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Part of book: High Pressure Measurements

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RESISTANCE MEASUREMENTS AT HIGH PRESSURES

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November 8, 1963

Resistance Measurements at High Pressures

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Introduction

The measurement of the resistance is one of the most accurate and precise determinations that can be made under ordinary conditions. It is also one of the most frequent measurements made at very high pressures. The special conditions required to obtain the very high pressures reduce the accuracy of the measurements by several powers of ten. A technique is described in a later section which might permit a precision approaching that at atmospheric pressure. However, the full potential of this technique has not as yet been explored. At the present time, it appears that the accuracy of resistance determinations as a function of pressure is no better than a few percent. The greater part of this uncertainty is due to the inaccuracy in the measurement of pressure.

The resistance is so complex a function that the detailed change of resistance with pressure is of little value for theoretical studies. Perhaps the greatest single use of resistance is the delineation of phase boundaries. In general, a change in the crystallographic, electronic, or magnetic structure will exhibit a discontinuity in the resistance. The first two of these types of changes usually show a discontinuity of the resistance, while the magnetic changes usually involve only changes in the slope of the resistance. The above experiments can be performed either

isobarically or isothermally. A second important use of the resistance is the determination of the gap of semiconductors as a function of pressure. These experiments are performed isobarically. The resistance can be used to determine the pressure gradient in the system.

One possible important kind of measurement has not as yet been performed. In principle, resistance measurements could be used to determine the Debye temperature of a solid as a function of pressure. At sufficiently low temperatures, the resistance of a metal is proportional to the fifth power of the temperature, while at temperatures near or above the Debye temperature, the resistance is a linear function of the temperature. If constants in both temperature regions are determined, a good estimate of the Debye temperature is possible. (1) The above by no means exhausts the useful aspects of resistance measurements, but they are certainly sufficient to warrant the past and many future investigations.

Experimental Methods

The techniques which are used are limited by the method of obtaining high pressures. In this discussion the pressure region is above 30 kbars. Since there is no available fluid at these pressures, solids are used to transmit the pressure to the sample. The use of a solid as the pressure transmission medium brings about a pressure gradient in the system. The sample under study may be essentially under uniform pressure, or it may exist under a non-uniform pressure. If the latter is the situation, the gradient is taken into consideration and true pressure-resistance dependence can be obtained.

The most usual method of generating high pressures is by the use of Bridgman anvils, (2) or some supported modification of the anvils such as developed by Drickamer. (3) & (4) Pressures as high as 400 kbars atmos may be obtained. The exact values of the pressures are not known. It appears that the most reliable pressure scale extends only to about 125 kbars. (5) The total volume in which this pressure is generated is of the order of a few hundreths to tenths cm^3. This limits the study to very small samples. The pressure chamber is of circular cross section, and may be as great at 7/16 in. in diameter and 0.010 in. high. The diameter can be decreased and the height increased. For pressures above about 150 kbars, the dimensions of the pressure measuring chamber are less than the above.

If the material under study is an insulator or semiconductor, it may be mounted directly between the anvils. If the material is a metal, then insulation is necessary. Silver chloride or pyrophylite are the two most common insulating materials that are used. The former has the advantage in that it has a lower pressure gradient than the pyrophylite. In general, the sample is mounted between two layers of the insulator, and electrical leads are run from the ends of the sample through each of the insulating layers. The contact of the leads through the insulators to the anvils, which are connected to the external circuitry, composes a simple electrical system.

The resistance now can be measured in the usual manner: by the use of a Wheatstone bridge, or by passing a constant current through the system and measuring the voltage drop. Either of the above can be as simple or

as sophisticated as desired.

As normally used, and described above, there are certain inherent difficulties in the measurements. The actual resistance values of the specimen can be very large. It may be well above 10^{12} ohms, or as low as .001 ohm, or even lower. The resistance may even vary by as much as 10^{12} in a single experiment. Such a variation is seen in the conversion of red phosphorous to the metallic state at room temperature. (6) The appropriate electrical techniques for studying very high resistances have not as yet been developed for work under high pressures. The precautions that are necessary to insure the current flowing through the sample between the contacts simply have not been taken, and the values quoted for very high resistance materials are probably low because of the contribution of surface conductivity and other effects.

With samples of very low resistance, another problem is present, namely that of contact resistances. The contact resistance may be as large or even larger than that of the sample. The contact resistance has been studied for several geometries, and some of the problems are treated by Jeans. (7) None of the old classical solutions apply to the geometries in use. A recent theoretical study by Harris, (8) has indicated that with certain geometries, the contact resistance can be 50 times that of a sample of copper. Attempts have been made to evaluate the contact resistance by direct experimentation; however, the results appear to be uncertain. The contact resistance can be avoided by the use of four lead measurements.

The technique for making four lead measurements in Bridgman anvils has been developed. (9) The description is for 1/2 in anvil faces. The diameter of the anvil face can be varied as long as the pyrophylite ring width and height are maintained at the given dimensions.

Figure 1 shows in a schematic manner the method of mounting a single sample. The two silver chloride disks, A, are punched from pre-rolled sheet of carefully controlled thickness to a diameter 0.010 inch less than the internal diameter of the pyrophylite ring. Gold electrical contacts, B, are inserted in 0.020 inch holes drilled near the edge of the rings. These plugs are of such a thickness that contact is made between the anvils and the wire, M, when the assembly is under load. The wire, M, is usually 0.003 inch in diameter and is bent in a circular arc, flattened at the ends to about 0.002 inch and mounted concentric to the center of the anvil face; such mounting insures a minimum pressure gradient in the sample. The ends of the lead wires, L, are also flattened at the ends where contact is made with the sample wire in order to reduce the tendency to pinch at the contact point. In order to facilitate mounting of the lead wires the containing pyrophlite gasket is made in two sections, 0.010 inch thick and 3/22 inch wide. On final assembly one gasket is placed on the anvil face, next the silver chloride assembly containing the sample and the lead wires is placed within this ring, and then the second ring is placed over the leads. The top and side views of a completed setup are shown in Fig. 2. The dimensions given are for 1/2 inch diameter anvil faces. For smaller anvil diameters the gasket thickness and sample clearances are used.

It is relatively easy to mount two separate samples in the same capsule by using three thinner silver chloride disks with an appropriate gold plug in the center disk to connect the two sample wires in series. To obtain more accurate voltage-drop data across each sample, separate leads are used This requires that four leads pass through the gasket for a double sample test. Several times we have attempted to mount three separate samples in the same capsule but we have not as yet been able to make a successful run because of the complexity of the assembly. An electical short or breaking of the circuit occurred each time within the silver chloride cell.

It was found that metals with a high modulus of elasticity such as tungsten, molybdenum, and platinum make the most successful lead-through wires. Wires of 0.005 inch diameter did not undergo shear failure. Platinum is the most desirable since it can be easily soldered; however, it has the disadvantage of lower shear strength than either tungsten or molybdenum and it fails about 125 kbar. Tungsten has the disadvantage of end fray during the flattening process. Mechanically molybdenum is superior and has been used for most of our tests despite its poor soldering qualities. A crimping procedure has been developed for connecting external lead wires to molybdenum and tungsten, which introduces relatively small contact errors. Both of these metals will successfully resist shear breakage to pressures of 200 kbar.

The electrical resistance of the samples is measured by passing a constant current through the entire sample stack connected in series. Current connections are made through the anvil faces. The potential drop is measured

across the individual samples with separate leads that pass through the split pyrophylite rings. Ohm's Law is then used to compute the resistance of the sample.

Figure 3 shows a typical determination by means of this technique. This was a two-sample assembly, one bismuth, the other manganin. The bismuth 1-2 and 6-8 transitions are used as an internal pressure calibration. The pressure is based on the assumption that the 1-2 transition occurs at 25.5 kbar and that the pressure is proportional to the load. There is some evidence that this latter assumption is not valid until pressures of about 30 to 35 kbar are reached.

The four lead technique is certainly the best manner of obtaining the resistance as a function of both the pressure and temperature. In principle, the results obtained by this method should be as accurate as ordinary resistance measurements. The ultimate limitation on the accuracy is the measurement of the pressure.

Resistance measurements can also be used to determine the pressure gradient in the system. The gradient has been extensively studied for anvils that are 1/2 in diameter, and for a wall thickness and height of 1/32 and 1/10 in respectively. For this geometry, and silver chloride as the pressure transmitting medium, the pressure P is given by

$$P = (0.725 + 0.468R)L$$

where R is the fractional displacement from the center of the anvil and L is the load in kbars per unit area over the entire anvil face.

Reference (5) should be consulted for the details of the manner in which these results were obtained.

In Fig. 3, the samples were mounted in the form of circular arcs so that the gradient was reduced to a minimum. The most common geometry for the sample is in the form of a strip. The sample is not under uniform pressure, and the measured resistance is an average over the load. All of Bridgman's results above 30 kbars used this geometry. However, if the pressure gradient is known, the results can be corrected to obtain the correct pressure-resistance relationship.

If there is a pressure gradient over the sample, the measured resistance R is

$$R = \int_{P_c}^{P_e} R(P)\text{-}dr$$

where $R(P)$ is the resistance at a pressure P, P_e and P_c the pressures at the center and the edge of the sample, and r the fractional distance from the center of the sample. A graphical differentiation of the measured data will give the correct functional relationship. An excellent method graphical differentiation for this data is the chord area method. If Bridgman's data are treated in this manner, the discrepancies between the resistance results and piston-cylinder measurements disappear. A prime test of this is in the determination of the pressure at which phase transitions occur. Table 1 shows the effect of the consideration of the pressure gradient in the determination of some phase boundaries. Before the correction is made there is violent disagreement between those obtained by resistance measurements, and those values that are well fixed by more

Table 1.

Effect of Considering Pressure Gradient on Some Fixed Pressure Points

Solid	Bridgman	Bridgman Corrected	Best Accepted Value
Hg	40	34	35
Tl	45	36	37
Cs	55	43	42
Se	56	44	—
Ba	80	63	60

standard techniques.

One last point of technique must be mentioned. When the system is at other than room temperature, a pressure gradient can be developed in the direction of axis of the anvil system. When this occurs, resistance readings must be taken with the current flowing in both directions through the system. The average of the two values is the correct value. The sign of the thermal EMF does give the sign of the majority carrier when the sample is a semiconductor.

Some Results

As indicated in the introduction, the resistance itself is too complex a function to consider theoretically at the present time. One of the important uses is its ability to determine phase boundaries, almost universally to the present time, crystallographic changes. The change in crystal structure usually brings about a finite discontinuity in the resistance. An example of its use in this manner is shown in Fig. 4 where part of the bismuth phase diagram is shown. (11) Many such results are available ranging from temperatures above 1000°K to temperatures below liquid nitrogen temperatures, and to pressures well above 100 kbars. Large samples are not necessary for these determinations. Figure 5 shows the α-β phase boundary as determined on a 400 microgram sample of plutonium. (11) Several other boundaries have been determined, but are not shown in this illustration. A few materials undergo a change in structure, but do not exhibit a change in the resistance. An example of this is lanthanum at

room temperature.(11) At elevated temperatures, there is a discontinuity in the resistance. The discontinuity becomes smaller as the temperature is decreased, and diminishes to the point that it is not detectable at about 400°K.

A purely electronic transition in a solid can also be detected by changes in electrical resistivity. The three definitely known examples, caesium, (2) cerium, (2) and ytterbium (12, 13) all exhibit very large discontinuities at room temperatures. The magnitude of the change decreases as the temperature is increased.

Changes in the electrical resistance have shown a large number of semiconductors or insulators to go metallic. Theoretically it has been long predicted that all matter would reach the metallic state at a sufficiently high pressure. Bridgman (2) found tellurium and silver sulfide to go metallic, Jura and co-workers (5) phosphorous and silver oxide, and Drickamer (14, 15) the group IV and 3-5 semiconductors. The pressures for this transition range upward from about 50 kbars for tellurium. In some of these transitions there is a detectable crystallographic change, in others not. Apparently, some times a higher band intersects the valence band, and at others, there is an approach or overlap the valence and conduction bands. Presumably, if there is a discontinuity, the bands must cross, while if there is a gradual approach to the metallic state, the bands overlap.

Recently, (12, 13) there has been the demonstration that a metal can become a non-metal under pressure. The investigations of ytterbium show

that the metal becomes a semiconductor under pressure. The gap measured on an impure sample, 99.8% ytterbium indicates that the gap reaches a value of 0.085 ev. (13) The possibility that ytterbium was a semiconductor was first suggested by Bridgman. (14) Just recently, P. C. Souers and this author have found that bismuth in phase 1 is a semiconductor. Investigation at liquid nitrogen temperatures shows that at 25 kbars the gap is 0.012 ev. This is low compared to kT at room temperature; consequently, bismuth appears to be metal.

The changes in magnetic properties under pressure have not been extensively studied. However, it is known that at 1 atmosphere there are discontinuities in the derivative of the temperature-resistance curves at both the Neel and Curie temperatures. Preliminary measurements of the Neel temperatures of europium and dysprosium have been made in this laboratory. The behavior of the temperature-resistance curves at constant pressure is analagous to those determined at one atmosphere.

From the preceeding, it is evident that resistance can be used to characterize quite completely the different phase regions in the P-T diagram. It is true, that on rare occasions, a change may be missed due to the fact that there is no detectable change in the resistance.

The other major use to which resistance measurements have been put is the determination of the gaps of semiconductors as a function of pressure. This kind of determination is best done at constant pressure and noting the resistance as a function of temperature. The relationship between the resistance, R and gap, Eg is given by

$$R = R_{\infty} \, \ell^{Eg/2KT}$$

where R_∞ is the first term of an expansion. This formula is valid when the gap is large compared to kT. It is apparent that if the log R is plotted against 1/T, a straight line results, and the slope yields the gap. Figure 6 shows such a plot for ytterbium, and Fig. 7 shows the gap as a function of the pressure.

The work on ytterbium had to be done at low temperatures because of the magnitude of the gap. For the more normal semiconductors, the measurements are made at high temperatures. The results of such determinations for a number of these, both organic and inorganic, are presented in Ref. (6).

Of particular interest is iodine. Here, the smallness of the gap, 0.08 ev., is of less interest than the change and magnitude of the pre-exponential term. Usually this term is practically independent of the pressure. For iodine, it decreases by three powers of ten. Since R_∞ has the product of the mobility and the number of carriers in the denominator, it is necessary that the mobility, or the number of carriers or both increase very rapidly with pressure. A similar effect is found in naphthalene. Several explanations are possible, but the ancilliary experiments which would permit the choice of the correct explanation have not as yet been performed.

At the present time, it does not appear that these experiments can be performed with sufficient precision to determine the variation of gap with temperature. Also, the necessary volume data are lacking to test the few general theories of conduction in semiconductors. Despite some shortcomings, it is evident that a large mass of useful information has, and can be obtained from resistance determinations.

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(16) P. W. Bridgman, Proc. Amer. Acad. Sci. 83, 1 (1954).

Figure 1. Schematic sketch of setup with leads through gasket.

Figure 2. Top and side views of assembly for multilead measurements.

Figure 3. Resistances of bismuth and manganin as determined simultaneously and independently with four-lead measurements.

Figure 4. Bismuth Phase Diagram.

Figure 5. Plutonium Phase Diagram in the region of the α-β transition.

Figure 6. Resistance-temperature determinations for ytterbium at several pressures. Circles refer to heating runs and triangles to cooling runs.

Figure 7. Energy gap of ytterbium as a function of pressure.

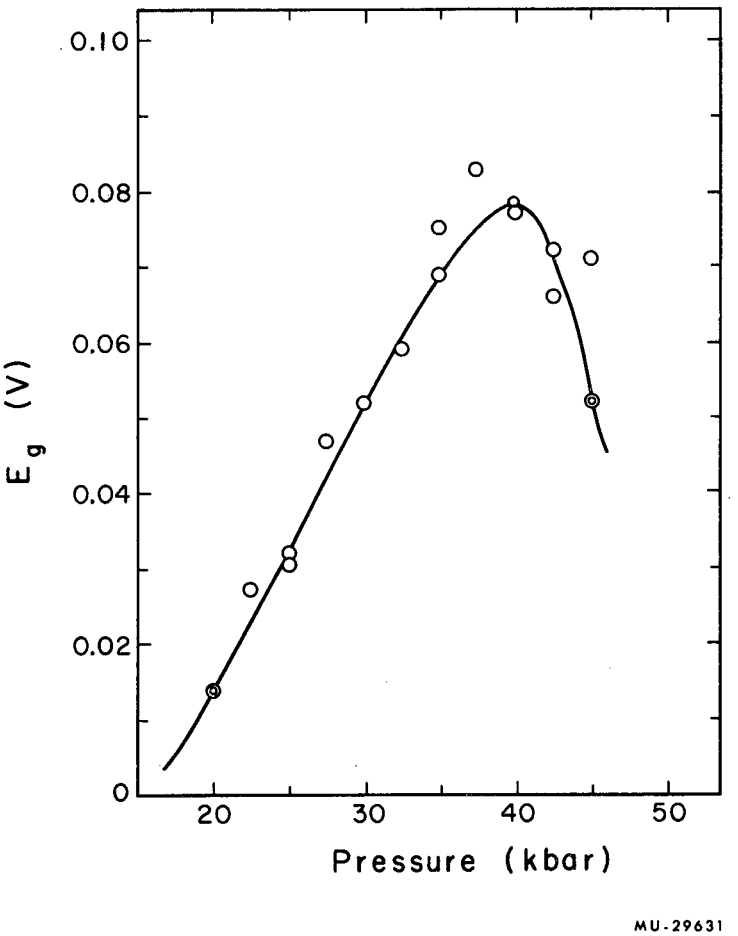


Fig. 1

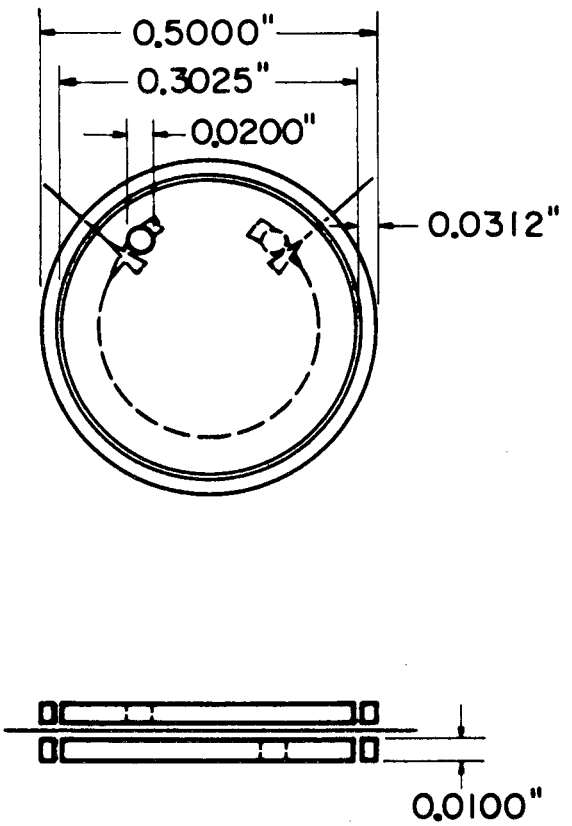
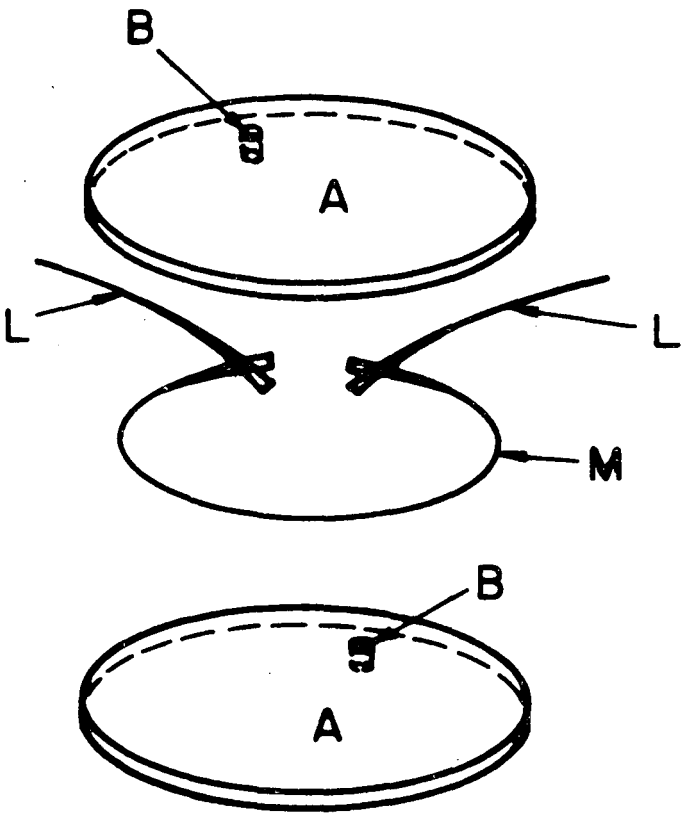


Fig. 2



MU-27498

Fig. 3

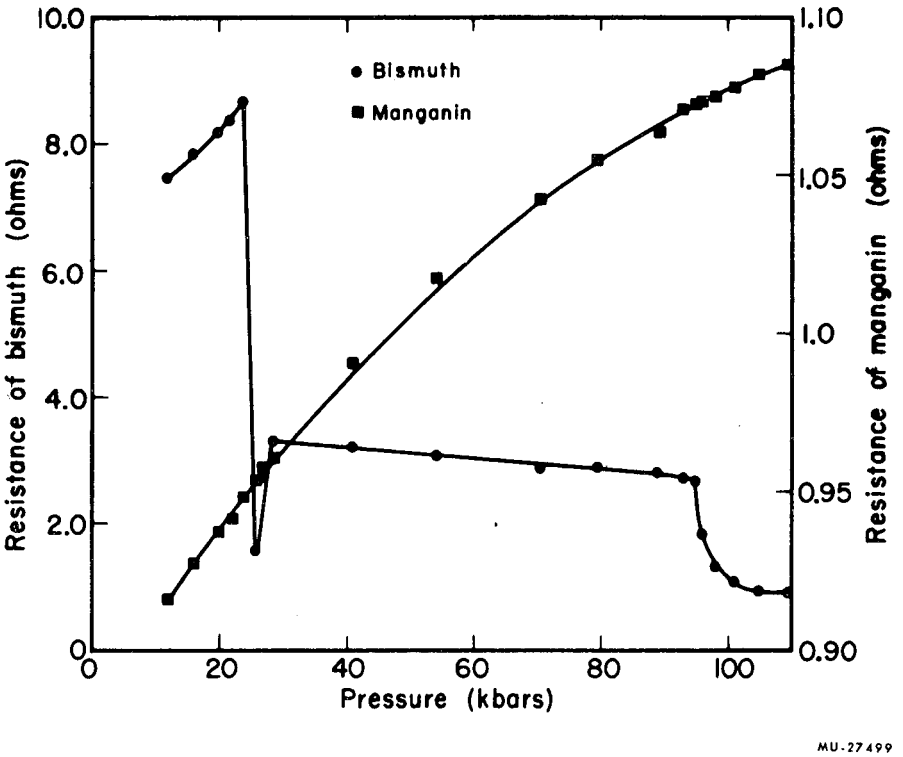

10.0
8.0
6.0
4.0
2.0
0
1.10
1.05
1.0
0.95
0.90
0
20
40
60
80
100
Pressure (kbars)
Resistance of bismuth (ohms)
Resistance of manganin (ohms)
Bismuth
Manganin
MU-27499

Fig. 4

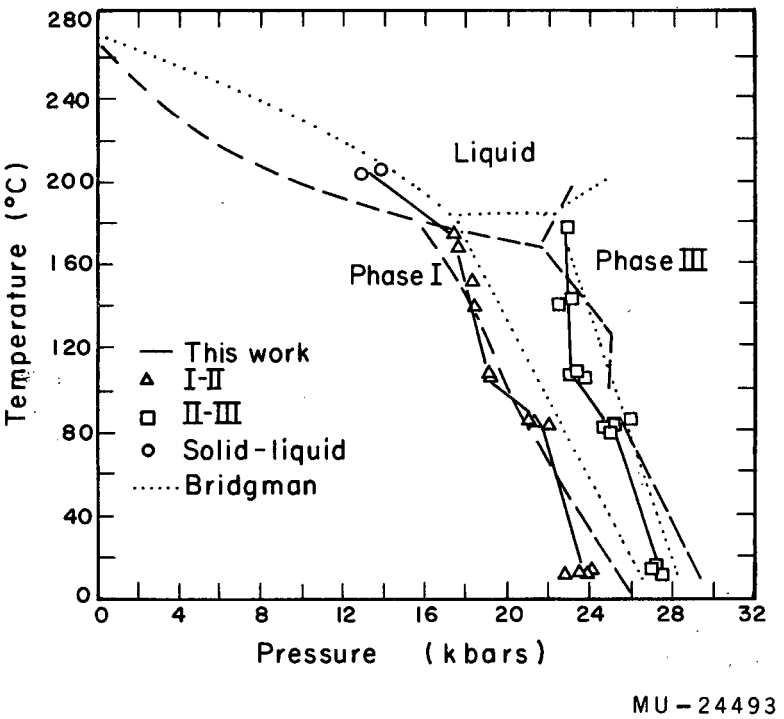

Temperature (°C)
280
240
200
160
120
80
40
0
0
4
8
12
16
20
24
28
32
Pressure (kbars)
Liquid
Phase I
Phase III
This work
I-II
II-III
Solid-liquid
Bridgman
MU-24493

Fig. 5.

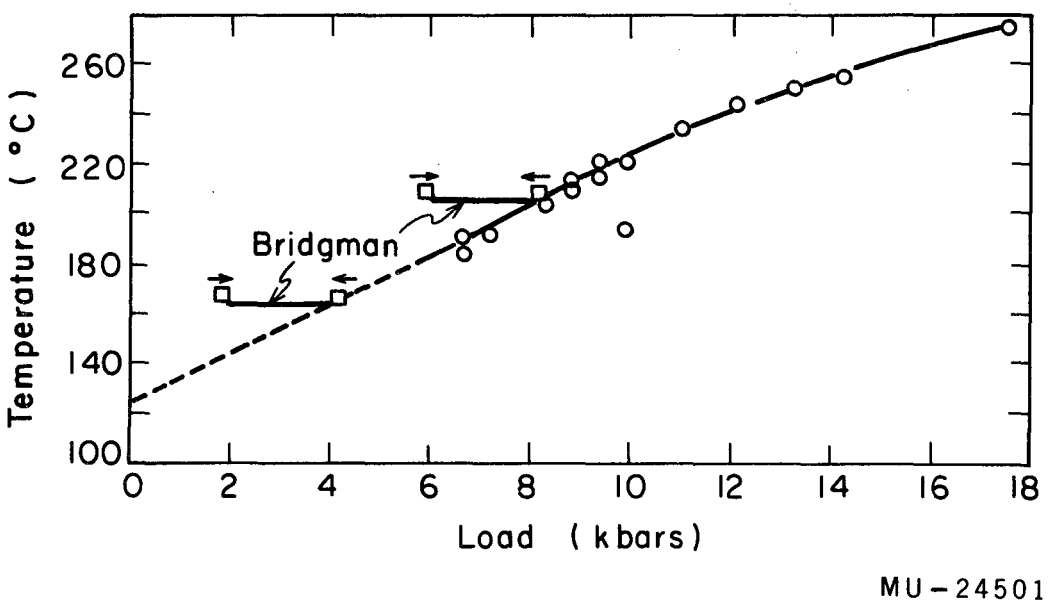

Temperature (°C)
260
220
180
140
100
0
2
4
6
8
10
12
14
16
18
Load (kbars)
Bridgman
MU-24501

Fig. 6

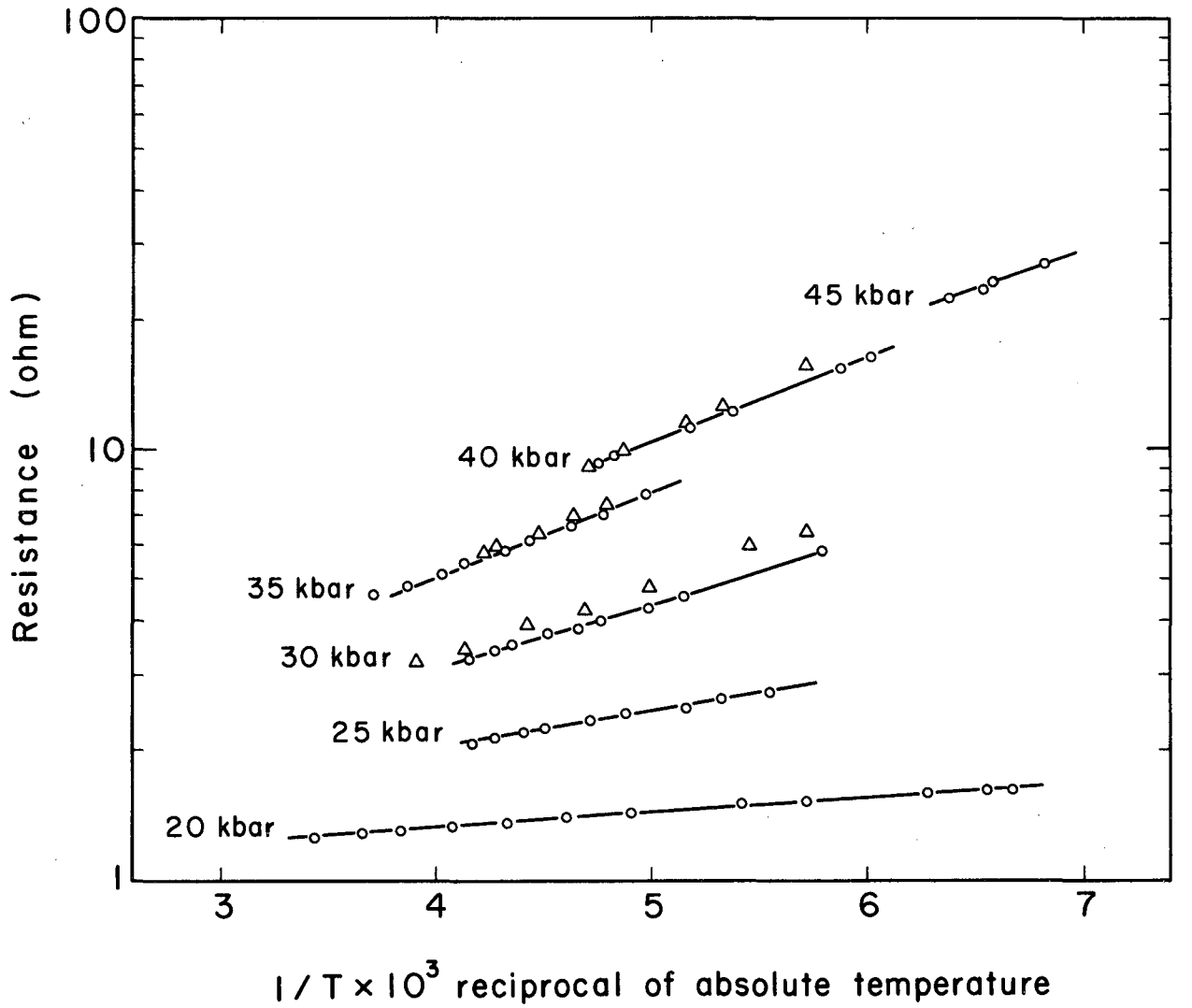

100
10
1
Resistance (ohm)
45 kbar
40 kbar
35 kbar
30 kbar
25 kbar
20 kbar
3
4
5
6
7
1 / T × 10³ reciprocal of absolute temperature
MUB-1645

Fig. 7

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