High-pressure and low-temperature study of electrical resistance of lithium

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The electrical-resistance behavior of Li is studied for pressures up to 410 kbar and temperatures from 300 K down to about 2 K. We found that between 220 and 320 kbar the electrical resistance of Li at low temperature exhibits a sharp drop around 7 K, suggesting a phase transition. It is suggested that Li transforms from the hcp to fcc phase near 260 kbar at low temperature.

I. INTRODUCTION

Lithium is the simplest of all metals. It has three electrons per atom and is one of the most important candidates for both theoretical and experimental investigations. However, aside from a few studies[1-3] on its electrical resistivity as a function of temperature at ambient pressure, there is very little information on the effect of pressure on its electrical behavior. Bridgman[4] measured the electrical resistivity of lithium up to about 100 kbar at room temperature. Stager and Drickamer[5] extended the investigation up to 200 kbar for room and liquid-N_2 temperatures only. In this paper, we report our measurements on the electrical-resistance behavior for lithium for pressures up to about 410 kbar and temperatures from 300 K down to 2 K.

In the pressure range from 220 to 320 kbar, we found a sudden electrical resistance drop for Li at around 7 K, suggesting that a phase transformation, possibly a superconducting transition, has occurred. In their early pseudopotential calculation of the mass enhancement and superconducting transition temperature of simple metals, Allen and Cohen[6] predicted that Li should be superconducting at low temperature. Aside from Cs,[7] this is the first time that a monovalent metal has indicated signs of possibly becoming superconducting at high pressures.

Recently, the s-d electron transfer in K, Rb, and Cs has been studied quite extensively by Takemura, Syassen, and colleagues.[8-10] It is believed, however, that such a mechanism should not play any role in the electrical behavior of Li and Na for pressures up to 410 kbar because their d states at these pressures are far above their Fermi level. Nevertheless, Stager and Drickamer[5] reported an electrical-resistance increase for both Li and Na in the 100 to 200 kbar region. Our result for Li also shows a large electrical-resistance increase beyond 150 kbar. The cause of such an increase will be discussed.

II. EXPERIMENTAL RESULTS

The pressure equipment used in this investigation is the cryogenic clamp type sintered-diamond-compact anvil apparatus. The experimental procedure and pressure calibration have been described elsewhere.[11-13]

The lithium metal of 99.9% purity was obtained from the Johnson Matthey Company. The samples were prepared under white oil by rolling freshly cut metal chips with carbide scriber to form thin foils about 0.07 mm thick. Specimens of a rectangular shape of approximately 0.13×0.6 mm^2 were cut and placed in the high-pressure cell as quickly as possible. Figure 1 shows the arrangement of the specimen, electrodes, and sample holder in the high-pressure cell. Because the sintered-diamond compacts are not good electrical conductors, the copper electrodes, in the form of long rectangular strips of about 0.05 mm thick and 0.13 mm wide, extend from both ends of the specimen all the way to the carbide part of the pistons. The resistance of the sample was monitored by sending through an exciting current of 10 mA and measuring the voltage drop across the pistons. The background electrode resistance, contributing about 0.05 Ω at 300 K and 0.01 Ω at liquid-helium temperatures, was subtracted from the total resistance to obtain the sample resistance. Gold electrodes were used initially, but were suspected to form an alloy with the lithium sample at high pressures and were thus not used.

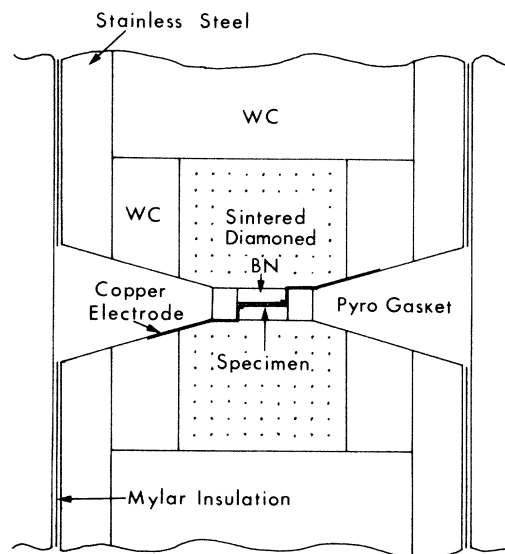Initially, a pyrophyllite sample holder (disks and ring)

FIG. 1. Sectional view of the arrangement of the specimen, electrodes, and sample holder in the high-pressure cell.

was used with various kinds of lining materials such as Teflon, Mylar, mica, epoxy coating, etc., to prevent the sample from oxidation. They were found to be unsatisfactory after at least 32 unsuccessful experiments. The sample resistance was found to increase indefinitely without approaching an equilibrium value, indicating a continuing oxidation. Later, a combination of prebaked boron nitride disks and ring was found quite successful with stable sample resistance readings and was thus used. On one of the BN disks, a groove of approximately $0.05 \times 0.13 \times 0.6$ mm^3 was made to accommodate the sample. This was found necessary to prevent the soft lithium metal from flowing in an uncontrollable manner. The whole sample preparation procedure was carried out in a plastic tent flushed with argon. Of the 21 runs at room temperature using the BN sample holder, 11 were successful.

Figure 2 shows a typical result of the electrical-resistance behavior of Li as a function of pressure at room temperature. The uncertainty in pressure scale is estimated to be ± 20 kbar. The initial resistance peak at 70 kbar reported by Stager and Drickamer[5] was smeared by the large reduction of the contact resistance in the loading cycle. This large reduction of the contact resistance is a typical characteristic of the sintered-diamond-compact device because the firm electrical contact is established on the conical flank through the long copper electrodes. The sample resistance reaches a minimum at about 120 kbar, starts to rise rapidly beyond 150 kbar, and exhibits several kinks up to about 300 kbar. Other higher-pressure runs indicate that the resistance continues to rise beyond 300 kbar. In a separate run, using tungsten carbide pistons with a much larger anvil face suitable for studies for the (0—100)-kbar pressure range, we reproduced the result of Stager and Drickamer[5] and found a sudden resistance drop at about 70 kbar. It is also shown in Fig. 2 as a dashed line. This resistance drop must be associated with the bcc→fcc phase transition recently found by Olinger
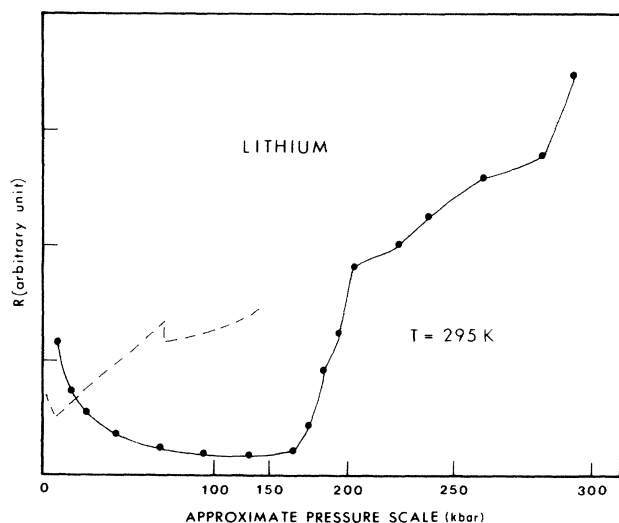
and Shaner.[14] Combining our experimental results using both the sintered-diamond-compact anvils and the tungsten carbide anvils, we believe that the resistance minimum that occured at about 120 kbar is an artifact due to the reduction of the contact resistance and that the electrical resistance of lithium increases monotonically with initial application pressure, makes a sudden drop at about 70 kbar, and continues to increase up to about 150 kbar. Beyond 150 kbar, the rate of the resistance increase with pressure becomes faster. After 200 kbar, the rate of the resistance increase slows down until about 290 kbar and goes up again. The region of slow resistance increase between 200 and 290 kbar is significant, because this is the region where we found sudden resistance drop at around 7 K in the low-temperature experiments.

Figure 3 shows the R versus T behavior at various fixed pressures from 160 to 410 kbar. Aside from that at 160 kbar which was a single run, the rest were the result of a continuous run accomplished by successively loading the clamp press between each temperature cycle to liquid-He temperature. They were done by loading the sample in the clamp press at room temperature, inserting the clamped rig into a cryogenic Dewar, lowering the temperature, to liquid-helium temperatures and below, and monitoring the resistance of the sample during the slow warm-up. The clamp press, designed to be temperature compensated, gives nearly constant cell pressure during the slow warm-up process. Each temperature cycle took about three days. The data were recorded by Keithley 195A Digital Multimeters along with a Keithley 705 scanner. The sample resistance was averaged with the exciting current in both forward and reverse directions to remove any thermal emf. Notice that from 220 to 410 kbar, the resistance at room temperature increases approximately 60 times. To include all the R versus T curves at various pressures in one plot, the logarithmic scale was used for the resistance.

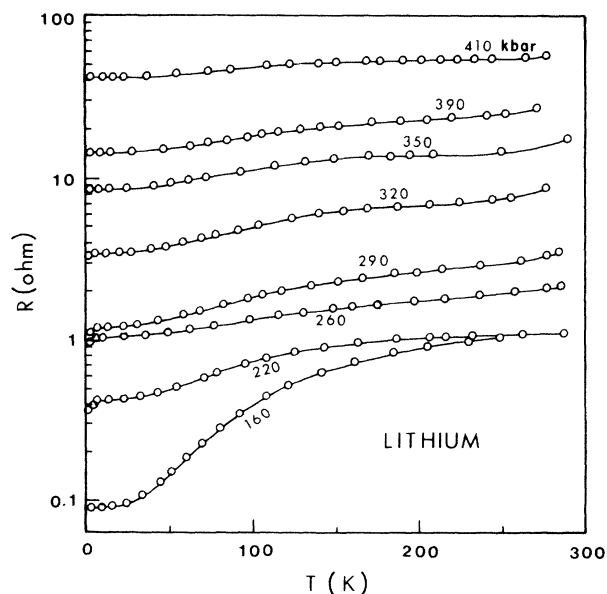FIG. 2. A typical room-temperature run for Li.

FIG. 3. Electrical resistance versus temperature at various pressures for Li.
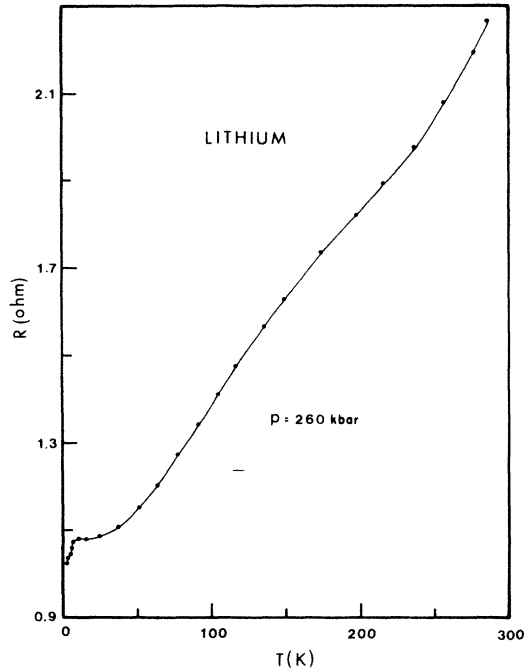
FIG. 4. Electrical resistance versus temperature at 260 kbar for Li.

Figure 4 shows the R versus T behavior for Li at approximately 260 kbar. The sudden resistance drop at about 7 K can be interpreted as a phase transition, possibly a superconducting transition. Because of the limitation of our temperature capability, we do not know if the resistance will continue to drop to the background resistance at lower temperatures. Figure 5 depicts the low-temperature electrical-resistance behavior of Li in a more
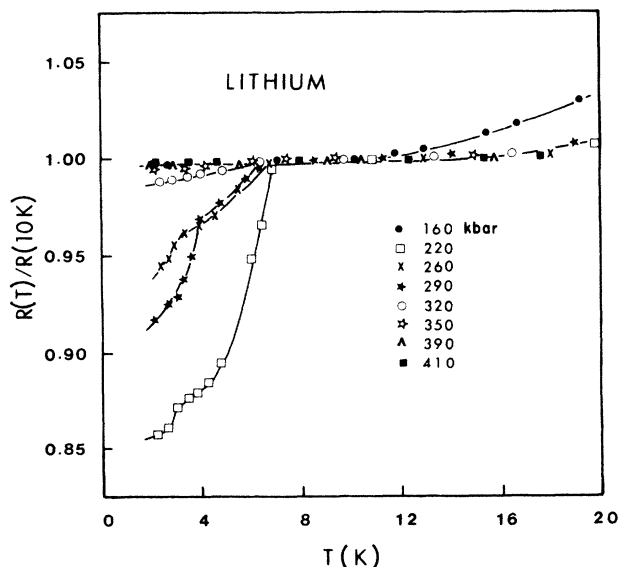

FIG. 5. Reduced-electrical resistance $R(T)/R(10\ \text{K})$ versus temperature at various pressures for Li.

clear manner. A resistance drop suggesting phase transition or possibly superconducting transition was not observed until 220 kbar. The drop starts at around 7 K. It disappears above 320 kbar. At least two more experiments were run and the same results were reproduced. The uncertainty in the temperature measurement is about ±0.1 K at low temperatures and ±1 K at higher temperatures.

III. DISCUSSION

Figure 3 shows an abnormally high residual resistance value for Li at high pressures. This may have been caused by the partial oxidation of the sample. However, the electrical resistance of the lithium sample increased only after the application of pressure between successive isobaric runs. It did not increase very much of its room-temperature value during the three-day temperature cycle. This observation is not compatible with the hypothesis of sample oxidation. Another explanation is that it is caused by the distortion of Fermi surface at high pressures. Recently, Boettger and Trickey[15] calculated the band structure of fcc Li at high pressures. They found, that fcc Li has an open Fermi surface with narrow necks centered on the L points touching the zone boundary. As the pressure is increased, the diameter of the necks in the Fermi surface increases. This change should increase the electron scattering, and hence, the electrical resistance. Perhaps most of the resistance increase is contributed from the large density of dislocations generated at high pressures due to the low flow stress of lithium. An early experiment by Dugdale and Gugan[1] showed that the electrical resistivity at 4.2 K increases linearly with strain. This may be a general feature for soft metals like Li and Na. It explains why Stager and Drickamer[5] also observed an electrical-resistance increase for Na in the 100—200 kbar range.

The low-temperature electrical behavior of Li is complicated by the presence of a martensitic transformation. As earlier work[1,3] at ambient pressure indicates, the bcc Li undergoes a spontaneous martensitic transformation to an hcp structure upon cooling through 75 K. The martensitic transformation start temperature M_s can be as high as 80 K for large-grained specimens of pure lithium and can be as low as 67.5 K for plastically deformed specimens. At 4 K, perhaps as much as 90% of pure lithium transforms to the hcp phase. Upon heating, reversion to the bcc phase does not begin until approximately 90 K and will not end until 160 K.

Barrett and Trautz[16] found that plastic deformation produced the fcc phase. Cold work at 78 K produced up to 50% of the fcc phase, and the lower the temperature of deformation the greater the fraction of fcc Li that was formed. Recently, using a Bridgman anvil device, Olinger and Shaner[14] found through x-ray-diffraction studies that lithium transforms from bcc to fcc structure at 69 kbar and 296 K. In our experiments, all the isobaric runs were at pressures higher than 69 kbar. Presumably, the lithium sample was in the fcc phase at high temperatures, i.e., 100—300 K. In order to understand the phase behavior of Li further, in the following we shall use the Grüneisen-

Bloch relation to study the electrical-resistance behavior of Li below 60 K.

To analyze our data, we take the limiting electrical-resistance value of Li at low temperature to be the residual resistance R_0, and subtract it from the total resistance R to obtain the ideal resistance R_T, i.e., $R_T = R - R_0$. Dugdale and Gugan[1] pointed out that the electrical behavior for Li at ambient pressure does not obey Matthiessen's rule. And usually, Matthiessen's rule is applied to cases where the residual resistance is small. Since we are not interested in studying the ideal resistance exactly and are only interested in exploring the general trend of the electrical-phase behavior of Li as a function of pressure, we shall temporarily ignore these limitations. Assuming a form of $R_T \sim T^n$ for each pressure in the low-temperature region, the ideal electrical resistance R_T can be plotted versus temperature in the logarithmic scale. Such a result is shown in Fig. 6. One notices that the data at 160, 220, and 260 kbar fall on a slope of $n = 3.2$, and starting from 290 kbar, the data gradually shift toward a slope of $n = 5$. This suggests that at pressures higher than 260 kbar, Li may have transformed to another phase at these low temperatures. This observation is quite close to Skriver's[17] predictions that Li transforms from hcp to fcc at 0 K around 210 kbar.

Using the simple form proposed by Grüneisen[18] and Borelius,[19] i.e.,

$$R_T/R_\Theta = 1.17(T/\Theta_R) - 0.17 , \qquad (1)$$

which represents the linear portion of the Grüneisen-Bloch relation in the temperature range $0.3 < T/\Theta_R < 1$, we obtain the electrical characteristic temperature Θ_R^{20}. The result is shown in Fig. 7. The data at zero pressure is a Debye temperature Θ_D obtained from the specific-heat
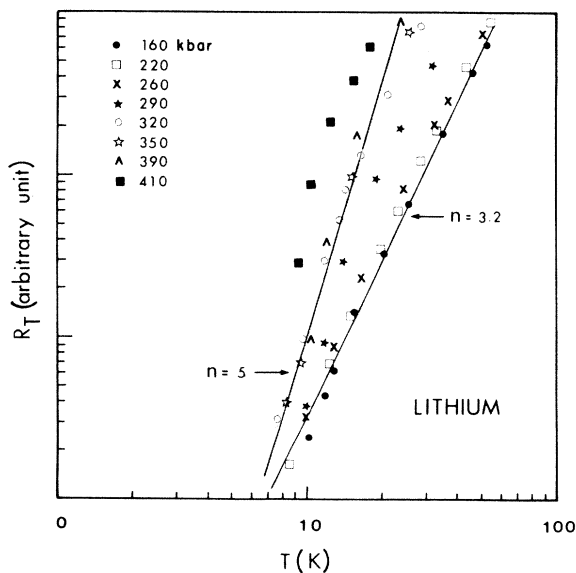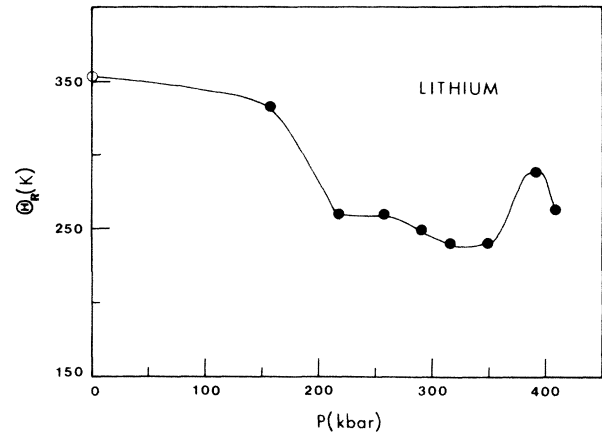

FIG. 7. Grüneisen characteristic temperature as a function of pressure.

measurement,[3] others were Θ_R determined from Eq. (1). Notice that the electrical-characteristic temperature decreases to a minimum around 220–350 kbar then goes up again. This behavior is reasonably consistent with our observation on Fig. 6 which suggests a phase transition near 260 kbar at low temperatures.

The phase stability of Li has been calculated by Young and Ross,[21] Skriver,[17] Boettger and Trickey,[15] and many others. Because very few experimental results on Li are available, there is yet no conclusive answer to the Li phase diagram. Based on the result of Olinger and Shaner[14] at room temperature, previous work on the martensitic transformation, and our present result on lithium's electrical behavior up to 410 kbar, we propose a tentative phase diagram for Li as shown in Fig. 8. The bcc-fcc phase line
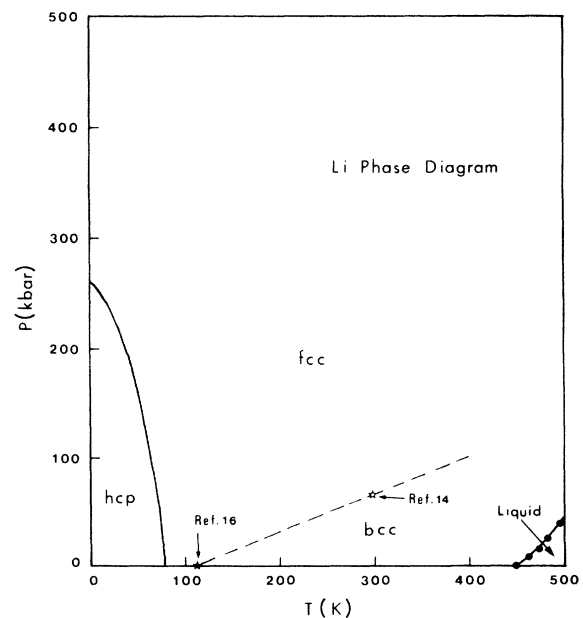

FIG. 6. Ideal electrical resistance R_T versus temperature at various pressures.

FIG. 8. Suggested phase diagram for Li.

was suggested by Olinger and Shaner.[14] The hcp-fcc phase line is based on our observation shown in Fig. 6, which suggests a phase transition near 260 kbar at low temperatures.

The superconductivity of Li was predicted by Allen and Cohen.[6] We are not certain that what we observed and showed in Fig. 5 is the superconducting transition. If it was truly a superconducting transition, it happened at the hcp region just before the lithium transformed to the fcc phase. Probably, the superconduction was due to the residual bcc Li which did not transform to the hcp phase. The residual bcc Li might be dispersed as small isolated particles in the hcp phase. This hypothesis explains why the resistance did not drop completely to the background resistance. The theoretical calculation recently made by Sundqvist et al.[22] on the electron-phonon interaction $\lambda(p)$ of bcc Li also supports our hypothesis. It is entirely possible that the observation shown in Fig. 5 was due to a phase transition of a different nature.

IV. CONCLUSION

Briefly summarizing our findings, we found the following:

(i) The electrical resistance of Li increases monotonically as a function of pressure, makes a sudden drop at around 70 kbar, and then continues to increase. The rate of increase becomes faster beyond 150 kbar, slows down between 200 and 290 kbar, and goes up again at higher pressures.

(ii) The data at 160, 220, and 260 kbar indicate that they are the same phase and that there is probably a phase transition of hcp→fcc near 260 kbar at low temperatures.

(iii) Lithium exhibits a sudden electrical resistance drop around 7 K between 220 and 320 kbar.

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