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The effect of pressure on the electrical resistance of lithium, sodium and potassium at low temperatures

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Measurements have been made of the electrical resistivity of lithium, sodium and potassium at temperatures between 2 and 300 °K and at pressures up to 3000 atm. From our results we have calculated the ideal electrical resistivity, ρ_i , and its volume derivative as functions of temperature for conditions of constant density. It is shown that, as predicted by simple theory, there is a linear relation between the temperature and volume coefficients of ρ_i for each metal. We conclude that the magnitude of the volume coefficient of ρ_i does not, at high temperatures at least, agree with present theoretical predictions and that this coefficient is closely connected with the high-temperature value of the thermoelectric power.

1. INTRODUCTION

In order to obtain a general understanding of how the effect of pressure on the electrical resistivity of a pure metal changes with temperature it is convenient to make use of the following simple expression for the ideal electrical resistivity of a metal:

$$\rho_i = \frac{KT}{M\theta_R^2} f(T/\theta_R). \quad (1)$$

θ_R is here a constant, having the dimensions of temperature, which characterizes the resistive properties of the metal, M is the mass of the metallic ions, and K is a parameter which measures the interaction between the conduction electrons and the lattice vibrations. f is a function which becomes constant at high temperatures and which at very low temperatures is expected to vary as $(T/\theta_R)^4$. One example of such a function occurs in the Bloch-Grüneisen expression for the temperature dependence of the ideal resistivity of a metal, but for our present purposes we do not need to make any assumption about the form of f except that it is independent of volume. We emphasize, however, that K and θ_R are assumed to be independent of temperature and to depend only on the volume.

Under these conditions, the *volume* coefficient of the ideal resistivity is related to the temperature coefficient of the ideal resistivity in the following way:

$$\left(\frac{\partial \ln \rho_i}{\partial \ln V}\right)_T = \frac{d \ln K}{d \ln V} - \frac{d \ln \theta_R}{d \ln V} \left\{ 1 + \left(\frac{\partial \ln \rho_i}{\partial \ln T}\right)_V \right\}. \quad (2)$$

At high temperatures ($T \gtrsim \theta$) $\partial \ln \rho_i / \partial \ln T$ tends to unity for most metals (at least at constant density) so that in this region we may write:

$$\partial \ln \rho_i / \partial \ln V = (d \ln K / d \ln V) + 2\gamma_R, \quad (3)$$

where $\gamma_R (= -d \ln \theta_R / d \ln V)$ is a parameter which is analogous to the Grüneisen parameter, γ_G . The Grüneisen parameter is defined as follows:

$$\gamma_G \equiv -d \ln \theta_D / d \ln V = V \alpha / C_v \beta, \quad (4)$$

where θ_D is the Debye temperature, α the volume expansion coefficient, β the compressibility, C_v the atomic heat at constant volume, and V the atomic volume.

On the not unreasonable assumption that $\gamma_R = \gamma_G$ it is possible to estimate values of $d \ln K / d \ln V$ from high temperature measurements alone and it is interesting to compare the values so deduced with those calculated theoretically. Lawson (1956) has made such a comparison with the predictions of several different theoretical models of a metal and in his notation we have

$$\frac{d \ln K}{d \ln V} = 1 + 2 \frac{d \ln C}{d \ln V} + 2 \frac{d \ln m^*}{d \ln V}, \quad (5)$$

where C is a coupling energy (different in the different models) of the same order as the Fermi energy, and m^* is the effective mass of the conduction electrons. The last term in equation (5), i.e. the variation of the effective mass with volume, has been calculated for the alkali metals by Brooks (1953) (see also Ham 1955), and it turns out to be negligible for sodium and potassium but quite large for lithium for which $d \ln m^* / d \ln V$ is -0.8 . Apart from the last term in equation (5), $d \ln K / d \ln V$ has been variously calculated for free electrons as -1 (Seitz 1940), $-\frac{1}{3}$ (Peterson & Nordheim 1937), both for the 'deformable ion' model, and -1 (Lenssen & Michels 1935) for the 'rigid ion' model. Using the 'tight binding' approximation, Lenssen & Michels obtained a value of $+1$.

The free-electron approximation is expected to hold rather well for sodium and potassium, much less well for lithium and copper (cf. Cohen & Heine 1958). It is therefore surprising to see from table 13 that the experimental values of $d \ln K / d \ln V$ for sodium and potassium (about $+2$) are quite different from the predicted values of -1 or $-\frac{1}{3}$. On the other hand, the agreement is better for lithium and copper, although certainly in copper and probably in lithium the Fermi surface is considerably distorted from the free electron sphere. It is thus evident that the present theory of the change of resistivity with volume is inadequate (at least for high temperatures), since it fails for those metals (sodium and potassium) for which it should be most successful.

This inadequacy in the theory of the volume dependence of electrical resistivity raises the question as to whether the assumption that $\gamma_R = \gamma_G$ is a sound one. Returning to equation (2), we see that, since both $d \ln K / d \ln V$ and $d \ln \theta_R / d \ln V$ are assumed to be independent of temperature, then $\partial \ln \rho_i / \partial \ln V$ should be linearly related to $\partial \ln \rho_i / \partial \ln T$. One purpose of these experiments was to find out whether this relation is valid. If it holds, it might then be possible to deduce separately the values of $d \ln K / d \ln V$ and $d \ln \theta_R / d \ln V$ and so test directly whether θ_R changes with volume in the same way as θ_D . In short, if equation (2) is valid, we may hope to find out how much of the pressure coefficient of resistivity derives from changes in the lattice properties of the metal and how much from changes in the properties of the conduction electrons.

The general inadequacy of theory in predicting correctly the volume dependence of electrical resistivity leads us also to the second purpose of these experiments. Theories which give incorrect predictions for the volume coefficient may, nevertheless, give correctly the temperature dependence of a quantity. To compare experimental results with such theories, however, it is necessary to be able to measure, or to be able to estimate from experimental data, the temperature dependence of the quantity at constant density. In the present work, therefore, we have made resistance-temperature measurements at effectively zero pressure between 2 and 300 °K from which, together with our high-pressure measurements, we have been able to deduce how the resistivities of lithium, sodium and potassium vary with temperature when their density stays constant; in such a highly compressible metal as potassium, for example, the differences between the temperature dependence at constant pressure and at constant density can be quite large (see figures 1 and 3).

Experiments comparable in scope with this work have already been made on copper (Dugdale & Gugan 1957). Less detailed studies have been made on rubidium (Dugdale & Hulbert 1957) and on a number of other metals (cf. Lawson 1956). Preliminary results of some of the present experiments have already been published (Gugan & Dugdale 1958*a, b*).

2. EXPERIMENTAL

We have described in detail elsewhere the methods by which we have made these measurements (references are given below). We shall therefore give here only a brief description of our methods.

2.1. *The specimens*

The specimens were made in the form of bare wires about 100 cm long and 0.5 mm in diameter. These were mounted on an insulating former and measured in either a high-pressure or a low-pressure apparatus. The resistance measurements were made by the potentiometer method. Further details of the preparation and mounting of specimens are given by Dugdale & Gugan (1960).

2.2. *The low-pressure apparatus*

This was designed after the principle of an adiabatic calorimeter so that accurate resistance-temperature curves could be obtained between about 2 and 300 °K at effectively zero pressure. Further details are given by Dugdale & Gugan (1960).

2.3. *The high-pressure apparatus*

This was an apparatus with which hydrostatic pressures of up to about 3000 atm could be applied to specimens using helium as the transmitting fluid. Below about 30 °K helium solidifies within the range of pressures that we could generate and in some cases we used solid helium as the pressure transmitting medium. The apparatus was designed so that the temperature of the specimen could be varied at fixed pressure. However, because of the long time needed to reach thermal equilibrium in the high-pressure bomb, we have made all our experiments under almost isothermal conditions, only a small correction being then necessary to allow for the change

of the bomb temperature during a run. Full details of the apparatus and the technique have been given by Dugdale & Hulbert (1957) and by Dugdale & Guban (1957).

2.4. The absolute resistivities

The absolute resistivities of our different specimens were measured at room temperature. The measurements were made on thick extruded rods of metal in the way described by Dugdale, Guban & Okumura (1961).

3. EXPERIMENTAL RESULTS

The numerical results we give in this paper are smoothed values from our original data. We explain in appendix A how we have obtained the results tabulated. In appendix B we give details of the values we have used for the equations of state of the metals we have studied; we use this information in calculating the resistive properties of our specimens under the conditions of constant density.

We present our results for the different metals in the following sections: 3.1, potassium; 3.2, sodium; 3.3, lithium. In each section we compare our data with those of other observers where these exist.

3.1. Potassium

Details of the specimens we have studied are given in table 1.

TABLE 1. DETAILS OF THE POTASSIUM SPECIMENS

specimen	$R_{0^{\circ}\text{K}}/R_{273^{\circ}\text{K}}$	comments	source of material
K (1)	0.124	commercial purity ($\sim 0.5\%$ sodium)	Messrs A. D. Mackay and Co., New York
K (2)*	7.5×10^{-4}	—	} Mine Safety Appliances Ltd., Toronto
K (3)	7.8×10^{-4}	—	
K (4)	8.2×10^{-4}	—	
K (5)	8.5×10^{-4}	—	
K (6)	—	same stock as K (2) to K (5)	

* The absolute resistivity of a specimen from this stock was $7.1_9 \times 10^{-6} \Omega \text{ cm}$ at 22.0°C (corrected for residual resistivity). The precision of this result is about 1%. Previous values at this temperature are $7.0_8 \times 10^{-6} \Omega \text{ cm}$ (Hackspill 1910) and $7.5_7 \times 10^{-6} \Omega \text{ cm}$ (Guntz & Broniewski 1909). Cf. also MacDonald *et al.* (1956).

3.1.1. The temperature dependence of ρ_i

Three specimens were studied in these measurements, namely K (3), K (4) and K (6); K (6) we measured only between about 8 and 20°K . The results were in satisfactory agreement in the region where they overlapped. The calculated values of ρ_i/T are given in table 2; the resistivity values have been normalized to our observed value of the absolute resistivity at room temperature (see table 1). The results are illustrated in figure 1.

Several anomalies in the temperature dependence of the resistivity of potassium have been reported: (a) kinks in the resistivity-temperature curve below 20°K

TABLE 2. THE IDEAL RESISTIVITY OF POTASSIUM AT ZERO PRESSURE, ρ_i ,
AND AT CONSTANT DENSITY, ρ'_i

T (°K)	ρ_i/T^* ($10^{-8} \Omega \text{ cm deg K}^{-1}$)	ρ'_i/T^\dagger ($10^{-8} \Omega \text{ cm deg K}^{-1}$)
8	0.080 ± 0.001	—
10	0.138	—
12	0.204	—
14	0.278	—
16	0.362	—
18	0.450	—
20	0.537	—
25	0.758	—
30	0.950 ₉	0.943 ₈
35	$1.110_0 \pm 0.0005^\ddagger$	1.098 ₉
40	1.240 ₂	1.224 ₄
45	1.348 ₈	1.327 ₈
50	1.437 ₈	1.410 ₉
55	1.511 ₉	1.478 ₉
60	1.573 ₈	1.534 ₃
70	1.667 ₂	1.611 ₈
80	1.736 ₄	1.661 ₀
90	1.790 ₁	1.692 ₄
100	1.835 ₉	1.715 ₅
110	1.876 ₅	1.732 ₆
120	1.911 ₅	1.743 ₅
130	1.943 ₉	1.751 ₈
140	1.974 ₃	1.757 ₇
150	2.003 ₂	1.761 ₈
160	2.031 ₅	1.765 ₄
170	2.058 ₆	1.767 ₃
180	2.086 ₁	1.769 ₂
190	2.113 ₅	1.771 ₁
200	2.140 ₆	1.771 ₆
210	2.168 ₇	1.772 ₅
220	2.197 ₉	1.774 ₁
230	2.227 ₃	1.774 ₉
240	2.257 ₄	1.776 ₆
250	2.288 ₀	1.778 ₀
260	2.319 ₀	1.779 ₄
270	2.350 ₂	1.780 ₅
273.1 ₅	2.360 ₁	1.780 ₇
280	2.383 ₂	1.782 ₆
290	2.418 ₂	1.785 ₄
295.1 ₅	2.436 ₀	1.786 ₃

* There is no significant difference below 30 °K between ρ_i and ρ'_i .

† The random error for these results is the same as for ρ_i/T , but there is in addition a possible systematic error (arising from uncertainties in the P - V - T data) which, at the higher temperatures, may be about twice as big as the random error.

‡ The random error in these values remains at $\sim \pm 0.0005$ above this temperature.

(MacDonald & Mendelsohn 1950); (b) a peculiar temperature dependence of ρ_i at quite high temperatures interpreted as due to a phase transformation (Bidwell 1924); and (c) a step-like anomaly at $\sim 150^\circ\text{K}$ (MacDonald 1952). We have observed none of these anomalies; the resistivity appears to vary smoothly with temperature down to the lowest temperatures measured ($\sim 2^\circ\text{K}$).

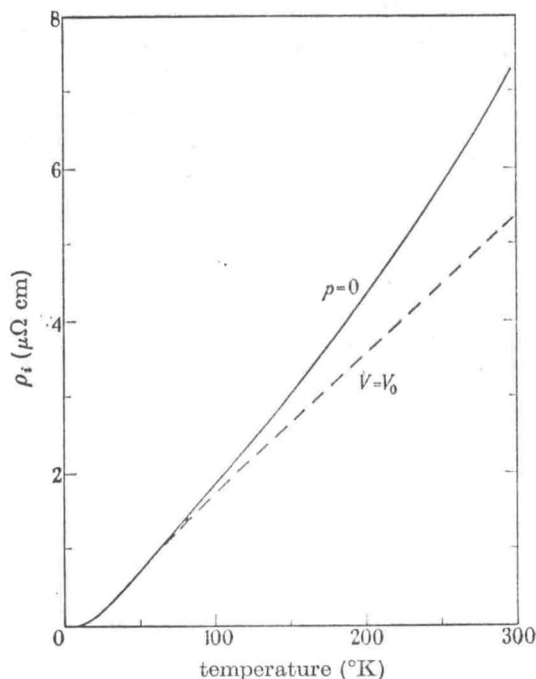


FIGURE 1. The ideal electrical resistivity of potassium as a function of temperature: —, at effectively zero pressure; ---, at a constant density equal to that at 0°K under zero pressure.

The results of other authors are compared with ours in table 3. It is clear that our values are systematically lower than those found in earlier work. We believe that the difference is real and that it and the anomalies found by other workers are due to the constraining effects of the capillary tubes which were used to contain the specimens in their experiments. We discuss this question in detail elsewhere (Dugdale & Guban, to be published) and conclude that in both potassium and sodium this effect can readily explain the discrepancy. We also conclude that for accurate work, capillary specimens are not satisfactory.

3.1.2. The dependence of resistance on pressure

Three specimens were studied in these experiments. *K*(1) was used only for a study of the effect of pressure on residual resistance; the pressure effect was studied over a wide temperature range on specimen *K*(2) and checked at several temperatures on *K*(5). The results of these experiments are given in Table 4 and are illustrated in figure 2. It will be seen that our results for the initial pressure coefficient of resistivity agree well with the values obtained by Bridgman (1921, 1925).

The shapes of the curves have been analyzed by constructing difference tables, as described in appendix A. If we express the resistance as a power series function of the pressure $R = R_0(1 + Ap + Bp^2 + Cp^3 \dots)$, the coefficients A, B, C may be obtained from the difference tables. Only these three coefficients are needed to express our experimental results; they are included in table 4.

TABLE 3. A COMPARISON OF RESULTS FOR THE IDEAL RESISTIVITY OF POTASSIUM AT ZERO PRESSURE

T ($^{\circ}\text{K}$)	ρ_i/T^* ($10^{-8} \Omega \text{ cm deg K}^{-1}$)			
	(1)†	(2)†	(3)	(4)
273.15	2.360 ₁	2.360 ₁	2.360 ₁	1.000
170.9 ₄	2.133 ₇	—	2.061	1.035
108.7 ₉	1.979 ₆	—	1.872	1.058
90.5 ₆	1.919 ₁	—	1.793	1.070
90.2 ₁	1.906 ₄	—	1.791	1.064
87.8 ₁	—	1.836 ₂	1.780	1.031
77.6 ₀	—	1.774 ₀	1.721	1.031
72.9 ₆	1.816 ₂	—	1.689	1.075
72.2 ₀	1.798 ₃	—	1.685	1.067
56.8 ₄	1.649 ₅	—	1.538	1.073
56.4 ₁	1.662 ₁	—	1.532	1.085
20.62	0.633 ₀	—	0.565	1.122
20.42	0.638 ₆	0.619 ₀	0.556	{ 1.150 1.113
18.47	0.533 ₈	—	0.471	1.144
17.19	0.471 ₂	—	0.414	1.138
16.39	0.432 ₆	—	0.379	1.141
14.27	0.336 ₄	—	0.288	1.168

* Normalized to $2.3601 \times 10^{-8} \Omega \text{ cm deg K}^{-1}$ at 273.15 $^{\circ}\text{K}$.

† Specimens in glass capillary tubes.

(1) Results from Woltjer & Kamerlingh Onnes (1924).

(2) Results from Moissner & Voigt (1930).

(3) This work.

(4) ρ_i (capillary specimen)/ ρ_i (bare wire).

3.1.3. The correction to constant density conditions

This correction is made in the way described in appendix A. The results of the calculations are given in tables 2 and 4 and they are also illustrated in figures 1 and 2. The systematic error given in table 2 arises from uncertainties in the equation of state of potassium; the error limits we have quoted are based on the supposition that at room temperature the error in the value of p' , the pressure required to increase the density of potassium to its value at 0 $^{\circ}\text{K}$ under zero pressure, is 3%.

3.2. Sodium

The results for sodium are similar in general form to those for potassium. Below about 40 $^{\circ}\text{K}$ there is, however, the extra complication of the martensitic transformation (cf. Dugdale & Gugan 1960). Details of the specimens studied are given in table 5.

TABLE 4. THE EFFECT OF PRESSURE ON THE IDEAL RESISTIVITY OF POTASSIUM

T (°K)	$-\partial \ln \rho_i / \partial p$ (10^{-6} atm $^{-1}$)	$-A$ (10^{-5} atm $^{-1}$)	B (10^{-9} atm $^{-2}$)	$-C$ (10^{-13} atm $^{-3}$)	$\partial \ln \rho_i' / \partial \ln V$
Specimen K (2)					
15.4 ₀	24.1 ± 0.4	23.2 ± 0.3	37 ± 5	60 ± 100	8.5 ₅ ± 0.15
20.3 ₅	22.8 ± 0.3	21.9 ± 0.2	29 ± 5	12 ± 100	8.1 ₅ ± 0.1
29.8	20.6 ± 0.2	19.6 ₅ ± 0.2	23 ± 2	11 ± 38	7.3 ₂ ± 0.1
61.1	17.0 ± 0.2	16.0 ± 0.2	17 ± 1	12 ± 29	6.0 ₂ ± 0.1
78.0	16.7 ± 0.2	15.7 ± 0.2	19 ± 2	15 ± 20	5.7 ₄ ± 0.1
116.7	16.9 ₅ ± 0.2	15.9 ₅ ± 0.2	17 ± 1	5 ± 18	5.7 ₀ ± 0.1
196.6	18.1 ± 0.1	17.0 ± 0.1	23 ± 2	17 ± 38	5.6 ₄ ± 0.1
273.7	19.0 ± 0.1	17.9 ± 0.1	22 ± 1	11 ± 41	5.7 ₅ ± 0.15
308.8	20.1 ± 0.2	18.9 ± 0.2	27 ± 1	18 ± 20	5.6 ₀ ± 0.15
308.8*	—	—	—	—	5.7 ₂ * ± 0.05
Specimen K (5)					
4.2 ₀ †	30 ± 3	—	—	—	10.7 ± 1
20.4 ₀	22.8 ₅ ± 0.2	21.9 ± 0.2	28 ± 5	-9 ± 100	8.1 ₀ ± 0.1
36.5	19.7 ± 0.2	18.8 ± 0.2	25 ± 2	23 ± 40	7.0 ₃ ± 0.1
79.2	16.8 ± 0.2	15.8 ± 0.2	19 ± 2	13 ± 50	5.8 ₀ ± 0.1
273.1 ₅	19.2 ± 0.1	18.1 ± 0.1	26 ± 1	21 ± 41	5.5 ₀ ± 0.15
Bridgman (1921, 1925)					
273.1 ₅	20.4 ± 0.5‡	—	—	—	—
298.0	19.6 ± 0.5	—	—	—	—
333.0	21.1 ± 0.5	—	—	—	—

* This point corresponds to the density at 308.8 °K.

† A large correction was necessary for the effect of pressure on residual resistivity.

‡ Estimated error.

TABLE 5. DETAILS OF THE SODIUM SPECIMENS

specimen	$R_{4.2 \text{ °K}} / R_{273 \text{ °K}}$	comments	source of material
Na (1)	6.9×10^{-4}	—	laboratory stock
Na (2)	7.1×10^{-4}	—	
Na (3)	4.0×10^{-4}	specimen in glass capillary*	N. V. Phillips, Eindhoven
Na (4)	2.0×10^{-4}		
Na (5)	2.9×10^{-4}	—	Messrs A. D. Mackay & Co., New York
Na (6)†	3.0×10^{-4}	—	
Na (7)	3.8×10^{-4}	—	
Na (9)	7.3×10^{-4}	—	laboratory stock

* We are grateful to Dr S. B. Woods for the loan of this specimen.

† The absolute resistivity of a specimen from this stock was $4.7_5 \times 10^{-6}$ Ω cm at 22.0 °C (corrected for residual resistivity). The precision of this result is about 1%. Previous values at this temperature are $4.7_0 \times 10^{-6}$ Ω cm (Hackspill 1910) and $4.8_4 \pm 0.1 \times 10^{-6}$ Ω cm (Bradshaw & Pearson 1956).

3.2.1. *The temperature dependence of ρ_i*

Specimens Na (3) to Na (7) were studied in the low-pressure apparatus. The results for the bare wire specimens were in excellent agreement with one another, whereas those for Na (4), which was a specimen enclosed in a glass capillary tube, were systematically different. We were able to obtain resistance-temperature curves of the pure body-centred cubic phase down to about 40 °K and the only uncertainty

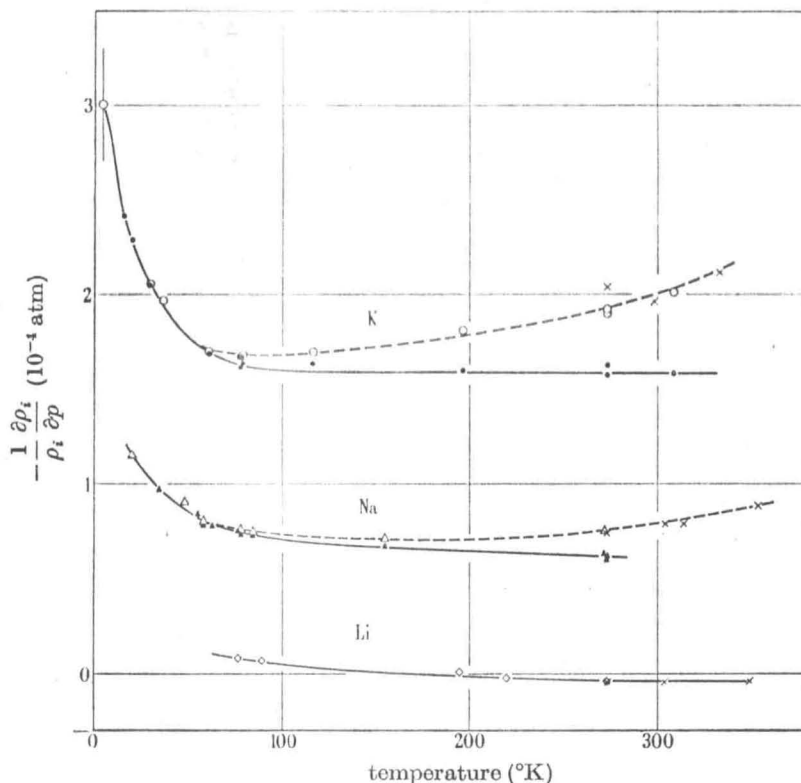


FIGURE 2. The pressure coefficient of the ideal resistivity of lithium (b.c.c. phase), sodium (b.c.c. phase) and potassium as a function of temperature: ---, at zero pressure, —, at a constant density equal to that at 0 °K under zero pressure. × Values from Bridgman (1921, 1925, 1938) for zero pressure.

in converting these to $\rho_i - T$ curves was that we had to measure the residual resistivity on a two-phase mixture. Our earlier work has shown that the residual resistivity is not much affected by the transformation (Dugdale & Guggan 1960) so we have used in our calculations the directly measured residual resistivity. These results are given in table 6.

Previous work on the resistivity of sodium as a function of temperature has been extensive. The most comprehensive work at low temperatures is that of MacDonald, White & Woods (1956), but as the effect of the phase transformation on the resistivity of sodium was not realized at that time, their results in general refer to two-phase mixtures of unknown proportions.

At higher temperatures there are experiments by Woltjer & Kamerlingh Onnes (1924), Meissner & Voigt (1930) and, more recently, a careful series of experiments by Bradshaw & Pearson (1956). These experiments were all on capillary tube specimens and we compare them with the results from our capillary and bare wire specimens in table 7. As in the case of potassium, there is clearly a systematic difference between the results of the capillary tube experiments and the experiments on bare wires. As before we attribute this to the capillary tube constraints.

TABLE 6. THE IDEAL RESISTIVITY OF B.C.C. SODIUM AT ZERO PRESSURE AND AT CONSTANT DENSITY

T (°K)	ρ_i/T^* ($10^{-8} \Omega \text{ cm deg K}^{-1}$)	ρ'_i/T^* ($10^{-8} \Omega \text{ cm deg K}^{-1}$)
50	0.6338	0.6284
60	0.7913	0.7815
70	0.9108	0.8954
80	1.0063	0.9845
90	1.0835	1.0543
100	1.1455	1.1080
110	1.1956	1.1487
120	1.2367	1.1797
130	1.2719	1.2040
140	1.3025	1.2231
150	1.3295	1.2382
160	1.3535	1.2503
170	1.3754	1.2605
180	1.3966	1.2688
190	1.4171	1.2763
200	1.4371	1.2831
210	1.4571	1.2894
220	1.4760	1.2946
230	1.4938	1.2985
240	1.5109	1.3014
250	1.5286	1.3047
260	1.5472	1.3082
270	1.5653	1.3109
273.15	1.5703	1.3115
280	1.5828	1.3127
290	1.6011	1.3149
295	1.6102	1.3160

* The random error in these values is $\sim \pm 0.0003$ at all temperatures. The systematic error in ρ'_i/T (cf. table 2) is about the same size as the random error.

3.2.2. The dependence of resistance on pressure

Four specimens were studied in these experiments, Na (1), Na (2), Na (3) and Na (9). The results of our experiments are given in tables 8 (for the pure b.c.c. phase) and 9 (for two-phase mixtures). In table 8 we have included values obtained by Bridgman (1921) from experiments on bare wires. Our results can be adequately represented by a quadratic dependence of ideal resistance on pressure, $R_i = R_0$

($1 + Ap + Bp^2$). We have tabulated B/A and $\partial \ln \rho_i / \partial p \equiv A + \frac{1}{3}\beta$ where β is the compressibility.

The pressure coefficient of ideal resistance of specimens in the two-phase region was correlated with the amount of low-temperature phase present. This was estimated from a measurement of the absolute resistivity of the specimen at 20.35 °K,

TABLE 7. A COMPARISON OF RESULTS FOR THE IDEAL RESISTIVITY OF B.C.C. SODIUM AT ZERO PRESSURE

T (°K)	ρ_i/T^* ($10^{-8} \Omega \text{ cm deg K}^{-1}$)				
	(1)	(2)	(3)	(4)	(5)
295	1.610 ₂	—	1.641 (1.019)†	—	—
273.15	1.570 ₃	1.608 ₅ (1.024)†	1.609 (1.025)	1.570 ₃ (1.000)	1.570 ₃ (1.000)
260	1.547 ₂	—	1.589 (1.027)	—	—
240	1.510 ₀	—	1.559 (1.032)	—	—
220	1.476 ₀	—	1.528 (1.035)	—	—
200	1.437 ₁	—	1.494 (1.040)	—	—
180.5	1.397 ₀	1.470 (1.052)	—	—	—
180	1.396 ₀	—	1.461 (1.046)	—	—
170.87	1.377 ₂	—	—	—	1.423 ₇ (1.034)
160	1.353 ₅	—	1.419 (1.048 ₅)	—	—
140	1.302 ₅	—	1.371 (1.052 ₅)	—	—
136.0	1.291 ₀	1.365 (1.058)	—	—	—
120	1.236 ₇	—	1.306 (1.056)	—	—
108.72	1.180 ₃	—	—	—	1.249 ₈ (1.051)
100	1.145 ₅	—	1.211 (1.057)	—	—
97.12	1.129 ₅	1.206 (1.068)	—	—	—
89.50	1.079 ₀	1.163 (1.078)	—	—	—
87.8	1.068 ₇	—	—	1.113 ₁ (1.041 ₅)	—
80	1.006 ₃	—	1.068 (1.061 ₅)	—	—
77.6	0.986 ₄	—	—	1.021 ₀ (1.036)	—
76.41	0.974 ₀	1.052 (1.080)	—	—	—
59.63	0.786 ₅	0.852 ₅ (1.084)	—	—	—
56.77	0.743 ₀	—	—	—	0.795 ₄ (1.071)
50.10	0.634 ₈	0.693 ₈ (1.093)	—	—	—
44.00	0.520 ₄	0.567 ₅ (1.091)	—	—	—

* Normalized to a value of $1.570_3 \times 10^{-8} \Omega \text{ cm deg K}^{-1}$ at 273.15 °K (except columns 2 and 3).

† The figures in brackets are the ratios $\frac{\rho_i \text{ (capillary)}}{\rho_i \text{ (bare wire)}}$.

(1) This work, bare wires. (2) This work, capillary tube specimen Na (4), normalized at 273.15 °K to the results of Bradshaw & Pearson. (3) Bradshaw & Pearson (1956), capillary tube specimen (these results include an unknown contribution from the residual resistivity). (4) Meissner & Voigt (1930), capillary tube specimen. (5) Woltjer & Kamerlingh Onnes (1924), capillary tube specimen.

in the manner described by Dugdale & Gugan (1960). The correlation seemed strongly to suggest that the two pure phases had appreciably different pressure coefficients of resistivity, and the apparent values estimated for the two pure phases are given in table 9. However, one important reservation must be made about the results for the two pure phases at 20.35 °K. It is known that the ideal resistivities of the two pure phases at this temperature differ by a considerably greater amount than the

TABLE 8. THE EFFECT OF PRESSURE ON THE IDEAL RESISTIVITY OF B.C.C. SODIUM

specimen	T (°K)	$\frac{-\partial \ln \rho_i}{\partial p}$ (10^{-5} atm $^{-1}$)	$-B/A$ (10^{-5} atm $^{-1}$)	$\frac{\partial \ln \rho_i'}{\partial \ln V}$
Na (1)	34.77	9.7 ± 0.2	8 ± 2	6.93 ± 0.15
	48.03	9.1 ± 0.2	7 ± 3	6.50 ± 0.15
	58.10	8.0 ± 0.2	7 ± 2	5.64 ± 0.15
	78.3	7.6 ± 0.2	10 ± 2	5.35 ± 0.15
	84.9	7.4 ± 0.2	6 ± 2	5.15 ± 0.15
	155.1	7.1 ± 0.2	6 ± 2	4.79 ± 0.15
	272.0	7.5 ± 0.2	6 ± 2	4.50 ± 0.15
Na (2)	55.57	8.5 ± 0.2	7 ± 1	6.00 ± 0.15
	78.0*	7.6 ± 0.1	6.5 ± 0.5	5.35 ± 0.07
	273.4	7.4 ± 0.1	6.0 ± 0.5	4.43 ± 0.07
Na (3)	77.0*	7.6 ± 0.1	6.5 ± 0.5	5.35 ± 0.07
	273.4	$7.2_5 \pm 0.1$	6.0 ± 0.5	4.32 ± 0.07
	(273.4)†	—	—	(4.60 ± 0.07)
Na (9)	63.07	7.9 ± 0.1	6.5 ± 1.5	5.57 ± 0.07
	78.7	7.4 ± 0.1	6.3 ± 0.5	5.21 ± 0.07
Bridgman‡	273.2	7.4 ± 0.2	9 ± 5	—
	303.2	7.9 ± 0.2	10 ± 5	—
	313.2	7.9 ± 0.2	10 ± 5	—
	353.2	8.8 ± 0.2	11 ± 5	—

* Average values from three different runs.

† This point corresponds to the density at 273.4 °K under zero pressure.

‡ Results from experiment on bare wires (Bridgman 1921).

TABLE 9. THE EFFECT OF PRESSURE ON THE IDEAL RESISTIVITY OF SODIUM IN THE TWO-PHASE REGION

specimen	f , fraction of h.c.p sodium in specimen at zero pressure	T (°K)	$\frac{-\partial \ln \rho_i}{\partial p}$ (10^{-5} atm $^{-1}$)	$-B/A$ (10^{-5} atm $^{-1}$)	$\frac{\partial \ln \rho_i'}{\partial \ln V}$
Na (2)	0.5 ± 0.1	20.35	10.1 ± 0.4	9 ± 2	7.2 ± 0.3
	0.0 ± 0.05	20.35	11.4 ± 0.4	—	$8.1_5 \pm 0.3$
Na (3)	0.1	20.35	11.3 ± 0.3	13 ± 2	8.1 ± 0.2
Na (9)	0.3_5	20.35	9.9 ± 0.2	8 ± 2	7.1 ± 0.2
Na (1)	$(0.3_5)^*$	20.35	10.3 ± 0.4	10 ± 3	$7.3_5 \pm 0.3$
	—	24.70	10.6 ± 0.3	10 ± 2	$7.5_5 \pm 0.2$
Na (b.c.c.)†	0	20.35	11.5 ± 0.4	—	8.2 ± 0.3
	0	24.70	11.6 ± 0.6	—	8.2 ± 0.4
Na (hex)†	1.0	20.35	7.8 ± 0.8	—	5.6 ± 0.6

* Estimated by interpolation of $\partial \ln \rho_i / \partial p$ at 20.35 °K.

† N.B. These values have been calculated on the assumption that there is no change of phase composition of the specimens with pressure (see text).

pressure induced change of resistance: if the proportions of the two phases change with pressure then our conclusion is invalid. It turns out that if we *assume* that the ratio of the resistivities of the two phases is independent of pressure, then quite a small change in the phase composition with pressure is sufficient to account for the apparent difference between the pressure coefficients of the two phases. For a 50-50 mixture of the two phases we find that at 20.35 °K the necessary change of composition is about 4% per 1000 atm, the change being such as to decrease the amount of close-packed phase present. The sign of this effect is consistent with the experiments of Basinski & Verdini (1959) on the specific volumes of the two phases of sodium. One also finds that a change of this amount would have only a small effect on the curvature of the resistivity-pressure relation. Our experiments on lithium show a similar effect and we believe that this is the more likely explanation of our results.

3.2.3. *The correction to constant density conditions*

This correction is made in the same way as for potassium. The results of the calculations are given in tables 6 and 8.

3.3. *Lithium*

The experiments on lithium proved to have several difficulties not found in those on potassium and sodium. In the first place the martensitic transformation, which occurs at about 75 °K in lithium, is more difficult to investigate than that in sodium (Dugdale & Guban 1961); secondly, the changes of resistance with pressure are relatively small and therefore not easy to determine accurately; and thirdly, these small changes are also often very irregular, even in specimens containing only the pure b.c.c. phase (cf. Guban & Dugdale 1958*a*). The results of the high pressure experiments were therefore often only of a qualitative nature, and although they showed several interesting new features, we shall discuss here only our simpler high pressure results. The specimens used for these measurements were similar to those used in our previous experiments on lithium (Dugdale & Guban 1961; Dugdale *et al.* 1961).

3.3.1. *The temperature dependence of ρ_i for lithium*

We have discussed this in detail elsewhere in connexion with the martensitic transformation in lithium (Dugdale & Guban 1961), and with the isotope effect (Dugdale *et al.* 1961); the results are given in table 10.

There are not many measurements of the resistivity of b.c.c. lithium with which to compare our results. Kelly & MacDonald (1953) give results for lithium between 4.2 °K and the melting point but only in the form of a small diagram. Meissner & Voigt (1930) give some results in the neighbourhood of 80 °K which probably refer to the b.c.c. phase although this is not certain because the thermal history of their specimens is not given in detail. Other experimental work (cf. MacDonald & Mendelsohn 1950; MacDonald *et al.* 1956; Rosenberg 1956) has been concentrated in the low-temperature range, i.e. in the two-phase region. Our values at 80 °K are about 10% lower than the values of Meissner & Voigt; this is probably connected with

departures from Matthiessen's rule since purer samples give lower values of ρ_i at low temperatures (this can in fact also be seen in the results of both MacDonald *et al.* (1956) and Rosenberg (1956)).

TABLE 10. THE IDEAL RESISTIVITY OF B.C.C. LITHIUM AT ZERO PRESSURE, ρ_i , AND AT CONSTANT DENSITY, ρ'_i

T (°K)	ρ_i/T^* ($10^{-8} \Omega \text{ cm deg K}^{-1}$)	ρ'_i/T^* ($10^{-8} \Omega \text{ cm deg K}^{-1}$)
80	1.244	1.24 ₁
100	1.714	1.71 ₀
120	2.081	2.07 ₆
140	2.359	2.35 ₃
160	2.571	2.56 ₆
180	2.728	2.72 ₈
200	2.852	2.85 ₆
220	2.941	2.95 ₆
240	3.013	3.03 ₈
260	3.075	3.10 ₆
273.15	3.110	3.14 ₆
280	3.126	3.16 ₆
290	3.150	3.19 ₂

* The random error in these results is about ± 0.001 at all temperatures.

3.3.2. The dependence of resistance on pressure

Because the effect of pressure on the electrical resistance of lithium is generally small, most of our experimental runs were made using liquid baths with the vacuum space around the high-pressure bomb flooded with exchange gas. This limited the pressure runs to comparatively few temperatures.

The density of lithium at a given temperature is almost linearly dependent on pressure so that we would expect the resistance of lithium also to depend nearly linearly on pressure. Indeed at 0 °C, this is what we find. Below this temperature, however, the behaviour of the electrical resistance of lithium under compression becomes quite erratic. We found hysteresis, zero shifts, marked curvature of the resistance-pressure curves and, in some cases, time effects; we emphasize that this is most unlikely to be due to any non-uniformity in the way the pressure is applied. Below about 100 °K these effects could be due to the martensitic transformation but we have also observed these effects at 200 °K in specimens which had never been cooled below that temperature and which we can hardly suppose to be affected by the phase transformation. Because of these irregularities we give in table 11 only the average initial pressure coefficients of the b.c.c. phase of our lithium samples, i.e. the coefficients for temperatures above 75 °K. We have also measured the change of resistivity of lithium six with pressure. This was similar to that of lithium of natural isotopic composition and, in particular, the values for the two materials were identical at 0 °C, within our experimental error.

3.3.3. *The correction of ρ_i to constant density conditions*

The value of $\partial \ln \rho_i / \partial \ln V$ is not very dependent on volume so that in view of the experimental uncertainties it has not seemed worth while making the correction to constant density for this quantity. On the other hand, we have corrected the values of the ideal resistivity of b.c.c. lithium to constant density and the results are given in table 10.

TABLE 11. THE EFFECT OF PRESSURE ON THE IDEAL RESISTIVITY OF B.C.C. LITHIUM

T (°K)	$\partial \ln \rho_i / \partial p$ (10^{-5} atm^{-1})	$\partial \ln \rho_i / \partial \ln V^*$
273.15	0.43 ± 0.01	-0.49
220	0.25 ± 0.1	-0.30
195	-0.09 ± 0.1	+0.11
90	-0.66 ± 0.1	+0.85
78	-0.73 ± 0.1	+0.94
273.2†	0.41 ₅	—
303†	0.42	—
348†	0.39	—

* Evaluated at zero pressure.

† Values from Bridgman (1921, 1938).

4. DISCUSSION

Before discussing the pressure coefficient of electrical resistivity we first consider briefly the temperature dependence of the resistivity (an introductory discussion of these topics has already been given by Dugdale (1961)). In the discussion which follows we shall generally be considering the conditions of constant density (i.e. constant volume) so that unless there is a statement to the contrary this may be assumed.

4.1. *The temperature dependence of ideal electrical resistivity*

In order to compare the resistivity-temperature curves of different metals it is often convenient to use the intermediary of some definite theoretical model, as one does when comparing experimental specific heat curves by means of the Debye model. For electrical resistivity the Bloch-Grüneisen model is a convenient one. According to this model the temperature dependence of the ideal resistivity is of the form of equation (1) and if we compare the logarithmic temperature coefficients of resistivity of our specimens with that predicted by the model we can specify our results by giving the variation with temperature of the Bloch-Grüneisen parameter θ_G † (cf. Kelly & MacDonald 1953).

We have done this for the metals we have studied and the results are shown in figure 3. The values of θ_G have been calculated from the resistivity at constant density; it is notable that when the correction to constant density is made to the results for lithium the temperature dependence of θ_G becomes stronger than before.

† We call this parameter θ_G to distinguish it from the more general θ_R of equation (1).

This is in marked contrast to the behaviour of sodium and potassium. Although in sodium and potassium there are rather large variations of θ'_G with temperature below about $\frac{1}{4}\theta$, it is seen that above this temperature θ'_G does not vary much, at least when it is evaluated at constant density. In fact it turns out that in all the monovalent metals for which reliable data are available (the data on rubidium and caesium are rather doubtful) the temperature dependence of the ideal resistivity above about $\frac{1}{4}\theta$ can be represented by an equation of the form of equation (1) with the same function f for all of them. Moreover, the function approximates quite closely to the Bloch-Grüneisen function.

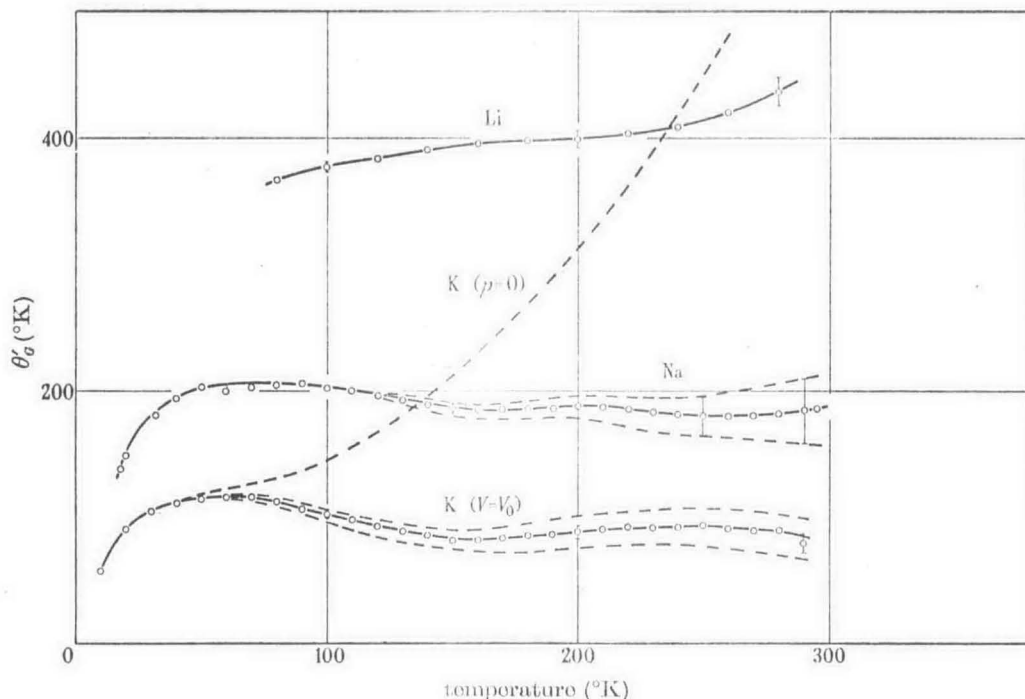


FIGURE 3. θ'_G for b.c.c. lithium, b.c.c. sodium and potassium. θ'_G was calculated by comparing the experimental temperature dependence of ρ_i at constant density with that predicted by the Bloch-Grüneisen formula. The bars indicate the approximate limits of random error, the dotted lines the approximate limits of systematic error which arise in the reduction of our experimental data to conditions of constant density. A curve of θ'_G for potassium corresponding to the results for $p = 0$ is also illustrated.

The existence of this reduced equation shows that the temperature dependence of ρ_i in the monovalent metals is not sensitive to the details of the phonon spectrum or the electronic band structure of the metal except at very low temperatures (cf. MacDonald & Mendelssohn 1950). For example, both sodium and copper obey the Bloch-Grüneisen relation very closely over a wide temperature range although they have different crystal structures and quite different shapes of Fermi surface. As we shall discuss below, the existence of this reduced equation at temperatures above about $\frac{1}{4}\theta$ has important consequences for the dependence of the pressure coefficient of ρ_i on temperature.

4.2. *The pressure coefficient of the ideal electrical resistivity*4.2.1. *The temperature dependence*

From our measurements on the pressure and temperature coefficients of electrical resistivity, we can deduce $\partial \ln \rho_i / \partial \ln V$ and $\partial \ln \rho_i / \partial \ln T$ at a fixed density for the metals potassium, sodium and lithium.† We can thus test whether $\partial \ln \rho_i / \partial \ln V$ is linearly related to $(1 + \partial \ln \rho_i / \partial \ln T)$ for these metals (cf. equation (2)). This is done in figures 4 and 5. The resulting curves are all representable by straight lines although in potassium, for which our measurements are most accurate, there are several points which lie further from the line than our estimated experimental error.

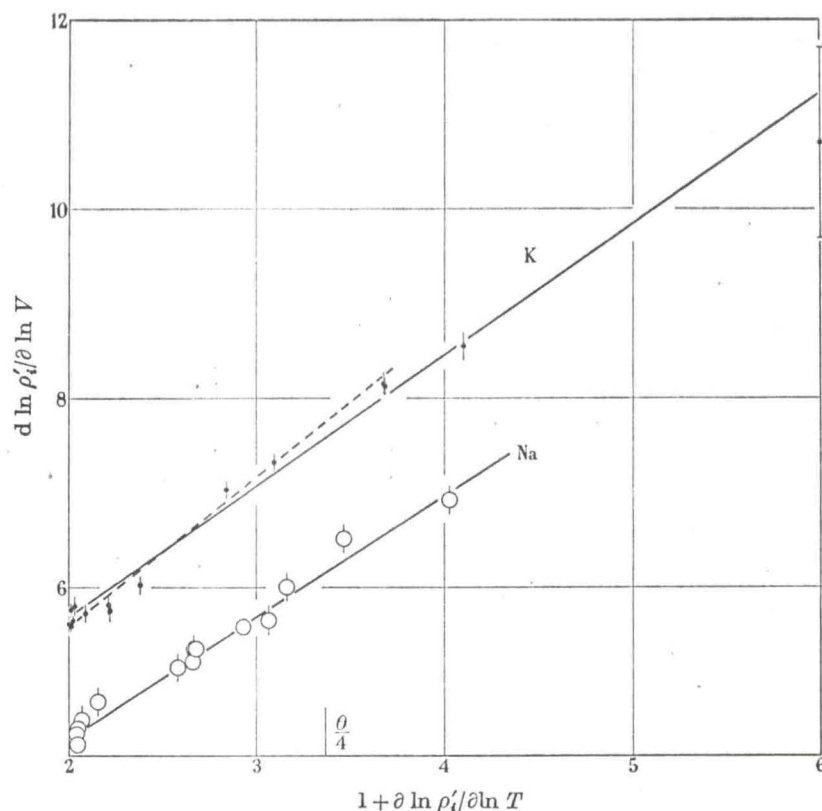


FIGURE 4. The volume coefficient of the ideal resistivity compared with the temperature coefficient of the ideal resistivity of sodium (b.c.c. phase) and potassium; ---, line drawn through points corresponding to temperatures above $\theta/4$ in potassium.

Since equation (2) is valid to a good approximation, we can determine the values of $\gamma_R (= -d \ln \theta_R / d \ln V)$ and $d \ln K / d \ln V$ from the experimental data on lithium, sodium, potassium and copper (the data on copper were taken from our earlier measurements (Dugdale & Gugan 1957)). These values are listed in table 12 in which we also include values of γ_G defined by the Grüneisen relation given in equation

† As explained above, the results for lithium have not been corrected to a fixed density since the corrections are small and probably less than our experimental error.

(4). It is seen that γ_G and γ_R have very nearly the same values.† Thus, just as the temperature dependence of ρ_i is given surprisingly well by the Bloch-Grüneisen expression, so the temperature dependence of the pressure coefficient agrees with the simple theory better than one would have expected from more sophisticated theoretical considerations.

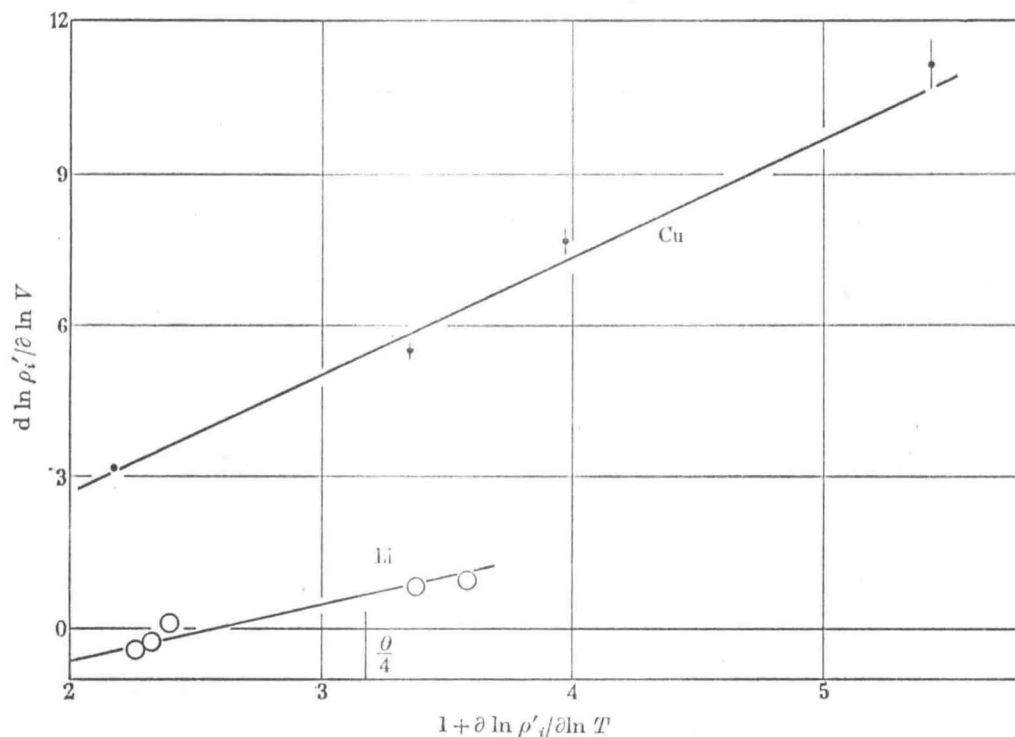


FIGURE 5. The volume coefficient of the ideal resistivity compared with the temperature coefficient of the ideal resistivity of copper and the b.c.c. phase of lithium.

TABLE 12. THE COEFFICIENTS γ_R AND $d \ln K/d \ln V$

	Cu	Li	Na	K	
				all T	$T > \frac{1}{4}\theta$
$\frac{d \ln K}{d \ln V}$	-2.0	-2.9	1.86	2.9	2.3
γ_R	2.3	1.1	1.3	1.4	1.6
γ_G	2.0	0.90	1.3		1.3

4.2.2. Departures from simple theory

It is interesting to consider why the simple theory works and what its limitations are. We can come to some conclusions about this by considering the $\rho_i - T$ curves of any one metal at different densities as though they were the properties of different

† We shall later be interested in the deviations from the linear relation predicted by equation (2) and we therefore include in Table 12 values of γ_R and $d \ln K/d \ln V$ for potassium which we deduce from results at 'high' temperatures, i.e. for temperatures greater than about $\frac{1}{4}\theta$.

metals. As we have already emphasized, there exists an approximate reduced equation for the resistivity of the monovalent metals at temperatures above about $\frac{1}{4}\theta$. *A fortiori* we may expect that this is also true for one metal at different densities. If equation (1) is valid at different densities over a certain temperature range, then equation (2) should be valid over this range for any single metal. This, we believe, is why the simple theory for the temperature dependence of $\partial \ln \rho_i / \partial \ln V$ works so well.

The differences in the temperature dependence of ρ_i that become conspicuous in the different metals below about $\frac{1}{4}\theta$ may arise from a number of different causes; two of the most important are differences in the phonon spectra of different metals and different degrees of distortion of the Fermi surfaces. Baily (1960) has investigated the first of these effects in detail and Collins & Ziman (1961) the second. Their results show that the differences in the functional form of the resistivity curves for different metals can indeed be explained on the basis either of anisotropies in the phonon spectrum or of distortion of the Fermi surface: this would also imply that if the effect of pressure (on any one metal) changes either of these anisotropies, then the functional form of the resistivity curve will change and that we should then expect deviations from equation (2). Indeed we would expect this to be the normal situation. For the metals we have studied it appears that (2) is obeyed fairly well on the whole. Only for potassium, however, do we have reasonably accurate results in much of the region below $\frac{1}{4}\theta$, and we find that here there appear to be departures from equation (2). In sodium the martensitic transformation makes uncertain the interpretation of our measurements at the lowest temperatures (see §3.2.2 above) so that we can only test equation (2) down to a temperature of about $\frac{1}{8}\theta$. Within this range, however, the equation does seem to hold for sodium.

We can understand this result for sodium because it is generally agreed that sodium has an almost spherical Fermi surface which remains practically unaffected by pressures of the order of those we have used,† and because, as one can deduce from the measurements of the pressure dependence of the elastic constants (Daniels 1960; Beecroft & Swenson 1961), the anisotropy of the phonon spectrum is also practically unaffected by pressure. For potassium there is no firm knowledge about either of these effects, but our results suggest that the anisotropy of the Fermi surface and/or that of the phonon spectrum is changing with volume.

We have seen that our results, broadly speaking, confirm that γ_R is almost equal to γ_G . It is clear that *exact* equality would be most unlikely even for $T \gtrsim \frac{1}{4}\theta$ since θ_R and θ_D are in fact different averages over the normal modes of the lattice vibrations. The ideas of Baily and of Collins & Ziman would certainly suggest that when pressure changes the anisotropy of either the phonon spectrum or the Fermi surface there will be, in addition to the deviations from equation (2) below $\frac{1}{4}\theta$, differences between γ_R and γ_G . It is perhaps significant then that for sodium, where we find no deviations from equation (2), we also find close agreement of γ_R and γ_G . For potassium, where there *are* deviations from equation (2), the average value of

† Measurements of the pressure dependence of the Hall constant of the alkali metals by Deutsch *et al.* (1961) indicate that even in sodium the Fermi surface probably changes shape at least slightly under such pressures.

γ_R over all temperatures is 1.4 (cf. $\gamma_G = 1.3$), but the value of γ_R from the region where (2) holds, above about $\frac{1}{4}\theta$, is 1.6.

4.2.3. The values of $d \ln K/d \ln V$

Since lithium has a positive pressure coefficient of resistance at high temperatures, its behaviour has long been regarded as anomalous. There have been several attempts to explain the anomaly, all of which recognized that compression of the metal must somehow change the electron properties in such a way as to offset the change in lattice vibrations which tends to decrease the resistance (cf. Mott 1934; Frank 1935; Cohen & Heine 1958).

Cohen & Heine (1958) interpreted the positive pressure coefficient of resistance in lithium as due to the close approach of the Fermi surface of lithium to the Brillouin zone boundary (or even to its contact with the zone boundary). They argued that the effect of pressure would be to increase the energy gap at the middle of the (110) face of the Brillouin zone and that this would thus increase the distortion of the Fermi surface (we are considering here only the b.c.c. phase). Such a distortion, they argued, would enhance the probability of Umklapp processes, and this together with possible changes in the average Fermi velocity of the electrons, would increase the electrical resistivity. No one has yet carried out a detailed calculation of these effects and the actual mechanism of the resistance increase is still uncertain (cf. Bailyn 1960).

TABLE 13. CORRELATION OF $d \ln K/d \ln V$ WITH THE THERMOELECTRIC POWER FOR THE MONOVALENT METALS

metal	$d \ln K/d \ln V$ †	α^*	$(d \ln K/d \ln V)/\alpha$
Li	-2.6	6.7	-0.4
Na	1.8	-2.7	-0.7
K	3.0	-4.0	-0.8
Rb	0.7	-2.5	-0.3
Cs	—	-0.2	—
Cu	-1.2	1.6	-0.8
Ag	-0.9	1.1	-0.8
Au	-0.7	1.5	-0.5

* See text.

† These values were calculated from the limiting high temperature values of $\partial \ln \rho_i / \partial \ln V$ by subtracting $2\gamma_G$ (see equation (3)). The value of $d \ln K/d \ln V$ for Cs is too uncertain for inclusion.

If, however, we accept the general argument of Cohen & Heine it should also apply to the noble metals. From the results of experiments on the anomalous skin effect, ultrasonic attenuation in a magnetic field and the de Haas-van Alpen effect, it is now well established that the Fermi surfaces of copper, silver and gold contact the Brillouin zone boundary. Cohen & Heine (1958) conclude from theoretical considerations that the effect of pressure on these metals should be to increase the area of contact of the Fermi surface and zone boundary; we therefore deduce, by the same argument as that applied to lithium, that this could account for the decidedly negative value of $d \ln K/d \ln V$ in the noble metals (see table 13).

In contrast, sodium and potassium are thought, from theoretical calculations and from a consideration of their transport properties, to have almost spherical Fermi surfaces (see, for example, Ham 1960; Cohen & Heine 1958). For these metals $d \ln K / d \ln V$ is about +2, and this implies that as the volume is decreased so the interaction between the electrons and the phonons decreases. This seems quite reasonable because one would expect *a priori* that as the electrons at the Fermi surface become more energetic, so their scattering for a given amplitude of vibration of the lattice would diminish.

According to the calculations of Ham (1960), the Fermi surfaces of all the alkali metals except sodium become more distorted under pressure. In sodium (according to these calculations) the Fermi surface remains effectively spherical up to moderate pressures but at higher pressures it too begins to become distorted. It is tempting to ascribe the minima that have been found by Bridgman in the resistance-pressure curves of the alkali metals at room temperature to a progressive distortion of the Fermi surface under pressure (cf. Dugdale 1961). In lithium the distortion of the Fermi surface is already large enough to make the resistance increase with pressure even at the lowest pressures; for the other alkali metals the increase of distortion with pressure (predicted by Ham) is, on this hypothesis, ultimately sufficient to cause the resistance of these metals also to increase with pressure (cf. also Frank 1935).

4.2.4. *The correlation of $d \ln K / d \ln V$ with the thermoelectric power*

The thermoelectric power of a metal at high temperatures ($T > \theta$) may be related to the energy dependence of electrical resistivity by the expression (which neglects phonon drag)

$$S = -\frac{\pi^2 k^2 T}{3e} \left(\frac{\partial \ln \rho(E)}{\partial E} \right)_{E=E_F} \quad (6)$$

Here $\rho(E)$ is the electrical resistivity of the metal for electrons of energy E and the derivative is to be evaluated at the Fermi level; e is the electronic charge and k is Boltzmann's constant. The significance of this expression is discussed by Ziman (1960). Equation (6) may be rewritten in the form

$$S = -\frac{\pi^2 k^2 T}{3e E_F} \left(\frac{\partial \ln \rho(E)}{\partial \ln E} \right)_{E=E_F}, \quad (6A)$$

where we have now introduced E_F , the Fermi energy measured from the bottom of the conduction band. From this expression and the measured values of S at high temperatures it is then possible to evaluate the quantity $(\partial \ln \rho(E) / \partial \ln E)_{E=E_F}$ (which for brevity we shall call x) for the monovalent metals†. This quantity x which measures the change in resistivity of the metal as the Fermi energy alters might be expected to be related in some way to the volume coefficient of electrical resistivity (cf. Friedel 1956). MacDonald & Pearson (1953) compared x directly with the logarithmic volume derivative of the electrical resistivity for the alkali metals and established that some correlation existed. It would seem, however, more appropriate to compare values of $d \ln K / d \ln V$ with the corresponding values of x , since in

† In doing this we shall use the free electron value for E_F .

$d \ln K/d \ln V$ changes due to the variation in the amplitude of the lattice vibrations, which have no counterpart in the thermoelectric powers, have been removed. In table 13 we make this comparison and in the last column we give the ratio $(d \ln K/d \ln V)/\alpha$ for the monovalent metals for which we have available reasonably reliable values of $d \ln K/d \ln V$. Since $d \ln E_F/d \ln V$ is $-\frac{2}{3}$ for quasi-free electrons, it is perhaps significant that for sodium and potassium, both of which approximate well to the free electron model of a metal, the ratio has a value of about -0.7 . This suggests that in these metals the dominant effect of the volume change on the electrons is simply to change their Fermi energy, E_F . The changes in electron properties which manifest themselves in the thermoelectric power then also manifest themselves in the changed electrical resistivity. Although this idea is attractive it is, as described in the introduction, hard to reconcile with the present theory of the volume dependence of electrical resistivity.

For the other monovalent metals the values of the ratio $(d \ln K/d \ln V)/\alpha$ are somewhat uncertain but they are all of comparable magnitude. It can at least be said that $d \ln K/d \ln V$ and α are closely related, and when the thermoelectric power of these metals is properly understood this should throw light on the magnitude of the pressure coefficient.

With regard to our earlier remarks about the minima in the resistance-pressure curves of the alkali metals, it follows that if there is a close relationship between $d \ln K/d \ln V$ and α , then when $d \ln K/d \ln V$ changes sign we might expect α also to change sign. Measurements on caesium at room temperature by Dugdale & Mundy (1961) show that this does indeed happen.

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APPENDIX A. THE TREATMENT OF THE EXPERIMENTAL DATA

(a) *The ideal resistivity of the b.c.c. phases as a function of temperature*

The immediate results given by our experiments were values of total resistance at temperature intervals of a few degrees for specimens of different shape factor. These we converted directly to resistivity-temperature results using the known equations of state (see appendix B). To convert from total resistivity to ideal resistivity we have in all cases subtracted the measured residual resistivity. This procedure is liable to lead to appreciable error for lithium because the observed residual resistance is that of a two-phase mixture and because lithium exhibits departures from Matthiessen's rule, but we believe that for our specimens the maximum error in our tabulated results (at 80 °K) is less than $\frac{1}{2}\%$ (cf. Dugdale & Guban 1961; Dugdale

et al. 1961). For sodium there should be little ambiguity in this procedure because we believe that here the residual resistivity is not much affected by the transformation (Dugdale & Guban 1960). Another objection to this method of correction for residual resistivity is that, since the residual resistivity is a function of density, the correction should vary with temperature. From our measurements of the volume dependence of the residual resistivity we were able to confirm that, for our high purity specimens, this effect is negligible within the limits of precision of our results.

In this way we have obtained curves of *relative* ideal resistivity as a function of temperature for specimens of different shape factor. We confirmed that the curves all had the same form (and were thus truly characteristic of the substance studied), and we then normalized the smoothed, average curve to the value of the *absolute* resistivity which we had measured at room temperature. The absolute accuracy of our results is thus limited by our value for the absolute resistivity at room temperature, and this we believe to be accurate to about one half per cent; the relative accuracy is of course much greater than this.

(b) *The pressure coefficient of ideal resistivity*

The immediate results given by our high-pressure experiments were values of total resistance at pressure intervals of a few hundred atmospheres for a series of constant temperatures. We first of all tested the resistance-pressure curves for smoothness by constructing tables of the divided differences; the smooth curves we then fitted to a polynomial expression (tables 4 and 8). From a knowledge of the equation of state we then calculated curves of total resistivity as a function of pressure, and by subtracting the curves for the measured residual resistivity we converted these to curves of ideal (relative) resistivity as a function of pressure. This last correction can be criticized for the same reasons that we have already given in (a) above, but where the correction is large (for example, the experiment on potassium at 4.2 °K) it is possible to make it with considerable accuracy, and in the conditions where the correction is less clearly defined (i.e. at high temperatures generally, and for sodium and lithium in *all* the b.c.c. region) it turns out that for our high-purity specimens, the correction is small. The limits of error we have given for the pressure coefficient of ideal resistivity do *not* include a specific contribution to include these uncertainties, but we believe that such a contribution would be very small even in the worst cases (e.g. lithium, where the pressure coefficient of residual resistivity depends on the phase composition of the material).

(c) *The ideal resistivity and the pressure coefficient of ideal resistivity at constant density*

As we mentioned in the introduction, the simplest theories of electrical conduction assume that the conductor remains at constant density. For metals with a large thermal expansion and a large value of $\partial \ln \rho_i / \partial \ln V$ it is obvious that the thermal expansion can have a considerable effect on the resistive behaviour. This is particularly true for the alkali metals and it has been recognized before (cf. Meixner 1940;

Kelly 1954; Bradshaw & Pearson 1956), but up till now the information needed to apply the corrections fully has not existed.

We have made a first attempt on this problem by calculating the resistive properties of sodium and potassium under the condition of constant density. We have chosen the density to be that of 0 °K under zero pressure, because all the high-pressure data needed to make such corrections to constant density lie in the range of our high-pressure experiments. It would be most interesting to be able to calculate what the resistive behaviour is for other densities too, but the accuracy of the basic data does not as yet warrant doing this.

The method we have adopted is to calculate from the data on the equation of state of our specimens the pressure required to compress them to the volume that they would occupy at the absolute zero under zero pressure; we call this new pressure p' . From the same data we also calculate the instantaneous compressibility at p' . From this information, and from our measured resistance-pressure curves, we are then able to calculate the resistivity and the pressure coefficient of resistivity at pressure p' ; these we call ρ'_i and $(\partial \ln \rho'_i / \partial p)$. We are of course interested in the temperature dependence of these quantities; in particular, from ρ'_i we calculate the quantities $(\partial \ln \rho'_i / \partial \ln T)$ and θ'_G as functions of temperature. We convert the values of $(\partial \ln \rho'_i / \partial p)$ to volume derivatives (using the values calculated for the instantaneous compressibility at p') and plot $(\partial \ln \rho'_i / \partial \ln V)$ against $(1 + \partial \ln \rho'_i / \partial \ln T)$ which gives us, according to equation (2), the quantities $(d \ln K / d \ln V)$ and γ_R appropriate to the density at 0 °K. That the difference between the coefficient evaluated at constant density and at constant pressure can be large is illustrated in figure 3 by the curves showing θ_G and θ'_G for potassium.

APPENDIX B. DATA FOR THE EQUATION OF STATE

We have tabulated in table A 1 the values *we have used* for the equations of state of lithium, sodium and potassium. The data are based on values of specific volume given by: Richards & Brink 1907 (K); Simon & Vohsen 1928 (K); Siegel & Quimby 1938 (Na); Pearson 1954 (Li); Barrett 1956 (Li, Na, K); Basinski & Verdini 1959 (Li, Na); and on values of volume compression given by: Bridgman, 1923 (Na), 1935 (Li, Na, K); Kleppa 1950 (K); Swenson 1955 (Li, Na, K); Nash & Smith 1959 (Li); Beecroft & Swenson 1961 (Na).

We have assumed that the shape of the P - V curves may be represented by the quadratic expression

$$V_p = V_0[1 + ap + bp^2] \equiv V_0[1 + ap(1 + cp)]. \quad (1A)$$

We have tabulated ' a ' ($\equiv \beta$, compressibility) as a function of temperature, and ' c ' ($\equiv b/a$) we have assumed to be independent of temperature. The quantity ' a ' is the value of ' a ' corresponding to the specific volume at 0 °K.

The units of pressure used in this paper are those of the normal atmosphere

$$1 \text{ atm} = 1.033_2 \text{ Kg wt./cm}^2 = 1.013_3 \text{ bar.}$$

TABLE A1. P - V - T DATA FOR LITHIUM, SODIUM AND POTASSIUM(a) Lithium of natural isotopic composition ($c = -1.1 \times 10^{-6} \text{ atm}^{-1}$)

T (°K)	$V(T)/V(0)$	$-a$ (10^{-6} atm^{-1})	$-a'$ (10^{-6} atm^{-1})
0	1.000 ₀	0.77 ₆	0.77 ₆
50	1.000 ₉	0.77 ₇	0.77 ₇
100	1.003 ₅	0.78 ₁	0.78 ₀
150	1.007 ₇	0.79 ₆	0.79 ₀
200	1.013 ₁	0.82 ₂	0.80 ₅
250	1.019 ₄	0.85 ₀	0.83 ₀
300	1.026 ₇	0.89 ₄	0.86 ₀

(b) Sodium ($c = -3.0 \times 10^{-6} \text{ atm}^{-1}$)

0	1.000 ₀	1.40 ₀	1.40 ₀
50	1.001 ₄	1.40 ₅	1.40 ₀
100	1.006 ₆	1.42 ₄	1.40 ₀
150	1.014 ₉	1.46 ₃	1.40 ₀
200	1.024 ₃	1.50 ₇	1.40 ₀
250	1.034 ₂	1.55 ₂	1.40 ₀
300	1.044 ₂	1.60 ₀	1.40 ₀

(c) Potassium ($c = -6.7 \times 10^{-6} \text{ atm}^{-1}$)

0	1.000 ₀	2.80 ₀	2.80 ₀
50	1.002 ₈	2.83 ₀	2.80 ₅
100	1.011 ₀	2.95 ₀	2.82 ₀
150	1.023 ₄	3.08 ₈	2.83 ₀
200	1.034 ₇	3.22 ₂	2.83 ₀
250	1.046 ₀	3.35 ₅	2.82 ₈
300	1.057 ₃	3.49 ₀	2.82 ₀

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