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THE EFFECT OF PRESSURE ON THE ELECTRICAL RESISTANCE OF RUBIDIUM[1]

J. S. Dugdale and J. A. Hulbert[2]

ABSTRACT

By using helium in both the solid and the fluid state as a pressure-transmitting medium, it has been possible to measure the resistance of rubidium over the temperature range from 2° K. to room temperature at pressures up to 2500 atmospheres. In particular the effect of pressure on the transition at ~200° K., on the low temperature ideal resistivity, and on the residual resistivity was examined.

INTRODUCTION

Until recently there have been scarcely any measurements on the effect of volume change on the electrical resistance of materials at very low temperatures. Fischer (1930) made measurements on some metals down to liquid hydrogen temperatures at pressures up to about 150 atm. Bridgman (1932) made measurements down to liquid oxygen temperatures up to 7000 atm. pressure using a gaseous transmitting medium. Sizoo and Kamerlingh Onnes (1925) studied superconductivity under small pressures and since then there has been considerable work on the change with pressure of the superconducting transition temperature. Hatton (1955), using solid hydrogen as the pressure-transmitting medium, has measured changes of residual resistance under pressures up to 5000 atm. in the helium temperature range. For further references, the reader is referred to a recent review by Lawson (1956) of the effects of hydrostatic pressure on the resistivity of metals.

Because of the great theoretical interest in the alkali metals we wished to make measurements on the properties of this group of metals over a wide temperature range under pressure. Pressure measurements of the resistance of these metals have hitherto been confined to the neighborhood of room temperature and above. The present apparatus is designed for measuring electrical resistance down to low temperatures (~2° K.) under moderately high pressures (up to 3000 atm.). With such a temperature range available, it now becomes possible to determine (assuming Matthiessen's rule) the effect of pressure both on the residual resistivity and on the "ideal" thermal component of resistance of the same specimen.

At low temperatures and under sufficient pressure all substances become solid so that a major problem of studying pressure effects at low temperatures is to find a suitable pressure transmitting medium. We have chosen helium since at a given pressure it retains its ideal fluid properties to a lower temperature than any other substance. Furthermore even in the solid state it is a useful pressure medium. In the pressure range with which we are concerned

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the equation of state of the solid is known (Dugdale and Simon 1953); it shows that at constant density, the pressure in the solid is only weakly temperature dependent. This means (*a*) that, if the temperature and density are known, the pressure in the solid can be deduced and (*b*) that, after applying the pressure at such a temperature that the helium is fluid, the system can be cooled at constant volume to the working temperature without serious loss of pressure. To show this, we give in Table I the pressures applied in the fluid state at the solidification point and the corresponding pressure in the solid after it has been cooled at constant volume to 2° K. About one-quarter of the pressure is lost in each case.

TABLE I

Filling pressure, atm.	Solidification temperature, ° K.	Pressure in solid at 2° K.
3000	28.3	2300
2500	25.2	1900
2000	21.9	1500
1500	18.2	1100
1000	14.1	730
500	9.1	350

THE APPARATUS

The pressure bomb, *A* (see Fig. 1), made of beryllium copper hangs from its high pressure input tube, *B*, inside an evacuated vessel, which itself is immersed in either liquid helium or liquid nitrogen contained in a glass dewar. A copper braid (not shown) is soldered at one end to a point on the tube about 30 cm. from the bomb and at the other end to the wall of the vacuum space. This serves to divert some of the heat flux down *B* to the helium or nitrogen bath. Helium exchange gas may be introduced into the vacuum space, *C*, to provide thermal contact with the refrigerant liquid and so cool the bomb; the temperature of the bomb may be raised by means of a constantan heater wound on the outside.

The specimen temperature is determined by either a platinum or a carbon resistance thermometer (*D* and *E*) mounted on the top of the bomb cap and shielded from external radiation by a copper screen.

The pressure-seal between the bomb and cap is made with a hardened steel lens ring, *F*. A seal which is reliable down to helium temperatures, and to pressures of helium up to 4000 atm., is achieved by using a ring of tool steel (e.g., Vasco "Speedcut"), hardened to 45–50 Rockwell "C". The contacting surfaces of the ring are ground to be accurately conical with an included angle of 60° and bear against the slightly chamfered square edges of the bomb body and cap. The high pressure input tube, a length of Aminco chrome–molybdenum steel (o.d. 1/4 in., i.d. 1/16 in.), is screwed and soft-soldered into the cap of the bomb. Occasional failures of this seal were ended by the application of a soldered, perforated soft copper disk to the inside of the seal.*

*This method was originally due to Mr. C. Chase of the Jefferson Laboratory of Harvard University. We are indebted to Dr. W. Paul of that laboratory for drawing our attention to it.

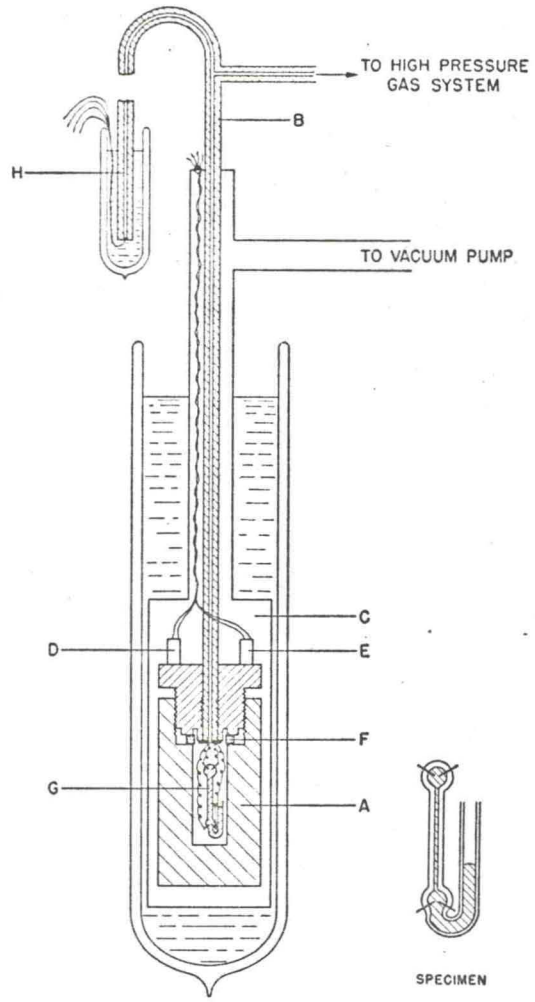

FIG. 1. Diagram of the apparatus for studying resistance under pressure over a wide temperature range (see text). Inset: rubidium specimen holder in soft glass with platinum electrodes.

The all-copper current and potential leads to the specimen, *G*, are introduced down the high pressure tube, entering through a frozen silicone oil seal contained in a side arm, *H*. Such a seal of oil kept frozen in liquid nitrogen has proved very satisfactory.

The high pressures are generated by an oil press and the pressure is transmitted to the helium gas through what is in effect a mercury-filled U-tube. The mercury separates the oil from the gas and thus prevents contamination of the helium. The dead volume in the high pressure part of the apparatus is kept to a minimum (about 4 cc.) in order to reduce the time required to reach the highest pressure and to minimize explosion dangers from the compressed gas.

The pressures were measured with a conventional Bourdon gauge to an accuracy of about 1%.

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THE SPECIMENS

The rubidium specimens were of the form shown in the figure (inset to Fig. 1). The container was of soft glass with platinum electrodes and was filled with rubidium under high vacuum. For most specimens the capillary had an inner diameter of 1 mm. and an approximate length of 5 cm. between the electrodes; for one sample, however, a capillary of 0.1 mm. diameter was used. The use of glass capillaries in pressure experiments is not entirely satisfactory even with materials as plastic as rubidium. Nevertheless because rubidium is such a highly reactive substance this has so far proved the only successful way of mounting a specimen of this element in the apparatus.

We assume that, since the deformation of the glass by the pressure (which acts both internally and externally on the specimen holder) is negligible, we are measuring resistivity directly as a function of pressure. In other words we assume that the dimensions of the specimen, which are determined only by the glass container, do not change appreciably with pressure.

ELECTRICAL MEASUREMENTS

The resistance of the platinum thermometer was measured by means of a potentiometer and the specimen resistance by a galvanometer amplifier (MacDonald 1947).

THE EXPERIMENTAL RESULTS

Measurements were made of electrical resistance over the entire range from helium temperatures to room temperature, in general at three different pressures (approximately 100, 1500, and 2500 atm.). Before the pressure effects are considered, the low pressure behavior of the resistance of rubidium as a function of temperature will be briefly discussed. Fig. 2 shows four examples of this behavior taken from the present measurements.*

Sample 1 is a rubidium specimen contained in a capillary of 0.1 mm. bore. The residual resistivity ratio $R_{0°K.}/R_{273°K.}$ was estimated from helium temperature measurements to be 1.3×10^{-2}.

Sample 2 was from the same batch of rubidium measured this time in a capillary of 1 mm. bore; its residual resistance ratio was 1×10^{-2}.

Sample 3 was prepared from rubidium chloride to be especially pure but in fact it was heavily oxidized. Its residual resistance ratio estimated from measurements down to nitrogen temperature only was $R_{0°K.}/R_{260°K.} = 3.8\times10^{-2}$. (We use R_{260} for reasons explained below.) It was contained in a 1 mm. bore tube.

Sample 4 was a further specimen in a wide bore tube (1 mm.) with a residual resistance ratio of just less than 1×10^{-2}.

(The material for all these samples except that of number 3 was obtained from Messrs. A. D. Mackay, New York.)

It is at once evident that the resistive behavior, particularly above about 200° K., varies from specimen to specimen.

*These measurements were made, for convenience, at helium cylinder pressure (about 100 atm.). This pressure changes the resistance by rather less than 1% of its value.

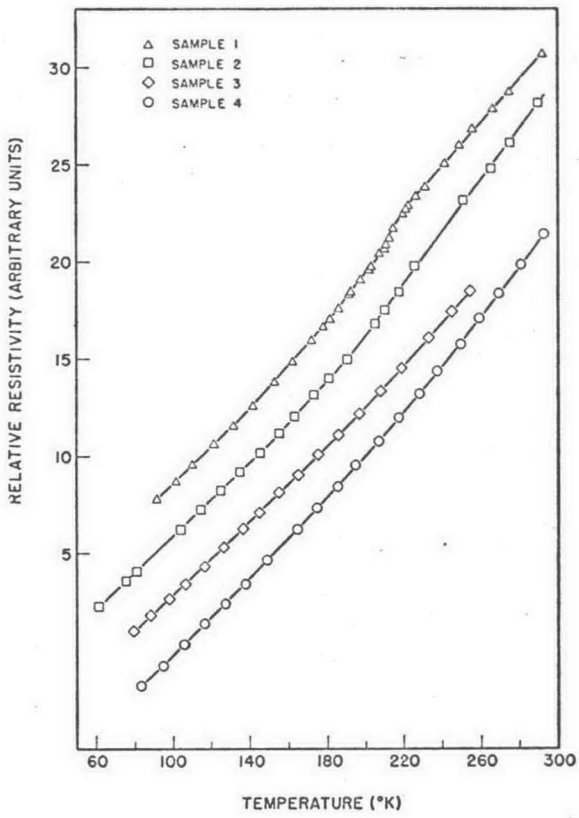

FIG. 2. The relative resistance of four rubidium samples as a function of temperature at low pressures (approximately 100 atm.). The resistances have been normalized to agree at 150° K. and then separated by intervals of 2 units to avoid overlapping.

MacDonald (1952) found an anomaly in the resistance of rubidium at about 180° K. and the present samples (except number 3) show this anomaly in various forms. In samples 1 and 2, the effect is quite evident, but in sample 4 the anomalous behavior takes the form of a gradual deviation from linearity with temperature which begins to be evident at about 150° K. Samples 1 and 2 showed marked thermal hysteresis in the neighborhood of the anomaly (cf. MacDonald 1952), the resistance measured with falling temperature being above that measured with rising temperature. To simplify the diagram only the falling temperature curves are shown here.

Sample number 3, which was heavily oxidized, shows little sign of the anomaly. (Its behavior is not shown above 260° K. since at this temperature premelting begins in this oxidized specimen and the resistance increases rapidly.) Other experiments in this laboratory (Hedgcock 1956) confirm that in highly oxidized rubidium the anomaly seems to be suppressed.

In addition to the work already referred to, Kelly and Pearson (1955) have investigated the anomaly in detail but at present its origin is still obscure.

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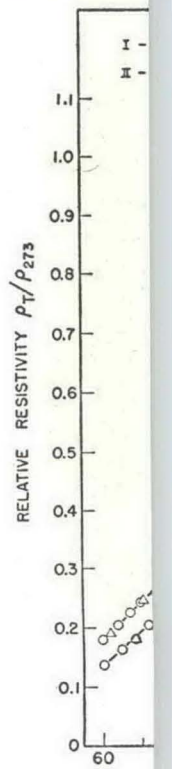

FIG. 3. The resistivity of a
temperature range.

PRESSURE EFFECTS

The isothermal change in resistance with pressure was measured in the neighborhood of room temperature on samples 1 and 2. As might be expected with such a fine capillary the change in resistance of sample 1 for a given pressure was appreciably lower than that in sample 2. Even with sample 2 the resistivity change at 2500 atm. was about 10% smaller than that deduced from Bridgman's measurements (Bridgman 1946) at higher pressures. (Bridgman's measurements refer to relative *resistance* changes of a given sample and have to be transformed into *resistivity* changes using the compressibility.) This difference is presumably due to the fact that we are using specimens melted into capillaries. The present experiments serve nevertheless to demonstrate that the general method is convenient and to give at least a qualitative picture of the pressure dependence of resistance down to very low temperatures.

In describing these results, it is convenient to divide the temperature range as follows:

(1) measurements between 50° K. and room temperature,

(2) measurements between 4° K. and 50° K.,

(3) measurement of the residual resistance.

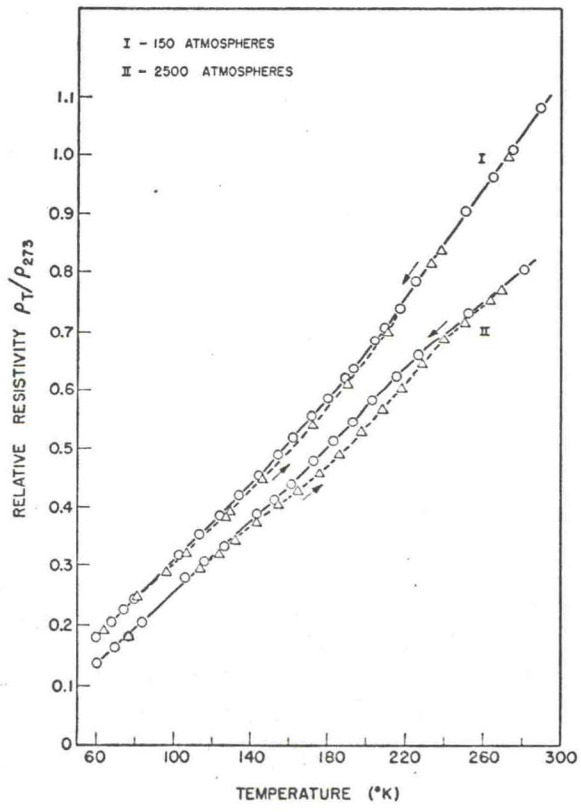

FIG. 3. The resistivity of a rubidium sample (sample 2) at two pressures in the higher temperature range.

(1) Fig. 3 shows the resistance of rubidium (sample 2) at two pressures (100 and 2500 atm.) in the temperature range around the anomaly, illustrating also the thermal hysteresis effects. It appears that because of temperature hysteresis and because the anomaly has no very well defined temperature it is impossible to judge from Fig. 3 whether the temperature of the anomaly is changed by pressure. However, the measurements on sample 1, for which the anomaly is more clearly defined, indicate that if there *is* a change it is certainly small.

The effect of pressure on sample 3 was also measured. It showed a considerably larger pressure coefficient than sample 2.

(2) In the lower temperature range, illustrated in Fig. 4, one sees that the high pressure and low pressure curves cross at about 6° K. This is because although the effect of pressure on the thermal component of resistance is always to lower it, the residual resistance (see below) is raised by pressure.

At about 25° K. helium under 2500 atm. pressure solidifies. Here we have approximately constant volume conditions since the pressure-filling tube is

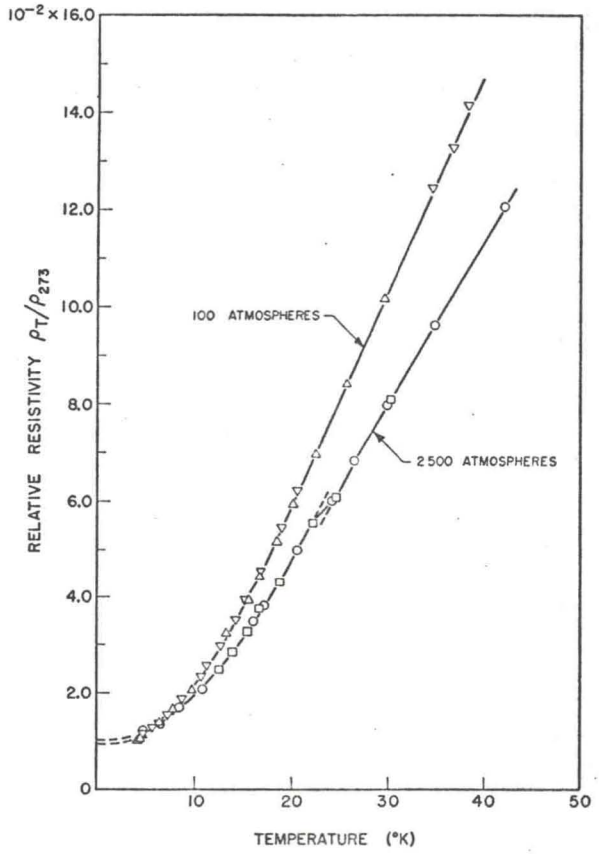

FIG. 4. The relative resistivity of a rubidium sample at low temperatures.

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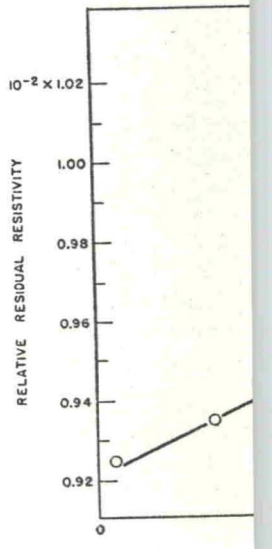

FIG. 5. The residual resi

arranged to be slightly colder than the bomb and so freezes first. Thus at 25° K. solidification of the helium begins and it is complete when the temperature has fallen to 22° K. The pressure is now very nearly 2000 atm. (see Dugdale and Simon 1953) and it falls slowly from this value to about 1900 atm. at the lowest temperatures.

Because of the marked pressure changes between 25° and 22° K. the resistance–temperature curve will be correspondingly modified in this temperature region. This is shown in Fig. 4.

After the measurements from nitrogen temperatures down to helium temperatures at three different pressures, the system was returned to its starting conditions at the nitrogen boiling point. The resistance was found to return to its initial value. The results of the low pressure measurements have been compared with values of the resistivity of rubidium obtained by White and Woods (private communication) and were found to agree satisfactorily.

(3) The effect of pressure on the residual resistivity was measured by applying the highest pressure (2500 atm.) at such a temperature (greater than 25° K.) that the helium is fluid and then cooling the system to 2° K. and measuring the resistance. The temperature was next returned to just above 25° K. and the pressure was lowered to 2000 atm. After this the system was again cooled to 2° K. and then the process repeated, the temperature being raised each time to a value sufficient to melt the solid helium before the pressure was lowered. The experimental points are shown in Fig. 5.

From these measurements we deduce a pressure coefficient of residual resistivity of about +4% per thousand atmospheres for sample 2.

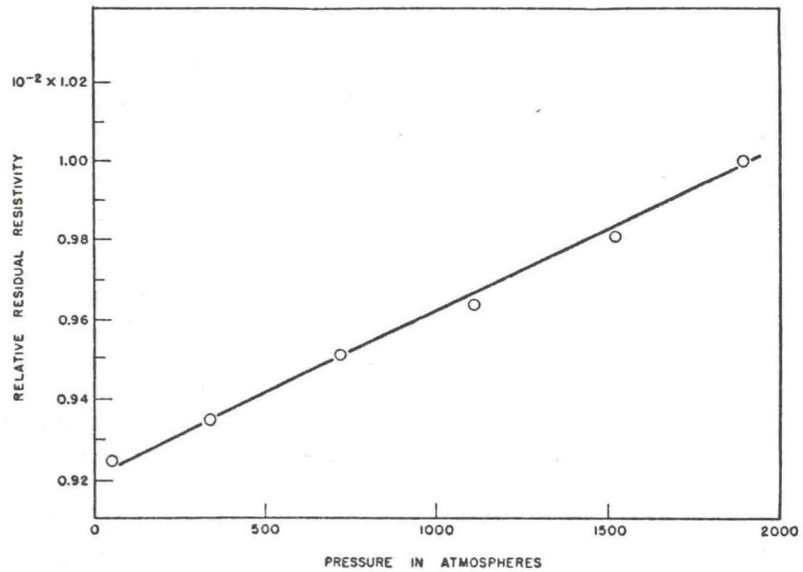

FIG. 5. The residual resistivity of a rubidium sample as a function of pressure.

DISCUSSION

(*a*) *The Thermal Component of Resistance*

A valuable summary of attempts to predict theoretically the effect of volume change on electrical resistivity and of comparisons with existing experimental data has recently been given by Lawson (1956). The main theoretical work on the volume dependence of resistivity at low temperatures is by Mott (1934) and by Grüneisen (1941). In these treatments, the Bloch–Grüneisen expression for the temperature dependence of resistivity was used as a basis for deriving the temperature dependence of the pressure coefficient.

For our present purpose this is not the best approach because the Bloch–Grüneisen theory does not describe at all satisfactorily the temperature dependence of the resistivity at constant volume of rubidium.

Consequently we have made a different comparison with theory. Instead of comparing the pressure coefficients directly, we have here computed the θ-values at several temperatures for two different pressures. The method used was that of comparing the logarithmic derivatives of resistivity with respect to temperature derived from experiment with those deduced from the Bloch–Grüneisen law (Kelly and MacDonald 1953). The results are given in Table II.

TABLE II

Temperature, ° K.	θ (100 atm.)	θ (2500 atm.)
10	45	45
20	58	58
30	63	65
45	50	65
50	46	65
60	50	65

We see thus that, as would be expected, the θ-value at a given temperature is usually increased when the volume is reduced, corresponding to a "stiffening" of the lattice under pressure, but that below about 30° K., although the ideal resistivities are markedly reduced by pressure, the θ-values appear to be unchanged.

(*b*) *The Residual Resistance*

Lenssen and Michels (1935) have discussed from a theoretical point of view the effect of pressure on the residual resistance. On the basis of the assumption that the electrons are truly free and that the scattering cross-section of the scattering centers is independent of volume, they deduce that $d \ln \rho_0 / d \ln V = -\frac{1}{3}$. If, on the other hand, the scattering centers are deformed by pressure in the same way as the dimensions of the specimen, then one deduces that $d \ln \rho_0 / d \ln V = +\frac{1}{3}$. From our measurements on sample II we deduce that for this specimen $d \ln \rho_0 / d \ln V = -1.1$.

ACKNOWLEDGMENTS

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