fig. 2).

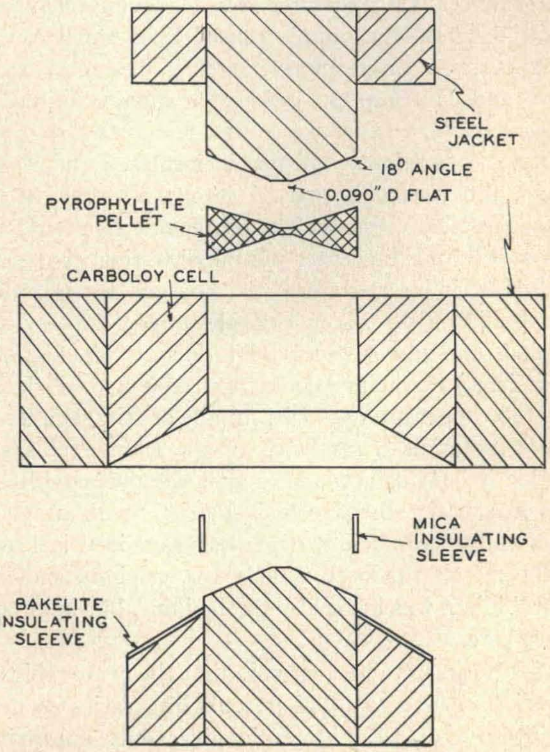

FIG. 1. Resistance cell—over-all schematic drawing.

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[1] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 72, 157 (1938).
[2] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 79, 125 (1951).
[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 82, 169 (1952); 83, 1 (1954); 74, 21 (1940).
[4] G. Jura, R. E. Harris, R. J. Vaisnys, and H. Stromberg, Proceedings of the Bolton's Landing Conference on Very High Pressure, June 1960 (to be published).
[5] F. P. Bundy, Phys. Rev. 110, 314 (1958).
[6] F. P. Bundy, Phys. Rev. 115, 274 (1959).
[7] H. T. Hall, Rev. Sci. Instr. 31, 125 (1960).

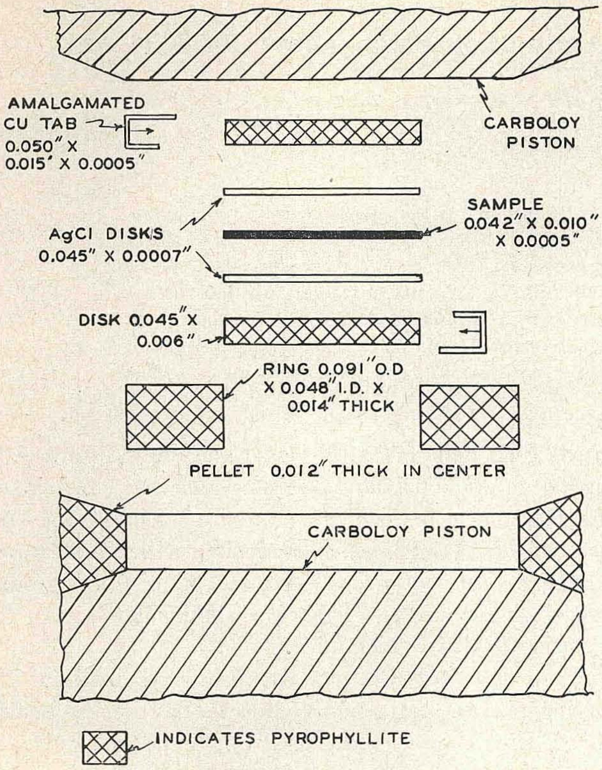

FIG. 2. Center assembly—high pressure resistance cell.

The force is applied with a home built press having 8-in. diam pistons. The stationary piston is insulated from the press by an 0.004-in. thick sheet of mica.

Resistances are measured by observing changes in potential across the sample caused by a small constant direct current. Electromotive force is measured using a Leeds and Northup potentiometer capable of measuring 1 μv.

After the stationary piston is insulated the weighed pyrophyllite pellet is pressed into the center at 2-kb average applied pressure. The center flat area is removed with a drill and the center pyrophyllite ring, coated with iron oxide, is inserted. Into the hole are fit, in order, a pyrophyllite disk, silver chloride plate, sample, silver chloride, and upper pyrophyllite disk. (See Fig. 2 for dimensions.) Secondary contacts of 0.0005-in. thick amalgamated copper are used with fragile or stiff samples. For ductile materials a sandwich of the sample plus silver chloride is bent as a whole around the pyrophyllite disk and contact with the pistons is made through an amalgamated copper tab. The two methods gave identical results for the metals run both ways (lead, calcium, and iron). The rubidium was loaded by method one, but in an argon atmosphere.

It is necessary to be very sure that the center thickness is precisely as desired. The pyrophyllite varies enough in density so that weighing it in gives only approximate thickness. The center thickness is accurately determined by inserting a series of ground metal cylinders of carefully micrometered height in the center hole after drilling and before loading.

After assembly 2-kb average pressure is applied to seal the center in. Resistance measurements were made in 0.2-−2.0-kb average pressure intervals.

The lowest center pressure at which satisfactory resistance measurements could be obtained varied from 30–80 kb.

The high pressure range obtained is due, in large part, to the possibility that Carboloy pistons could be work hardened considerably without damage. A new set of pistons is hardened using a pyrophyllite pellet with 0.015 in. center thickness. No silver chloride is used. Grade 999 pistons were hardened to 14-kb average pressure, grade 883 to 25 kb. The plastic deformation and degree of regrinding is illustrated in Fig. 3. Usually in making a resistance run both pistons were destroyed. In a few cases the stationary piston remained intact (this only occurred with a very few 883 pistons). The hardening procedure permitted an extension of the pressure range of from 75–100%.

A number of modifications of the design were tried including variations in piston diameter and tapers, center thickness, pressure transmitting medium and Carboloy grade (including the use of compound pistons). None of these proved as satisfactory as the design described above.

CALIBRATION

The basic data used for calibration of the cell include the barium and upper bismuth transition, the extrapolation of Bridgman's 30 000 kg/cm^2 data for lead, platinum, and indium, and a transition found in lead at 161 kb.

The bismuth and barium transitions were run repeatedly in optical apparatus described elsewhere.[8] The barium transition fell at 58–60 kb, and the bismuth transition at 89–92 kb. The values used were 59 kb for barium and 90 kb for bismuth.

It was found possible to correlate Bridgman's[1,2] resistance and p-v data measured in his 30 000 kg/cm^2 apparatus to

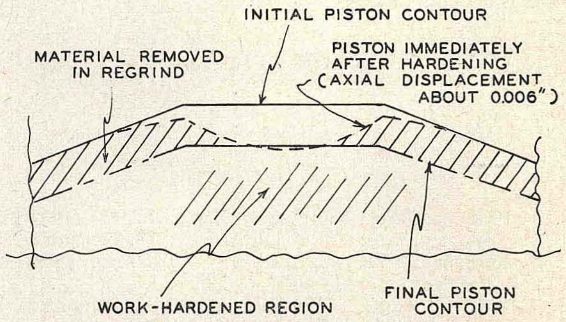

FIG. 3. Deformation of piston during hardening.

[8] R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, J. Opt. Soc. Am. 47, 1015 (1957).

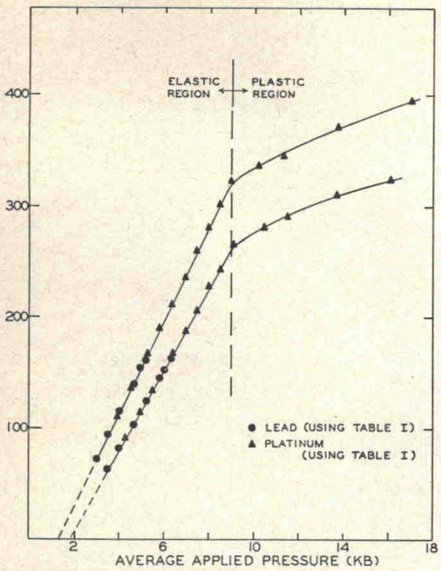

FIG. 4. Typical calibration runs for grade 999 work-hardened Carboloy pistons.

obtain slowly varying functions of density, either as ρ/ρ_0-1 vs R/R_0-1 or $[1-(v/v_0)]$ vs $[(R/R_0)-1]$ or as $\ln R_0/R$ vs $[(\rho/\rho_0)-1]$. The data were extended using the p-v data of Rice, McQueen, and Walsh[9] extrapolated to 25°C.

The extrapolated values of R/R_0 are shown in Table I for platinum, indium, and lead. These metals were chosen because their resistance-density curves varied less than did those for most metals, and because at least two different extrapolations gave consistent resistance changes at the higher pressures.

A transition was observed in lead exhibiting a 23.2% increase in resistance. Bismuth and lead were run consecutively using the same hardened pistons. The bismuth transition at 90 kb was used as a reference point. The lead data of Table I were than employed to calculate the transition pressure. The average of five sets of runs gave 161±3 kb. The calibration thus generated gave a straight line plot of center pressure versus applied pressure from 50–161 kb (see Fig. 4).

The calibration above 161 kb was obtained using the calculated resistance-pressure curves for platinum and indium of Table I. Using the same hardened pistons consecutive runs were made with lead and with platinum or indium. A plot of calculated center pressure versus average pressure was consistently linear to 9-kb average pressure (corresponding to 250-—350-kb center pressure, depending on the hardness of the particular piston set). Two typical sets of data are shown in Fig. 4. Above 9-kb average pressure significant plastic deformation occurred, but apparently in a consistent manner from set to set. Figure 5 shows the ratio of the center pressure for any applied average pressure to the center pressure at 9-kb average pressure.

TABLE I. Resistance (relative to zero pressure resistance) versus pressure-extrapolation of Bridgman's data.

P (kilobars)	R/R_0 (platinum)	R/R_0 (indium)
50	0.917	0.653
100	0.585	0.514
150	0.813	0.436
200	0.778	0.384
250	0.751	0.347
300	0.731	0.319
350	0.714	0.296
400	0.700	0.278
450	0.690	0.262
500	0.681	0.249

P (kilobars)	R/R_0 (lead)
30	0.704
60	0.556
90	0.478
120	0.425
150	0.386
161	0.374

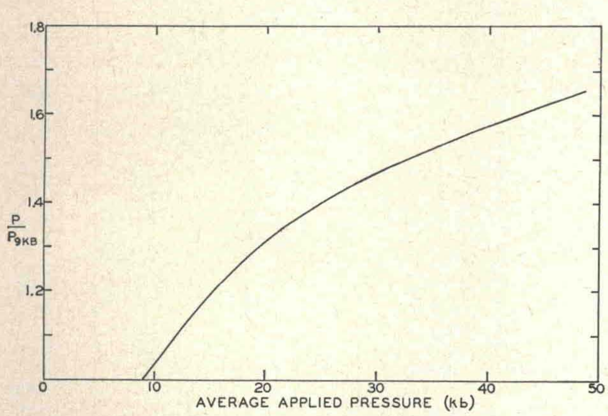

FIG. 5. Calibration—(pressure at center)/(pressure at center for 9 kb av pressure) versus average pressure.

The procedure used in operation is to harden a set of pistons and run the lead resistance, thus obtaining a straight line which is extrapolated to 9-kb average pressure. The curve of Fig. 5 is used to obtain the higher pressures. The sample is then run on the same pair of pistons. It is necessary to use great care to ensure that the center thickness is the same for the lead run and the sample run.

RESISTANCE OF LEAD, IRON, BARIUM, CALCIUM, AND RUBIDIUM; NEW CALIBRATION POINTS

Figure 6 shows the resistance of lead to 230 kb. The data were normalized at 90 kb and, from 90–161 kb, represent the extrapolation in Table I. The transition was reversible although the high pressure phase showed great metastability on release of pressure, as indicated by a rise

[9] M. H. Rice, R. G. McQueen, and J. M. Walsh, *Solid State Physics* (Academic Press, Inc., New York, 1958) Vol. 6, p. 1.

of resistance considerably above the maximum with increasing pressure. ("Reversibility" is used throughout this section to describe phenomena such as are shown in Fig. 11. Due to irreversible deformation of the pyrophyllite, the pressure calibration does not apply on releasing applied pressure.) The 23.2% increase across the transition is the average of 22 runs.

Since lead is in the face-centered-cubic structure at atmospheric pressure, the transition is probably electronic in nature.

Figure 7 illustrates the resistance of iron to 425 kb. A transition (almost certainly the $\alpha \rightarrow \gamma$ transition) was observed at 133 kb $\pm 1.5\%$ on four runs (the temperature was about 20°C). The resistance change below the transition was fit to an extrapolation of Bridgman's[1,2] 30 000 kg/cm² data as discussed for lead, etc. The calculated resistance increase across the transition was 366%.

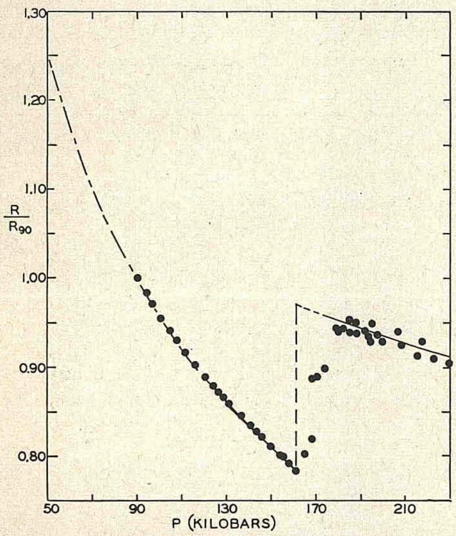

FIG. 6. (Resistance at P)/(resistance at 90 kb) versus pressure—lead.

The transition pressure of 133 kb at 20°C agrees very well with the shock wave results for iron (131 kb–37°C).[10] This also gives confirmation of our extrapolated pressure scale. The results do not agree well with those of Strong[11] although it is not certain that we are using the same transition "point."

The effect of pressure on the resistance of barium is shown in Fig. 8. After the transition at 59 kb the resistance rises linearly to 144 kb where a second transition occurs with an increase of 42% in resistance. Above this point the relative resistance decreases. Both transitions are reversible. The data shown are the average of four runs. The change of resistance across the 59-kb transition was fitted to Bridgman's data.

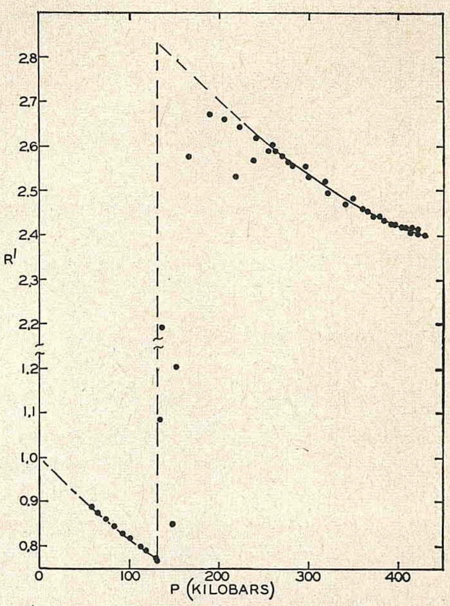

FIG. 7. Relative resistance versus pressure—iron.

Figure 9 shows the relative resistance of calcium to 525 kb. A maximum occurs at 375±15 kb obtained as the average of four runs. Points below 100 kb were difficult to obtain with accuracy for calcium (and rubidium) and are not shown. Because of this difficulty and the relatively large corrections used by Bridgman for these substances, no attempt was made to fit with his data, and the points are shown uncorrected. The resistance at 375 kb is 6.78 times the resistance at 100 kb.

The effect of pressure on the resistance of rubidium is shown in Fig. 10. In this case also the data are uncorrected. A transition occurs at 193 kb with a 147% increase in resistance. The resistance just before the transition is 3.31

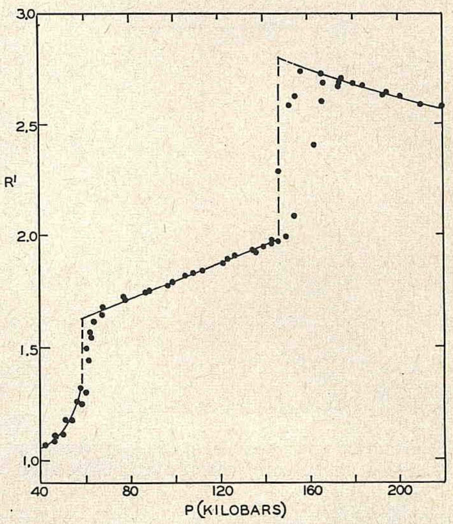

FIG. 8. Relative resistance versus pressure—barium.

[10] D. Bancroft, E. L. Peterson, and S. Minshall, J. Appl. Phys. **27**, 291 (1956).

[11] H. M. Strong, Proceedings of the Bolton's Landing Conference on Very High Pressures, June, 1960 (to be published).

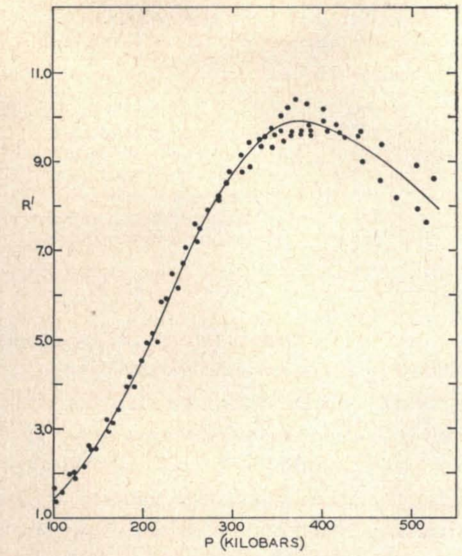

FIG. 9. Relative resistance versus pressure—calcium.

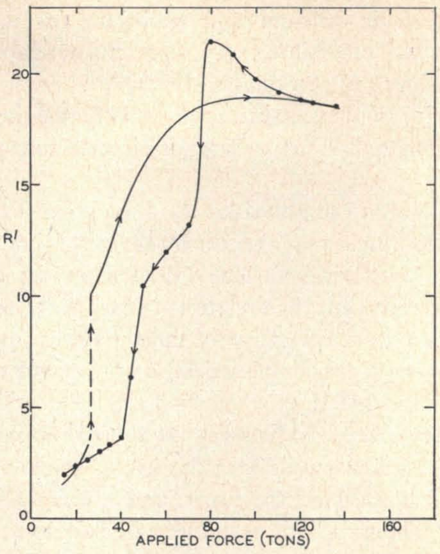

FIG. 11. Relative resistance versus pressure (increasing and decreasing pressure)—rubidium.

times that at 100 kb. Above the transition a maximum in the resistance occurs at 425 kb. Both maximum and transition are reversible as shown in Fig. 11. The metastability is illustrated by the sharp rise with decreasing pressure and the displacement of the maximum to lower pressures. Calcium showed qualitatively similar behavior.

Bundy[6] observed a transition in rubidium at 107 kb (75–80 kb on our scale), accompanied by an increase of 8–10% in resistance. Because of the rapid rise in resistance and our difficulties with pressure in this range it is impossible to say whether it occurs in our samples.

A phenomenon of interest occurs immediately above the maximum in both calcium and rubidium. As an increment of pressure is applied the pressure rises slightly and then drops to a steady value. As one gets well beyond the maximum this phenomenon disappears.

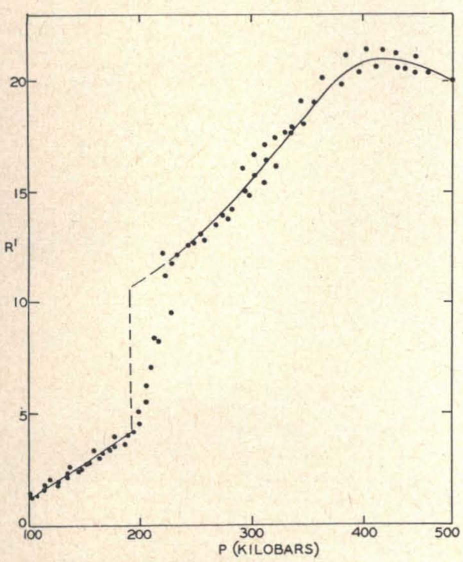

FIG. 10. Relative resistance versus pressure—rubidium.

The results obtained at higher pressure for barium, calcium, and rubidium help explain their anomalous low pressure behavior and aid in predicting the possible behavior of other metals. Sternheimer[12] explains the transition in cesium as a discontinuous increase in the *d* character of the valence electron. Lawson[13] explains the large increase in resistance near the transition as due to scatter of conduction electrons into vacant *d* states whose density at the Fermi surface increases with pressure. Lawson also indicates that the anomalies in cerium and ytterbium are due to an increase (either discontinuous or gradual) of the *d* character of the 4*f* electrons. Manning and Krutter[14] show that the *d* band of calcium overlaps the first Brillouin zone at 1 atm; the overlap increases with decreasing interatomic distance.

It appears that all metals which have a vacant *d* band at energies slightly above the filled levels of conduction band at 1 atm may exhibit qualitatively similar behavior. It is proposed that the transition in rubidium and the 144-kb transition in barium are electronic in nature, qualitatively similar to the transition in cesium. The maxima in calcium and rubidium have some of the characteristics of gradual transitions as noted earlier.

In general, the behavior of this class of metals may be due to the fact that in the lower pressure region the increase in vacant *d* states at the Fermi surface is controlling. At sufficiently high pressures the stiffening of the lattice determines the change of resistance. It is not certain whether the latter extreme has been reached in any metals studied.

[12] R. Sternheimer, Phys. Rev. **78**, 235 (1950).
[13] A. W. Lawson, Progr. in Metal Phys. **6**, 1 (1956).
[14] M. F. Manning and H. M. Krutter, Phys. Rev. **51**, 761 (1937).

The maxima in calcium and rubidium (as well as in strontium and ytterbium) may represent overlap with the first set of levels of predominantly *d* character. In this case the behavior of the resistance beyond the maximum may still be anomalous. Further work is planned to explore this point.

In Table II are summarized the fixed points established in this work (including also the 90-kb transition noted by Bridgman[3] and Bundy[5]). The values listed for the sharp transitions represent the pressure of onset of the transition. This appeared always as a very sharp point. ($\frac{1}{4}$ to $\frac{1}{2}$ of the transition could be completed in 5 kb beyond the point indicated in Table II.)

The main differences between the present apparatus and normal Bridgman anvils are; the use of smaller flat size, the use of support on the taper, and a greater degree of work hardening, which is made possible by the other changes.

The small center flat makes it possible to use smaller blocks of Carboloy (allowing greater Carboloy uniformity) and also a smaller press. On the other hand, the smaller flat size increases markedly the difficulty of loading.

The method of calibration is subject to criticism and possible error due to the gross extrapolation. However, the results are presented in a form such that it should be easy for future workers to translate our results in terms of their pressure scales. It should be pointed out that the extrapolations and calibration were quite consistent from run to run, and the iron transition checks shock wave work.

The pressures are undoubtedly not truly hydrostatic, so that the fractional changes of resistance may not be quantitative. The "fixed points" should, however, be quite accurate, and it appears to the authors that any pressure calibrations in the higher range will be determined by fixed points.

TABLE II. Calibration points.

Elements	Pressure (kb)	Character of change	
Bismuth	90	Sharp drop in resistance	250–300%
Iron	133	Sharp rise in resistance	366%
Barium	144	Sharp rise in resistance	42%
Lead	161	Sharp rise in resistance	23.2%
Rubidium	193	Sharp rise in resistance	147%
	425	Maximum in resistance	
Calcium	375	Maximum in resistance	

ACKNOWLEDGMENTS

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