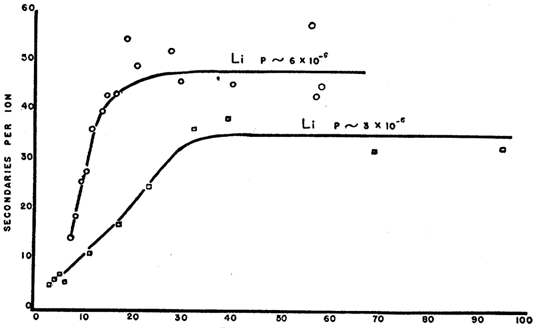

FIG. 5. Effect of elapsed time on freshly formed lithium targets, with 1.32 mv ions.

tion of the effect. In the light of the high values and the great speed of the lithium reaction as compared to the others it seems likely that the surface change is neither a modification of properties that is directly proportional to the thickness of the adsorbed layer, nor a simple replacement of the lithium by a gas film as the emitter.

The action of the alpha-rays has been studied by Thomson,[5] Logeman,[6] Bumstead and McGougan,[7, 8] Becker[9] and others, and it has been found that the number of secondaries per alpha-particle is of the order of 10, but depends upon experimental conditions. The energies of the secondaries lie in the range zero to two or three thousand electron volts with the great majority having a value of only a few volts; these energies are compatible with the theory that the maximum velocity a secondary can have is twice the velocity of the incident alpha-particle. This allows a maximum energy of about 10 volts for the secondaries produced by 1.32 mv. mercury ions, but about 10 percent of the electrons leaving the target have greater energy. It seems likely that these more energetic particles are photoelectrons. In this connection it should be pointed out that Coates[3] has found that x-rays of several thousand volts energy are produced by the swiftly moving mercury ions.

The author takes pleasure in expressing his gratitude to Professor Ernest O. Lawrence who suggested the problem and has been an inspiration and the source of invaluable suggestions.

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[5] J. J. Thomson, Proc. Camb. Phil. Soc. **8**, 49 (1904).
[6] W. H. Logeman, Proc. Roy. Soc. **A78**, 212 (1906).
[7] H. A. Bumstead, Phil. Mag. **26**, 233 (1913).
[8] H. A. Bumstead and A. G. McGougan, Phil. Mag. **24**, 462 (1912).
[9] A. Becker, Ann. d. Physik **75**, 217 (1924).

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The Effect of Pressure on the Electrical Conductivities of the Alkalies

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The observed effects of pressure on the resistance of lithium and of sodium are explained by taking into account the change of binding of the conduction electrons of these metals with pressure. A method of interpreting the experimental results is given and it is shown that from the theoretical calculations of Slater and of Millman one can predict the observed behavior of these metals. Thus no special assumptions are necessary to explain the "abnormal" behavior of lithium.

INTRODUCTION

It is well known that the alkalies in common with most other metals become better conductors of electricity when compressed, with the notable exception of lithium, which becomes a poorer conductor under pressure than at zero pressure. Besides lithium, calcium and strontium also display an abnormal pressure coefficient of resistance, but these elements are divalent and this abnormal behavior can readily be explained.[1] The normal effect has been qualitatively explained by Grüneisen[2] as follows: When a metal

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[1] See N. F. Mott, Proc. Phys. Soc. **46**, 691 (1934).
[2] Grüneisen, Verh. d. D. physik. Ges. **15**, 186 (1913).

is subjected to high pressure, the atoms are held in equilibrium positions which are closer together than at zero pressure, and the forces which hold the atoms in these positions are stronger than at normal separation. Hence, for a given thermal energy, the amplitudes of oscillations of the atoms decrease with increasing pressure, and since the scattering of the conduction electrons by the lattice varies with these amplitudes, we should expect a decrease in resistance when the metal is compressed.

The wave-mechanical theory of the structure of sodium and lithium,[3] and the modern theory of electrical conductivity[4] have been developed sufficiently so that we are in a position to attempt an explanation of the pressure effects in these metals. According to a general theorem of Bloch, the state of an electron in a metallic lattice is defined by a wave function of the form

$$u = e^{i(\mathbf{k}\cdot\mathbf{r})}\psi_{\mathbf{k}}(x, y, z)$$

with an energy E which is a function of the components of the vector **k**. For free electrons, **k** is the wave vector and is proportional to the momentum of the electron. In the case that the energy E is a function only of the magnitude of **k**, a condition which is well fulfilled for Na and Li for the values of **k** which determine the conductivity, Bethe gives the following expression for the conductivity σ at high temperatures,

$$\sigma = \frac{n_0}{\pi^3}\frac{k}{C^2}\left(\frac{dE}{dk}\right)^2\frac{2\pi k_0}{ha_0}\frac{M}{m}\frac{\Theta^2}{T}. \tag{1}$$

In this expression n_0 is the number of conduction electrons per atom, k_0 Boltzmann's constant, a_0 the radius of a hydrogen atom, M the mass of the metallic ion, Θ the Debye characteristic temperature. The quantities k, dE/dk refer to the maximum of the Fermi distribution and C is a constant which measures the scattering power of a metal ion.

For the purpose of discussing the variation of conductivity with pressure, we may write Eq. (1) more conveniently as

$$\sigma \sim (k/C^2)(dE/dk)^2\Theta^2, \tag{1a}$$

all the other factors being independent of pressure for a given metal. The characteristic temperature Θ increases with increasing pressure (the Grüneisen effect mentioned above), and we must attribute the abnormal behavior of lithium to changes in the other factors.

1. Interpretation of the Experimental Results

The changes of resistance of most of the metals under pressures up to 12,000 atmospheres have been measured by Bridgman.[5] In the case of sodium, he finds that the electrical resistance drops (at 12,000 atmos.) by about 57 percent from its value at zero pressure, whereas for lithium, the electrical resistance increases by about 9 percent under the same conditions. In order to compare the experimental results with the theory, it is necessary first of all to correct for the factor Θ^2 in (1a). The variation of Θ with pressure may be obtained with the help of the thermodynamic relation[6]

$$(1/\Theta)(\partial\Theta/\partial p)_T = (1/C_v)(\partial V/\partial T)_p,$$

where V is the volume of the metal and C_v its heat capacity at constant volume. This relation may also be written as

$$(\partial \ln \Theta/\partial p)_T = \beta/c_v,$$

with β the thermal expansion coefficient of the metal, and c_v the heat capacity per unit volume. c_v may be considered constant up to pressures of 20,000 atmos., but β decreases rather sharply with pressure. The variation of β with pressure has been determined by Bridgman.[7] For lithium, β decreases by about 50 percent at a pressure of 20,000 atmos., and for sodium, by about 60 percent. With the help of these results, one may directly calculate the variation of Θ with pressure and hence values of σ/Θ^2 as a function of pressure.

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[3] J. C. Slater, Rev. Mod. Phys. **6**, 210 (1934); Phys. Rev. **45**, 794 (1934); Also see the following paper by J. Millman.

[4] See the article by A. Sommerfeld and H. Bethe, Handb. d. Physik **XXIV**/2 (1933).

[5] P. W. Bridgman, Proc. Am. Acad. Arts and Sci. **56**, 61 (1921).

[6] Grüneisen, Handb. d. Physik **10**, Chapter 1 (1926).

[7] I should like to express my thanks to Professor Bridgman for supplying me with these as yet unpublished experimental values.

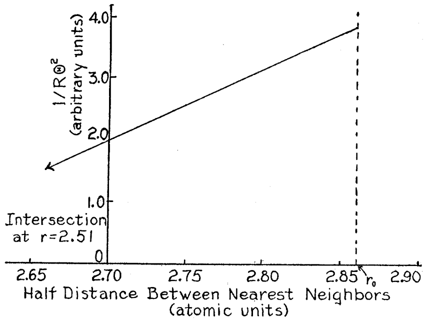

FIG. 1. $1/R\Theta^2$ plotted as a function of half distance between nearest neighbors for lithium.

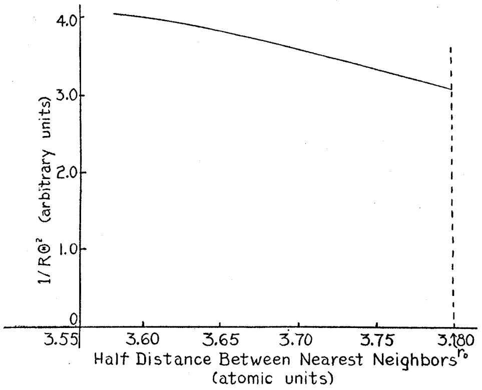

FIG. 2. $1/R\Theta^2$ plotted against half distance between nearest neighbors for sodium.

For reasons which we shall discuss in the next section, it is more convenient for our purposes to calculate $1/R\Theta^2$ as a function of pressure, where R is the measured resistance of the metal sample, uncorrected for the changes in volume due to pressure. The results are shown in Figs. 1 and 2 for Li and Na, respectively, where $1/R\Theta^2$ in arbitrary units is plotted as a function of the lattice constant, or more precisely, as a function of r, the half distance between nearest neighbors in the lattice. The conversion of the independent variable from pressure to r is easily made with the help of the known compressibilities of these metals. For Li the decrease of $1/R\Theta^2$ with r is practically linear up to 20,000 atmos., whereas for Na, there is a rise in $1/R\Theta^2$, and there seems to be an indication that the curve is approaching a maximum.

2. COMPARISON OF THE EXPERIMENTAL RESULTS WITH THE THEORY

To obtain a comparison of experiment and theory, we refer again to the relation (1a) which we rewrite as

$$\sigma/\Theta^2 \sim (k/C^2)(dE/dk)^2.$$

If the metal sample has a length l and cross section A, the resistance R is related to the conductivity σ by $R=(1/\sigma)(l/A)$, or $\sigma=(1/R)\cdot(l/A)$, so that we may write

$$(1/R\Theta^2)\cdot(l/A) \sim (k/C^2)(dE/dk)^2.$$

Now the number of conduction electrons per unit volume (equal to the number of atoms per unit volume for the alkalies) varies as the cube of k, so that k itself varies inversely as the linear dimension of the crystal. Thus, the variations of l/A and k with pressure cancel, and we have as a final result

$$1/R\Theta^2 \sim (1/C^2)(dE/dk)^2.$$

As far as order of magnitude is concerned, it seems reasonable to place C independent of pressure over the range utilized in the experiments, and to compare directly the values of $1/R\Theta^2$ as shown in Figs. 1 and 2, with the theoretical values of $(dE/dk)^2$.

In the case both of Na and Li, the first Brillouin zone is half full and up to this point the energy can be taken practically independent of the direction of the wave normal. If one plots E *vs.* k for the first zone, one obtains the familiar curve shown in Fig. 3. The curvature of the parabolic portion which alone interests us is almost that for free electrons in the case of sodium, but much less in the case of lithium, indicating a tighter binding of the electrons in the latter metal. Now the slope dE/dk at the edge of the Fermi distribution will clearly decrease as the energy breadth of the first Brillouin zone decreases. In Figs. 4 and 5 are plotted the lowest energy states for Li and Na, respectively, as function of the half distance between nearest neighbors in the lattice. On these curves the breadth of the first Brillouin zone ΔE is indicated at normal separation. If we now imagine the metals compressed, we see that for Li the breadth ΔE of the zone decreases and hence dE/dk decreases. This behavior was first pointed out by Professor Slater as a means of

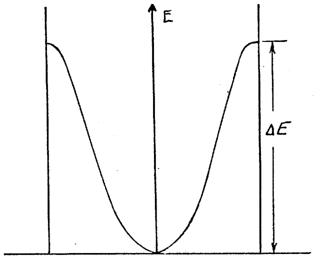

FIG. 3. Energy *vs.* wave number in the first Brillouin zone.

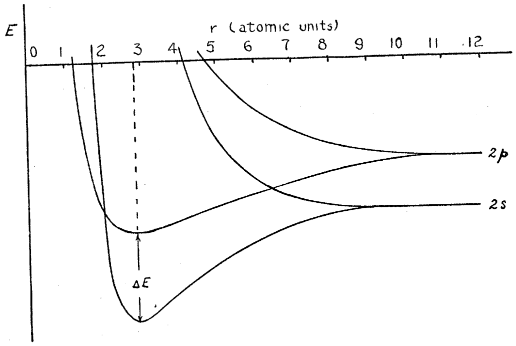

FIG. 4. Energy bands for Li *vs.* half distance between nearest neighbors.

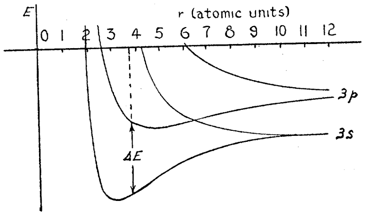

FIG. 5. Energy bands for Na *vs.* half distance between nearest neighbors.

explaining the abnormal pressure coefficient of lithium. At about 2.1 atomic units, where the lowest 2*s*-state and the lowest 2*p*-state intersect, we should expect the slope to become zero. On the other hand, in the case of sodium, the breadth of the zone increases somewhat with decreasing r and then eventually gets smaller. Thus, we should expect an initial increase in the freedom of the electrons for sodium as it is compressed and eventually a decrease as it is compressed further. Although it has not been possible to attain pressures high enough to cause a reversal in the resistance-pressure curve for sodium,[8] such a behavior has been observed by Bridgman[5] for Cs, and this affords a very satisfactory check on the general theory.

Turning now to the quantitative aspects, Mr. Millman has kindly calculated the slopes dE/dk as a function of r for propagation in the 110 direction for Li. This indicates a drop of about 10 percent at a pressure of 12,000 atmospheres, and hence $(dE/dk)^2$ drops by about 20 percent at this pressure. From Fig. 1 we see that at $r=2.78$ atomic units (corresponding to $p=12{,}000$ atmos.) there is a drop in $1/R\Theta^2$ of about 25 percent. Thus, we find a satisfactory check for this phenomenon. If one extrapolates the curve in Fig. 1, it indicates infinite resistance for about $r=2.5$ units, whereas Millman's calculations give 2.1 units. The reason for this discrepancy is easy to give. The calculations for lithium were made using a potential function for the free atom. This is only a rough approximation, and gets worse as the metal is compressed. Certainly the real potential curve lies lower in the metal than in the free atom, and we should accordingly expect the lowest 2*p* level to drop faster and intersect the lowest 2*s* level at larger separation than 2.1 units. In sodium, the free atom potential is a much better approximation at the actual distance of separation, since the lattice constant of sodium is much larger than that of lithium. The observed increase in $1/R\Theta^2$ with increasing pressure corresponds to the predicted initial increase of ΔE. Furthermore, the fact that the rate of increase of $1/R\Theta^2$ decreases as the pressure increases, indicates that at higher pressures ΔE will decrease as expected.

To summarize, we may say that wave mechanics has led to a satisfactory explanation of the observed pressure effect on resistance for the alkalies, including the abnormal behavior of lithium, without any special assumptions, and predicts the correct order of magnitude of these changes. When one takes into account the approximate nature of the theory, the fact that it holds at the absolute zero and that the experimental results are obtained at room temperature, the quantitative agreement between theory and experiment must be regarded as highly satisfactory.

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[8] Professor Bridgman has informed me that such a reversal would take place at about 24,000 atmospheres.