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# Phase Diagram of Rubidium to 150 000 kg/cm$^2$ and 400°C

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A room temperature transition was found in rubidium at 107 000 kg/cm$^2$. It is characterized by an abrupt increase in electrical resistance of about 12 to 15%. The melting temperature increased with pressure in a normal manner up to about 25 000 kg/cm$^2$; then the rate of rise diminished rapidly until a maximum melting point of about 280°C was reached at 50 000 kg/cm$^2$. Beyond this the melting point decreased with increasing pressure. A triple point at 112 000 kg/cm$^2$, 200°C occurred at the junction of the solid I–II line and the melting line. Only electrical resistance type measurements were made. Other transitions might be shown by volume measurements.

## I. INTRODUCTION

THE alkali metals, having one hydrogen-like valence electron per atom, might be expected to form relatively simple solid states, the properties of which could be predicted. Although progress has been made in the application of modern solid-state theory to these metals the results are only approximate, especially in the behavior at very high pressures.

The work on rubidium presented here was stimulated by a suggestion by Brooks[1] that a cesium-like resistance cusp transition might be expected in rubidium at a pressure of about 130 000 kg/cm$^2$. The suggestion was based on some theoretical work on the solid state of alkali metals done at Harvard University.

To provide a background of comparison, the behavior of cesium will first be presented. Figure 1 shows the volume transitions in cesium at room temperature, as reported by Bridgman.[2] The first transition occurs at 22 500 kg/cm$^2$ and the second at about 44 000 kg/cm$^2$. Both are polymorphic transitions. Figure 2 shows the electric resistance behavior with pressure, at room temperature, again as found by Bridgman.[3] A slight change of resistance appears at 22 500 kg/cm$^2$, but nothing shows at 44 000 kg/cm$^2$ where the large polymorphic transition occurs. The remarkable "resistance-cusp" electronic transition referred to above takes place at 55 000 kg/cm$^2$. This is the type of transition that was suggested might occur in rubidium at roughly 130 000 kg/cm$^2$.

## II. EXPERIMENTAL

A high-pressure apparatus similar to that of Hall[4] was used. The test cells were similar to those used in the author's studies of bismuth.[5] Most of the experiments were carried out with the simple cell shown in Fig. 3. The rubidium was enclosed in a very thin-walled glass capillary tube for convenience in handling and loading into the cell. The silver chloride sleeve around the rubidium core served as an approximate hydrostatic medium so that the rubidium sample would be subject to moderately uniform pressure. The stone cylinder around the silver chloride provided additional thermal insulation between the sample and the cold walls of the pressure vessel. The rubidium was heated directly by passage of electric current through it. The temperature was maximum at midspan because of extra heat losses through the electrical connections at the ends of the cell. The temperature was calibrated in terms of heating power by observing the heating power required

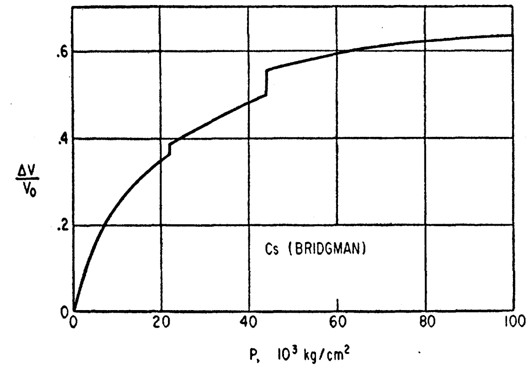

FIG. 1. Fractional volumetric compression of cesium *vs* pressure (Bridgman).

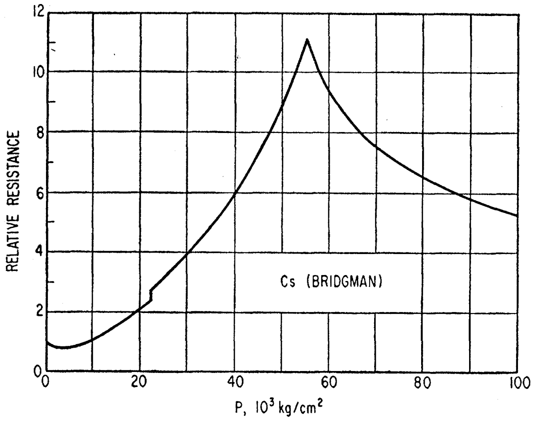

FIG. 2. Relative resistance of cesium *vs* pressure (Bridgman).

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[1] Harvey Brooks (private communication).

[2] P. W. Bridgman, *The Physics of High Pressure* (G. Bell and Sons, London, 1952).

[3] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 190 (1952).

[4] H. T. Hall (unpublished).

[5] F. P. Bundy, Phys. Rev. **110**, 314 (1958).

to melt the rubidium at a number of "low" pressures for which Bridgman[2] had already given data. Resistance and heating power were obtained from readings of the applied voltage and current.

The rubidium used was triply vacuum distilled and had a sharp melting point. It was stored in sealed glass capsules. Prior to a series of experiments a capsule was cracked under cool white mineral oil, then heated to slightly above the melting point and the rubidium sucked up into the thin-walled capillary tubes and solidified.

The test cells were loaded under mineral oil by passing the tube of rubidium into the hole in the cell, pinching it off at the ends and inserting nickel pin heads to seal it. Additional sealing and improved electrical contact was provided by 0.002-in. soft gold caps which were pressed into place as the cell was removed from the mineral oil.

For more refined work, done after the phase diagram had been "roughed-out" with use of the simple cell, the indirectly-heated, thermocouple-equipped, cell shown in Fig. 4 was used. In this cell heat was provided by the carbon heater sleeve which surrounded the rubidium assembly. The resistance of the rubidium sample was monitored through electrical connections coming out through the sides of the cell and through special pressure seals in the pressure vessel. Temperatures were measured by a chromel-alumel thermocouple lying near the midspan of the sample inside the carbon heater sleeve. The thermocouple wires were run directly through pressure seals in the pressure vessel so that no stray thermal emf's due to dissimilar materials were involved.

Only resistance measurements were made. No attempt was made to observe volume changes of the rubidium. Thus any polymorphic transitions not accompanied by electrical resistance changes would have escaped notice.

## III. RESULTS

The results of the experiments are summarized in Fig. 5. At room temperature a new, reproducible, reversible transition was discovered at 107 000 kg/cm$^2$. This transition is characterized by a 12 to 15% rise of resistance and is quite independent of temperature. As the temperature is increased the resistance change at this transition gets smaller, and almost vanishes at the triple point at about 200°C, 112 000 kg/cm$^2$.

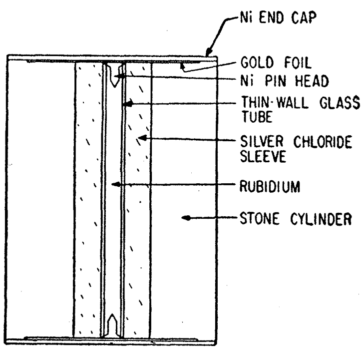

FIG. 3. Simple cell with direct heating.

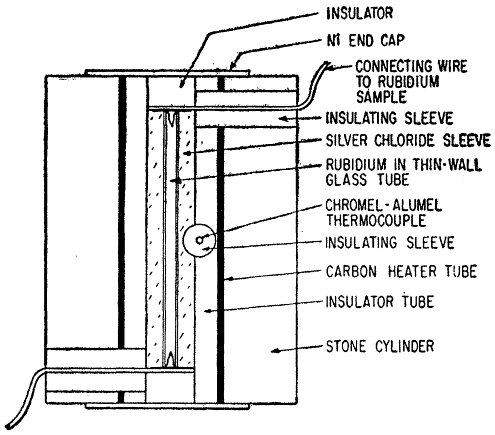

FIG. 4. Indirectly heated cell with thermocouple.

The melting line starts out with a rapid rise, in close agreement with Bridgman's data to 4000 kg/cm$^2$, then gradually levels out, and finally descends with increasing pressure. The resistance rise associated with melting gets progressively larger as the pressure is increased. When the rubidium was heated much above its melting point the pressure gradients in the cell walls tended to pinch it off, causing the resistance to rise, and in some cases causing open circuit. The behavior of the samples in this regard was about the same at 10 000 kg/cm$^2$, 250°C; 50 000 kg/cm$^2$, 300°C; or 130 000 kg/cm$^2$, 220°C. At all temperature-pressure positions in the solid phase areas the sample was very stable mechanically and electrically. In Fig. 5 the circles mark melting points determined in the indirectly heated cells with thermocouples, while the area bounded by dashed lines shows area of scatter of the results from the simple directly heated cells.

When the first results indicating a descending melting line were obtained, it was considered that the phenomenon might be caused by such other things as

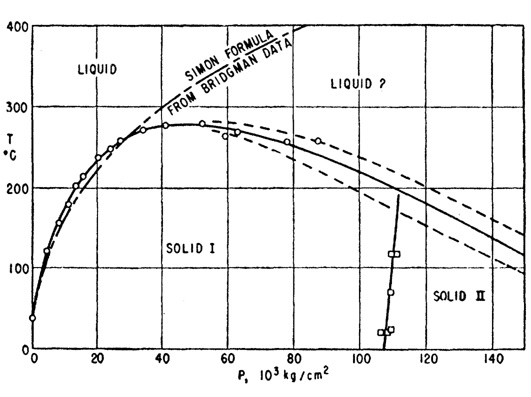

FIG. 5. Phase diagram of rubidium deduced from resistance measurements.

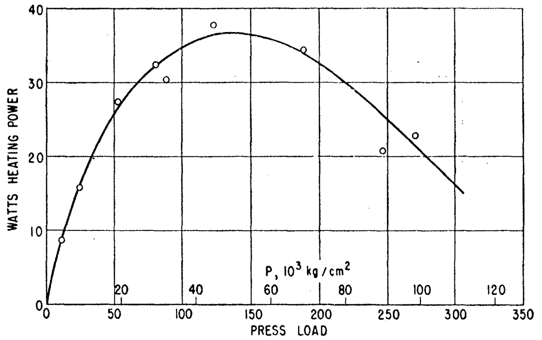

FIG. 6. Melting line *vs* pressure for rubidium in stone sleeve cell.

chemical reaction of the rubidium with the silver chloride sleeve, or with the glass capillary, or that the silver chloride was undergoing a phase transition. Examination of the glass after test runs showed it to be cracked into platelets but intact chemically. Also a small series of test runs was made in which the silver chloride was omitted. The results of these tests are shown in Fig. 6 as the heating power at which the transitions occurred plotted against the press load and approximate cell pressure. The shape of the transition curve is essentially the same as for the cells with silver chloride. Furthermore, the observed transitions were reversible with pressure or temperature. Reversibility almost certainly would not be true of a chemical reaction.

Figure 7 shows the resistance behavior of a sample at room temperature. The minimum in the resistance at about 30 000 kg/cm$^2$ is in agreement with Bridgman's observations. The abrupt increase at 107 000 kg/cm$^2$ is the newly discovered transition.

A typical melting transition at 14 000 kg/cm$^2$ is presented in Fig. 8. Melting starts at 206°C at the mid-span of the cell and continues until the thermocouple reads 220°C. This shows a temperature spread of about 14°C from the center to the ends of the rubidium sample in the cell used. After melting is completed the resistance line takes on a steeper slope which would indicate a higher temperature coefficient of resistance for the liquid. However, the cooling line shows that while the sample was in the liquid state it deformed enough to take on a permanently higher resistance. When this effect is taken into account the temperature coefficient of resistance of the liquid comes out about the same as for the solid at this pressure.

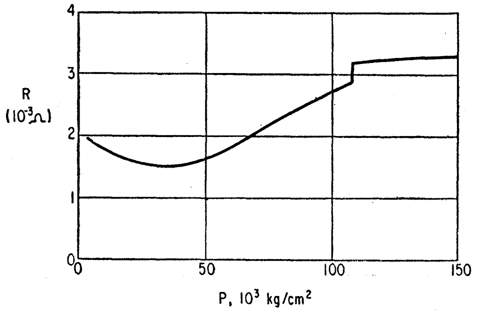

FIG. 7. Resistance *vs* pressure for rubidium sample at room temperature.

Figure 9 shows a melting cycle at 60 000 kg/cm$^2$. The resistance change at this pressure is considerably greater than at 14 000 kg/cm$^2$. There is the same permanent increase of resistance of the sample due to deformation during the period it was in the liquid phase.

The apparatus was calibrated for cell pressure in terms of applied press force by substituting bismuth, cesium, or barium for the rubidium in the cell and observing the known pressure-induced transitions in these elements, as determined by Bridgman. Figure 10 shows the resistance of a bismuth sample plotted against press load. Also plotted against press load is the cell pressure (right-hand ordinate scale). The bismuth transitions at 25 000 and 125 000 kg/cm$^2$ occur at press loads of 70 and 303, respectively. The cesium points shown are those at 22 500 and 55 000 kg/cm$^2$ which were presented in Fig. 2. The barium transition takes place at 80 000 kg/cm$^2$. Points for the very low-pressure part of the curve were established by observing the melting point of bismuth as a function of the press load, then deducing the cell pressure from the melting points as determined in hydrostatic apparatus by Bridgman,[6] and by Butuzov *et al.*[7] The absolute accuracy of the barium and high bismuth points is only about ±3 or 4% as discussed in reference 5 and hence the accuracy of the high part of the calibration curve can be no better.

## IV. CONCLUSIONS

The tests reported here do not show a resistance-cusp transition in rubidium. The solid I → II transition

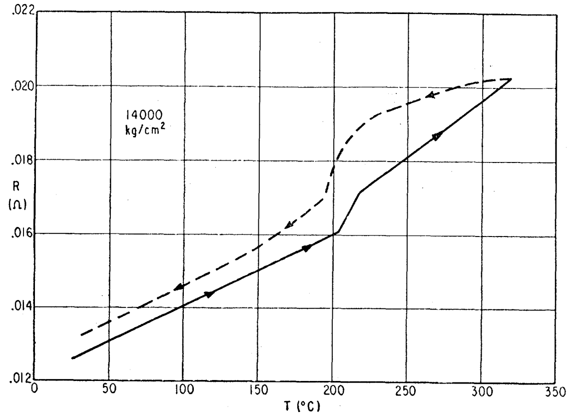

FIG. 8. Resistance *vs* temperature for rubidium sample at 14 000 kg/cm$^2$.

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[6] P. W. Bridgman, *American Institute of Physics Handbook* (McGraw-Hill Book Company, New York, 1957).

[7] Butuzov, Gonikberg, and Smirnov, Dolady Akad. Nauk. S.S.S.R. **89**, 651 (1953) (translation: National Science Foundation tr-76).

found at 107 000 kg/cm$^2$ shows more resemblance to the cesium transition at 22 500 kg/cm$^2$. If these are truly analogous, one would look for a cusp transition in rubidium at about 2.4 times the first transition, *viz.*, at about 250 000 kg/cm$^2$. However, this state might never be reached if the melting line continues the rate of decrease shown in Fig. 5, as melting would occur at room temperature at about 200 000 kg/cm$^2$.

Bridgman's data on the melting point of rubidium to 4000 kg/cm$^2$ can be fitted by a Simon-type[8] fusion equation, *viz.*,

$$(P+a)/a=(T/T_0)^c,$$

where $T$ is the melting temperature at pressure $P$, $a$ is an "internal pressure," $T_0$ is the melting temperature at $P=0$, and $c$ is a constant. The best fit to Bridgman's data is obtained by $a=3500$ kg/cm$^2$ and $c=4.20$. This line is shown in Fig. 5. The present results are fitted better from 0 to 20 000 kg/cm$^2$ by $a=2720$ kg/cm$^2$ and $c=4.43$.

The present experiments do not prove for certain that the transition line extending from 280°C, 40 000 kg/cm$^2$ to 140°C, 140 000 kg/cm$^2$ is a melting line. It is definite that the phase on the high-temperature side of this line is liquid-like in its mechanical properties. Several test runs were made into the $P,T$ region, above 300°C, suggested by the Simon formula for the melting line. In this region the sample always increased in resistance with time and eventually increased catastrophically to open circuit, or very high resistance. Examination afterward showed the sample to have necked down and pinched off.

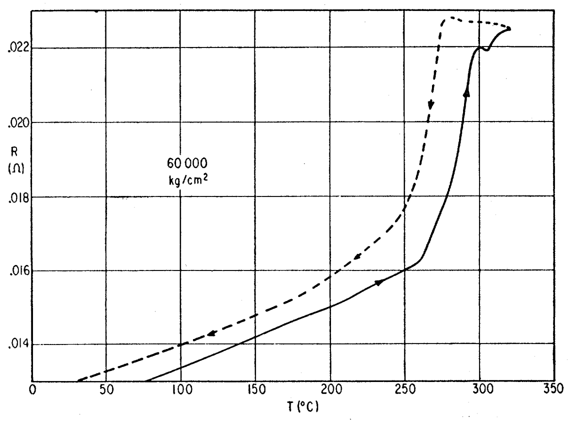

FIG. 9. Resistance *vs* temperature for rubidium sample at 60 000 kg/cm$^2$.

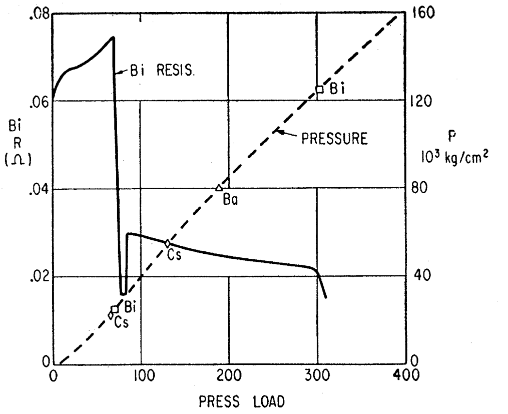

FIG. 10. Pressure calibration of the apparatus used in the rubidium experiments. Bismuth resistance dubbed in to show location of the two bismuth calibration transitions.

In 1952, MacDonald[9] reported a transition in rubidium at about −93°C and atmospheric pressure. It was manifested by increase of slope of resistance with temperature, and was reversible. This was investigated further as a function of pressure and temperature by Dugdale and Hulbert.[10] The transition at −93°C at low pressure was verified. However at 2500 kg/cm$^2$ it was rather spread out in temperature and showed some hysteresis upon change of direction of temperature, but occurred at roughly the same temperature. The character of the resistance change, and its slope on the $T,P$ diagram make it seem unrelated to the 107 000 kg/cm transition found in the present work.

Experimental measurements of the volume changes with pressure of rubidium are needed to complete the phase diagram in the pressure-temperature area reported here. At room temperature Bridgman found no discontinuities in the volume up to 100 000 kg/cm$^2$.

## ACKNOWLEDGMENT

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[8] F. Simon, Z. Elektrochem. **35**, 618 (1929); Trans. Faraday Soc. **33**, 65 (1937).

[9] D. K. C. MacDonald, Phil. Mag. **43**, 479 (1952).

[10] J. S. Dugdale and J. A. Hulbert, Can. J. Phys. **35**, 720 (1957).