Resistivity of Pure Metals at Low Temperatures I. The Alkali Metals
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ivity. The resulting diffusive system has been worked out in detail for flow over a short grass surface. It is observed that the application of this system leads to good agreement of theory and experiment with regard to the vapour distribution at all points over a finite short grass surface, bounded by a parabolic curve and contaminated uniformly with liquid. It appears probable that this system of equations may be applied with equal success to surfaces of other shapes, such as the finite rectangle problem discussed by the author (Davies 1950, I), as long as attention is confined to the region over the surface. The extension of the work to the region down-wind of the surface is being investigated.

I am indebted to the Chief Scientist, Ministry of Supply, for permission to publish the experimental figures of tables 1 and 2 which appeared in a Ministry of Supply Report.

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Resistivity of pure metals at low temperatures
I. The alkali metals

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A technique is described for measuring resistance in the temperature interval between 1·5 and 20° K continuously. The resistivity of the alkali metals has been determined in this temperature region, and the results have been discussed in comparison with theory. The resistivity of sodium has been found to agree closely with theory, while in the case of the other metals the hypothesis of quasi-free conduction electrons does not seem to be fully justified. Certain observations suggest that small impurities may give rise to anomalies other than the phenomenon of 'residual' resistance.

1. INTRODUCTION

The modern analysis of the behaviour of the electrical resistance rests essentially on three separate fundamental features:

(1) There is first the nature of the ionic lattice-electron interaction; that is to say, the characteristics of the electric field due to the crystal and the degree of binding of the valence electrons. The information required is summarized more or less

adequately by a specification of the Brillouin zone structure together with a knowledge of the boundaries of the Fermi energy surface, in so far as it may be known. This essentially classifies the intrinsic conductivity of the metal irrespective of thermal vibration or lattice faults.

(2) Secondly, the electron scattering due to the thermal vibration of the lattice, which clearly must be closely linked with the entropy of the latter. The quantitative relation of the scattering to be expected is given by the well-known Grüneisen-Bloch formula for the resistivity of an ideal metal, namely,

$$\rho \sim \left(\frac{T}{\Theta}\right)^5 \int_0^{\Theta/T} \frac{x^5\,dx}{(\mathrm{e}^x - 1)(1 - \mathrm{e}^{-x})}, \tag{1}$$

where T = absolute temperature and Θ = Debye temperature of the lattice. Certain fundamental assumptions underlie this formula as, for instance, that of a quasi-free electron gas of isotropic characteristics. In so far as these are met, equation (1) should then give universally the temperature dependent component of the electrical resistance.

(3) Finally, scatter due to physical or chemical irregularities of the lattice have to be taken into account. Their effect is expressed through the empirical rule of Matthiessen as an additional resistance which is independent of temperature. This 'residual' resistance can be interpreted theoretically if one assumes essentially that the collisions with the thermal Debye waves and with the fault centres are independent of one another.

For very low temperatures ($T \ll \Theta$) the integral in (1) yields a constant value, and hence

$$\rho \sim T^5, \tag{2}$$

as first derived by Bloch (1929). For high temperatures, on the other hand, one sees readily that, since the integral approximates to $\frac{1}{4}(\Theta/T)^4$,

$$\rho \sim T. \tag{3}$$

In general, then, progressive deviation from (3) with falling temperature indicates the onset of quantization phenomena. It is not generally appreciated, however, that in this field significant deviations from the classical conditions, yielding (3), can only be expected to arise for temperatures *well below* Θ. This becomes clear when one compares the variation of classical and quantal entropy of a regular crystal (see figure 1). In order to study significantly the temperature variation of resistivity in comparison with (1) it is thus necessary to work at temperatures below $\sim 0{\cdot}4\Theta$. For most metals, this requires observation below the temperature of liquid air, and for many below the temperature of liquid hydrogen. On the other hand, the dominance of residual resistance at very low temperatures greatly decreases the value of measurements at liquid helium temperatures in this respect.

The great number of existing observations (cf. Meissner & Voigt 1930) carried out at isolated fixed temperatures (liquid air, liquid hydrogen, liquid helium) is therefore quite inadequate for the comparison with theory envisaged above. Only one series of continuous measurements (de Haas & van den Berg 1936) on a number of metals exists so far. It was therefore decided to begin a systematic determination of the resistance of all metals in dependence on temperature, particularly in the region between 4 and 20° K. A short note on some of the results has been published recently (MacDonald & Mendelssohn 1948).

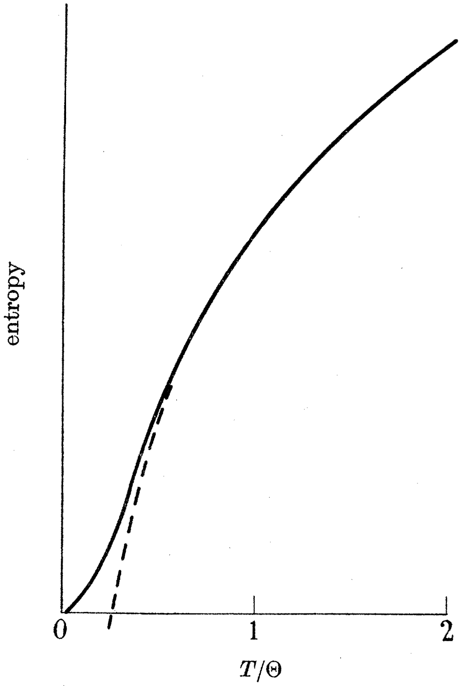

FIGURE 1. Entropy of crystal lattice: ——, Debye theory; — — —, classical theory.

2. EXPERIMENTAL PROCEDURE

It is well known that when investigating physical properties in relation to temperature an awkward gap occurs between 4 and 14° K. Above the latter temperature liquid hydrogen boiling under reduced pressure provides a convenient temperature bath; below the former, liquid helium is available. Although solid hydrogen may be pumped down to 10° K or even somewhat lower, considerable difficulties arise owing to its poor thermal conductivity. The Simon desorption method, using helium adsorbed on charcoal, may be used to cover this region, and the Leiden workers have used this method in determining some electrical conductivities over the range 1 to 20° K.

We have, however, been able to use successfully a Simon expansion helium liquefier to cover this whole range continuously with most satisfactory consistency and accuracy, and, in fact, also in a number of cases to cover the range from as high as 90° K (liquid oxygen) with fair accuracy.

In this particular liquefier, devised by Daunt & Mendelssohn (1938), access is provided to the liquid helium container by a long thick-walled tube extending to the top of the whole apparatus (see figure 2), which is normally sealed with a high-pressure nut during the liquefaction process. For this investigation this tube was used to enable a gas thermometer bulb, adjacent to which the specimen was placed, to be inserted for the period of the experiment. This bulb communicates through a fine capillary with an accurate large-scale vacuum gauge mounted on the top of the apparatus; the whole is filled with very pure helium gas at about 1 atm. at room temperature. Suitable choice of the ratio of bulb volume to that of the gauge (cf. Mendelssohn 1931) enables one to arrange for the scale to be very 'open' over a more or less arbitrary temperature interval. In our case about 30 cm. of scale interval corresponded to the range 4 to 20° K.

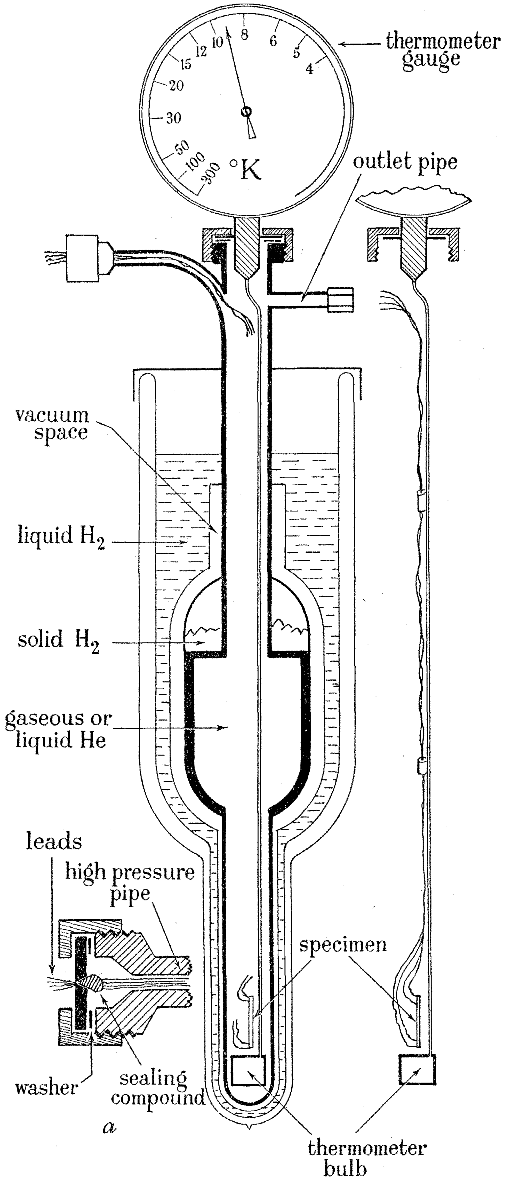

FIGURE 2. Cryostat (not to scale).

Each specimen was provided with separate current and potential leads, and these were brought out through a high-pressure seal. Considerable effort went towards providing an effective simple seal. Fair success was achieved with a seal of the type shown in figure 2*a*, where the insulated leads emerge through a conical aperture terminating in a very small hole in a brass boss and are sealed in with hot sealing-wax. Although Bridgman (1931) advocates such a seal for pressures of 100 or 200 atm. considerable difficulty was met with in trying to make the wax adhere satisfactorily to the metal boss. Hard Bakelite or similar materials for the boss proved unsatisfactory owing to distortion under pressure. Ultimately, the best solution was found in the use of small commercial Kovar glass-to-metal seals soldered to a brass cap. The tubular type of seal was used, since this allowed the potential leads to come straight through without the intervention of a thermo-electric junction with the Kovar metal.

Finally, an outlet equipped with a small high-pressure nut was provided so that after liquefaction of the helium the nut could be removed under atmospheric pressure and connexion made to a vacuum pumping system to reduce the temperature still further.

The essential feature of the method then is that, particularly below 20° K, the highly compressed helium gas in the liquefier, in which the specimen and thermometer capsule are situated, provides a large heat capacity, practically equivalent to a liquid bath. It should be borne in mind that the density of the helium gas before expansion may well exceed that of the final liquid helium. Furthermore, since the gas is enclosed in a vessel of high heat conductivity, excellent thermal equilibrium is to be expected. During the first part of the run, from 20 to $\sim 12°$ K, constant temperatures may readily be achieved by control of the pumping-off rate of the hydrogen condensed inside the expansion liquefier, and during the latter part, ~ 12 to 4° K, by adjustment of the expansion rate of the helium gas. Adjustment could be made by manual control of a needle valve in the expansion line to give a temperature constancy of 0·1° K or better. By suddenly changing the trend of the temperature drift and simultaneously observing the resistance of the specimen it could be established that the latter followed the indications of the thermometer without appreciable delay. Finally, after production of liquid helium, connexion may be made to a constant-pressure pumping device (cf. Mendelssohn 1936) and constant temperatures down to $\sim 1{\cdot}5°$ K attained.

3. ELECTRICAL MEASUREMENTS

A galvanometer amplifier using simple selenium photo-voltaic cells was designed to measure the small potentials developed. Galvanometer amplifiers have been used before in this field (e.g. Milner 1937; Kapitza & Milner 1937), but in these cases the photo-cell amplification has been used solely to improve the sensitivity of null detection in a bridge circuit. Systematic or random drift is generally rather troublesome in such systems, and although a relatively straightforward optical circuit is intrinsically capable of providing an enormous magnification, only a very small fraction can be usefully employed under these circumstances. The incorporation of negative feed-back in such a galvanometer amplifier enables the 'unwanted' amplification to perform valuable service in a number of ways. By returning a large fraction of the output of the photo-cell in opposition to the input voltage rather than 'neglecting' it in a step-down potentiometer one can provide a greatly enhanced stability of the overall system, a considerably reduced response time and a high linearity while still leaving ample net gain for the purpose in hand. Preston (1946) used such a system with the feed-back arranged in parallel with the input terminals, which has the effect of greatly lowering the effective input impedance to the system—a valuable feature when it is desired to record from a low-resistance source such as a thermocouple, essentially a current-generating device. In our case, it was desired to record directly from the potential leads of the specimens in which it is necessary, to avoid the effect of contact resistance, to draw practically *no* current; that is, a device with a very high input impedance is called for. This is achieved by modifying the system (MacDonald 1947; cf. Frankenhaeuser & MacDonald 1949) so that the feed-back is generated in series with the input; this results in an input resistance at d.c. of at least several thousands of ohms which may certainly be neglected in comparison with any contact resistance likely to be encountered in such work.

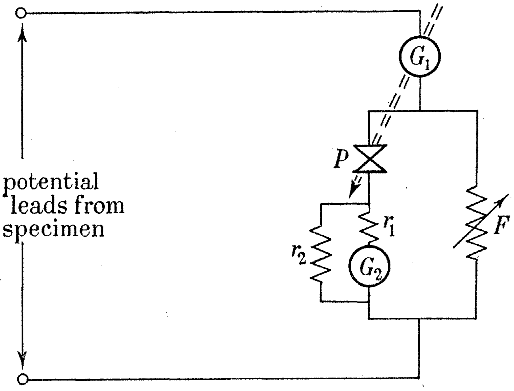

FIGURE 3. Basic circuit of galvanometer amplifier. G_1, amplifying galvanometer; G_2, recording galvanometer; r_1, r_2, local shunt for G_2; P, split photo-cell; F, feed-back control resistance. $<==$, optical beam reflected from G_1 mirror to P.

The circuit diagram of the galvanometer amplifier is shown in figure 3. The galvanometer, G_1, was a Tinsley high-sensitivity galvanometer ($R \approx 30\ \Omega$, ~ 1000 mm./μA), while the recording galvanometer, G_2, was a Cambridge high-sensitivity short-period galvanometer ($R \approx 450\ \Omega$, ~ 1500 mm./μA); a scale length of 1 m. was used with a 3 m. optical throw with an image which could be read to $\sim \frac{1}{2}$ mm. An upper limit of relative accuracy $\sim 1/1$–2000 was thus available. This appears entirely adequate for this type of investigation. Furthermore, when a pure metal specimen at very low temperatures provides a total potential difference of only ~ 5–$10\,\mu$V with a measuring current ~ 100 mA, there is no advantage in seeking for a sensitivity greater than $\sim 10^{-8}$ V. The greatest advantage of a direct-reading system for these high sensitivities lies in the fact that no variable contacts exist in the potential measuring circuits. The only switch that occurs is in the *current* network where thermal and contact e.m.f.'s are of no consequence. In a potentiometer or other nulling circuit such e.m.f.'s are *in principle* compensated for by commuting the circuits. Should the disturbing e.m.f. vary too rapidly commuting must fail to achieve the object. With a direct-reading system, however, the effect of any disturbing e.m.f. is continually visible and may be readily corrected for. The method used by Kapitza & Milner (1937) of overcoming this difficulty in a potentiometer by rapid-action switches was tried but proved unsatisfactory.

The problem of stability as related to the choice of a particular photo-cell lies outside the scope of this paper, and is being discussed elsewhere (MacDonald 1950).

4. PREPARATION OF SPECIMENS

In view of the great chemical activity of the alkali metals, particular care had to be taken in the preparation of the specimens. The four metals (Na, K, Rb, Cs) were prepared in soft glass capillary moulds with platinum electrodes sealed in. The glass apparatus was thoroughly cleaned and washed out with distilled water. It was then pumped under hard vacuum for an hour or two whilst being heated at ~ 150° C. Pure helium to 1 atm. was then admitted; the glass capsule containing the metal was broken and immediately inserted through a cone and socket joint. In the case of rubidium and caesium the capsules were severed under benzene previously dried thoroughly with sodium wire.

The capsule was inserted, and the system was rapidly re-evacuated before the film of benzene had evaporated from the cut surface. Formation of oxide was by this means practically entirely obviated. After melting, the metal was forced into the capillary by admitting pure helium gas at 1 atm. The specimen was then allowed to cool very slowly under this pressure. It was rare that any sample prepared under these circumstances did not then form a continuous specimen, whose resistance agreed satisfactorily with that computed from the geometry of a solid wire. When cool, the specimen tubes were cracked off (under benzene where necessary), sealed over with Plasticine and covered finally with a suitable sealing compound (Durofix). When this has hardened a satisfactorily air-tight seal is formed. To avoid the risk that small cracks, which might develop in the seal on cooling to helium temperatures, would vitiate a future experiment, the specimens were kept between runs in dried petrol ether.

In the case of lithium, this technique cannot be employed because as soon as the lithium melts (m.p. 186° C) and comes into contact with ordinary glass a relatively violent reaction occurs, the glass cracking almost immediately. Lithium glass,* on the other hand, proved to be extremely soft and very difficult to work, and it has not yet been possible to make suitable capillary specimens. The following technique was finally adopted for lithium. The metal was melted in a stainless steel crucible, in a closed atmosphere of pure helium. A glass capillary mould with open end was

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* We are indebted to the British Thomson Houston Co. Ltd for kindly undertaking to make this glass for us.

then quickly inserted into the molten metal after the surface oxide had been skimmed off. A tap connecting the upper end of the capillary with a vacuum bottle was then immediately opened. Lithium then rushed up into the mould and froze almost immediately without having had time to react appreciably. Suitable specimens resulted on about one occasion in three; difficulty was always found, however, with the upper contacts, as the metal normally only covered the lower electrodes, having frozen in the capillary before reaching the upper contacts in sufficient quantity. Fine needles were therefore inserted by hand into the metal to provide the remaining pair of electrodes, and proved quite satisfactory. The specimen was then sealed off as before.

5. Experimental results

(1) *Sodium*

The results on sodium are discussed first, since their interpretation appears simplest from the theoretical standpoint. Metal of high purity was kindly given to us by Messrs British Thomson Houston Co. Ltd. It was supplied after triple distillation in hard vacuum of commercial sodium in sealed boro-silicate glass tubes.

Spectrographic analysis* gave the following result:

(parts in 10^6)	not detected (parts in 10^6)
B: 2000	Cs: <200
	Hg: <200
Si: 2000	Sn: <10
	Pb: <5
K: 500	Rb: <5
	Li: <1

It was later confirmed that the boron and silicon impurities had come from the glass in the preparation of the specimen for analysis, and the intrinsic purity of the metal as used by us may therefore be taken as 99·95 %.

Specimens Na 1 and Na 2 of $\sim 150\,\mu$ diameter exhibited entirely similar behaviour. Some forty observations were made on specimen Na 1 in liquid helium at temperatures from 4·2 to ~1·5° K, and the resistance was found strictly constant within 0·4 % with no systematic variation. Subsequent experiments on Na 1 and Na 2 were made covering the range from ~20 to 4·2° K. The resulting curves were essentially coincident after the residual resistance had been subtracted, and the data for Na 2 appear in figure 4. A logarithmic plot of the data is given in figure 5. If we assume that the ideal resistance is representable by an expression $R \sim T^n$, then the slope of the logarithmic plot gives the index n.

The value $n \approx 4{\cdot}85$ is found for the specimen Na 2. This index agrees very closely with the theoretical value 4·89 expected for the temperature range 8–20° K as computed from equation (1). The value of exactly 5 for the index (cf. equation (2)) will not of course be reached except for vanishingly low temperatures, and it is in fact impossible to deduce reliable values for the ideal resistance of sodium below

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* This analysis as well as that of the caesium metal was kindly furnished by A.E.R.E. Harwell.

about 8° K because of the extreme steepness of the curve. The ratio of the resistance at 4·2° K to that at 0° C or at room temperature is frequently quoted as a rough measure of the purity (chemical and physical) of the material and for Na 2 $R_{4\cdot2^\circ\mathrm{K}}/R_{290^\circ\mathrm{K}} \approx 7 \times 10^{-4}$. It is immediately obvious that this ratio may be used validly for comparison of the purity of various specimens of the *same* metal, since the resistance at 4° K is generally dominantly 'residual' resistance. More strictly, of course, one should use the value of resistance as $T \to 0^\circ$ K. On the other hand, the value at 0° C acts effectively as a normalizing factor to remove the necessity of including the geometry of the particular specimen. This again is valid, since for all reasonably pure metals the scattering at such a high temperature is effectively purely thermal in origin and thus independent of purity.

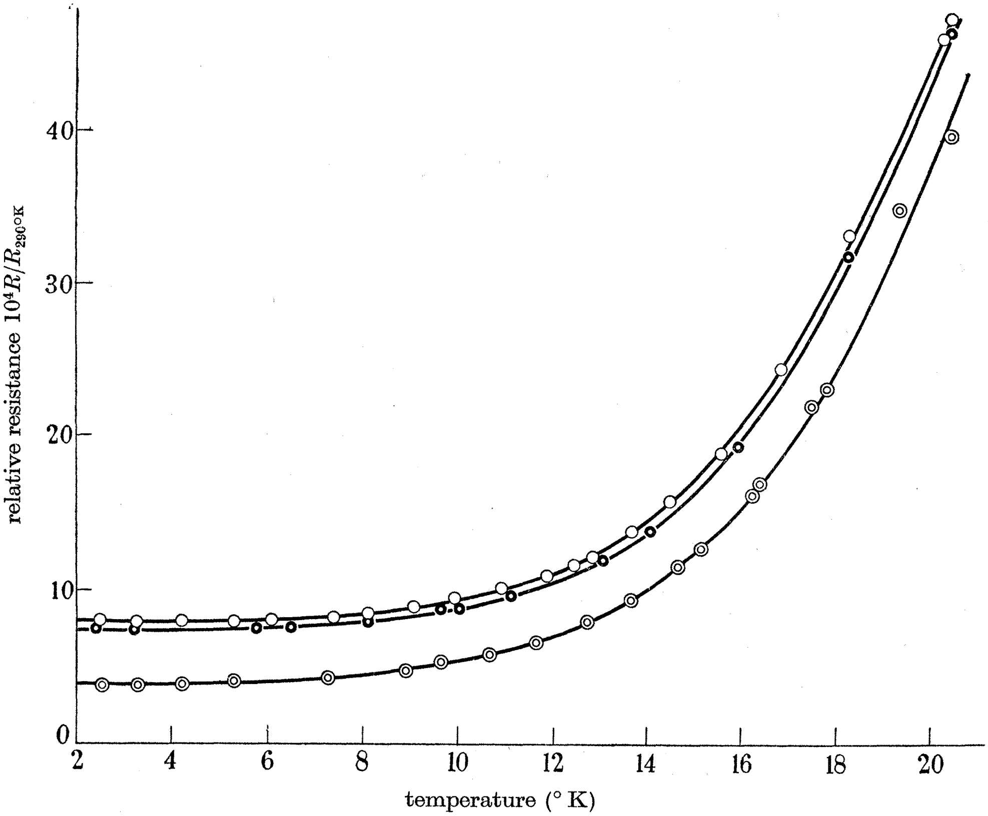

FIGURE 4. Resistance of sodium below 20° K. Specimens: o, Na 2; ◎, Na 3; ○, Na 4.

The matter is less obvious when one tries to compare different metals. One may, on the one hand, turn to the theoretical conductivity expressions and try thus to determine the significance of the ratio for different metals. Unfortunately, the expressions then involve such factors as the effective number of free electrons per atom which are by no means certain *a priori* theoretically. One therefore approaches the problem more directly. At 0° K the mean free path is given by

$$l_{0^\circ\mathrm{K}} = \frac{1}{n_i A_i} = \frac{\Omega_0}{x_i A_i},$$

where n_i = number of impurity atoms/cm.^{3}, x_i = number of impurity atoms per cent of parent metal, Ω_0 = atomic volume of parent metal, A_i = scattering cross-section of impurity (and where, if more than one kind of impurity is present, x_iA_i is to be replaced by Σx_iA_i). Therefore

$$x_iA_i = [r]\,\frac{\Omega_0}{l_{0^\circ\,\mathrm{C}}},$$

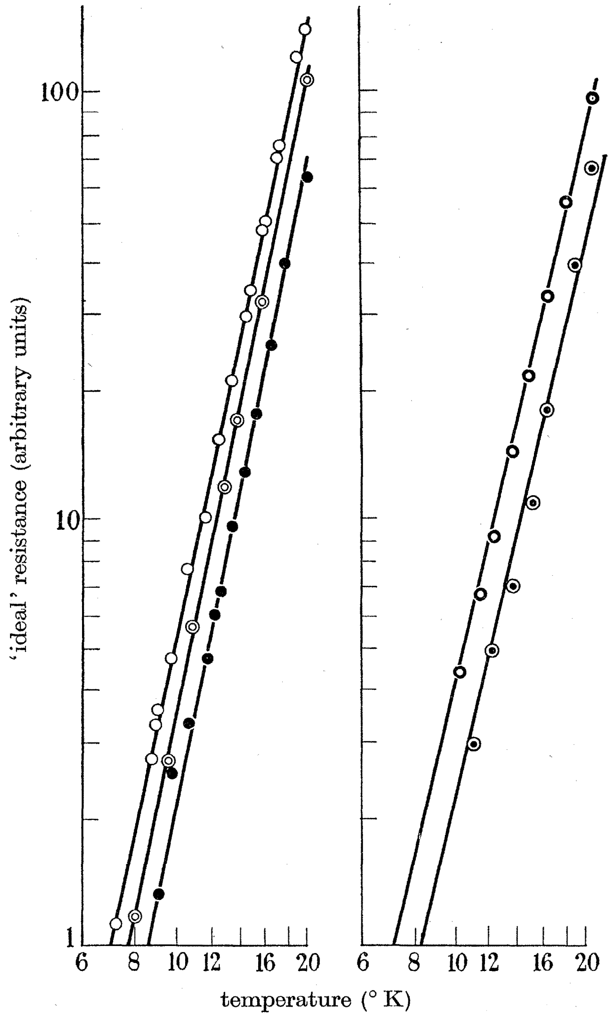

FIGURE 5. Logarithmic plots of the results for sodium and lithium. ◎, Na2; ○, Na3; ●, Na4; o, Li1; ⊙, Li3.

where $[r]$ is the ratio of resistance $R_{0^\circ\,\mathrm{K}}/R_{0^\circ\,\mathrm{C}}$. Thus it is clear that the ratio $\Omega_0/l_{0^\circ\,\mathrm{C}}$ is to be regarded as characteristic of each metal in determining its effective impurity content x_iA_i. We will then accept the experimental values of $l_{0^\circ\,\mathrm{C}}$ (cf. Mott & Jones 1936, p. 268) and can thus calculate the appropriate factor for each metal. For the alkali metals in particular we find the following values for the parameter $\Omega_0/l_{0^\circ\,\mathrm{C}}$, normalized to unity for sodium:

metal	Li	Na	K	Rb	Cs
$\Omega_0/l_{0^\circ\,\mathrm{C}}$	1·6	1	1·74	3·6	6·2

TABLE 1. SODIUM: $\Theta = 202°$ K

		$r_{\text{obs.}}$		
T (° K)	$r_{\text{calc.}}$	(1)	(2)	(3)
273·2	1·0000	1·0000	1·0000	1·0000
170·87	0·5672	—	0·5672	—
108·72	0·3135	—	0·3168	—
90·0	0·2600	—	—	0·2420
87·8	0·2279	0·2279	—	—
77·6	0·1860	0·1849	—	—
56·77	0·1022	—	0·1055	—
20·4	0·00327	0·0034	—	0·00326
15·95	0·00100	—	—	0·00098
14·1	0·00055	—	—	0·00051
13·1	$0{\cdot}00038_4$	—	—	$0{\cdot}00036_5$
11·05	$0{\cdot}00015_4$	—	—	$0{\cdot}00017_3$
9·65	$0{\cdot}00009_3$	—	—	$0{\cdot}00010_2$
8·1	0·00004	—	—	0·00005
4·2	0·00000	—	—	0·00000

Key: (1) Meissner & Voigt (1930); (2) Woltjer & Kamerlingh Onnes (1924); (3) present work.

TABLE 2. LITHIUM: $\Theta = 363°$ K

		$r_{\text{obs.}}$		
T (° K)	$r_{\text{calc.}}$	(1)	(2)	(3)
374·5	1·433	1·443	—	—
329·7	1·243	1·247	—	—
273	1·000	1·0000	1·0000	1·0000
90·9	0·1692	—	0·1621	—
90	0·166	—	—	0·171
86·3	0·1492	—	0·1464	—
80·1	0·1236	—	0·1252	—
77·7	0·1139	—	0·1169	—
20·4	0·0004	—	0·0013	$0{\cdot}0013_3$
17·8	$0{\cdot}0002_2$	—	—	$0{\cdot}0007_6$
16·05	0·00015	—	—	$0{\cdot}0004_5$
14·8	0·00011	—	—	0·00029
13·55	0·00008	—	—	$0{\cdot}0002_1$
12·3	0·00004	—	—	$0{\cdot}0001_4$
11·4	$0{\cdot}00002_4$	—	—	0·00009

Key: (1) Meissner (1920); (2) Meissner & Voigt (1930); (3) present work.

TABLE 3. LITHIUM: $\Theta = 268°$ K

		$r_{\text{obs.}}$	
T (° K)	$r_{\text{calc.}}$	(2)	(3)
273	1·0000	1·0000	1·0000
90·9	0·222	0·1621	—
80·1	0·174	0·1252	—
20·4	$0{\cdot}0013_3$	0·0013	$0{\cdot}0013_3$
14·8	$0{\cdot}0002_5$	—	$0{\cdot}0002_9$
12·3	$0{\cdot}0001_2$	—	$0{\cdot}0001_4$

Key: as for table 2.

Thus it is clear that in fact the ratio $[r]$ alone can only be regarded as a very rough guide to provide comparative purities. In our case, however, the inclusion of $\Omega_0/l_{0^\circ \mathrm{C}}$ merely serves to emphasize the remarkable purity attainable in the case of sodium.

A specimen (Na 3) was kept after manufacture for many months at room temperature. The resistance ratio (see figure 4) had now dropped to $\sim 3{\cdot}8 \times 10^{-4}$ which presumably indicates that a considerable degree of annealing had occurred, probably leading to the formation of a monocrystalline sample. This then appears to be the purest sodium specimen recorded. The power index deduced was practically identical ($n \approx 4{\cdot}83$) with that for the earlier specimens, thus providing confirmation of Matthiessen's rule. A further sample (Na 4) was made in a very wide capillary (~ 1 mm.). Sufficient measurement sensitivity was achieved by winding about 30 cm. of the capillary in spiral form. This specimen of large diameter was examined in order to eliminate the possibility that a limitation of electron mean free path by the physical size of the specimen might modify the observed data. The results on Na 4 (see figures 4 and 5) agree closely with those on the previous specimens, yielding an index 4·86.

A more detailed comparison with theory may be made by comparing the observed values of resistance with those computed from equation (1) over a wide temperature range. Table 1 collates the data of a number of investigations, including the present paper, covering the range from $\sim 0^\circ$ C to $\sim 10^\circ$ K. The agreement with the Bloch-Grüneisen theory is seen to be excellent, and one should note particularly that a single value of the parameter Θ (namely, $\Theta = 202^\circ$ K) suffices throughout. It is very interesting to compare this value with that deduced from the temperature variation of the specific heat. The value of the Debye temperature necessary to give reasonable agreement with the experimental data at low temperatures (~ 10 to 60° K) is about 150° K. Simon, however (1926, 1930), has pointed out that the values for sodium and lithium derived from specific-heat data are inconsistent with those obtained from the electrical resistivity and the Nernst-Lindemann formula. He has interpreted therefore, as previously in the case of grey tin, the data as composed of a normal Debye spectrum plus an 'anomalous' transformation obeying a Schottky (1922) function. It seems therefore significant that our work on the electrical conductivity has yielded a much higher value of Θ for sodium, namely, 202° K as postulated by Simon, covering the whole temperature range. It thus appears that the postulated internal excitation is of such a nature as not to affect the electrical conductivity. The resulting Schottky contribution has a characteristic temperature of 95° K. On the other hand, the possibility that the true vibrational spectrum of an alkali metal crystal deviates considerably from a simple Debye spectrum as suggested by more recent theoretical work (e.g. Blackman 1937*a*, *b*; Kellerman 1940, 1941) cannot be excluded. Support for this view arises from the considerable elastic anistropy of the alkalis (cf. Fuchs 1936).

Observations were also made on Na 2 throughout the range 20–4° K of resistance in a uniform transverse magnetic field of 4000 gauss, and no change as great as $\sim 0{\cdot}25\,\%$ could be detected.

Thus our results without and with a magnetic field give no indication of the small specific heat anomaly at $\sim 8^\circ$ K found in sodium by Simon & Pickard (1948).

Since the entropy change in this anomaly was very much less than $R \ln 2$, it was suspected to be of electronic origin and might possibly have shown up in conduction experiments. Equally, we have found in none of our specimens any indication whatsoever of a rise in resistivity with falling temperature below 4° K such as reported by Meissner & Voigt (1930).

(2) *Lithium*

Metal from three sources was examined. Li 1 was made from metal received through the courtesy of the late Dr R. A. Hull, and it is believed that its original source was Kahlbaum. Li 2 was made from metal supplied by Messrs New Metals and Chemicals Ltd., while the metal for Li 3 was obtained through the courtesy of Dr W. Hume-Rothery. All three samples appear to be of approximately the same overall purity, judged from the residual resistances ($\sim 3{\cdot}3 \times 10^{-3}$; $\sim 4 \times 10^{-3}$; $\sim 5 \times 10^{-3}$ respectively).

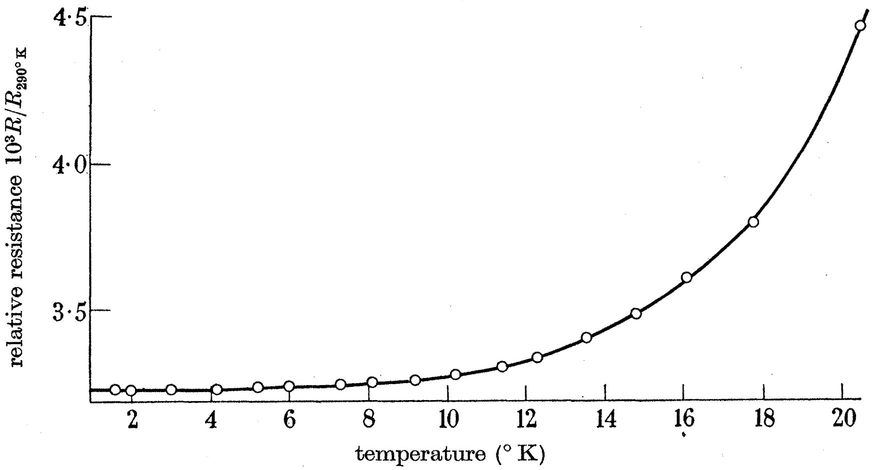

FIGURE 6. Resistance of lithium (specimen Li 1) below 20° K.

Resistance measurements were made on all three specimens, but the results on Li 2 showed appreciable scatter not normally encountered, and therefore only the results from Li 1 and Li 3 were utilized. The resistance was measured for both these specimens down to $\sim 1{\cdot}8$° K and presented no obvious abnormalities; in particular, the resistance was constant below ~ 4° K. The resistance-temperature curve for Li 1 is shown in figure 6. A logarithmic plot for Li 1, after subtraction of residual resistance (figure 5), shows quite definitely an index $n = 4{\cdot}52$. The data for Li 3 are somewhat less certain, but a line of slope $n = 4{\cdot}56$ fits the data satisfactorily.

We thus find disagreement with theory in this case, since lithium with a Debye temperature of 380–400° K would be expected to obey a T^5 law almost rigorously below 20° K. The observed behaviour concurs with the progressive departure from Grüneisen's formula towards low temperatures (20° K) found by previous workers (Meissner 1920; Meissner & Voigt 1930). A value of $\Theta = 363$° K (in general satisfactory agreement with specific heat data) is necessary to secure reasonable agreement between room temperature data with those in the region 70–90° K, but considerable deviation is then already evident at 20° K (see table 2, where the data on Li 1 have been collated with those at higher temperatures of earlier workers). If, on the other hand, we enforce agreement at $\sim 20°$ K we find a value $\Theta = 268°$ K is called for. It seems very difficult to assume such a low value, although it must be admitted that the Debye temperature deduced from the specific heat is falling off progressively at low temperatures (at 80° K, $\Theta = 380°$ K, while at 20° K, $\Theta = 340°$ K). It would therefore seem very valuable to have further specific heat data for lower temperatures, and this remark applies also to the other alkali metals yet to be discussed. A selection of resistance values has been calculated in table 3 with $\Theta = 268°$ K for comparison with the data, and while reasonably good agreement below 20° K is then obtainable, serious discrepancies now emerge in the upper region, as might be expected. The data have also been expressed in the form of a curve representing the variation of Θ with temperature as necessary to procure agreement with Grüneisen's formula and are presented along with data from rubidium in figure 7.

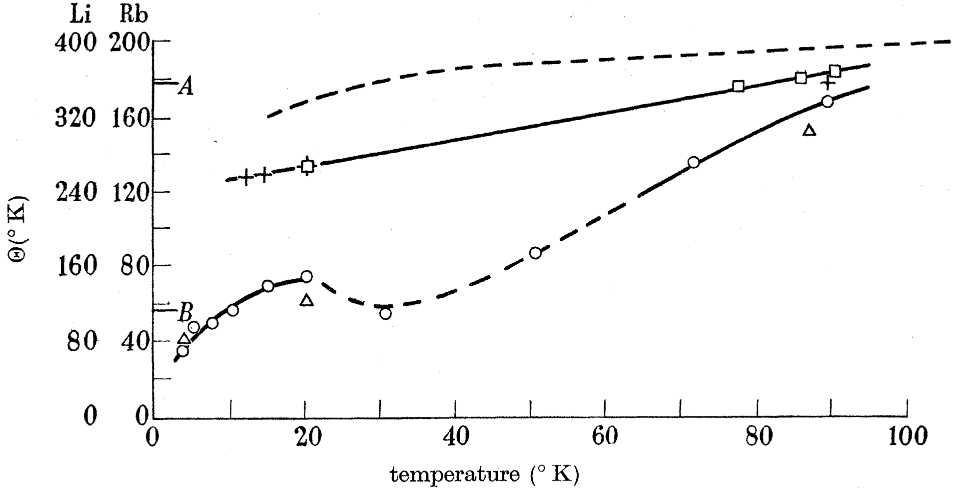

FIGURE 7. Variation of Θ with temperature.

	present work	deduced from data of Meissner & Voigt (1930)
Rb	○	△
Li	+	□

The top dashed line represents Θ for Li as deduced from specific heat data. *A* is the limiting value of Θ for Li deduced from the elastic constants and *B* is the value of Θ for Rb deduced from Lindemann's melting-point formula.

(3) *Potassium*

A rather detailed investigation was carried out on this metal and seven specimens in all were examined. The sources, treatment and residual resistance ratios are tabulated below, the latter giving a qualitative trend of purity:

specimen	source	treatment	residual resistance ratio
K1	Hopkins and Williams Commercial; suppliers unable to quote any analysis	melted under vacuum into capillary as received	$\sim 1 \times 10^{-1}$
K2	G.E.C. ex B.D.H. (quoted 'typical' analysis Na 0·1 % Cl 0·01 % SO_4 0·01 % NH_3 0·01 % heavy metals 0·002 %)	melted under vacuum into capillary as received	$\sim 5 \times 10^{-2}$
K3	Dr R. A. Hull (E. Bolton King; reported once distilled)	melted under vacuum into capillary as received	$\sim 3 \times 10^{-2}$
K4	G.E.C. (once distilled by them)	melted under vacuum into capillary as received	$\sim 4{\cdot}2 \times 10^{-2}$
K5	as K3	distilled twice in Pyrex glass by us	$\sim 1{\cdot}75 \times 10^{-2}$
K6	as K3	distilled five times in Pyrex with rejection of final top-fraction distillate	$\sim 1{\cdot}45 \times 10^{-2}$
K7	as K3	remainder of previous sample re-distilled twice in potassium glass (B.T.H.)	$\sim 7{\cdot}5 \times 10^{-3}$

The first sample examined, when plotted logarithmically over the range 20 to 6° K, gave a law $R \sim T^{3\cdot 2}$. This agrees with van den Berg's observation (1938) that a cubic index is valid over the range 14 to 20° K. Difficulty again arises here in essaying comparison with theory. From about 70° K upwards satisfactory agreement is found with Grüneisen's formula if Θ is taken $\sim 163°$ K. On the other hand, a value $\Theta \sim 70°$ K would be called for to procure agreement in the low-temperature region, while the Debye temperature deduced from specific heat data from ~ 14 to 80° K is about 100° K. In view of this conflict of evidence and the general uncertainty in our knowledge of the vibrational spectrum it is unreasonable to be dogmatic in interpreting these results. We can, however, suggest that the upper value of Θ does indicate the basic spectrum as in the case of sodium and lithium on Simon's hypotheses (1926, 1930), and we have then to explain the slow decrease in electrical resistance at the low temperatures.

The resistance curve also showed, however, a slight anomalous hump centred about 12° K and extending roughly from 10 to 14° K. This anomaly had a magnitude only $\sim 1/3$ %, but in view of the high consistency of all the measured points it was felt to be significant. A somewhat purer specimen, K2, exhibited the anomaly more strongly, and a detailed experiment on the specimen located a cusp of about 1 % magnitude at 13·4° K. In the experiments on K3 and K4, again of slightly higher purity, the original anomaly remained, but a second one at $\sim 10°$ K became evident. The experimental points for K 4 and K 6 appear in figure 8. These anomalies were also confirmed in specimens K 5 and K 6, which showed a further improvement in purity.

It will be noticed that little significant improvement in residual resistance occurred with the repeated distillation of K 6 over K 5. It was presumed that this must be due to collection of impurity atoms from the glass, compensating the improvement by distillation. Messrs British Thomson-Houston Co. Ltd. kindly undertook then to manufacture some potassium glass for us, and this was used for distillation to produce K 7. This specimen then showed a satisfactory decrease in residual resistance and also the anomalies had disappeared. We therefore deduce that these resistive anomalies must be characteristic of a relatively small number of impurity atoms in solid solution. On the one hand, the pure metal does not exhibit the phenomenon, while of course any serious amount of impurities produces so much random scattering in any case that any coherent effect due to their presence is entirely masked by a high residual resistance. In view of the later results on barium* it seems very probable that the significant impurity is sodium.† Hard glass was in fact used for the earlier distillations, because of its lower sodium oxide

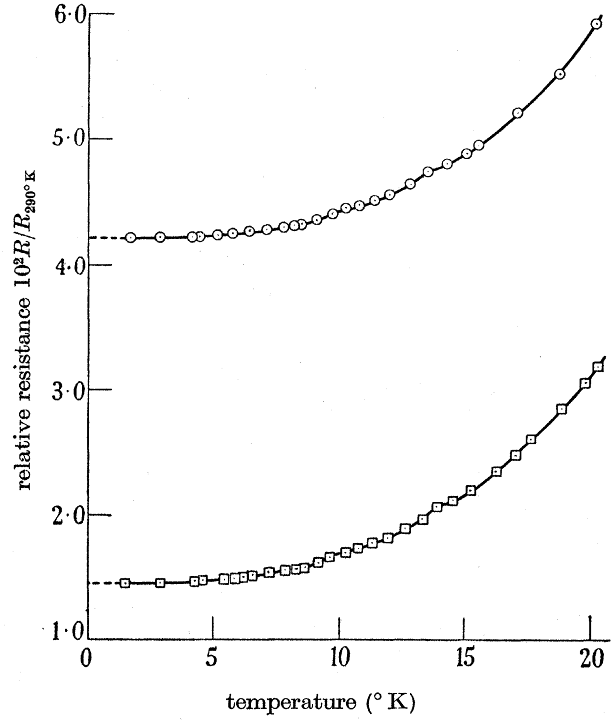

FIGURE 8. Temperature-variation of potassium below 20° K. Specimens: ⊙, K 4; ⊡, K 6.

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* In course of publication.

† Cf. also the quoted analysis for K 2.

content than soft glass;* the percentage content of sodium oxide is none the less quite considerable.

It is interesting in relation to these experiments to notice that if van den Berg's data on his first potassium specimen—of the same order of purity as our K3—are plotted, it is quite possible to fit a curve showing similar cusps, although there is a paucity of data in the relevant region. On the other hand, no sign of anomaly appears in his second specimen, which was of rather higher purity than our specimen K7.

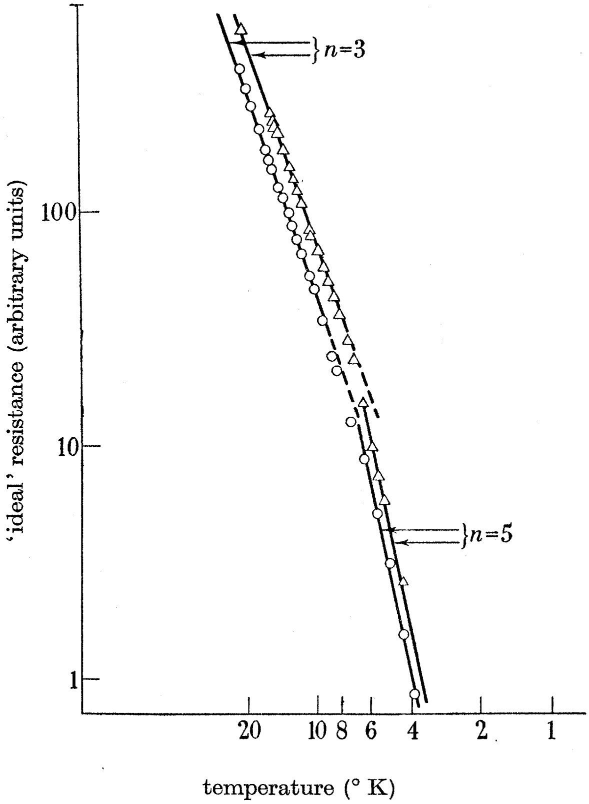

FIGURE 9. Resistance of potassium specimens plotted logarithmically.
Specimens: ○, K5; △, K7.

Our purer specimens (K5 and K7) are plotted logarithmically (in figure 9), and enable an accurate determination of power-law variation to be made down to ~ 4° K. The data of the purest (K7), in particular, show an excellent T^3 variation down to 8° K and a T^5 law from 6·5° K downwards, as shown. This latter agrees well with van den Berg's observations of a T^5 law from 3 to 7° K, although he suggests an increase above the cubic power law below 14° K.

* Chance Hysil G.H. 1: SiO_2: 80·4 % B_2O_3: 12·4 %, Na_2O: 4·2 % CaO: 0·3 %, Al_2O_3: 2·7 %.
Chance (soft) G.W. 1: SiO_2: 74 % Na_2O: 16 %, Al_2O_3: 1 % CaO: 7 %, Sb_2O_3: 1·3 %.

(4) *Rubidium*

The metal was obtained from Messrs New Metals and Chemicals Ltd. This had been distilled to a high purity for use in photo-electric cells. The ratio of resistance in liquid helium at 4·2° K to that at room temperature was about 3×10^{-2} and $1 \cdot 8 \times 10^{-2}$ for our two specimens, which are rather better values than those of the specimens used by Meissner & Voigt.

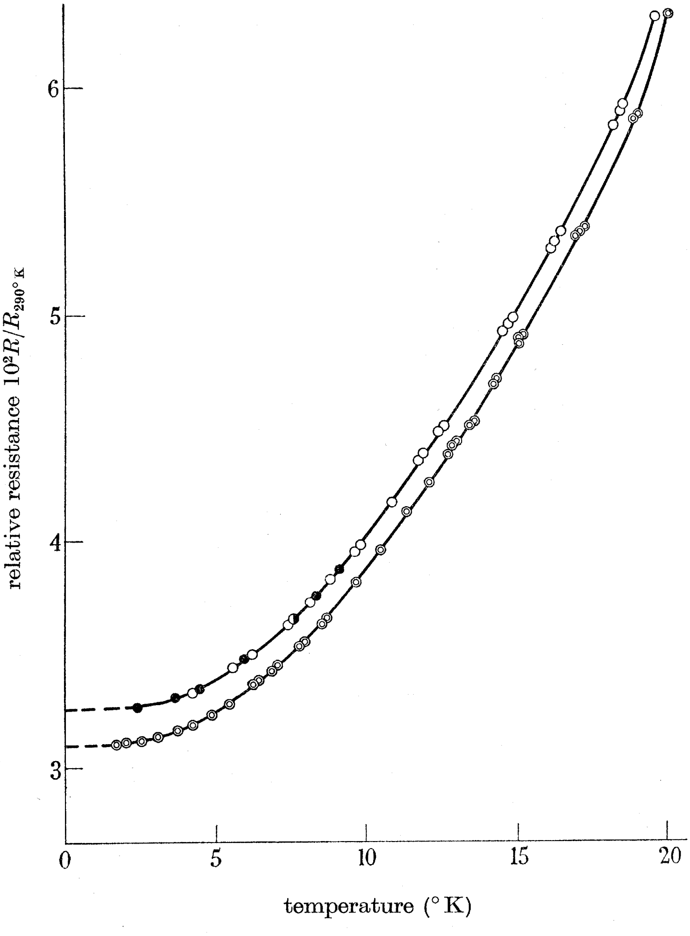

FIGURE 10. Resistance of rubidium (specimen Rb 1) below 20° K. Dates of experiment (1948): ○, 22 January; ●, 29 January; ◎, 5 February.

A number of experiments were made from 20° K downwards; no significant anomaly was detected anywhere in this region.* We may say at once that the resistance does not follow Grüneisen's law, but since on general grounds (cf. Seitz 1940, p. 532) one should expect a T^5 law to hold in any case for *sufficiently* low temperatures, a detailed examination was made in the liquid helium region down to ~ 1·5° K.

Experimental results for rubidium are shown in figure 10, and logarithmic plots for both specimens are given in figure 11. Meissner & Voigt did not attempt to

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* Apart from possibly a *very* slight extended 'hump' from 7 to 12° K.

compare their data with equation (1) but tried to fit an earlier empirical law due to Grüneisen, viz. $R \sim ATC_p$, where A is a constant and C_p the specific heat. This leads to $R \sim T^4$ for low temperatures. They were probably led to this course, since the decline of the resistance with temperature is much too slow for the Bloch-Grüneisen law with constant Θ. Even then the agreement is not good. We have therefore derived a curve of the variation with temperature of the required Debye temperature, Θ (see figure 7), in the same fashion as one exhibits specific heat data that do not follow the Debye law strictly. One sees immediately that the data for rubidium are highly anomalous. It should be pointed out that the reality of the minimum above 20° K cannot be guaranteed, since the value of Θ deduced in this region is found to be rather sensitive to temperature and high accuracy is not claimed for temperature measurement in this region. If the deviation from theory of the electrical resistance for the alkali metals, except sodium, is in fact ultimately to be attributed to the departure of the lattice vibrations from the Debye law, then this curve is of significance and suggests that a determination of the specific heat of rubidium would be of very considerable interest; the same applies with equal weight to caesium. In this respect the qualitatively similar trend of Θ for Li when deduced from both sources of data may be significant. On the other hand, if the source of the anomalous behaviour is an intrinsic deviation of the electronic structure of a metal from that of the ideal metal, then of course the curve is only to be regarded as a convenient mode of data presentation.

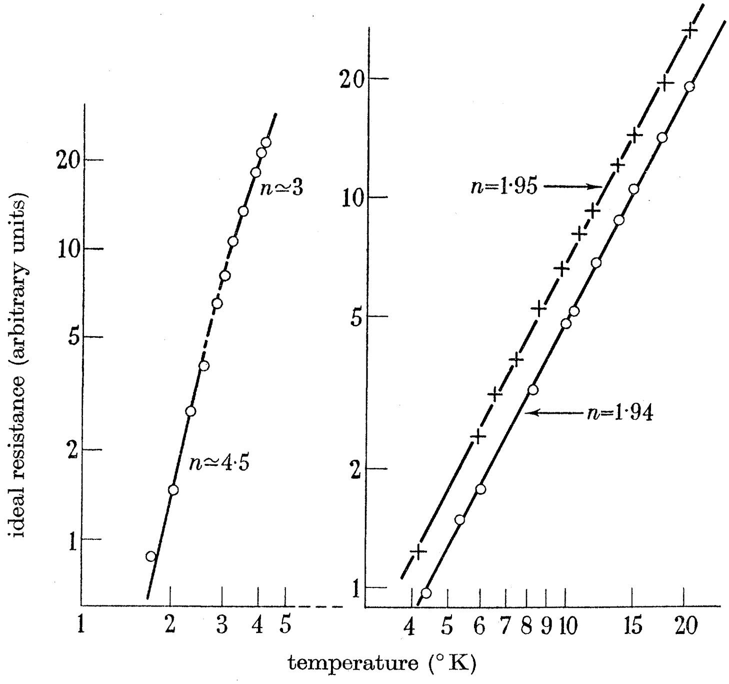

FIGURE 11. Logarithmic plot of resistance of rubidium.

Two experiments were made to examine closely the resistance variation below ~ 4° K; these agree well with one another and are shown in figure 12. The data are plotted logarithmically in figure 11, and indicate clearly that at sufficiently low temperatures the T^5 law does hold. The fact, however, that this does not occur until probably below ~2° K indicates a very low limiting Debye temperature (~25° K) in good agreement with the variation of Θ shown in figure 7. Of the various possible sources of anomalous behaviour in general, only electron-electron collisions (Baber 1937) leading to a T^2 component of resistivity appear likely to prevent the ultimate inception of a T^5 law, and such collisions would be expected to play a very small part in the alkali metals.

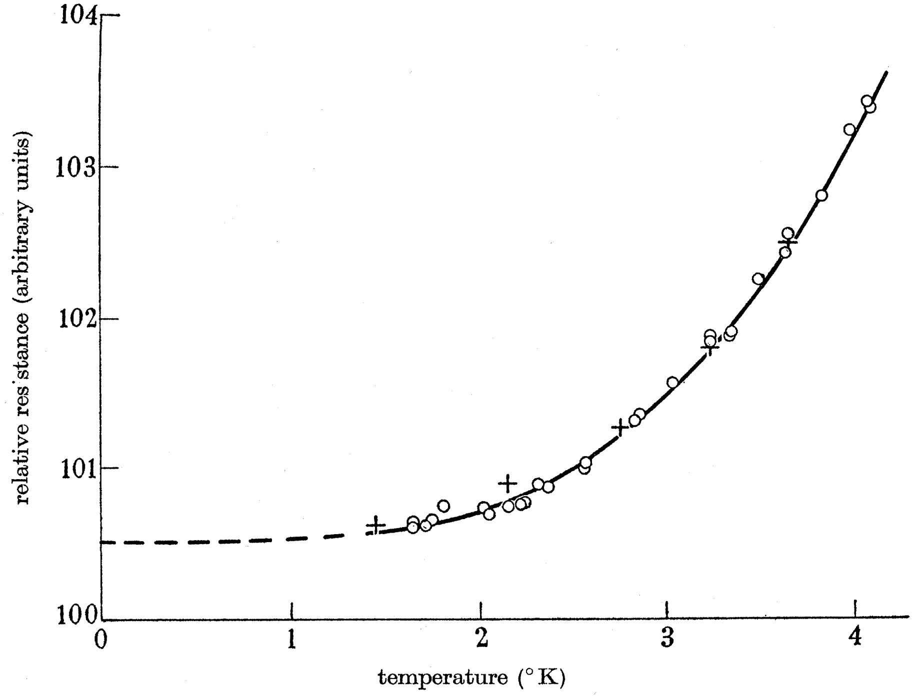

FIGURE 12. Resistance of rubidium at low temperatures. +, Experiment 1; ○, Experiment 2.

(5) *Caesium*

This metal was also obtained from Messrs New Metals and Chemicals Ltd., and the preparation before despatch to us was similar to that for rubidium. Two capsules containing about 1 g. each were received, and spectrographic analyses obtained through the courtesy of A.E.R.E. Harwell furnished the following data:

sample I (Cs 1)	parts in 10^6	sample II (Cs 2)	parts in 10^6
K	500	Na	200
Si	500	K	200
Rb	300	Rb	300
Pb	300	Pb	50
Na	1000	*Not detected*	
Li	5	Li	(<1)
Sn	20	B	(<50)
Not detected		Hg	(<200)
B	(<50)	Sn	(<10)
Hg	(<200)	Si	

Judging also from the residual resistance ratios (2 to 1×10^{-2}) the metal was rather purer than that used by Meissner & Voigt.

The first results on caesium showed quite anomalous behaviour. The curve of resistance from 20 to ~1·5° K showed two marked 'kinks' (cf. MacDonald & Mendelssohn 1948), the first at ~6° K, the second, more severe, at ~4° K. Subsequent experiments clearly confirmed these anomalies. A second specimen, from the other capsule of metal, also showed anomalies, somewhat less marked, at ~4 and ~11° K (see figure 13). It is interesting to note that Meissner & Voigt suspected a resistance anomaly between 4 and 20° K.

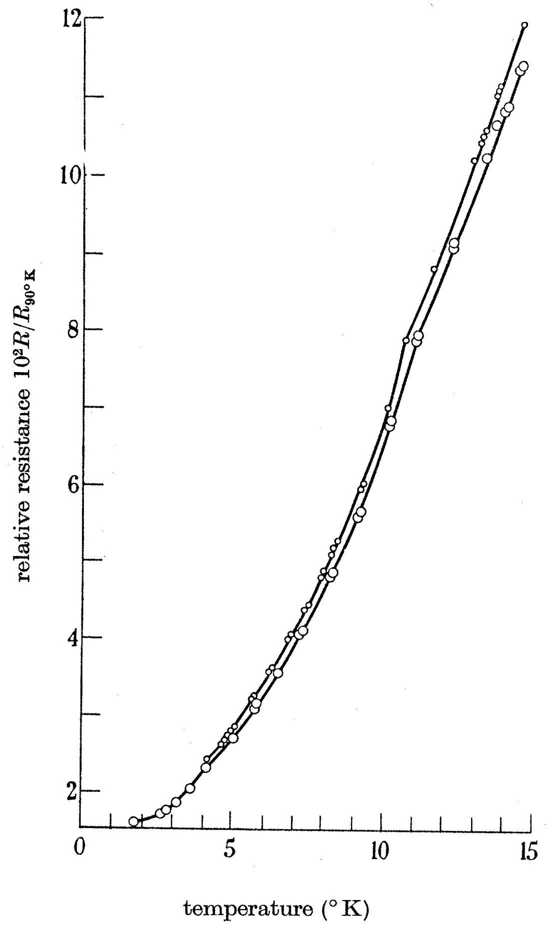

Figure 13. Resistance variation at low temperatures of caesium (specimen Cs 2). Dates of experiment (1948): o, 19 February; ○, 26 February.

When relatively slowly cooling the first specimen to liquid oxygen the resistance showed a discontinuity; the specimen was re-warmed to room temperature and then successfully carried down to liquid oxygen temperature by extremely slow cooling. After the low-temperature work, investigations were made between −183° C and room temperature using a thermo-couple for the temperature determination. One of these experiments is shown in figure 14, and a discontinuity on first warming is seen at ~ -20° C which did not arise, after re-cooling, in the second experiment up to room temperature. It is clear that this anomaly is responsible for the radically different behaviour of the specimens observed by McLennan, Niven & Wilhelm (1928) and by Meissner & Voigt in this temperature region.

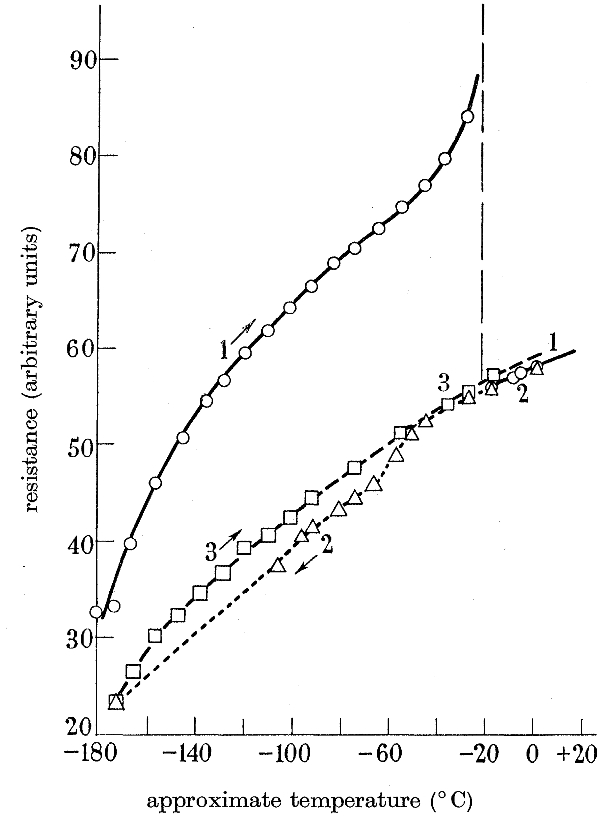

Figure 14. Variation of resistance of caesium (specimen Cs 1) at temperatures above liquid oxygen. Temperature scale based on linear interpolation of Cu-constantan thermocouple:

experiment	key	temperature
1	○	increasing
2	△	decreasing
3	□	increasing

The electrical behaviour at -20° C may possibly be ascribed to some anomaly in the thermal contraction in this region, since it appears likely that only such a mechanism could produce effectively infinite resistance.

In view of the unusual behaviour of the metal, in particular at very low temperatures, leading to uncertainty in the true value of residual resistance it does not appear profitable to try to compare the data in detail with the theoretical conductivity law. We mention, however, that ignoring the anomalous behaviour, the apparent Debye temperature for Cs 1 deduced from data over the range ~ 8 to 20° K is only 35° K (cf. figure 15), while even below 4° K the resistance follows an approximate power law of index only ~ 2·75, obviously still deviating markedly from the Bloch law.

Since the sodium content of Cs 1 is considerably greater than in Cs 2 (see analysis) it seems likely that the low temperature anomalies are again attributable to this source as in the case of potassium.

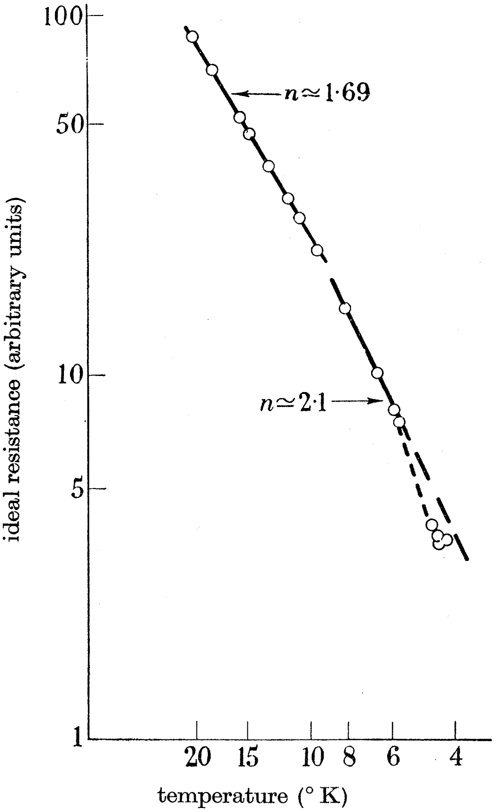

FIGURE 15. Logarithmic plot for caesium (specimen Cs 1).

CONCLUSIONS

The specific features of the results have already been discussed in the case of each metal in turn. Surveying the data generally under the headings of the introduction it appears that sodium follows the theory remarkably well throughout. This confirms indications from other sources that sodium may be regarded as an excellent example of the quasi-free electron model in all respects. The results on the other alkali metals seem to show, however, that sodium presents a singular case in this respect. There are two ways in which the deviations from the simple theory can be interpreted. On the one hand the lattice vibrations may depart markedly from the Debye law, resulting in a different law of variation of resistance with temperature. The second possibility is that the conduction electrons may not be legitimately regarded as quasi-free. In the case of lithium the screening of the valence electron from the nucleus may be inadequate. On the other hand, in the later alkalis the growth of the ion may be sufficient to interfere with the freedom of the outer electron.

An entirely new phenomenon is presented by the small anomalies observed in potassium and caesium which have been correlated with the presence of very slight impurity. Although the phenomena are not conspicuous they appear to be of particular interest because so far impurity scatter has not been known to create any effect except the residual resistance. This temperature-independent component of the resistance which forms the basis of Matthiessen's rule can under plausible assumptions be accounted for theoretically (cf. Mott & Jones 1936, pp. 287–288), but there does not seem to be any simple way of interpreting these small anomalies in a similar way. It is hoped to obtain further information on these questions from resistance measurements on other metals, and these are now in progress.

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