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PRESSURE-TEMPERATURE-RESISTANCE properties of Lanthanum, Bismuth Neptunium, Plutonium, and Americum to 450°C and 30kb.

D. McWhan, P. W. Montgomery, H. D. Stromberg and G. Jura

August 1961

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University of California, Berkeley, California

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ABSTRACT

The actinide elements neptunium, plutonium, and americium are materials of considerable interest to the high pressure investigator. The possibility of pressure induced electronic transitions such as those in cerium and cesium is suggested by the electronic configurations of the actinides. Such transitions are usually detectable by a discontinuous change in the electrical resistance of the sample. A matter of additional interest is the known one atmosphere polymorphism of plutonium with six allotropic forms between room temperature and its melting point, of neptunium with two allotropic forms, and a suspected allotropism in americium. The program therefore involved the following:

- development of apparatus capable of developing high pressures and temperatures which
  - could allow electrical resistance measurements to be made on milligram quantities of metal;
  - and was resistant to breakage or blowout which could contaminate the laboratory, permanent equipment and, of course, laboratory personnel.

APPARATUS

The apparatus, called the cavity anvil, is shown in Fig. 1. It consists of a shallow ½ inch diameter cavity in a hardened steel or tungsten carbide cylinder. The cylinder is supported with a steel jacket in the same fashion as the tungsten carbide inserts in the Bridgman type anvils.[1] The bottom of the cavity consists of a jam fit high speed tool steel plug, in order to alleviate rounded corner effects in the bottom of the cavity. The piston is of the same hardened steel as the bottom plug, being kept as short as possible, to obtain maximum column strength. Originally tungsten carbide pistons, bottom plugs, and cylinders were used, but they were prone to frequent breakage. Analysis of the breaks indicated that failure occurred due to tension stresses. The use of hardened steels with their higher tensile strengths has eliminated the breakage problem. Repeated runs to 30kb and 450°C did not result in any apparent serious deformation of the high speed steel components.

Electrical resistance is measured by a four lead technique using a two channel Leeds and Northrup Speedomax Recorder to record current and potential drop across the sample. Electrical contact can be made in two ways: one by spring loaded probes located on the bottom side of the cavity plug and directly on top of the piston by copper plates inserted between the anvils and the heat blocks. With the probe method the potential contacts are made at the ends of the probes and the current is brought in through a side contact on the probe to minimize end effects. When Cu plates are used the current and potential contacts are made on separate tabs. Iron-constantan thermocouples are located in the tips of both the top and bottom probes. Heat is supplied by an external heater. For safety and ease of transportation the cavity anvil, when assembled, is wrapped with .010" stainless steel sheet, secured with hose clamps. This

is insulated from the top and bottom by asbestos sheet. This allows radioactive metals to be loaded in glove boxes and then safely transported to the pressure laboratory.

An enlarged view of the sample cell is shown in Fig. 2. The metal sample is in the form of a fine wire or sliver mounted vertically in a disc of silver chloride which serves as the pressure transmitting medium. The silver chloride is coated with acrylic lacquer to prevent reaction with the metal. The metal should protrude very slightly (.001") on each side and be faced off with .001" platinum foil to improve electrical contact between the sample and steel. Sample lengths varied from .010" to .050" depending upon the amount of material available. The silver chloride disc is placed in the cavity inside an iron oxide coated pyrophyllite ring of the same height as the silver chloride. The pyrophyllite ring serves as a gasket, preventing extrusion of the silver chloride past the piston. The piston is insulated from the wall of the cylinder by coating with several coats of a mixture of iron oxide and Bisonite. The Bisonite is a phenolic resin having good high temperature properties, the iron oxide improves the mechanical strength of the coating which has a tendency to chip off on loading. There is .0025" radial gap between the piston and cylinder wall. It should be noted that it is important that the height of the ring match the height of the silver chloride disc. If this is not done the load will not be distributed evenly and erroneous pressures will be obtained. The radial thickness of the ring is not critical, in these experiments it was .032".

Calibration

In designing the cavity anvil it was hoped that by keeping the sample

cell and piston configuration as simple as possible there would be negligible friction so that the pressure in the cell could be calculated from the load exerted on the ½" diameter piston. The calibration was carried out using the transitions in Bismuth at around 25 kbs. The phase diagram for these has been carefully worked out by Bridgman[2] using a truly hydrostatic pressure chamber. Fig. 3 gives the phase diagram obtained in the cavity anvil superimposed upon that of Bridgman for comparison. For the I-II transition at room temperature the average transition pressure for 15 runs was 24.1kb with a scatter of ± 1.5kb. The temperature uncertainty is taken as ½ the difference between the top and bottom thermocouples which is generally less than 5 degrees. The I-II transition in bismuth is taken as the standard for calibration. The II-III transition provides a useful secondary check but in practice proves to be more sluggish and irreproducible.

Single crystal silver chloride is used to transmit pressure to the sample. It has a tendency to react with the metals involved in this study and during the calibration work pyrophyllite was used in one run at room temperature to determine its suitability as a pressure medium. Experience has shown that a good measure of the hydrostatic nature of a substance is the sharpness of the bismuth transitions in the material. Fig. 4 shows the results of two room temperature runs, one in silver chloride and the other in pyrophyllite. The spread of the transition in pyrophyllite ruled it out as a substitute for silver chloride. Qualitatively similar results to those of pyrophyllite were obtained when Teflon was used as the pressure transmitting medium.

One valuable feature of the cavity anvil is that it may be cycled up and down in pressure as often as desired. In this respect the cavity anvils

behave in a fashion similar to the conventional piston-cylinder apparatus, provided the pressure is above 6-8 kbars.

While calibrating the cavity anvil it was found that the AgCl disc, which holds the sample, forms an effective thermal barrier which upon suitable arrangement of the heater insulation allows thermal gradients as high as 20° to develop between the top and bottom thermocouples. Since it has not been possible to develop more than a 3° gradient when there is no AgCl in the cavity (piston to piston) it is reasonable to assume that the whole temperature difference between the thermocouples occurs across the sample. This fact allows rough measurements to be made of the thermal emf of the sample and the effect of pressure thereon. In the case of Bismuth the thermal emf was seen to go from 8 microvolts in phase I to approximately zero in phase II and III. The thermal emf measured is Bismuth-Tungsten Carbide superimposed on the Tungsten Carbide-Copper thermal emf where the leads leave the apparatus.

Neptunium

The neptunium used in this work was prepared by a lithium reduction technique and contained 0.015 wt percent calcium and .0015 wt percent lithium. The material required handling in a dry nitrogen atmosphere.

The room temperature resistance-pressure curve shows no evidence of transitions between 4kb and 27kb. In all, four runs were made on two different samples. The phase diagram in Fig. 5 shows the effect of pressure on the alpha-beta transition temperature which involves a transition from an orthorhombic to a tetragonal structure.

The very shallow slope of the extrapolated transition curve to one atmosphere gives a dP/dT of about 1.1kb per degree. Using the density values of Zachariasen[3] a heat of transition of 4.8 kilocalories per mole is obtained,

which is probably no better than 50% due to difficulties in estimating the small slope, and a $\pm 5^{\circ}$ uncertainty 1 atmosphere transition temperature.

Plutonium

The plutonium studied was 99^{+}% pure obtained from Los Alamos. Although there are seven polymorphic transitions between room temperature and its melting point at 640°C only the alpha-beta transition gave a resistance change large enough and sharp enough to establish the onset of a transition beyond doubt. Other features in the resistance temperature curves were observed but the small magnitudes involved, together with difficulties in pressure phenomena has led us to omit these details until further work clarified the complex situation present.

All data were taken by isobaric heating. The transitions were sharp, running over not more than 5°C. The transition temperature is taken at the onset of the transition with increasing temperature. A hysteresis of 30°C to 50°C between the alpha and beta transitions was observed by us as well as previous investigators at atmospheric pressure. Fig. 6 shows our work together with that of Bridgman[4] which was determined by volume measurements.

Bridgman's phase diagram was obtained by the method of piston displacement at constant temperature, the general idea being to manipulate the pressure to force the material to be approximately equally divided between the two phases. Two points were obtained at each temperature: a high pressure point at which the transition would just begin to run from beta to alpha, and a low pressure point at which the transition would begin to run from alpha to beta. The difference between these values is referred to as the "region of

indifference" by Bridgman.

In this work all points were taken by heating at constant pressure. The transition is sharp, running to completion within 10° at a heating rate of 2° to 5° per minute. No attempt was made to establish an equilibrium situation. In the one constant pressure run in which he cooled from beta to alpha Bridgman observed the same hysteresis found in this work.

The discrepancy between our work and Bridgman's is probably attributable to two impurity effects. Bridgman's material was the best available in 1945 but contained around 0.1 wt % impurity. In addition Bridgman encased his plutonium in a lead capsule. It is possible that alloying effects at the temperature of the alpha-beta transition between the lead and the plutonium effected the results. Another possibility is, of course, the fact that the initial volume changes may not correspond to the initial change in resistance.

Americium and Lanthanum

Americium was of interest to us because early x-ray studies indicated that it existed in both an expanded and collapsed double hexagonal close packed structure with the expanded form being the low temperature form. This is similar to the situation in cesium where it is believed that the collapsed structure involves an electronic transition from the 6s to the 5d level.

Americium was studied using both isothermal compressions and isobaric heatings. No reproducible feature was detected at room temperature from 4kb to 36kb. Americium proved to be very sensitive to heating. The resistance behavior became erratic and rose irreversibly above 70°C. On at least one occasion the resistance increased by a factor of a thousand. We could not establish whether this was due to chemical or metallurgical changes in the americium. The sample was always clean and shiny when removed from the acrylated AgCl and did not show evidence of oxide in its x-ray pattern.

At very high temperatures americium goes into a face centered cubic phase and early in this work we decided to look at lanthanum which undergoes a hexagonal to face centered cubic transformation at 310°C (atmospheric pressure). This involves a negative volume change and was therefore believed to be the same transformation observed by Bridgman in his compressibility studies at room temperature and 24Kb. Bridgman was unable to detect this transition using resistance measurements.

The lanthanum used in this work was 99+% pure and was loaded in a nitrogen atmosphere. The phase diagram is shown in Fig. 7. Above 13Kb the transition could not be detected in our measurements. The reason for this is shown in Fig. 8, where the relative change in resistance at the transition, $\frac{\Delta R}{R}$, is plotted as a function of pressure. It falls rapidly and drops below the limits of detection by 14Kb. That the transition still occurs is shown by the point at room temperature, due to Bridgman's compressibility work. Fig. 9 shows the resistance-temperature curve for La at 4-4Kb.

It is interesting to note that after being heated from the alpha to the beta phase, the transition could not be seen on cooling, nor could it be found on subsequent heating. This change in subsequent compression of lanthanum was observed by Bridgman[5] in isothermal compressions.

Key to Fig. 1

A: Ferrovac 609 steel heat treated to a hardness of Rc 48-50.

B: Tungsten Carbide (6% Cobalt Binder) or Rex AA toolsteel hardened to Rc 64. The "Fracture Line" is the point at which the cylinder eventually fails. This failure can be delayed by grinding the bottom of the jacket back so that the cylinder protrudes about .020". If this is done the Cavity Anvil may be used after fracture occurs without any noticeable effect on the results.

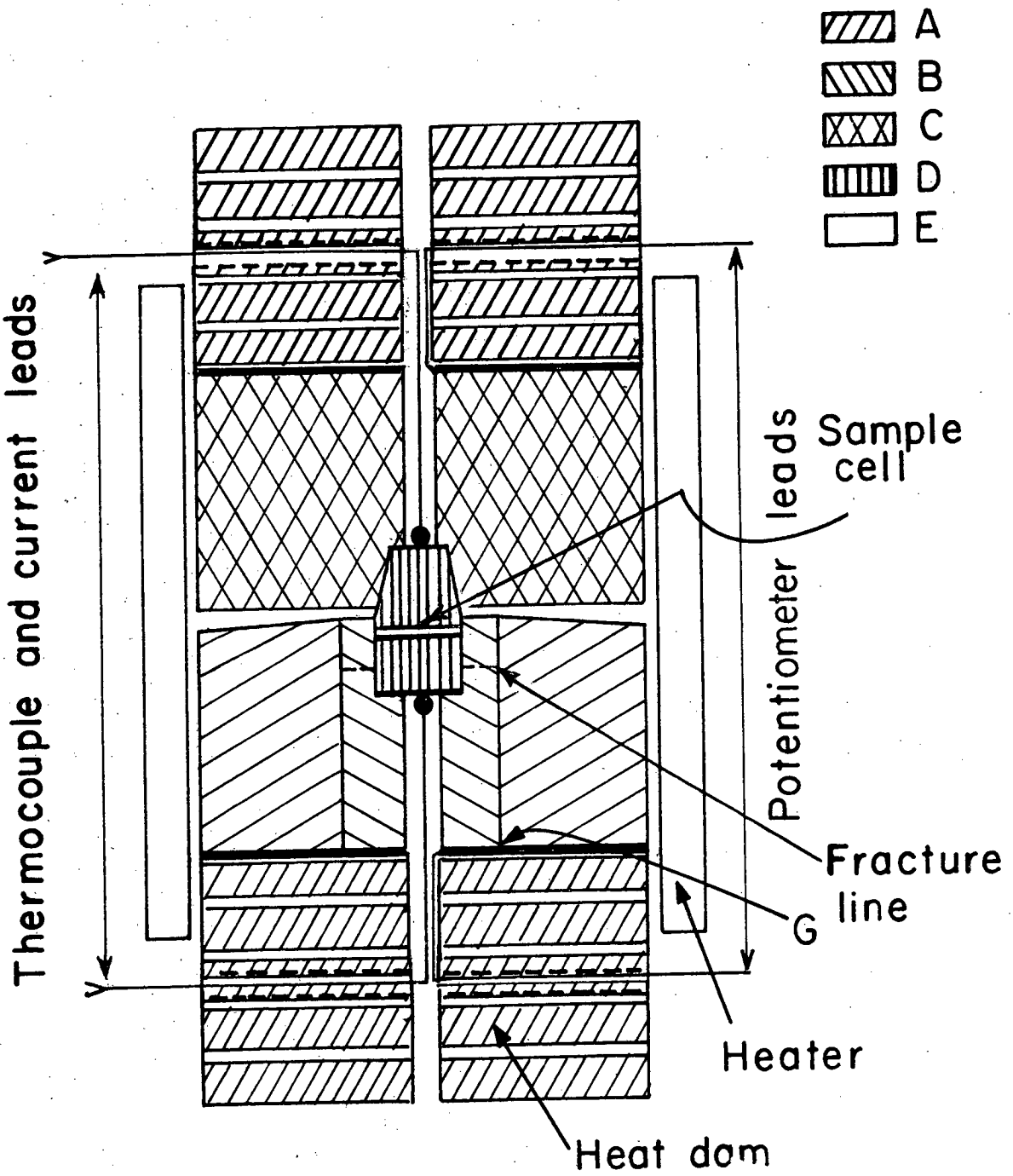
C: Ferrovac 609 steel heat treated to a hardness of Rc 52-54.

D: Rex AA steel heat treated to a hardness of Rc 64.

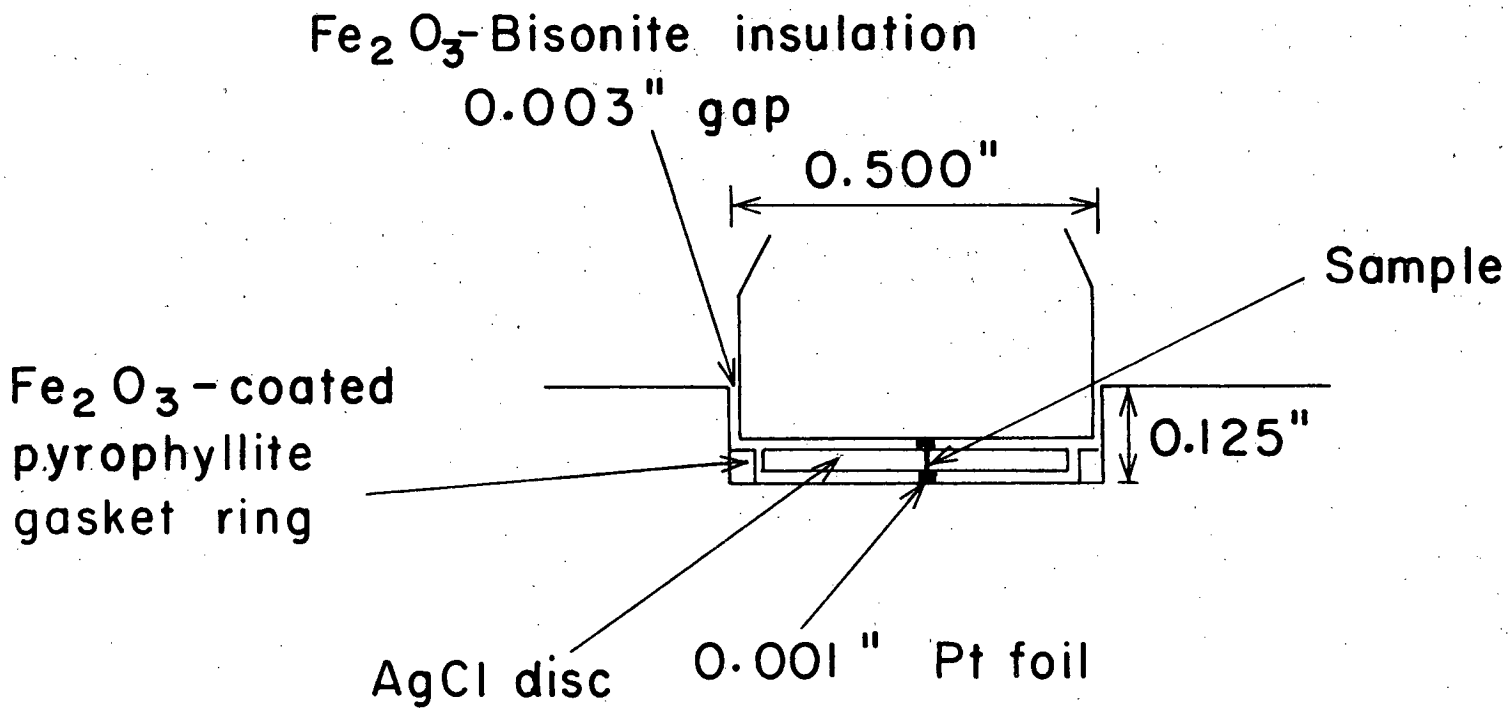
E: Transite heat dam material.

References

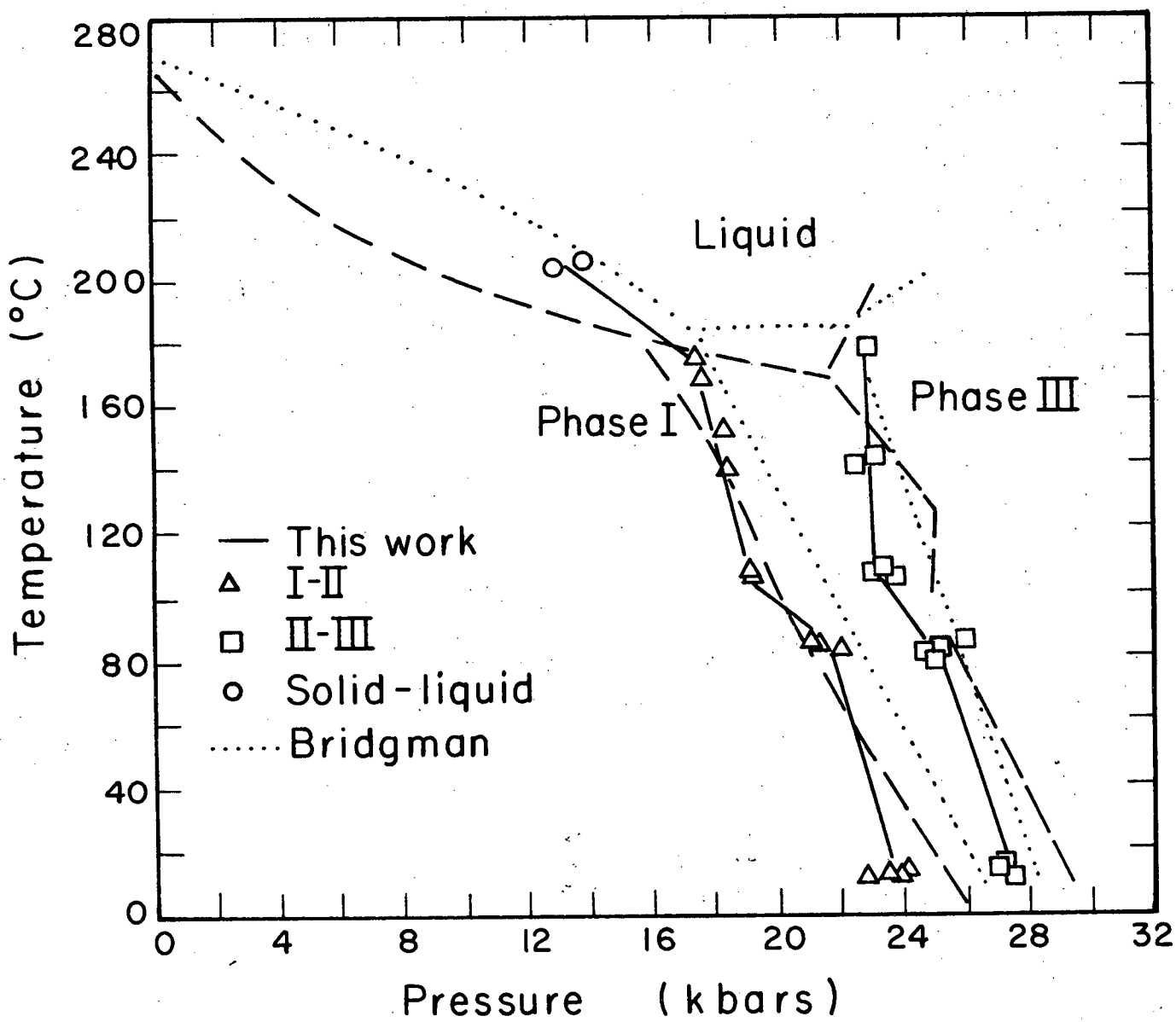
1. R.E. Harris, R.J. Vaisnys, H. Stromberg and G. Jura, Progress in Very High Pressure Research, John Wiley and Sons, New York, N.Y. (1961).
2. P.W. Bridgman, Phys. Rev., 48,893(1935).
3. W.H. Zachariasen, Acta Crystallographica, 5, 664(1952).
4. P.W. Bridgman, J. Appl. Phys., 30, 214(1959).
5. P.W. Bridgman, Proc. Acad. Arts and Sciences, 81, 165(1952).


A
B
C
D
E
Thermocouple and current leads
Potentiometer leads
Sample cell
Fracture line
G
Heater
Heat dam

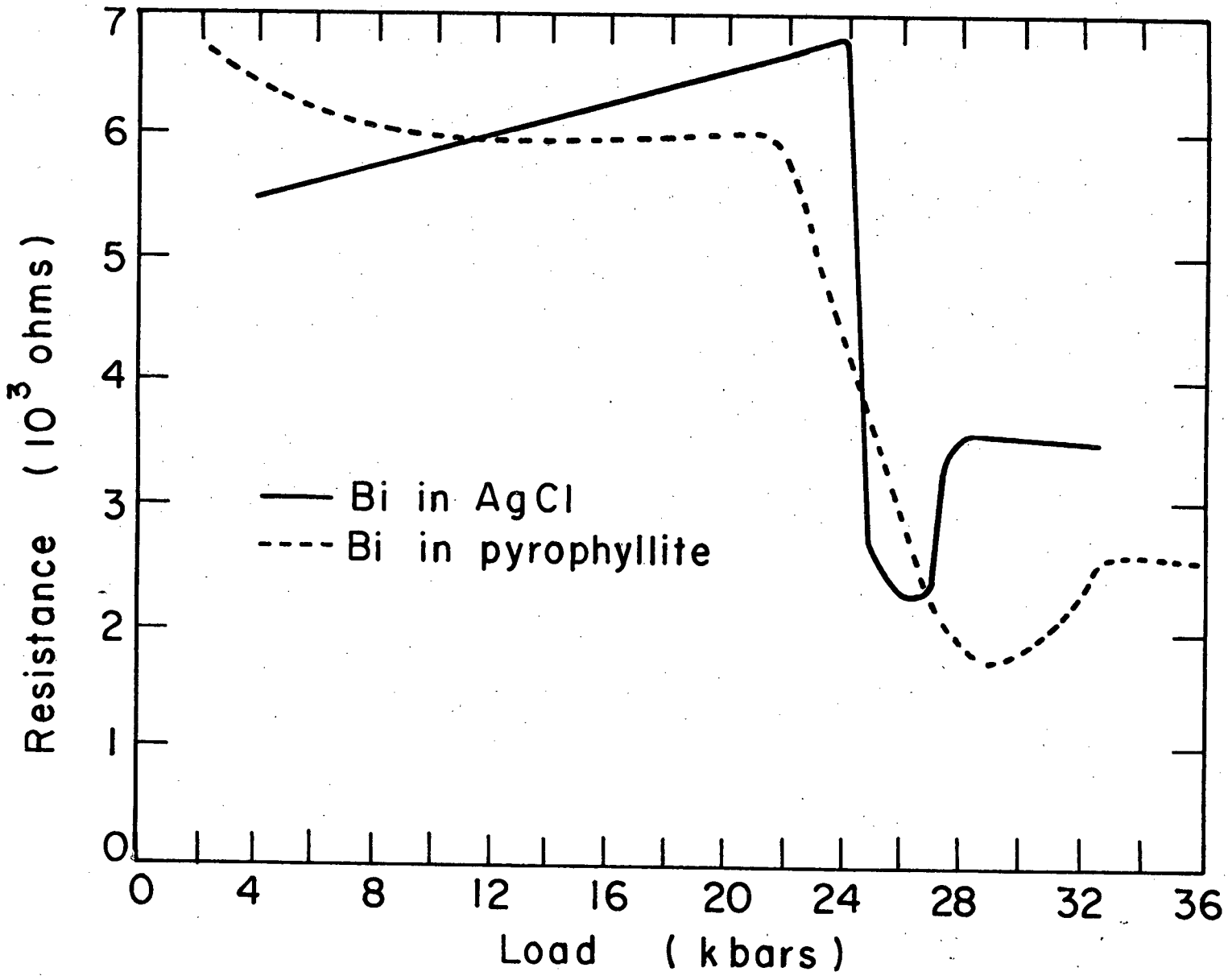
6065-3-1


Fe_2O_3-Bisonite insulation
0.003" gap
0.500"
Sample
Fe_2O_3-coated pyrophyllite gasket ring
0.125"
AgCl disc
0.001" Pt foil

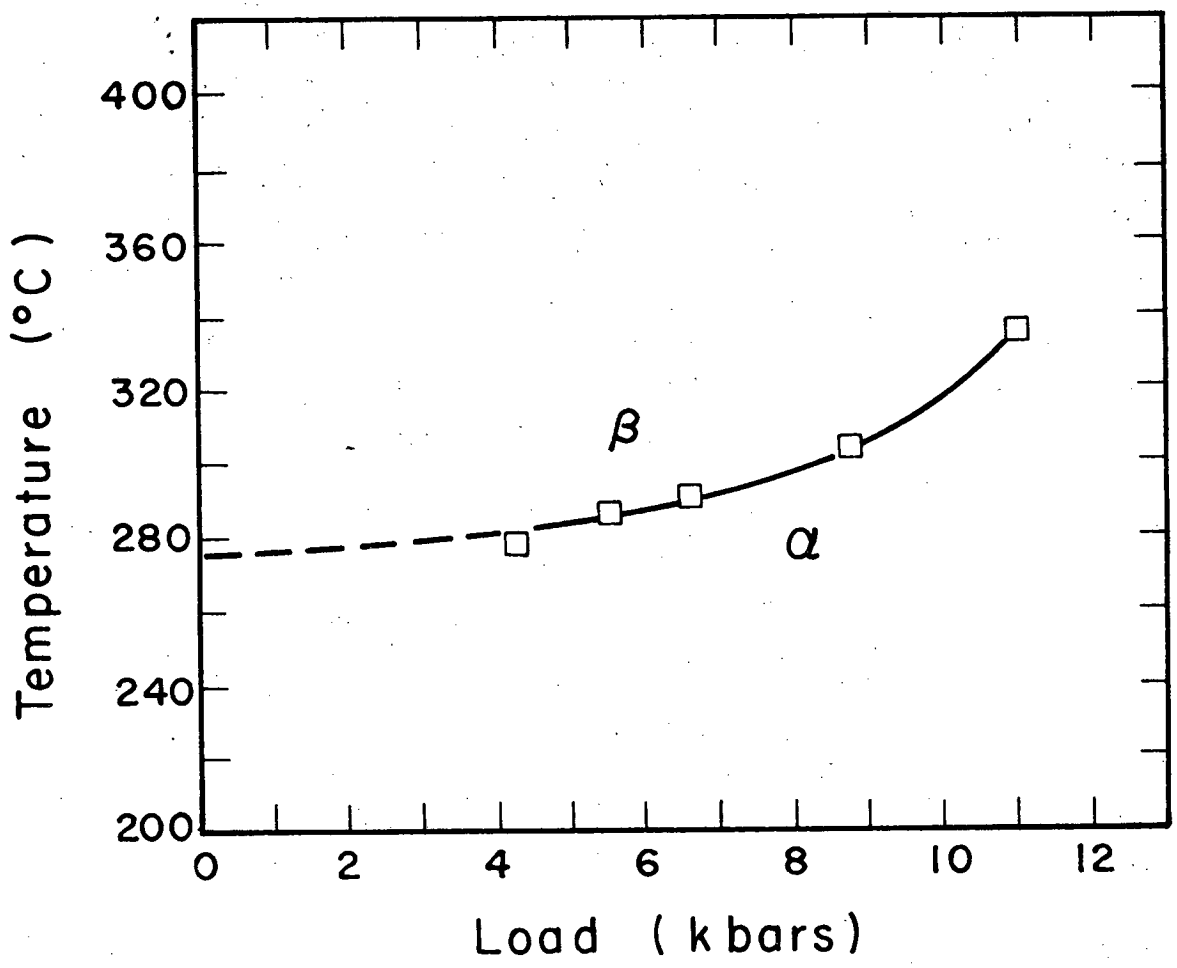
E0644-1


Temperature (°C)
Pressure (kbars)
Liquid
Phase I
Phase III
This work
I-II
II-III
Solid-liquid
Bridgman
0
40
80
120
160
200
240
280
0
4
8
12
16
20
24
28
32

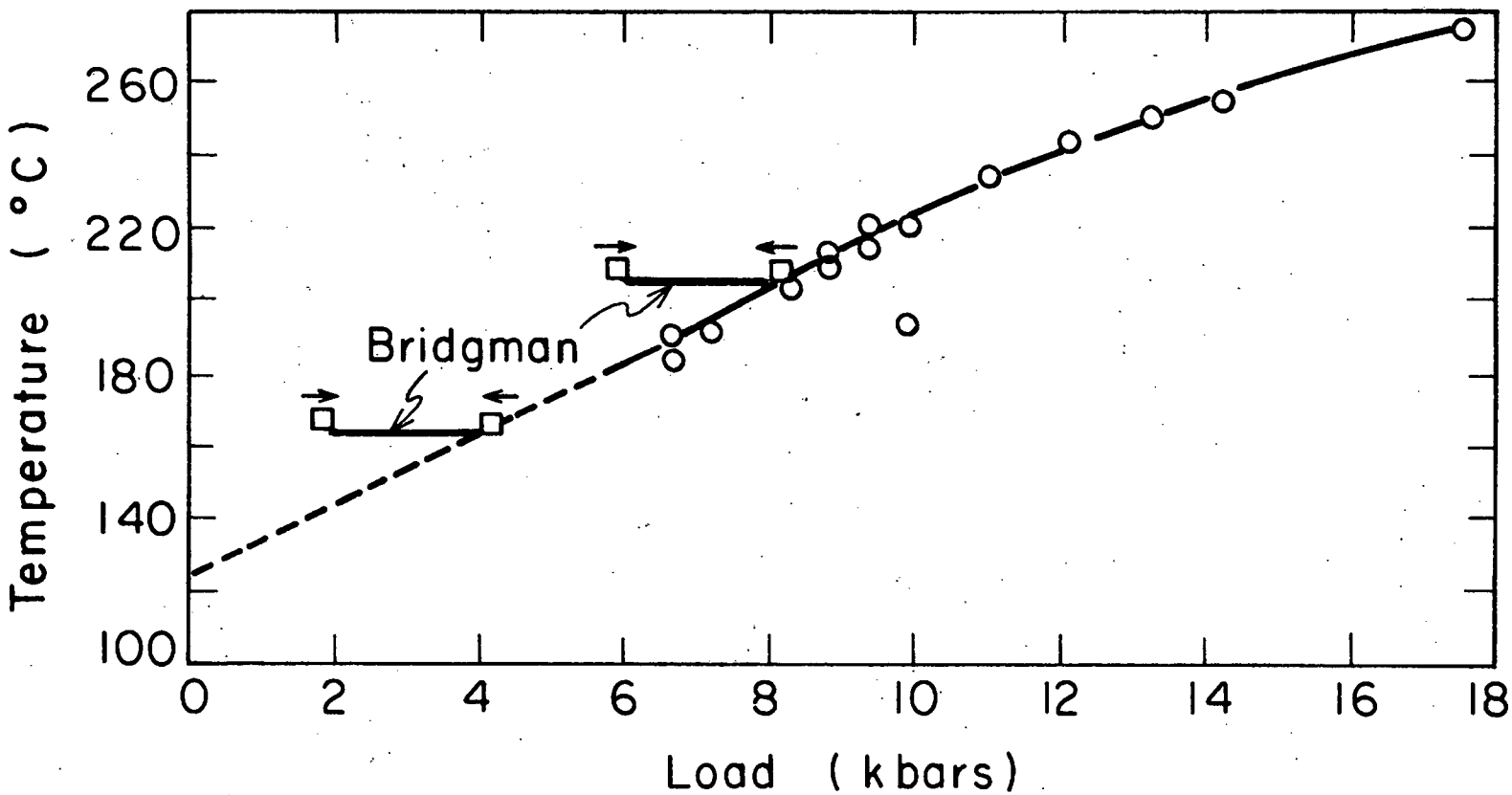
63647-1


Resistance (10^3 ohms)
0
1
2
3
4
5
6
7
0
4
8
12
16
20
24
28
32
36
Load (kbars)
Bi in AgCl
Bi in pyrophyllite

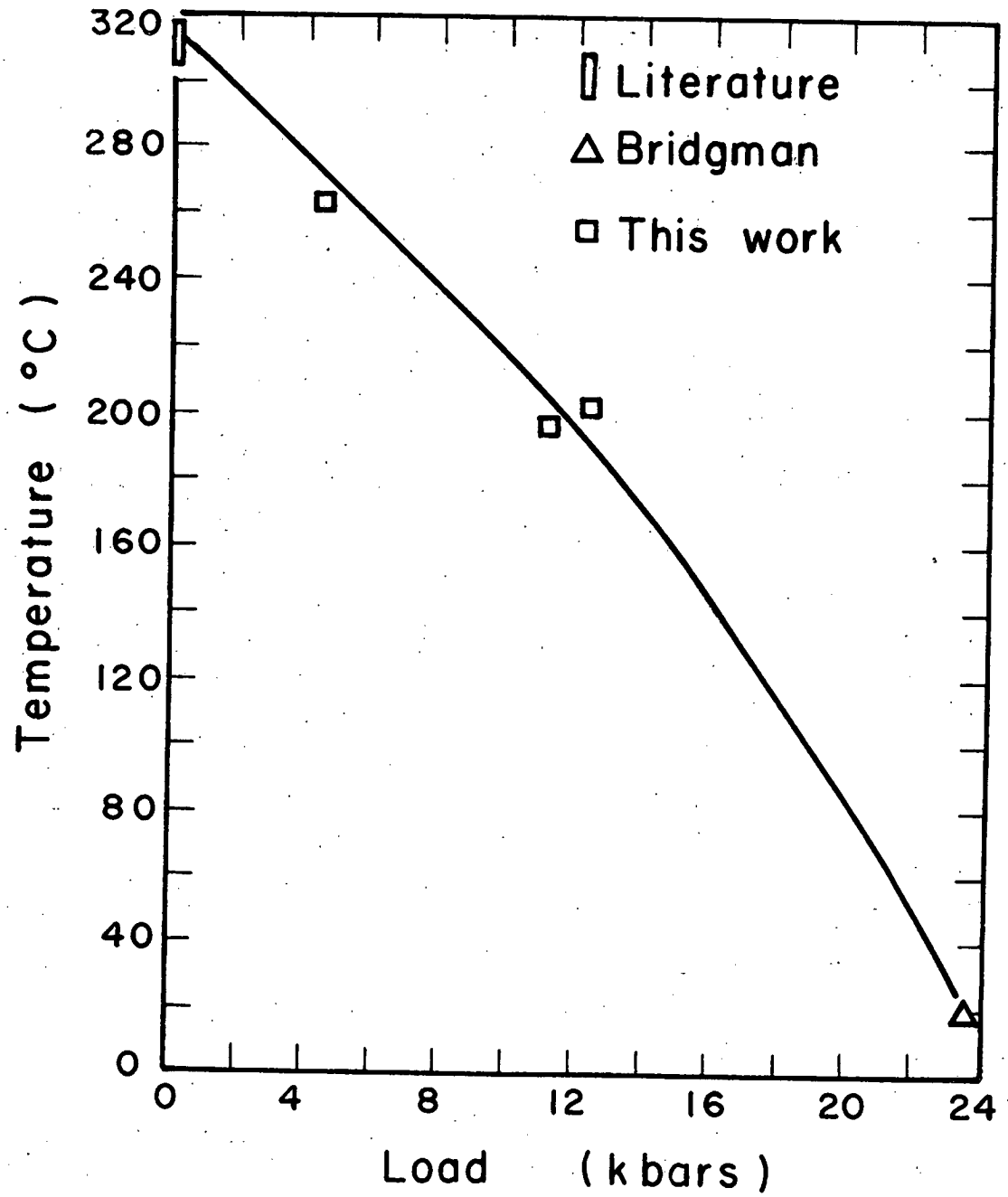
6063-4-1


400
360
320
280
240
200
Temperature (°C)
0
2
4
6
8
10
12
Load (kbars)
β
α

60 652-1


Temperature (°C)
260
220
180
140
100
0
2
4
6
8
10
12
14
16
18
Load (kbars)
Bridgman

60655-1


Literature
Bridgman
This work
Temperature (°C)
320
280
240
200
160
120
80
40
0
0
4
8
12
16
20
24
Load (k bars)

60650-1

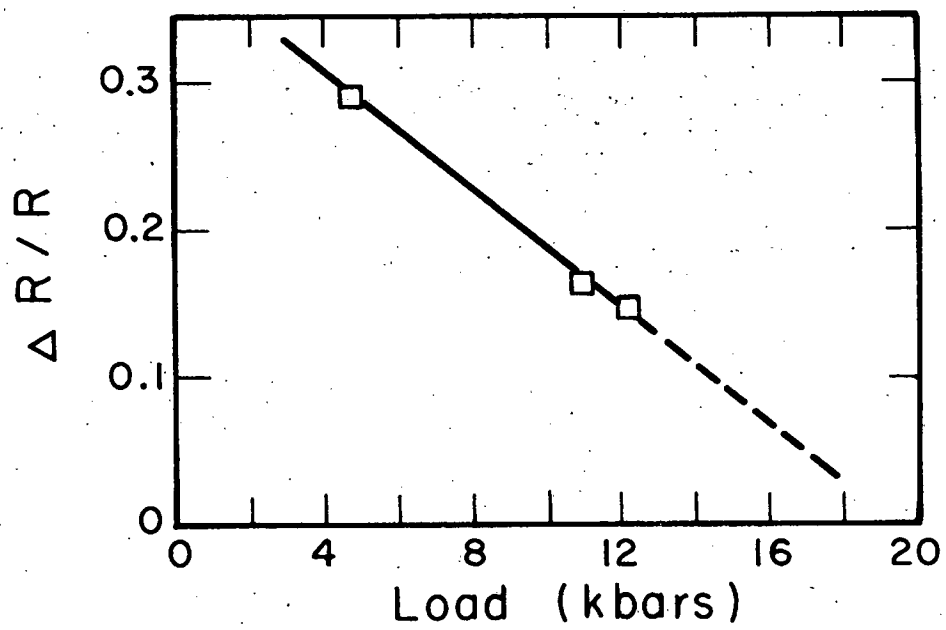
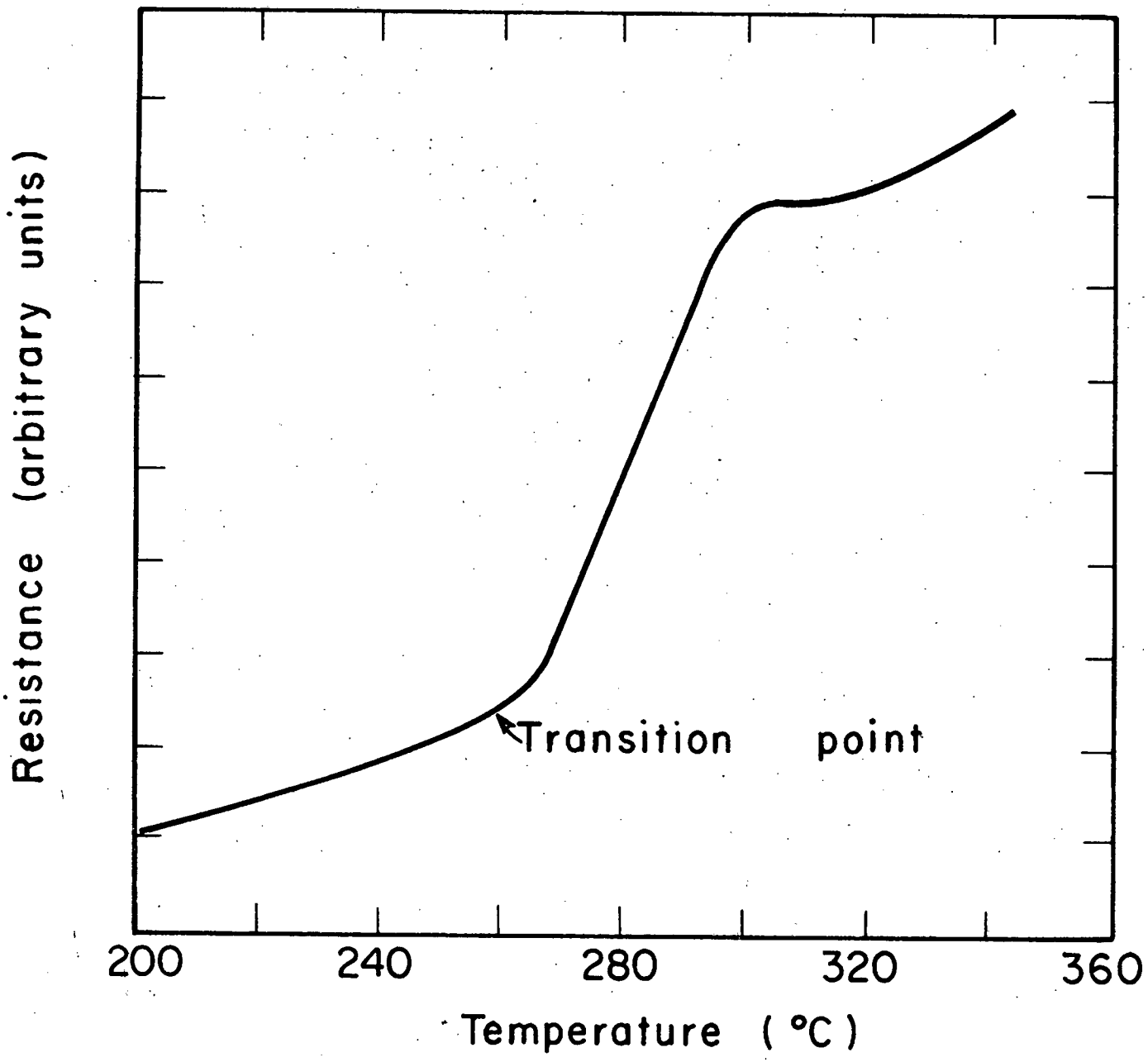


Fig 5

60648-1


Resistance (arbitrary units)
Transition point
200
240
280
320
360
Temperature (°C)

56

60651-1