

This gives

$$\alpha_0 = \mathcal{L}[2\alpha_0\beta J(\mathbf{k}_0)]. \quad (15)$$

It is easily seen that configuration (8) with $\alpha = \alpha_0$ is a solution of (4). This is an explicit verification of the remarks above (6). Figure 2 is a schematic representation of the pertinent sets of configurations and is useful for visualizing the course of the proof.

Although we used the classical formulation, the quantum mechanical treatment using the density matrix is the same in all essentials. Of course, the Langevin function is then replaced by a Brillouin function, and the spin length appears explicitly. On the other hand, the theorem and proof can be modified and extended only to certain special cases⁷ of anisotropic interaction and/or non-Bravais lattices. For example, we expect further results are obtainable when some form of generalized Luttinger-Tisza method^{4,8} is successful in rigorously determining the ground state. However, it is clear that the technique is not adequate to deal with the general case. For it has been shown⁹ that in at least some non-Bravais lattices, even with only Heisenberg interactions, the angles between spins in the classical ground state

⁷ The hcp lattice is an example of a non-Bravais lattice to which the proof may easily be extended.

⁸ M. J. Freiser, *Phys. Rev.* **123**, 2003 (1961).

⁹ D. H. Lyons, T. A. Kaplan, K. Dwight, and N. Menyuk, *Phys. Rev.* **126**, 546 (1962)

fail to satisfy the very plausible translational invariance condition,

$$\mathbf{S}_{n\nu} \cdot \mathbf{S}_{m\mu} = f_{\nu\mu}(\mathbf{R}_m - \mathbf{R}_n).$$

Here ν and μ label the sublattices and m and n label the unit cells. The ground state is, therefore, probably very complex and no method is known for discovering it. This difficulty is compounded at temperatures higher than $T=0$.

Finally, a word about the use of the molecular field idea. As it stands, the theorem has precise meaning for $T>0$ only in the context of the molecular field or independent spin approximation. One may wonder whether the theorem reflects a similar precise statement true for the exact canonical distribution. We feel this to be unlikely, if only for the reason that the concept of a spiral configuration for $T>0$ loses its precision outside of the molecular field approximation. Rather, the molecular field results suggest a single high peak in the transform of the spin correlation function $\langle \mathbf{S}(\mathbf{R}_n) \cdot \mathbf{S}(\mathbf{R}_n + \mathbf{R}) \rangle$. Of course, this transform is essentially what is measured in neutron diffraction experiments on magnetic ordering.

ACKNOWLEDGMENT

I would like to thank T. A. Kaplan for helpful comments.

Effect of Temperature and Pressure on the Resistance of Four Alkali Metals*

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(Received 27 May 1963)

The electrical resistance of lithium, sodium, potassium, and rubidium has been measured as a function of pressure to over 500 kbar at 77°K and 296°K. Lithium exhibits an initial rise in resistance, a first-order phase transition at 70 kbar with a large resistance drop, and a very gradual rise in resistance at high pressure. Sodium has a rise in resistance with pressure at both 77 and 296°K. The high-temperature isotherm exhibits a very broad maximum at high pressure. For potassium, the 296°K isotherm shows a rise by a factor of 50 in 600 kbar. The 77°K isotherm shows a sluggish transition at 280 kbar and a very sharp transition at 360 kbar. The latter is almost certainly martensitic. Both isotherms for rubidium have qualitatively similar behavior: a rise in resistance which accelerates with increasing pressure, a discontinuous rise at 190 kbar (210 kbar at 77°K), and a broad maximum at high pressure. The discontinuous rise is probably due to a electronic transition.

THE effect of pressure to over 500 kbar has been measured on the electrical resistance of lithium, sodium, potassium, and rubidium at 296 and 77°K. At appropriate pressures isobars were also measured. The experimental techniques have been previously de-

scribed.^{1,2} The methods for preventing sample oxidation are mentioned in a previous paper on alkaline earth metals.³ The metals used in this work are c.p. materials.

¹ A. S. Balchan and H. G. Drickamer, *Rev. Sci. Instr.* **32**, 308 (1961).

² H. G. Drickamer and A. S. Balchan, in *Modern Very High Pressure Techniques*, edited by R. H. Wentorf, Jr. (Butterworths Scientific Publications, Ltd., London, 1962).

³ R. A. Stager and H. G. Drickamer, *Phys. Rev.* **132**, 124 (1963).

* This work was supported in part by the U. S. Atomic Energy Commission.

Bridgman⁴ has previously measured the resistance of these elements to 65–70 kbar.

A quantitative comparison of our data with Bridgman's is not simple for several reasons. In the first place our data are least reliable below 50 kbar which covers much of this range. In the second place we report resistances, not resistivities, since it is not clear just how the correction for contact, etc., should be made. Thirdly, Bridgman tentatively assumed a pressure range of 100 kbar for his apparatus, but it is now clear that the range was nearer 65–70 kbar. On the basis of his assumptions he made rather complex corrections for contact resistance by fitting his 30 kbar and high-pressure data in the low-pressure range. Nevertheless, some comparison is possible.

For lithium, Bridgman showed an (uncorrected) resistance increase of 47% over his range. He corrected this to 70%. We show a rise in resistance of 39% from 10 kbar to the transition. Doubtlessly this would be larger if corrected for contact. For sodium he showed a

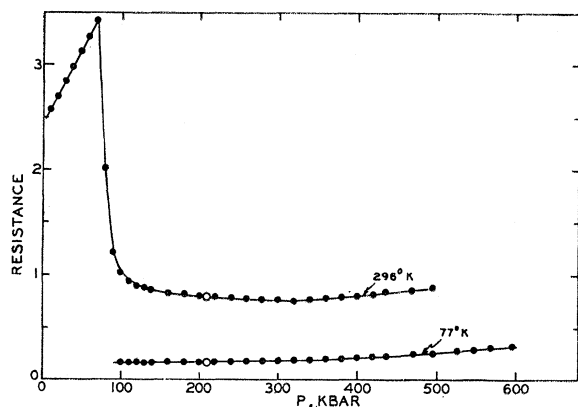


FIG. 1. Resistance versus pressure—lithium.

minimum in resistivity at about 46 kbar on his scale (about 40 kbar by present pressure scales). We obtained a minimum in resistance between 30 and 40 kbar.

Bridgman showed a minimum in the resistivity of potassium at 25 kbar. We find a minimum in resistance at the same pressure as nearly as such a low pressure can be determined in our apparatus. Bridgman found a minimum in resistivity for rubidium near 17 kbar, which is below the range where we can measure. In summary it can be said that the features of his data and ours are qualitatively the same, and the quantitative comparison is very reasonable in view of the differences in technique, pressure calibration, etc.

Theoretical work on the alkali metals has been done by Frank,⁵ Bardeen,⁶ and Ham.⁷ A review of earlier work is given by Lawson.⁸ It is difficult to apply these

⁴ P. W. Bridgman, Proc. Am. Acad. Arts Sci. **81**, 165 (1952).

⁵ N. H. Frank, Phys. Rev. **47**, 282 (1935).

⁶ J. Bardeen, J. Chem. Phys. **6**, 367 (1938).

⁷ J. S. Ham, Phys. Rev. **128**, 2524 (1962).

⁸ A. W. Lawson, Progr. Metal Phys. **6**, 1 (1956).

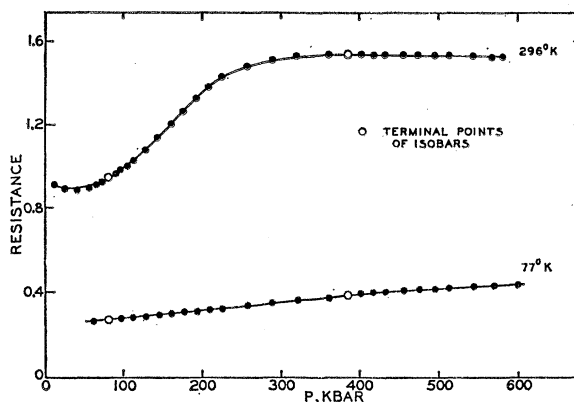


FIG. 2. Resistance versus pressure—sodium.

theoretical results to our data except in the most general fashion, in part due to the existence of high-pressure phases of undetermined structure.

LITHIUM

Figure 1 shows the two resistance-pressure isotherms for lithium. The open circles are terminal points of isobars. At 296°K the resistance rises to a maximum value at 70 kbar and then drops abruptly. Beyond this drop the resistance exhibits a minimum. At 77°K the drop in resistance was found to be smeared out and subsequent data was taken after first pressing to 100 kbar at 296°K and then cooling. As observed in the diagram, the resistance rises slowly but continuously at higher pressures.

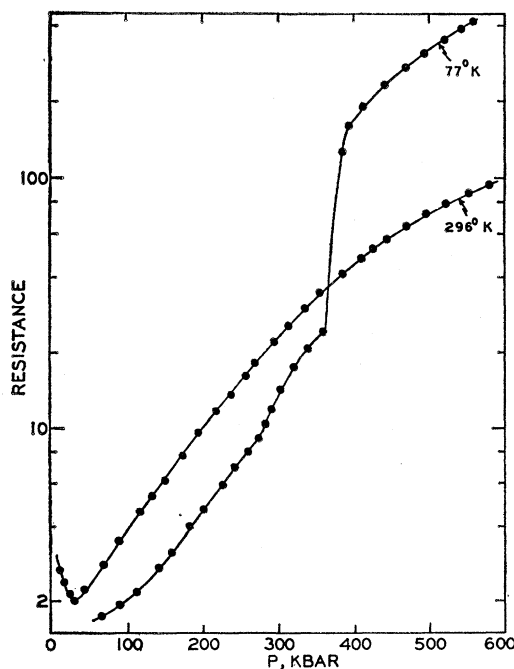


FIG. 3. Resistance versus pressure—potassium.

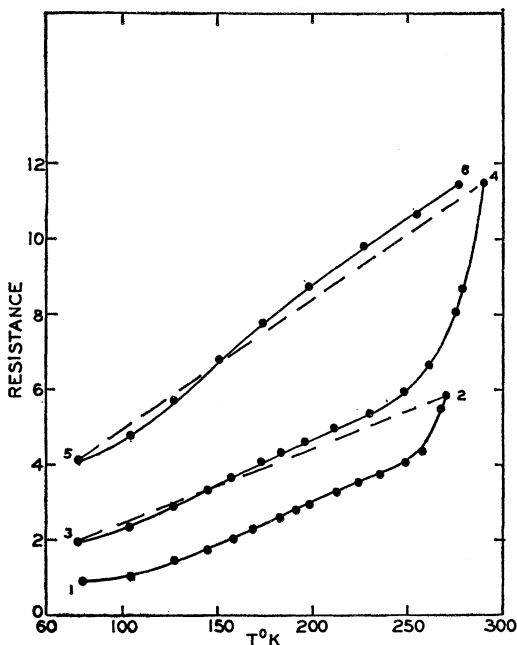


FIG. 4. Resistance versus temperature—potassium (320 kbar).

Since at atmospheric pressure and room temperature lithium has a bcc structure, a transformation to a closer packed structure such as fcc or hcp is the most likely explanation of the discontinuity in resistance. The smearing out of the transition at 77°K suggests a first-order, diffusion-controlled transformation. The slow rise in resistance with pressure at high pressures may be due to narrowing of the conduction band, as has been suggested by several authors.

SODIUM

At 296°K a minimum in resistance is observed at 40 kbar, after which there is a continuous rise ending in a very broad shallow maximum at about 360 kbar (Fig. 2). The 77°K curve, starting after the 50 kbar room temperature minimum, shows a similar, but less pronounced, rise, which never reaches a maximum even at 600 kbar (Fig. 2).

While it is not surprising that the rise in resistance with pressure at 296°K becomes less and less with increasing pressure, the particular shape of the curve may indicate sufficient increase in the Debye temperature θ_D to bring sodium into the region of $T/\theta_D < 0.15$. Below 0.15 the resistance is less sensitive to changes in θ_D and so should be less sensitive to pressure at higher pressures.

POTASSIUM

The resistance of potassium as a function of pressure is shown in Fig. 3 for isotherms obtained at 296 and 77°K.

The main feature of the 296°K isotherm is the very large continuous rise of resistance with pressure. The

increase is by a factor of about 50 in 500 kbar, and contrasts markedly with the modest rises in sodium and lithium. Evidently, some form of interband scattering is taking place here, as there is no evidence from Ham's⁷ calculations that there could be sufficient band narrowing to give this result.

The 77°K isotherm has two unusual features in addition to the large rise exhibited by the 296°K isotherm. At about 280 kbar there is a distinct discontinuity in slope of the resistance-pressure curve. The size of the discontinuity varied from run to run, as would be expected from a sluggish phase transition. At 320 kbar a series of isobars were obtained by alternately heating and cooling between 77°K and room temperature until the same terminal values were obtained for successive cycles, as shown in Fig. 4. The new phase is metallic and is apparently stable at room temperature when established in this fashion. It is not clear why the transition does not occur during a 296°K isotherm.

At 360 kbar and 77°K a second transition took place, with a very sharp increase in resistance in contrast to the one discussed above. The high-pressure phase also showed a large increase in resistance with increasing pressure. An isotherm obtained at 197°K was very similar to that at 77°K.

It is believed that this second transition can be explained with the aid of the isobars shown in Figs. 5 and 6.

From Fig. 5, it is seen that the resistance drops with increasing temperature (points 1 to 2) to about 230°K, then increases to 270°K (2 to 3). The sharp drop at 270°K (3 to 4) is the reverse transition. On cooling

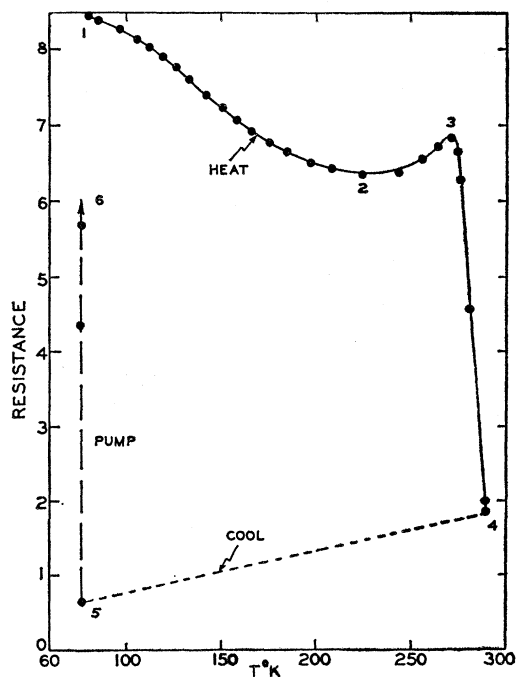


FIG. 5. Resistance versus temperature—potassium (500 kbar).

(4 to 5) the material remains metastable in the lower resistance phase, but transforms back immediately when pressure is applied. Evidently, the slight shear accompanying pressure application is sufficient to initiate the transition. From Fig. 5, one could conclude that the high-pressure phase is a semimetal with an energy gap at low temperatures and overlapping bands at high temperatures. Figure 6, however, shows a cycle where the heating is interrupted at 160°K by recooling (2 to 3) to 77°K. The resistance-temperature curve (1 to 2) is not reversible. On reheating, the material returns to its former state at point 2 (now state 5). The cycle then continues.

The 360 kbar transition is very likely martensitic on the basis of the following observations:

(a) There is a temperature above which the transition does not run with pressure, which is between 197 and 296°K;

(b) The transition is sharp at temperatures at which a diffusion-controlled, first-order transition is usually very metastable;

(c) Martensitic transitions have been found in lithium and sodium at atmospheric pressure, but not in potassium (Barrett⁹). The behavior is qualitatively similar for these transitions;

(d) Upon heating up the reverse transition occurs at about 270°K, depending slightly on the pressure. This would be the M_a (martensitic critical) temperature.

The irreversible nature of the initial resistance drop in Figs. 5 and 6 could indicate that this drop is due to

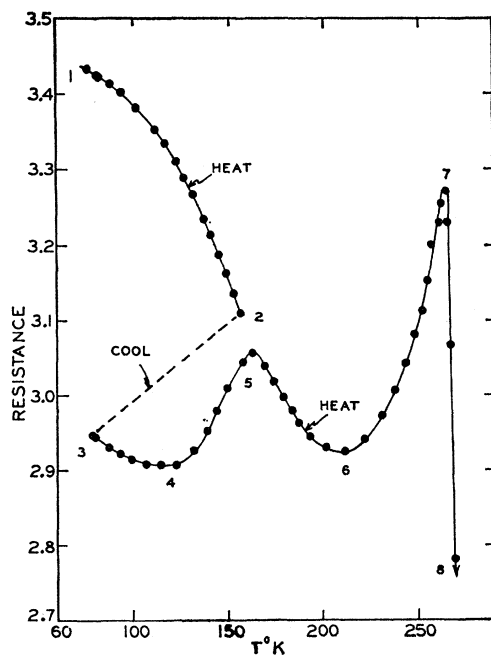


FIG. 6. Resistance versus temperature—potassium (490 kbar) heating to 160°K, recooling, and reheating.

⁹ C. S. Barrett, J. Inst. Metals 84, 43 (1955).

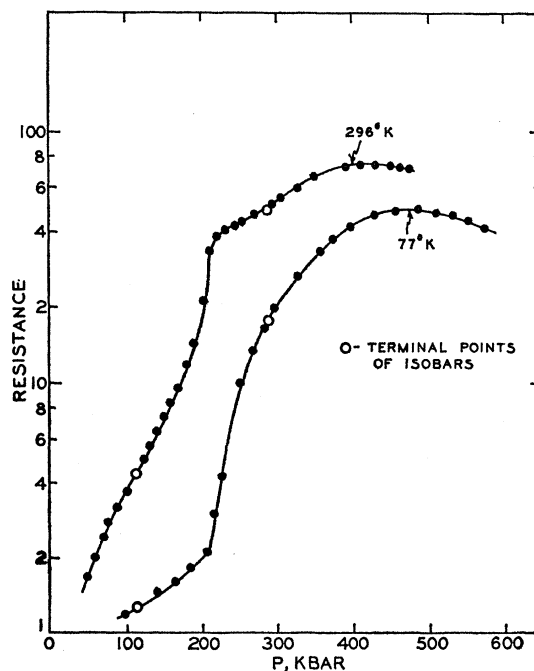


FIG. 7. Resistance versus pressure—rubidium.

the removal of strain in the sample. The subsequent rise would then indicate that the high-pressure phase is metallic.

RUBIDIUM

Room temperature data were first obtained by Balchan and Drickamer,¹ and have been confirmed and extended in this work. The resistance rises with pressure at the lowest pressures obtainable in this work. There is a distinct discontinuity in slope near 70 to 75 kbar, which is undoubtedly the transition (probably bcc to fcc) observed by Bundy.¹⁰ Above this point the resistance rises with increasing slope. Near 190 kbar there is an abrupt rise accompanied by much drifting upward with time. At higher pressures a downward drift initiates, and there is a broad maximum near 425 kbar. The higher pressure features are similar but sharper at 77°K. The abrupt rise is at 210 kbar and the maximum at 510 kbar. Typical isotherms and terminal points of isobars are shown in Fig. 7.

The sharp rise at 190 kbar and 296°K could be melting, judging by the extension of Bundy's¹⁰ melting curve which showed a negative slope at high pressures. In view of the fact that it occurs at only slightly higher pressure at 77°K, it would seem more likely that it is an electronic transition, analogous to the 41 kbar transition in cesium.

ACKNOWLEDGMENTS

The authors wish to thank J. Bardeen and F. Seitz for very helpful discussions.

¹⁰ F. P. Bundy, Phys. Rev. 115, 274 (1959).