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## The effect of pressure and temperature on the electrical resistance of rubidium and caesium

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Measurements have been made of the electrical resistivity of rubidium and caesium at temperatures between 1.5 and 300 °K and at pressures up to 3000 atm. From our results we have calculated the ideal resistivity and its pressure derivative both at constant pressure and at constant density. The results are compared with those of the lighter alkali metals and with theoretical predictions.

### I. INTRODUCTION

In an earlier paper (Dugdale & Gugan 1962)† the effect of pressure on the electrical resistance of lithium, sodium and potassium at low temperatures was described. In this paper we present comparable results on rubidium and caesium. In this way we are able to compare the resistivity of all the alkali metals from low temperatures (*ca.* 2 °K) up to room temperature both at constant pressure (effectively zero) and at constant volume. In addition, we are able to compare the volume coefficients of resistivity and their dependence on temperature for the whole series of alkali metals.

Except for Bridgman's work and that described in I, most of the previous experiments on the resistivity of alkali metals have been done on specimens contained in capillary tubes. In the present series of experiments bare wires were used since these are essential if accurate measurements under pressure are to be made. As Bridgman (1925) has pointed out and as our earlier experience on the lighter alkali metals (Dugdale & Gugan 1963) showed, even for measurements of the temperature dependence of resistivity capillary specimens are unsatisfactory. This is particularly true of rubidium and caesium. Indeed, the thermal contraction of caesium is so large relative to glass that in some of the previous experiments in which glass capillaries were used the results showed very marked anomalies and in extreme cases the specimens became open circuit during cooling or heating. In rubidium, too, the anomaly originally found by MacDonald (1952) is almost certainly to be ascribed to the fact that the specimens were contained in glass capillaries.

In I it was pointed out that the present theory of electrical resistivity could not account for the volume dependence of the electrical resistivity of any of the metals discussed there. In particular, it was emphasized that even for sodium and potassium which appear to approximate well to the free electron model of a metal the theory was unsatisfactory. Since then there have been new theoretical

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† In what follows we shall refer to this paper as I.



calculations which agree rather well with experiment for these two metals and these calculations will be referred to later when we discuss our results on rubidium and caesium.

## 2. EXPERIMENTAL

The experimental techniques of measurement were essentially similar to those already described or referred to in I. Measurements were made of the resistance of the specimens as a function of temperature between *ca.* 2 and 300 °K at effectively zero pressure. In a second apparatus the pressure dependence was measured in a similar temperature range. The pressure transmitting medium was helium: in its fluid form at the higher temperatures and in the solid phase at the lowest temperatures. The pressure range was up to 3000 atm.

The main differences from the earlier experimental techniques were in the preparation and mounting of the specimens. Because rubidium and caesium, particularly the latter, are highly reactive metals which ignite spontaneously in a humid atmosphere the handling of the specimens had to be carried out either in a vacuum or in a dry box with an inert gas atmosphere.

The specimens consisted of wires about 40 cm long and 1 mm in diameter wound on a former similar to that described by Dugdale & Guban (1960). The metal was removed from its original glass capsule and melted into an extruding cell under vacuum of the order of  $10^{-5}$  to  $10^{-6}$  mmHg. The cell was then transferred into a stainless steel dry box of the conventional type, filled with clean dry helium. The metal wire was extruded into dry transformer oil, at about  $-5$  °C, under which it was wound onto the former; the former was then mounted on the apparatus, the excess oil brushed off with a fine artist's brush and the high pressure vessel screwed on. The whole was then transferred from the dry box to the cryostat, the high pressure connexions were made and the cryostat was then filled with liquid nitrogen.

During the experiments we had some trouble with oxidation of the specimens. In general high pressures seem to inhibit this effect and we found it safest at temperatures above about 180 °K to keep a pressure of at least 100 atm on the specimens in the high pressure apparatus. This was also experimentally convenient although it had the disadvantage that we had to obtain the zero pressure value of the resistance for each pressure run by extrapolation. In one of our experiments on caesium near room temperature we found the 'transition' reported by Bridgman (1923) which occurs when a specimen becomes appreciably oxidized. This shows up as a step in the resistivity-pressure curve at temperatures near 0 °C and is presumably related to the change with pressure of the eutectic temperature of the caesium oxide-caesium metal system. If the specimen is not contaminated, a smooth dependence of resistance on pressure is found with only slight effects due to oxidation.

In the low pressure apparatus we had similar problems. At temperatures above 140 °K in the case of rubidium (specimen 4) and 180 °K in the case of caesium (specimen 2) we found that the resistance of the specimen increased slowly while the temperature was kept constant. We attributed this to oxidation at the surface

of the specimens, and to improve the accuracy of the measurements in this region we rapidly cooled the specimens after each reading to a low temperature at which no reaction could occur. By measuring the resistance at this low temperature and comparing it with its previous value we were able to make a correction for the change in shape factor of the specimen. Any oxidation of the specimen during cooling was, we believe, negligible compared with that during the slow warming up.

### 2.1. The specimens

Details of the various specimens used are summarized in tables 1 and 2. The rubidium for specimen Rb (5) was distilled in this laboratory in order to reduce its residual resistivity. The distillation was carried out in three stages in a quartz apparatus specially designed for the purpose. The first and third fractions were

TABLE 1. THE RUBIDIUM SPECIMENS

no.	source of material	resistance ratio	residual resistance
1*	L. Light and Co. Ltd., Colnbrook, England	$\frac{R_{78}}{R_{4.2}} = 52$	0.00042 $\Omega$
2*			
3*		$\frac{R_{78}}{R_{4.2}} = 54$	0.00037 $\Omega$
4†		$\frac{R_{78}}{R_{4.2}} = 146, \frac{R_{273}}{R_{4.2}} = 615$	0.00009 <sub>0</sub> $\Omega$
5‡		$\frac{R_{78}}{R_{4.2}} = 230$	0.000044 $\Omega$
6§		$\frac{R_{295}}{R_{4.2}} = 580$	
7§			
8§			

\* High pressure apparatus.

† Low pressure apparatus.

‡ Redistilled in this laboratory.

§ Used for absolute resistivity measurements.

TABLE 2. THE CAESIUM SPECIMENS

no.	source of material	resistance ratio	residual resistance
1*	A. D. Mackay and Co., New York	$\frac{R_{78}}{R_{4.2}} = 67$	0.00029 $\Omega$
2†		$\frac{R_{78}}{R_{4.2}} = 74, \frac{R_{273}}{R_{4.2}} = 298$	0.00024 $\Omega$
3*		$\frac{R_{78}}{R_{4.2}} = 73$	0.00025 $\Omega$
4‡	L. Light and Co. Ltd., Colnbrook, England	$\frac{R_{295}}{R_{4.2}} = 250$	—
5‡			
6‡			

\* High pressure apparatus.

† Low pressure apparatus.

‡ Used for absolute resistivity measurements.



discarded and only the middle fraction kept. This fraction was then melted into the extruding cell and transferred into the glove box in the usual way. Such a distillation improved the resistance ratio of the rubidium by a factor of nearly 5.

### 2.2. *Absolute values of the resistivity*

To measure the absolute resistivities of rubidium and caesium we extruded a wire (2 mm in diameter for rubidium and 3 mm for caesium) under distilled paraffin oil. We then put a length of this into a transparent, rigid plastic tube of about 3 mm diameter. Next we pushed four platinum electrodes through holes in the tube into the wire. These electrodes were used as current and potential leads for the measurement of the resistance of the wire. The distance between the potential electrodes was determined afterwards from the distance between the holes in the plastic tube which held these electrodes.

To determine the diameter of the wire a known length of it (equal to the total length of the plastic tube) was allowed to react with ethyl alcohol. The solution formed in this way was then titrated against a standard acid solution to determine the amount of metal. From the mass of metal and its density the diameter of the wire could then be found. (Dr Z. S. Basinski suggested this method of determining the diameter and we are grateful to him for the idea and for carrying out the titrations.) The reaction of cold ethyl alcohol with the rubidium was fairly slow but with the caesium it was rather fast; fortunately, this did not cause any liquid to spill out of the spherical flask which held the alcohol.

Apart from holding the electrodes and fixing the total length of the specimen, the plastic tube also served to keep down the oxidation of the specimens by protecting them from the bulk of the oil in the open tank. Chemical reaction in the caesium specimens was further reduced by having the oil cool (about 9 °C for specimen 6 and about 2 °C for specimens 7 and 8). These precautions seemed sufficient since the specimens stayed bright and shiny and their resistance did not increase appreciably with time (except for caesium specimen 7 which may have contained some oxide). The error in the absolute resistivities determined in this way is probably about  $\pm 2\%$ .

## 3. EXPERIMENTAL RESULTS

### 3.1. *Absolute resistivity*

Our values of absolute resistivity are compared with those of other observers in table 3; it is seen that there are large discrepancies among these values (up to 15% for rubidium). It is clear from Hackspill's (1910, 1911) account of his experiments that they are more reliable than those of Guntz & Broniewski (1909). The measurements by MacDonald, White & Woods (1956) of *absolute* resistivity were incidental to their main objective and their methods were not very reliable as they themselves admit in discussing the unreproducible values they found for potassium. Our results confirm those of Hackspill and we believe that there is now no serious doubt (within  $\pm 2\%$ ) of the values to be adopted for the absolute resistivities of rubidium and caesium.



## 3.2. Temperature dependence of resistance

The results of the resistance measurements obtained with the low pressure apparatus are converted into resistivity values in the following way. We first derive the ideal resistance,  $R_i$ , by assuming Matthiessen's rule

$$R = R_i + R_0.$$

Here  $R$  is the total measured resistance at any temperature and  $R_0$  the limiting low temperature value of the resistance.  $R_i$  is then assumed to be the resistance due to the lattice vibrations. Strictly this relationship should be applied only to measurements at constant density but the corrections to  $R_0$  due to thermal expansion are small enough to be neglected. On the other hand, departures from Matthiessen's rule itself could be appreciable at low temperatures, perhaps 10% of  $R_0$  at  $\frac{1}{4}\theta$ .

TABLE 3. ABSOLUTE RESISTIVITIES

metal	temperature (°K)	resistivity ( $\mu\Omega$ cm)	observer
rubidium	295	12.6*	present work (average of three specimens)
	295	14.2	G. & B.
	295	12.6	H.
	295	14.6	M., W. & W.
	caesium	275.6	18.2†
	275.6	19.5	G. & B. (interpolated value)
	275.6	18.3	H. (interpolated value)
	282.3	19.9†	present work (specimen possibly oxidized)
	282.3	20.1	G. & B.
	282.3	18.8	H. (interpolated)

(For an estimate of accuracy, see text.)

G. & B.: Guntz & Broniewski (1909). H.: Hackspill (1910). M., W. & W.: MacDonald, White & Woods (1956).

\* In deducing this value we took for the density of rubidium at 20 °C the value 1.53 g/cm<sup>3</sup>.

† In deducing these values we took for the density of caesium at 20 °C the value 1.87 g/cm<sup>3</sup>.

From the values of the ideal resistance we now wish to determine the resistivities. The first correction is for the change in dimensions of the specimen with temperature; since the thermal expansion data on rubidium and caesium are rather uncertain, this procedure can introduce a systematic error (up to  $\frac{1}{2}\%$ ) into the values for the resistivity. However, the results can readily be corrected when more accurate volumetric data become available and, for this purpose, we give in table 6 the values for the changes in volume with temperature which we have assumed. The resistance data so corrected give *relative* resistivity values.

To find the *absolute* values we extrapolate our measured values of relative resistivity to the temperature region in which the absolute resistivities are known (above 0 °C). The relative resistivity values are then scaled to have the right magnitude; this process involves an extrapolation over a temperature interval of about 12 degC for rubidium and about 3 degC for caesium.



The resistivity values (effectively at zero pressure) obtained in this way are shown in tables 4 and 5. These values normalized to the ice point resistivity are compared with the results obtained by other observers in tables 7 and 8. This comparison shows that for the most part our values are systematically lower than those of previous workers. Take, for example, the data of Meissner & Voigt (1930); there is a systematic difference between our results and theirs which increases at

TABLE 4. THE IDEAL RESISTIVITY OF RUBIDIUM AT ZERO PRESSURE,  $\rho_i$ , AND AT CONSTANT VOLUME,  $\rho'_i$

$T$ (°K)	$\rho_i/T^*$ ( $10^{-8} \Omega \text{ cm/deg}$ )	$\rho'_i/T^\dagger$ ( $10^{-8} \Omega \text{ cm/deg}$ )	$T$ (°K)	$\rho_i/T^*$ ( $10^{-8} \Omega \text{ cm/deg}$ )	$\rho'_i/T^\dagger$ ( $10^{-8} \Omega \text{ cm/deg}$ )
2	0.01 <sub>2</sub>	0.01	120	3.53 <sub>8</sub>	3.21 <sub>2</sub>
4	0.15 <sub>6</sub>	0.16	130	3.57 <sub>4</sub>	3.21 <sub>7</sub>
6	0.40 <sub>3</sub>	0.40	140	3.61 <sub>0</sub>	3.22 <sub>3</sub>
8	0.70 <sub>3</sub>	0.70	150	3.64 <sub>4</sub>	3.22 <sub>8</sub>
10	1.00 <sub>0</sub>	1.00	160	3.67 <sub>8</sub>	3.23 <sub>5</sub>
12	1.29 <sub>1</sub>	1.29	170	3.71 <sub>3</sub>	3.24 <sub>4</sub>
14	1.56 <sub>9</sub>	1.57	180	3.74 <sub>6</sub>	3.25 <sub>3</sub>
16	1.80 <sub>7</sub>	1.81	190	3.78 <sub>3</sub>	3.26 <sub>7</sub>
18	2.00 <sub>4</sub>	2.00	200	3.82 <sub>4</sub>	3.28 <sub>5</sub>
20	2.16 <sub>5</sub>	2.16	210	3.86 <sub>4</sub>	3.30 <sub>4</sub>
30	2.68 <sub>8</sub>	2.66	220	3.90 <sub>4</sub>	3.32 <sub>7</sub>
40	2.97 <sub>6</sub>	2.92	230	3.94 <sub>5</sub>	3.34 <sub>6</sub>
50	3.14 <sub>7</sub>	3.05 <sub>4</sub>	240	3.98 <sub>6</sub>	—
60	3.25 <sub>2</sub>	3.12 <sub>6</sub>	250	4.00 <sub>4</sub>	—
70	3.31 <sub>9</sub>	3.16 <sub>1</sub>	260	4.07 <sub>2</sub>	—
80	3.37 <sub>5</sub>	3.18 <sub>3</sub>	270	4.11 <sub>5</sub>	—
90	3.42 <sub>2</sub>	3.19 <sub>6</sub>	280	4.15 <sub>8</sub>	—
100	3.46 <sub>1</sub>	3.20 <sub>3</sub>	290	4.20 <sub>8</sub>	—
110	3.50 <sub>0</sub>	3.20 <sub>7</sub>	300	4.28 <sub>4</sub>	—

\* *Random* error at all temperatures is  $\pm 0.002$  in the units used in the table. The *systematic* errors are estimated to be as follows: (a)  $\pm 2\%$  due to uncertainty in the absolute value of  $\rho_i$ ; (b)  $\pm \frac{1}{2}\%$  due to uncertainties in the equation of state of the metal; this decreases at higher temperatures; (c)  $\pm 2\%$  at low temperatures (around 10 °K) due to departures from Matthiessen's rule; this error should be appreciably smaller than the residual resistivity itself at all temperatures; (d)  $\pm 1\%$  above *ca.* 140 °K due to oxidation of the specimens (see text).

† The random errors are similar to those in  $\rho_i$ . The systematic errors in  $\rho'_i$  include those in  $\rho_i$  together with a high temperature error of about  $\pm 1\%$  due to uncertainty in the equation of state.

lower temperatures. Some of this (down to 20.4 °K in rubidium) could be due to capillary constraints in the specimens of Meissner & Voigt (cf. Dugdale & Guban 1963), but this alone could not account for the differences by factors of 2 or 3 that are observed at the lowest temperatures in both rubidium and caesium. This sort of difference might be due to cavitation. As we have already emphasized, there is a large volume contraction in cooling these two metals from room temperature to helium temperatures (nearly 10% in caesium) and in capillary specimens this can cause large, unreproducible changes in resistance (see figure 14 of MacDonald & Mendelssohn 1950). This sort of behaviour presumably comes about because if the stress in the specimen (due to the differential contraction between glass and metal)



becomes large enough the metal breaks away from the glass or forms voids which can then increase the resistance unpredictably.

On the other hand it is seen that we get quite good agreement with the results of MacLennan, Niven & Wilhelm (1928) on caesium and with limited data of MacDonald *et al.* (1956) on both metals. Both these sets of results were obtained with capillary specimens so that it is not obvious why we should get such good agreement. The clue to this may again be cavitation. MacDonald *et al.* mention that in their caesium specimens cavitation may have occurred even at room

TABLE 5. THE IDEAL RESISTIVITY OF CAESIUM AT ZERO PRESSURE,  $\rho_i$ , AND AT CONSTANT VOLUME,  $\rho'_i$

$T$ ( $^{\circ}$ K)	$\rho_i/T^*$ ( $10^{-8}$ $\Omega$ cm/deg)	$\rho'_i/T^*$ ( $10^{-8}$ $\Omega$ cm/deg)	$T$ ( $^{\circ}$ K)	$\rho_i/T^*$ ( $10^{-8}$ $\Omega$ cm/deg)	$\rho'_i/T^*$ ( $10^{-8}$ $\Omega$ cm/deg)
2	0.08 <sub>9</sub>	0.90	120	5.72 <sub>8</sub>	5.28 <sub>7</sub>
4	0.63 <sub>8</sub>	0.64	130	5.77 <sub>0</sub>	5.28 <sub>7</sub>
6	1.38 <sub>0</sub>	1.38	140	5.81 <sub>1</sub>	5.29 <sub>0</sub>
8	2.24 <sub>2</sub>	2.24	150	5.85 <sub>3</sub>	5.29 <sub>0</sub>
10	2.94 <sub>9</sub>	2.95	160	5.89 <sub>8</sub>	5.30 <sub>0</sub>
12	3.42 <sub>2</sub>	3.42	170	5.94 <sub>8</sub>	5.30 <sub>8</sub>
14	3.75 <sub>0</sub>	3.75	180	6.00 <sub>2</sub>	5.31 <sub>9</sub>
16	3.99 <sub>3</sub>	3.99	190	6.05 <sub>4</sub>	5.33 <sub>4</sub>
18	4.20 <sub>8</sub>	4.21	200	6.11 <sub>0</sub>	5.34 <sub>7</sub>
20	4.41 <sub>2</sub>	4.39 <sub>5</sub>	210	6.16 <sub>7</sub>	—
30	4.93 <sub>8</sub>	4.88 <sub>7</sub>	220	6.22 <sub>8</sub>	—
40	5.16 <sub>3</sub>	5.07 <sub>3</sub>	230	6.28 <sub>9</sub>	—
50	5.31 <sub>0</sub>	5.16 <sub>1</sub>	240	6.35 <sub>5</sub>	—
60	5.40 <sub>8</sub>	5.20 <sub>9</sub>	250	6.42 <sub>4</sub>	—
70	5.47 <sub>0</sub>	5.22 <sub>7</sub>	260	6.49 <sub>4</sub>	—
80	5.53 <sub>0</sub>	5.24 <sub>1</sub>	270	6.56 <sub>3</sub>	—
90	5.58 <sub>7</sub>	5.25 <sub>5</sub>	280	6.64 <sub>1</sub>	—
100	5.63 <sub>7</sub>	5.26 <sub>7</sub>	290	6.72 <sub>3</sub>	—
110	5.68 <sub>5</sub>	5.28 <sub>0</sub>			

\* The estimated errors, both random and systematic, are similar to those for rubidium except that oxidation effects begin at *ca.* 180  $^{\circ}$ K and may be rather larger by room temperature.

temperature (presumably during the solidification process after filling the capillary with liquid metal). Moreover, their rubidium and potassium specimens gave quite inaccurate values for absolute resistivity and this again suggests that cavitation may have occurred. If this is so, then the metal in their specimens may not have completely filled the cross-section of their glass capillaries and this might prevent the building up of any appreciable negative pressure. This question is of some interest because in recent work on the Fermi surfaces of the alkali metals there has been considerable uncertainty about the actual lattice parameter of the specimens in the helium range of temperatures. The metals have been either coated with petroleum jelly (Shoenberg & Stiles 1964) or held in glass capillaries (Okumura & Templeton 1962, 1963) and this introduces uncertainties about the degree of constraint in the specimens. The resistivity data seem to indicate that in the lighter alkali metals (which do not contract so much on cooling) cavitation is probably unusual but much commoner in rubidium and caesium

We next wish to derive values of the resistivity as a function of temperature at *constant density*. For this we have to use the results of our measurements of resistance under pressure (see following section). Consider first the resistivity at

TABLE 6. *P-V-T* VALUES ASSUMED FOR RUBIDIUM AND CAESIUM\*

$T(^{\circ}\text{K})$	$V(T)/V(0)$	$-\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T (10^{-5} \text{ atm}^{-1})$ at $p = 0$	$\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T (10^{-5} \text{ atm}^{-1})$ at $V = V_0$
(a) rubidium			
0	1.000	3.56	3.56
30	1.003	3.61	3.56
60	1.009	3.77	3.56
90	1.016	3.94	3.56
120	1.023	4.12	3.56
150	1.030	4.29	3.56
180	1.037	4.47	3.56
210	1.044	4.64	3.56
240	1.052	4.81	3.56
270	1.059	4.99	3.56
300	1.066	5.16	3.56
(b) caesium			
0	1.000	4.40	4.40
30	1.003	4.46	4.40
60	1.013	4.75	4.40
90	1.023	5.13	4.40
120	1.033	5.40	4.40
150	1.042	5.72	4.40
180	1.052	6.05	4.40
210	1.062	6.38	4.40
240	1.072	6.71	4.40
270	1.082	7.03	4.40
300	1.092	7.36	4.40

\* For full references to the sources of experimental data, see Martin (1965).

TABLE 7. A COMPARISON OF RESULTS FOR THE IDEAL RESISTIVITY OF RUBIDIUM AT ZERO PRESSURE

$T(^{\circ}\text{K})$	$\rho_i(T)/\rho_i(273.15)$			
	1	2	3	4
273.15	1.000 <sub>0</sub>	1.000 <sub>0</sub>	1.000	1.000
87.8 <sub>1</sub>	—	0.277 <sub>2</sub>	—	0.268
77.6 <sub>0</sub>	—	0.241 <sub>7</sub>	—	0.233
20.4 <sub>2</sub>	0.43 <sub>2</sub>	0.045 <sub>9</sub>	0.038	0.040 <sub>3</sub>
14.0 <sub>0</sub>	0.021 <sub>9</sub>	—	—	0.019 <sub>5</sub>
4.20	$\left\{ \begin{array}{l} 0.0013 \\ 0.0008 \end{array} \right.$	0.001 <sub>7</sub>	0.0007	0.000 <sub>6</sub>

1, Justi (1948); 2, Meissner & Voigt (1930); 3, MacDonald *et al.* (1956); 4, This work.

a fixed density corresponding to that of the solid at the absolute zero under zero pressure. To obtain these values of  $\rho_i$  at any temperature we have worked out from thermal expansion and compressibility data (see table 6) the pressure ( $p'$ ) required at any temperature to compress the metal to the given density. The change in



resistance  $\Delta R_i$  due to this pressure was then read off from our pressure measurements and this together with our original  $R_i$  versus temperature curves at zero pressure gives  $R'_i$  the resistance at constant density over the whole temperature range. This is then converted to resistivity by a single conversion factor determined from the known resistivity above 0 °C. Values of the resistivity calculated in this way are included in tables 4 and 5.

TABLE 8. A COMPARISON OF RESULTS FOR THE IDEAL RESISTIVITY OF CAESIUM AT ZERO PRESSURE

$T$ (°K)	$\rho_i(T)/\rho_i(273.15)$				
	1	2	3	4	5
273.15	1.000	1.000	1.000	1.000	1.000
87.8 <sub>1</sub>	—	0.302 <sub>2</sub>	—	—	0.272
82	—	—	—	0.248	0.253
77.60	—	0.269 <sub>0</sub>	—	—	0.238
20.6	—	—	—	0.051	0.051 <sub>8</sub>
20.4 <sub>2</sub>	0.057 <sub>6</sub>	0.095 <sub>7</sub>	—	—	0.051 <sub>2</sub>
14.0 <sub>0</sub>	0.032 <sub>9</sub>	—	—	—	0.028 <sub>8</sub>
4.2 <sub>0</sub>	0.001 <sub>6</sub>	0.002 <sub>9</sub>	0.0017	0.002 <sub>1</sub>	0.001 <sub>6</sub>

1, Justi (1948); 2, Meissner & Voigt (1930); 3, MacDonald *et al.* (1956); 4, McLennan *et al.* (1928); 5, This work.

To work out  $\rho'_i$  (the prime is used to indicate that  $\rho_i$  is evaluated at fixed density) at other densities we assumed that the compressibilities of rubidium and caesium were independent of temperature at a fixed density. Then we could work out the resistance changes at each temperature in a similar way for pressures of  $(p' + 1000)$  and  $(p' + 2000)$  atm and proceed as before. The values of  $\rho'_i$  obtained in this way are plotted in figures 1 and 2.

We can illustrate how the ideal resistivity of rubidium and caesium depends on temperature in a different way. In this we compare their resistivities (at constant density) with that predicted by the Bloch-Grüneisen formula. To do this we compare values of  $(\partial \ln \rho_i / \partial \ln T)_V$  for the actual metal with that deduced from the Bloch-Grüneisen function and choose the value of the characteristic temperature  $\theta_G$  involved in this function to make the two agree at each temperature (Kelly & MacDonald 1953). The results showing how  $\theta_G$  varies with temperature for rubidium and caesium are shown in figure 3. The general behaviour is not unlike that of the lighter alkali metals (see I).

### 3.3. Pressure dependence of resistance

Tables 9 and 10 show the variation of ideal resistance of rubidium and caesium with pressure at various temperatures. They are smoothed curves of direct readings taken with the high pressure apparatus, Matthiessen's rule being applied to determine the ideal resistance.

In the solid helium range, the procedure was to plot curves of variation of resistance with temperature at several different pressures; the curves for rubidium specimen 3 are shown in figure 4. The residual resistances, indicated by arrows



on this diagram were determined by linear extrapolations of plots of  $R$  against  $T^5$ . Figure 5 shows a typical set of results obtained in the liquid hydrogen range of temperature. It illustrates what happens when the helium, which transmits the pressure, solidifies; this is shown by the abrupt increase in slope of the resistance-temperature curve when solidification begins and an abrupt decrease in slope again when solidification is complete.

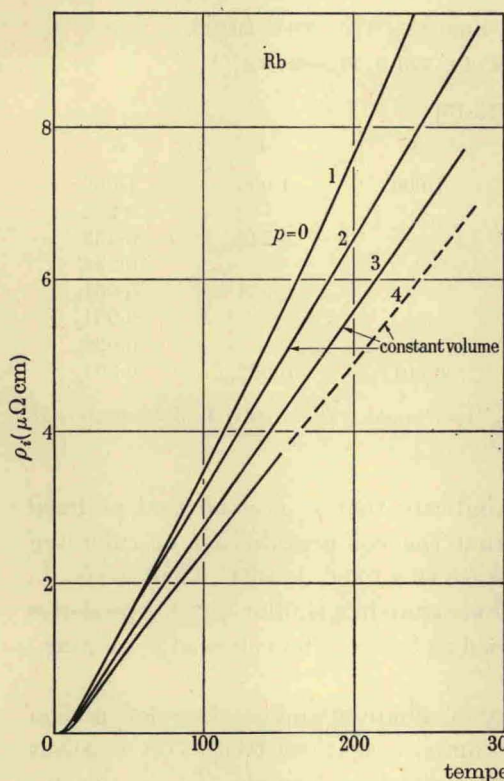


FIGURE 1

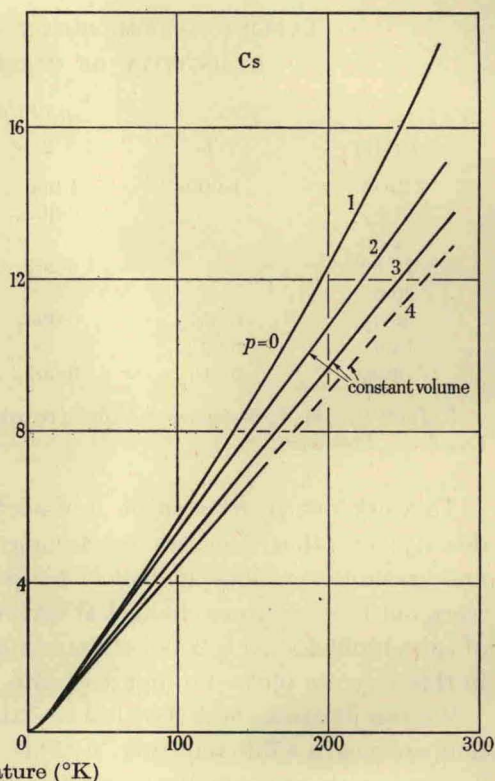


FIGURE 2

FIGURE 1. The ideal resistivity of rubidium as a function of temperature. Curve 1 is at constant pressure ( $p = 0$ ); the rest at constant density. The densities are those of the solid at  $0^\circ\text{K}$  and the following pressures: curve 2, zero; curve 3, 1000 atm; curve 4, 2000 atm. The dashed line is an interpolation between our results at lower temperatures and a point based on Bridgman's data at the ice point.

FIGURE 2. The ideal resistivity of caesium as a function of temperature. Curve 1 is at constant pressure ( $p = 0$ ); the rest at constant density. The densities are those of the solid at  $0^\circ\text{K}$  and the following pressures: curve 2, zero; curve 3, 1000 atm; curve 4, 2000 atm. The dashed line is an interpolation between our results at lower temperatures and a point based on Bridgman's data at the ice point.

Table 9 shows the effect of pressure on the resistance of two samples of rubidium of very different purity; this enables one to test the validity of Matthiessen's rule for determining the pressure coefficient of ideal resistivity at low temperatures. Consider in particular the results obtained at  $4.2^\circ\text{K}$ . Specimens 1 and 3 which are of similar purity give concordant results, whereas specimen 5 which was much less impure (by



a factor of 5) gives an appreciably bigger pressure dependence for  $\rho_i$ . The initial pressure coefficients for the specimens of different purity are not too different but the difference appears to increase with pressure. Since the departures from Matthiessen's rule are probably mainly due to different anisotropies of  $\tau(k)$  for phonon and impurity scattering, one can only assume that these are changing

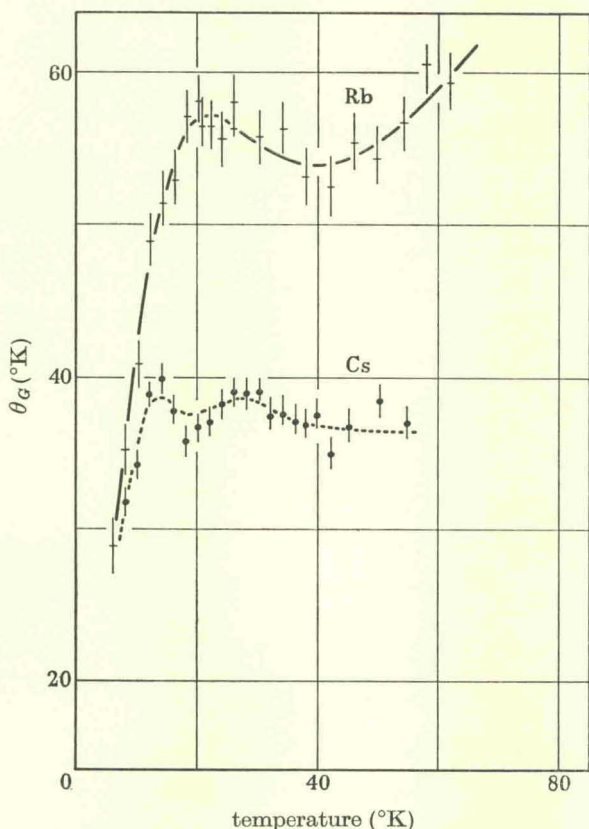


FIGURE 3. Values of  $\theta_G$  as a function of temperature for rubidium and caesium.  $\theta_G$  is obtained by comparing the ideal resistivity of the metal with that predicted by the Bloch-Grüneisen relation.

differently in the two sets of specimens. This does, however, show that in this region the pressure coefficients are as yet not very reliable. At higher temperatures, the results from specimens of different purity agree well (cf. the results on rubidium specimens 1, 3 and 5 near 20 °K).

### 3.3.1. The minimum in the $R$ - $p$ curve for caesium

Bridgman (1925) found that the resistance versus pressure curve of caesium went through a minimum (cf. figure 7); at 0 °C this minimum occurs at a pressure of about 4000 atm. Since our measurements extend only to 3000 atm, we do not observe this minimum, but we can make some deductions from our results about its temperature dependence.



Figure 2 shows that at three different densities the ideal resistivity of caesium is directly proportional to the absolute temperature down to quite low temperatures. It is reasonable to suppose that this would also be true at the slightly higher densities corresponding to and beyond that at which the minimum occurs. If this were so then the minimum would be associated with one particular density at all temperatures, at least in the region where the ideal resistivity (at fixed density) is directly proportional to  $T$ . This enables us to estimate how the pressure at which the minimum occurs changes with temperature.

TABLE 9. THE PRESSURE DEPENDENCE OF THE ELECTRICAL RESISTANCE OF RUBIDIUM

The listed values give  $R_i(p)/R_i(p=0)$ .

pressure (atm)	4.2 °K {Rb 1, 3}	4.2 °K {Rb 5}	12.3 °K {Rb 1}	14.3 °K {Rb 1}	20.3 °K {Rb 1}	20.3 °K {Rb 3}	20.7 °K {Rb 5}
0	1.00	1.00	1.00	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>
250	—	—	0.95	0.95 <sub>0</sub>	0.95 <sub>9</sub>	0.96 <sub>0</sub>	0.95 <sub>9</sub>
500	0.92	0.90	0.92	0.92 <sub>0</sub>	0.92 <sub>2</sub>	0.92 <sub>2</sub>	0.92 <sub>3</sub>
750	—	—	0.88	0.88 <sub>2</sub>	0.88 <sub>6</sub>	0.88 <sub>5</sub>	0.88 <sub>7</sub>
1000	0.85	0.81	—	—	0.85 <sub>3</sub>	0.85 <sub>1</sub>	0.85 <sub>4</sub>
1250	—	—	—	—	0.82 <sub>0</sub>	0.82 <sub>0</sub>	0.82 <sub>1</sub>
1500	0.80	0.69	—	—	0.79 <sub>0</sub>	0.79 <sub>0</sub>	0.79 <sub>1</sub>
2000	0.72	0.59	—	—	—	—	—
2500	—	—	—	—	—	—	—
	29.5 °K {Rb 1}	55.9 °K {Rb 1}	67.9 °K {Rb 1}	78.4 °K {Rb 1}	78.8 °K {Rb 5}	79.5 °K {Rb 3}	90.7 °K {Rb 1}
0	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>
500	0.92 <sub>3</sub>	0.907	0.93 <sub>0</sub>	0.92 <sub>9</sub>	0.92 <sub>9</sub>	0.92 <sub>9</sub>	0.92 <sub>8</sub>
1000	0.85 <sub>8</sub>	0.86 <sub>8</sub>	0.86 <sub>7</sub>	0.86 <sub>4</sub>	0.86 <sub>6</sub>	0.86 <sub>4</sub>	0.86 <sub>4</sub>
1500	0.79 <sub>9</sub>	0.80 <sub>8</sub>	0.81 <sub>1</sub>	0.80 <sub>8</sub>	0.81 <sub>2</sub>	0.80 <sub>8</sub>	0.80 <sub>8</sub>
2000	0.74 <sub>4</sub>	0.75 <sub>8</sub>	0.76 <sub>0</sub>	0.75 <sub>8</sub>	0.76 <sub>1</sub>	0.75 <sub>9</sub>	0.75 <sub>8</sub>
2500	0.70 <sub>1</sub>	0.71 <sub>1</sub>	0.71 <sub>5</sub>	0.71 <sub>3</sub>	0.71 <sub>8</sub>	0.71 <sub>5</sub>	0.71 <sub>4</sub>
	113.2 °K {Rb 1}	160.5 °K {Rb 1}	195.0 °K {Rb 1}	195.3 °K {Rb 3}	230.9 °K {Rb 1}	273.2 °K {Rb 2}	273.2 °K {*}
0	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>
500	0.92 <sub>3</sub>	0.92 <sub>5</sub>	0.92 <sub>3</sub>	0.94 <sub>5</sub>	0.91 <sub>6</sub>	0.91 <sub>1</sub>	—
1000	0.85 <sub>9</sub>	0.85 <sub>8</sub>	0.85 <sub>9</sub>	0.87 <sub>4</sub>	0.84 <sub>4</sub>	0.83 <sub>8</sub>	0.85 <sub>4</sub>
1500	0.80 <sub>2</sub>	0.80 <sub>0</sub>	0.80 <sub>2</sub>	0.81 <sub>4</sub>	0.78 <sub>2</sub>	0.77 <sub>7</sub>	—
2000	0.75 <sub>2</sub>	0.74 <sub>9</sub>	0.75 <sub>0</sub>	0.76 <sub>1</sub>	0.72 <sub>9</sub>	0.72 <sub>5</sub>	0.73 <sub>9</sub>
2500	0.70 <sub>7</sub>	0.70 <sub>5</sub>	0.70 <sub>5</sub>	0.71 <sub>6</sub>	0.68 <sub>4</sub>	0.67 <sub>6</sub>	—

\* P. W. Bridgman.

On the basis of our assumptions about the equation of state of caesium we estimate that the pressure required to keep the density of the metal constant increases by about 2.5 atm/degC around room temperature. So we would expect the pressure of the minimum to change by a similar amount. Between 0 and 100 °C Bridgman (1925) has measured this pressure directly. If we take into account only his reproducible measurements on bare wires and ignore his data on capillary specimens or the values which were quite different with increasing and

decreasing pressure we find that our estimate is consistent with Bridgman's findings. The change in pressure at the minimum is not very big and it is difficult to measure accurately but from the general agreement between our findings and Bridgman's it seems probable that the minimum occurs at the same *density* at all temperatures from about 40 °K up to near the melting point.

TABLE 10. THE PRESSURE DEPENDENCE OF THE ELECTRICAL RESISTANCE OF CAESIUM AT VARIOUS TEMPERATURES

The listed values give  $R_i(p)/R_i(p=0)$ .

pressure (atm)	3.2 °K {Cs 1, 3}	4.2 °K {Cs 1}	4.2 °K {Cs 3}	14.0 °K {Cs 1}	14.0 °K {Cs 3}	16.0 °K {Cs 1}	16.0 °K {Cs 3}
0	1.00	1.00	1.00	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>
500	0.88	0.94	0.91	0.93 <sub>2</sub>	0.94 <sub>2</sub>	0.93 <sub>4</sub>	0.94 <sub>2</sub>
1000	0.84	0.88	0.85	0.87 <sub>1</sub>	0.88 <sub>5</sub>	0.87 <sub>9</sub>	0.88 <sub>9</sub>
1500	0.75	0.82	0.79	0.82 <sub>7</sub>	0.83 <sub>6</sub>	0.83 <sub>7</sub>	0.84 <sub>4</sub>
2000	0.72	0.75	0.75	0.79 <sub>2</sub>	0.79 <sub>7</sub>	0.80 <sub>0</sub>	0.80 <sub>6</sub>
	18.0 °K {Cs 1}	18.0 °K {Cs 3}	20.4 °K {Cs 1}	20.6 °K {Cs 3}	29.7 °K {Cs 1}	48.0 °K {Cs 1}	65.5 °K {Cs 1}
0	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.000 <sub>0</sub>	1.000 <sub>0</sub>	1.000 <sub>0</sub>
500	0.94 <sub>2</sub>	0.94 <sub>1</sub>	0.94 <sub>0</sub>	0.95 <sub>1</sub>	0.932 <sub>8</sub>	0.944 <sub>5</sub>	0.945 <sub>4</sub>
1000	0.89 <sub>0</sub>	0.89 <sub>0</sub>	0.88 <sub>7</sub>	0.88 <sub>6</sub>	0.879 <sub>8</sub>	0.897 <sub>9</sub>	0.921 <sub>9</sub>
1500	0.84 <sub>3</sub>	0.84 <sub>8</sub>	0.84 <sub>3</sub>	0.84 <sub>6</sub>	0.844 <sub>4</sub>	0.861 <sub>5</sub>	0.863 <sub>1</sub>
2000	0.80 <sub>4</sub>	0.81 <sub>0</sub>	0.80 <sub>9</sub>	0.81 <sub>0</sub>	0.815 <sub>3</sub>	0.832 <sub>4</sub>	0.833 <sub>8</sub>
2500	—	—	—	—	0.789 <sub>8</sub>	0.808 <sub>8</sub>	0.810 <sub>9</sub>
	78.3 °K {Cs 1}	79.3 °K {Cs 3}	89.8 °K {Cs 1}	159.3 °K {Cs 1}	195.2 °K {Cs 1}	259.4 °K {Cs 1}	273.2 °K {*}
0	1.000 <sub>0</sub>	1.000 <sub>0</sub>	1.000 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>	1.00 <sub>0</sub>
500	0.944 <sub>3</sub>	0.944 <sub>1</sub>	0.943 <sub>6</sub>	0.94 <sub>3</sub>	0.93 <sub>4</sub>	0.91 <sub>7</sub>	0.92 <sub>7</sub>
1000	0.897 <sub>7</sub>	0.897 <sub>8</sub>	0.898 <sub>5</sub>	0.89 <sub>4</sub>	0.88 <sub>2</sub>	0.85 <sub>2</sub>	0.88 <sub>2</sub>
1500	0.861 <sub>7</sub>	0.860 <sub>9</sub>	0.862 <sub>4</sub>	0.85 <sub>8</sub>	0.84 <sub>4</sub>	0.79 <sub>9</sub>	0.81 <sub>5</sub>
2000	0.832 <sub>7</sub>	0.831 <sub>8</sub>	0.833 <sub>4</sub>	0.82 <sub>7</sub>	0.81 <sub>5</sub>	0.76 <sub>4</sub>	0.77 <sub>1</sub>
2500	0.808 <sub>3</sub>	0.809 <sub>5</sub>	0.810 <sub>5</sub>	0.80 <sub>5</sub>	0.79 <sub>5</sub>	0.73 <sub>6</sub>	0.75 <sub>1</sub>

\* P. W. Bridgman.

#### 4. DISCUSSION

##### 4.1. Theoretical calculations of $\rho_i$

There are three main elements to be considered in the calculation of  $\rho_i$ : (1) the perturbing potential; (2) the dispersion relations of the lattice waves (more briefly the phonon spectrum); and (3) the Fermi surface. Let us consider each of these briefly.

##### 4.1.1. The perturbing potential

Following the original work of Bloch (1928, 1930), the most important calculation from first principles of the ideal resistivity of the monovalent metals was that due to Bardeen (1937). In this the perturbing potential which scatters the conduction electrons was calculated by a self-consistent method. This potential is



considered as the sum of two terms, (1) the change in the potential due to the displacement of the ions, and (2) the change in the potential of the valence electrons which move so as to screen the ionic potential produced by (1). It turns out that, at least to the extent that electrons can be treated as effectively free, the effect of the screening of the conduction electrons can be written as a factor which simply

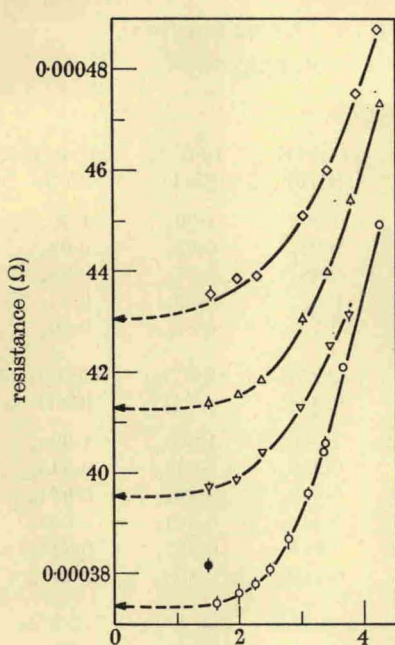


FIGURE 4

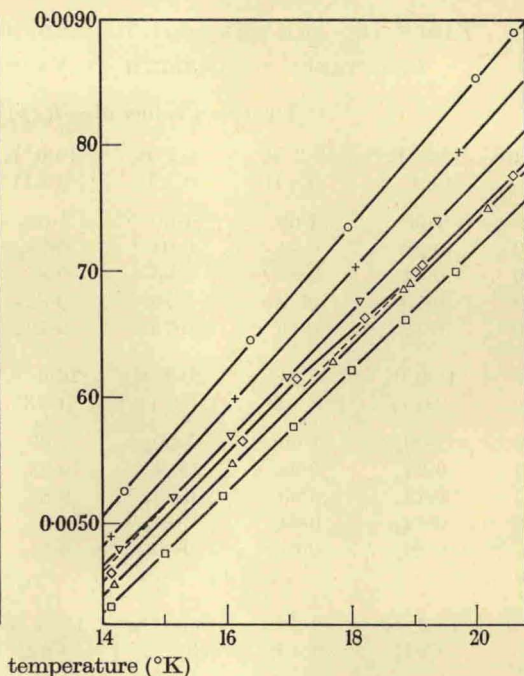


FIGURE 5

FIGURE 4. Resistance of rubidium specimen 4 at different pressures as a function of temperature below 4°K:  $\circ$ ,  $p = 0$  (initially);  $\bullet$ ,  $p = 0$  (finally);  $\nabla$ ,  $p = 640$  atm;  $\triangle$ ,  $p = 1360$  atm;  $\diamond$ ,  $p = 2080$  atm. The pressures were applied by means of solid helium.

FIGURE 5. Resistance of caesium specimen 1 at different pressures as a function of temperature in the hydrogen range of temperatures. The approximate pressures are as follows:  $\square$ , 2140 atm;  $\triangle$ , 1670 atm;  $\diamond$ , 1610 to 1240 atm;  $\nabla$ , 1120 to 990 atm;  $\times$ , 650 atm;  $\circ$ , 150 atm. The top two curves correspond to the fluid phase of helium and the bottom two to the solid phase only. In the middle two curves a change of phase takes place and this causes the slope of the curves to change.

multiplies the matrix elements associated with the unscreened ionic potential. In his calculations Bardeen used a Debye approximation for the phonon spectrum since at the time no other information was readily available; in addition, he considered only spherical Fermi surfaces. Nevertheless, his approach has remained the basis of nearly all the subsequent developments.

#### 4.1.2. *The phonon spectrum*

The recurring theme of much of the work since Bardeen has been the overriding importance of umklapp processes in the alkali metals (Ziman 1954; Bailyn & Brooks 1956; Bailyn 1960). An umklapp process tends to be more important than



a normal process for electrical resistivity because it can produce scattering through larger angles. This is particularly important at low temperatures where normal processes can cause only small angle scattering.

It turns out that the elastic properties of the alkali metals are very strongly anisotropic (this point has been particularly stressed by Bailyn 1960) and this can have the effect of enhancing umklapp scattering, particularly at low temperatures. Indeed, it is mainly for this reason that umklapp processes are found to predominate in the resistivity of the alkali metals right down to the lowest temperatures of practical interest (Bailyn 1960).

In table 11 we list values of the elastic anisotropy parameter  $C_{44}/2(C_{11}-C_{12})$  for those alkali metals for which elastic measurements have been made. (We are referring now only to the b.c.c. phases.) For an isotropic material the parameter would be 1. The square root of this parameter measures the ratio of the velocities of shear waves in the (100) and (110) directions. From the values in the table it is seen that in some of the metals these velocities can differ by a factor of as much as 3.

TABLE 11. ELASTIC ANISOTROPY PARAMETERS IN THE ALKALI METALS

metal	$2C_{44}/(C_{11}-C_{12})$		
	Bailyn's* values	experimentally observed	observer
lithium	9.60	9.35	Nash & Smith (1959)
sodium	11.06	7.14	Daniels (1960)
potassium	10.27	6.71	Smith & Smith (1964)
rubidium	10.15	—	—
caesium	9.77	—	—

\* Bailyn (1960).

Quite recently, Woods, Brockhouse, March, Stewart & Bowers (1962) have determined directly the phonon dispersion relations in sodium by means of thermal neutron diffraction and this has stimulated a number of theoretical studies of the resistivity of the lighter alkali metals, in particular sodium. These calculations produce fairly good agreement with experiment and we shall refer to them later.

#### 4.1.3. *The Fermi surface*

Table 12 summarizes the experimental information about the Fermi surfaces of the alkali metals; it is seen that in sodium and potassium the surfaces are effectively spherical, in rubidium nearly so, while in lithium and caesium the surfaces are appreciably different from spheres. Ham (1962) has made theoretical calculations of the properties and shapes of the Fermi surfaces of the alkali metals. His calculations overestimate the distortions of the surfaces but they give the right qualitative sequence of distortion through the series; in addition, Ham has calculated how the properties of the Fermi surfaces should change with volume. Although again these calculations may be quantitatively in error, it seems probable that they will give the correct qualitative picture.

Attempts to infer the shapes of the Fermi surfaces from various physical properties of the metals have tended to ignore elastic anisotropy and, perhaps for



this reason, have also overestimated the distortion of the Fermi surfaces (Cohen & Heine 1958; Ziman 1959; Dugdale 1961; Collins & Ziman 1961). The important point is that elastic anisotropy and distortion of the Fermi surface can produce similar effects on transport properties and without further knowledge their effects are hard to distinguish.

Bearing in mind these ideas, let us now look at the experimental results. To help in understanding the heavier alkali metals we shall find it useful to make some comparisons between all the alkali metals, particularly since we now have comparable experimental data on the resistivity of all of them.

TABLE 12. ANISOTROPY OF THE FERMI SURFACE IN THE ALKALI METALS

metal	maximum radial distortion from a sphere	observer
lithium	about 5%	Stewart <i>et al.</i> (1964)
sodium	probably $< 5 \times 10^{-4}$	Shoenberg & Stiles (1964)
potassium	$15 \times 10^{-4}$	
rubidium	1%	
caesium	about 5%	Okumura & Templeton (1965)

#### 4.2. *The magnitude of the resistivity*

Bailyn has calculated the magnitude of the resistivities of all the alkali metals. In table 13 we make a comparison of these calculated values with the most recent experimental values. It is seen that apart from lithium the agreement is everywhere within a factor of 2 and for sodium, potassium and rubidium is much closer still. Bailyn assumed in his calculations that the Fermi surfaces were spherical, although he recognized that for lithium this was a poor approximation. More recent calculations of the resistivity of lithium by Hasegawa (1964), which take account of the distortion of the Fermi surface, have improved the agreement for this metal. The comparatively small distortions of the Fermi surfaces of rubidium and caesium, which we now know to exist, might be enough to account for the remaining discrepancies between the theoretical and experimental values of  $\rho_i$  in these metals.

TABLE 13. RESISTIVITIES ( $\mu\Omega\text{cm}$ )

	lithium	sodium	potassium	rubidium	caesium
temperature ( $^{\circ}\text{K}$ )	297	125	70	211	158
$\rho$ (theor.)*	2.0	1.4	1.4	5.6	5.0
$\rho$ (exp.) ( $p = 0$ )	9.4	1.5 <sub>6</sub>	1.1 <sub>7</sub>	8.1	9.4
$\rho$ (exp.) ( $V = V_0$ )†	9.5	1.4 <sub>9</sub>	1.1 <sub>3</sub>	6.9	8.5

\* Bailyn (1960).

†  $V_0$  is the molar volume of the solid at 0  $^{\circ}\text{K}$  under zero pressure.

#### 4.3. *How the resistivity depends on temperature*

Figures 1 and 2 show that if we plot the resistivity as a function of temperature at constant density, the resistivity at high temperatures for both rubidium and caesium is linear and very closely proportional to the absolute temperature. This is true both at the density corresponding to zero pressure at 0  $^{\circ}\text{K}$  and at the two



higher densities for each metal. There is thus *no* anomalous behaviour in the high temperature resistivity of rubidium as described by MacDonald (1952). The effects that he found can almost certainly be ascribed to capillary constraints in his specimens.

Bailyn (1960) has calculated the temperature dependence of the resistivity of all the alkali metals. He found reasonable agreement with experiment for caesium and poor agreement for the others. (For lithium the agreement was good but, as already mentioned, the model used was not strictly appropriate to this metal.) Bailyn was inclined to attribute this poor agreement to the phonon spectra he used. The values he adopted for the anisotropy parameters are shown in table 11, together with the experimental values where these are known. It seems that his values of the anisotropy for sodium and potassium were indeed too large and this may account for much of the discrepancy. The more recent calculations of Bross & Holz (1963) and of Hasegawa (1964) used the neutron data on sodium and the specific heats as a check on their calculated dispersion relations. They then found reasonably good agreement with experiment for the temperature dependence of the resistivity of sodium, potassium and lithium. (For lithium the fact that the Fermi surface is not spherical had to be taken into account.)

Working more directly from the neutron data, Darby & March (1964) also found reasonable agreement for sodium. Still more recently Greene & Kohn (1965) have calculated the temperature dependence of the resistivity of sodium using the neutron data directly to give information about the motion of the ions. They have made what are probably the most refined calculations so far and find some disagreement with experiment. They discuss whether the discrepancy could be due to non-equilibrium of the phonons, although they think this unlikely. By comparing their results with those of Darby & March they conclude that anharmonic effects are important, in particular the change in elastic constants with temperature, and when they take this into account they find agreement with experiment within an accuracy of about  $\pm 20\%$ .

It seems therefore that although the agreement for sodium is not as complete as might have been expected these calculations are generally speaking successful. We may therefore expect that when we know the phonon dispersion curves for rubidium and caesium it will then be possible to calculate successfully the temperature dependence of their resistivities.

#### 4.4. *How the resistivity depends on pressure*

At high temperatures ( $T > \theta_0$ ) we may think of the resistivity as proportional to the square of the amplitude of the lattice vibrations and write for the ideal resistivity  $\rho_i$  at temperature  $T$

$$\rho_i = KT/M\theta^2, \quad (1)$$

where  $M$  is the mass of the ions,  $\theta$  is the characteristic temperature of the lattice and  $K$  represents all the factors associated with the interaction of the electrons with the lattice waves. We may then write

$$\left(\frac{\partial \ln \rho_i}{\partial \ln V}\right)_T = 2\gamma_G + \frac{d \ln K}{d \ln V}.$$



In this we have assumed that the changes in the amplitude of the lattice vibrations can be taken account of through the Grüneisen parameter  $\gamma_G$ . In table 14 we have listed the values of  $d \ln K/d \ln V$  calculated in this way.  $\gamma_G$  has been evaluated from the thermal expansion, compressibility and specific heat of the solid. For rubidium and caesium some of these data are rather uncertain.

At low temperatures the ideal resistivity varies more strongly with temperature than at high temperatures (approximately as  $T^5$  at the lowest temperatures). This means in effect that  $\rho_i$  depends more strongly on the amplitude of the lattice vibrations at low temperatures than at high. We may therefore expect that this will also show up in the pressure dependence of  $\rho_i$  (since pressure also changes the amplitude of the lattice vibrations) and that the pressure coefficient of  $\rho_i$  will

TABLE 14

metal	$\frac{\partial \ln \rho_i}{\partial p}$	$-\frac{1}{V} \left( \frac{\partial V}{\partial p} \right)_T$	$\frac{\partial \ln \rho_i}{\partial \ln V}$	$\frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P$	$\gamma_G^*$	$\frac{d \ln K}{d \ln V}$	$\frac{d \ln K \dagger}{d \ln V}$
	$0^\circ\text{C}$ ( $10^{-5} \text{ atm}^{-1}$ )	$0^\circ\text{C}$ ( $10^{-5} \text{ atm}^{-1}$ )	$0^\circ\text{C}$	$0^\circ\text{C}$ ( $10^{-5} \text{ per } ^\circ\text{C}$ )		(expt.)	(theory)
lithium							
$p = 0$	+0.43	0.87 <sub>5</sub>	-0.49	14	0.9 <sub>0</sub>	{-2.3}	-3.7
$V = V_0$	—	—	—	—			
sodium							
$p = 0$	-7.3	1.58	4.6	21	1.3	{2.0}	1.8
$V = V_0$	-6.2	1.40	4.4 <sub>6</sub>	—			
potassium							
$p = 0$	-19.1	3.43	5.6	25	1.3	{3.0}	1.9
$V = V_0$	-15.8	2.82	5.6	—			
rubidium							
$p = 0$	-21	5.0	4.3	24	1.0	{2.3}	—
$V = V_0$	-17	3.6	4.7	—			
caesium							
$p = 0$	-22	7.1	3.1	29	1.0	{1.1}	—
$V = V_0$	-14	4.4	3.2	—			

\* The data are not available to calculate  $\gamma_G$  at  $V = V_0$  so we have assumed that the values at  $p = 0$  and at  $V = V_0$  are the same.

† Hasegawa (1964).

become more negative at low temperatures. This effect can be seen in figure 6 which shows how the pressure coefficient of ideal resistivity (at constant density) varies with temperature for all the alkali metals. (The data for lithium, sodium and potassium are taken from I.) As already stressed, the very low temperature values tend to be uncertain because of departures from Matthiessen's rule. Nevertheless, the tendency to become more negative at low temperatures in rubidium and caesium (as in the other metals) is clearly evident and qualitatively reliable. At higher temperatures the coefficient tends to be constant; the changes near room temperature may be real or they may be only a consequence of using slightly wrong data for the equation of state.

To show how the resistivity of the alkali metals varies with pressure over a wider pressure range, we show in figure 7 the relative resistivity  $\rho/\rho_0$  as a

function of relative volume  $V/V_0$  for all the alkali metals at  $0^\circ\text{C}$ . The data are taken from Bridgman (1925).\*  $\rho_0$  is the resistivity at the volume  $V_0$  at which  $p = 0$  and  $\rho$  is the resistivity corresponding to the volume  $V$ . Let us now consider how far theory can account for the pressure dependence of the ideal resistivity.

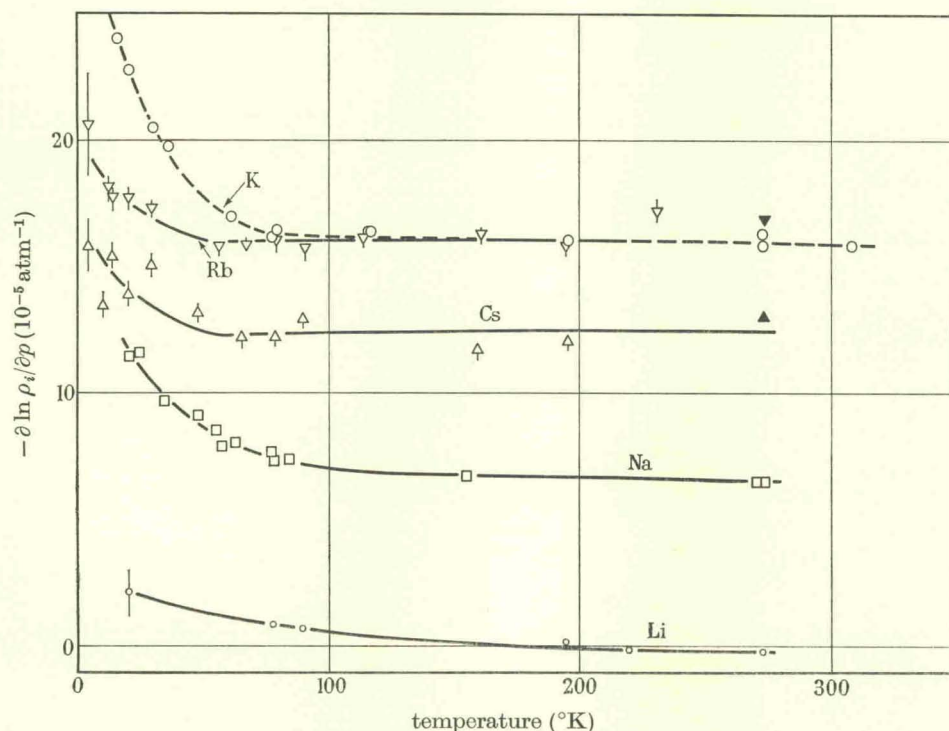


FIGURE 6. The pressure coefficient of the ideal resistivity of the alkali metals as a function of temperature. The data for lithium, sodium and potassium are taken from I; the solid points are from Bridgman (1925).

#### 4.4.1. Rubidium

If we look at table 14 we see that  $d \ln K / d \ln V$  for rubidium is quite similar in magnitude to that for sodium or potassium; indeed the general dependence of resistivity on volume (figure 7) is rather similar for sodium, potassium and rubidium over the first 25% change in volume. To understand the behaviour of rubidium, therefore, let us look briefly at how Hasegawa (1964) has interpreted the pressure dependence of  $\rho_i$  in sodium and potassium. Hasegawa assumes that the Fermi surfaces of these metals are spherical (see table 12) and that they remain

\* Bridgman (1952) has made measurements on the resistivity of the alkali metals up to considerably higher pressures (nominally up to 100 kbar). More recently Stager & Drickamer (1963) have made measurements up to 500 kbar on the four lighter alkali metals and have found many strange and complicated effects. Here we have concentrated on Bridgman's results at lower pressures since they are the only ones which can be compared directly with the present work. Moreover, they are in the region where we have the best hope of a quantitative comparison with theory.



so under modest pressures (cf. Ham 1962). In addition he assumes that the anisotropy of the phonon spectrum does not change significantly with volume; as far as one can tell from the elastic constants this is true (see Daniels (1960) for sodium and Smith & Smith (1964) for potassium).

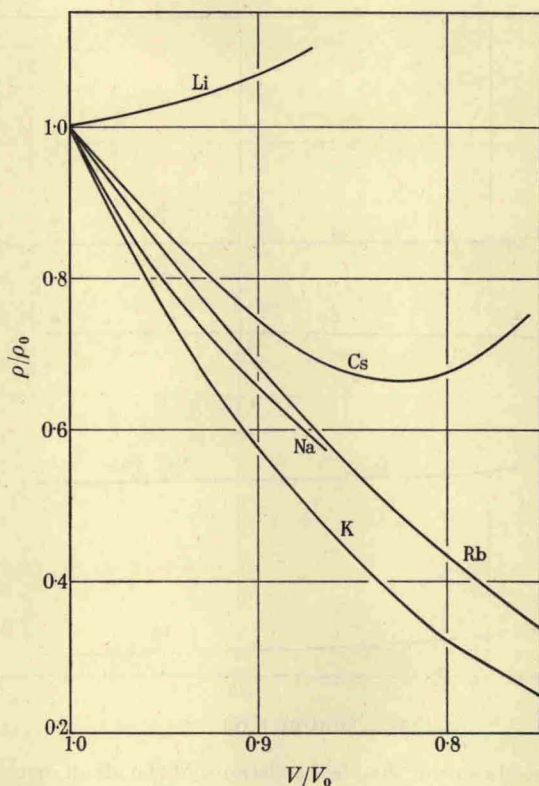


FIGURE 7. Relative resistivity plotted against relative volume for the alkali metals at 0°C (from the data of Bridgman (1925)).

Since the anisotropy of the phonon spectrum and that of the Fermi surface do not change, and since the relative size of the Fermi surface and Brillouin zone does not alter under compression, the geometry in  $k$  space of all the phonon electron scattering processes is unchanged by the volume change. This means that the proportions of normal and umklapp processes are likewise unchanged.

Hasegawa finds that the major part of the change with volume of the parameter  $K$  (equation (1)) is due to the change in the matrix elements themselves. In essence, the increase in the kinetic energy of electrons on compression diminishes the effect of the scattering potential. Hasegawa finds quite good numerical agreement with experiment; see table 14.

We know that although rubidium has a slightly distorted Fermi surface it is nevertheless nearly spherical. In the absence of other information, therefore, it seems probable that the sort of considerations already applied to sodium and potassium might be sufficient to explain the pressure dependence of  $\rho_i$  in rubidium.

## 4.4.2. Caesium

In caesium the Fermi surface is appreciably distorted (see table 12). According to Ham's calculations the Fermi surface of caesium distorts under pressure, thereby causing those parts of the surface near the zone boundaries to get nearer. This could then account for the minimum in the resistivity-pressure curve illustrated in figure 7. The general idea is that the distortion of the Fermi surface enhances the probability of umklapp processes; presumably this effect eventually overrides that due to the diminishing amplitude of the lattice vibrations and other effects which tend to reduce the resistivity. (Hasegawa has shown that this kind of explanation can account for the anomalous pressure dependence of  $\rho_i$  in lithium.) However, as we emphasized earlier, there could be changes in the anisotropy of the phonon spectrum which would have a similar effect. To find out which effect is more important we need further experiments to find out both how the Fermi surface and how the elastic constants change with pressure.

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