

# Electrical and Thermal Resistivity of the Transition Elements at Low Temperatures

G. K. White and S. B. Woods

*Phil. Trans. R. Soc. Lond. A* 1959 **251**, 273-302

doi: 10.1098/rsta.1959.0004

## Email alerting service

Receive free email alerts when new articles cite this article - sign up in the box at the top right-hand corner of the article or click [here](#)

To subscribe to *Phil. Trans. R. Soc. Lond. A* go to: <http://rsta.royalsocietypublishing.org/subscriptions>

## ELECTRICAL AND THERMAL RESISTIVITY OF THE TRANSITION ELEMENTS AT LOW TEMPERATURES

BY G. K. WHITE\* AND S. B. WOODS

*Division of Pure Physics, National Research Council, Ottawa**(Communicated by N. F. Mott, F.R.S.—Received 5 August 1958)*

## CONTENTS

	PAGE		PAGE
1. INTRODUCTION	273	3. EXPERIMENTAL RESULTS	282
1.1. Aim of the experiments	273	3.1. Electrical resistivity	282
1.2. Theoretical	274	3.2. Thermal resistivity	288
1.3. Previous experimental work	276	4. DISCUSSION	292
2. EXPERIMENTAL PROCEDURE	278	4.1. Electrical resistivity	292
2.1. Cryostat and associated equipment	278	4.2. Thermal resistivity	295
2.2. Accuracy of results	279	5. CONCLUSIONS	297
2.3. Specimens	281	APPENDIX	298
		REFERENCES	300

The results of measurements on 20 transition elements are reported giving values for the thermal resistivity,  $W$ , from 2 to about 140 °K and for electrical resistivity,  $\rho$ , from 2 to about 300 °K. Values of the 'ideal' resistivities,  $W_i$  and  $\rho_i$  (due to scattering of the electrons by thermal vibrations), are deduced from these and tabulated for various temperatures. Comparisons are made with values for Cu, Ag, Au and Na and with the predictions of the 'standard' theory, i.e. solutions of the transport equation developed by Bloch, Grüneisen, Wilson, etc. Excepting Mn,  $\rho_i$  follows a Bloch-Grüneisen function tolerably down to  $\theta_D/5$ , although slight anomalies are shown by V, Cr, Fe, Co and Ni; at low temperatures behaviour is varied but below 10 °K in Mn, Fe, Co, Ni, Pd, Pt and perhaps in W and Nb,  $\rho_i$  appears to vary nearly as  $T^2$ . The parameter,  $\rho_i M \theta_D^3 \Omega^{\frac{1}{2}}$  (at 273 °K) has rather similar values for different members of each group, e.g. for Ti, Zr and Hf of group IVA.

The ideal thermal resistivity,  $W_i$ , can generally be approximated by the relation,

$$W_i/W_\infty = 2(T/\theta)^2 J_3(\theta/T),$$

although for many elements,  $W_i$  falls more rapidly than  $T^2$  below  $\theta/10$ . Measurements on the relatively poor conductors, e.g. Ti, Zr and Hf, suggest the presence of an appreciable lattice conductivity, which affects the confidence with which values can be deduced for  $W_i$  in these elements.

## 1. INTRODUCTION

1.1. *Aim of the experiments*

Some years ago one of us took part in a study of the electrical and thermal conductivity of the alloy systems Ag+Pd and Ag+Cd, at low temperatures (see, for example, Kemp, Klemens, Sreedhar & White 1956). These experiments were specifically intended to investigate the result of changing the effective number of conduction electrons on the lattice component of the heat conductivity and on the electronic transport processes. During this

\* Now at National Standards Laboratory, C.S.I.R.O., Sydney, Australia.

work measurements were also made on pure palladium (Kemp, Klemens, Sreedhar & White 1955) and later on iron and nickel (Kemp, Klemens & White 1956). Analysis of the results indicated that at quite low temperatures ( $T \ll \theta_D$ ) the 'ideal' or intrinsic thermal resistivity and the electrical resistivity varied approximately as  $T^2$  and  $T^3$ , respectively. This suggested that the theory of the effect of interband transition on resistivity (as developed by Wilson 1938) might be applicable over quite a wide temperature range.

This stimulated our interest in the behaviour of the transition elements, particularly as it appeared that, for a large number of them, little information was available concerning their conduction properties. Indeed, for some the room-temperature values of electrical resistivity quoted in different standard texts and tables are widely at variance with one another.

### General

#### 1.2. Theoretical

We shall briefly quote some results of the basic theory of electron transport processes founded on the work of Sommerfeld, Bloch and others and refer for a complete description to Wilson (1953). Among recent reviews which deal with this topic and with the shortcomings of this standard theory are those of Jones (1956), Klemens (1956, dealing chiefly with thermal transport) and Sondheimer (1957). To a first approximation the total resistivity is obtained by the addition of the residual resistivity produced by static defects ( $\rho_0, W_0$  in the electrical and thermal cases, respectively) and the 'ideal' component produced by thermal vibrations of the lattice ( $\rho_i, W_i$ ), that is

$$\rho = \rho_0 + \rho_i \quad (\text{Matthiessen's rule}) \quad \text{and} \quad W = W_0 + W_i; \quad (1)$$

further the residual resistivities are related by the Wiedemann–Franz–Lorenz (W.-F.-L.) relation

$$\rho_0/W_0 T = L \simeq 2.45 \times 10^{-8} \text{ W } \Omega \text{ deg}^{-2} \quad (2)$$

and the ideal resistivities should be given by

$$\rho_i = 4A(T/\theta)^5 J_5 \quad (3)$$

and

$$W_i = \frac{4A}{LT} (T/\theta)^5 \left[ \left\{ 1 + \frac{3}{2\pi^2} \frac{\zeta}{D} \left( \frac{\theta}{T} \right)^2 \right\} J_5 - \frac{1}{2\pi^2} J_7 \right], \quad (4)$$

where

$$J_n(\theta/T) = \int_0^{\theta/T} \frac{x^n dx}{(e^x - 1)(1 - e^{-x})}. \quad (5)$$

In these expressions,  $A$  is a constant, proportional to the square of the electron-lattice interaction constant  $C$ ,  $\zeta$  is the Fermi energy, and the parameter,  $\zeta/D = 2^{3/2} N^{3/2}$ , where  $N$  is the effective number of conduction electrons per atom. At high and low temperatures (3) and (4) have exact solutions yielding the following proportionalities:

$$\rho_i \propto T^5, \quad W_i \propto T^2 \quad \text{for} \quad T \ll \theta,$$

and

$$\rho_i \propto T, \quad W_i \simeq \text{constant} \quad \text{for} \quad T > \theta.$$

### Electrical resistivity

As Wilson and the review authors have discussed,  $\rho_i$  may be adequately represented over a fairly wide temperature range by a suitable choice of  $\theta$ , but no single  $\theta$  value gives good agreement from high to very low temperatures.

For high temperatures the free electron model leads to a value

$$\rho_i \simeq 4.8 \times 10^{-2} \left(\frac{C}{\zeta}\right)^2 \left(\frac{T}{M\theta^2 \Omega^{\frac{1}{3}}}\right) \text{ ohm cm,} \quad (6)$$

where the atomic volume  $\Omega$  is expressed in cubic ångströms. As  $C/\zeta$  is expected to be of the order of unity, the parameter  $\rho_i M\theta^2 \Omega^{\frac{1}{3}}/T$  should not vary greatly among metals to which the model is at all applicable (see Mott 1936, or Mott & Jones 1936). In fact the average of the experimental values for the alkali metals is  $\sim 0.06$  (cf. theoretical 0.048), and for Cu, Ag and Au is  $\sim 0.08$ , but for transition elements is an order of magnitude higher. Mott (1936) suggested that the high probability of electron transitions from the  $s$ - to the  $d$ -band in these latter elements produced the high resistivity responsible for this, and later Wilson (1938) showed that

$$\rho_i(sd) = d \left(\frac{T}{\theta}\right)^3 \int_{\theta x/T}^{\theta/T} \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})} = d(T/\theta)^3 J_3(\theta/T), \quad (7)$$

where  $d$  is a constant, so that if at low temperatures  $s$ - $d$  transitions are not prohibited by conservation laws,  $\rho_i(sd)$  should vary as  $T^3$ . If on the other hand,  $s$ - $d$  transitions become very unlikely below a characteristic temperature,  $\theta_E$ , then we should expect

$$\rho_i(sd) \propto e^{-\theta_E/kT}.$$

Finally, we may mention the effect of electron-electron interactions examined theoretically by Baber (1937) and more recently in the collective electron treatments (see, for example, Pines 1955, 1956). These may contribute a component of resistivity proportional to  $T^2$  which may be appreciable at very low temperatures in the transition elements, and explain earlier observations made by de Haas & de Boer (1933) on platinum.

#### *Thermal resistivity*

Equation (4) leads to a low-temperature relation  $W_i = BT^n$  ( $n = 2.0$ ), so that

$$W = W_0 + BT^n \quad (T \leq \theta/10), \quad (8)$$

where

$$B = \beta N^{\frac{2}{3}} W_\infty / \theta^2, \quad (9)$$

$W_\infty$  is the ideal thermal resistivity at high temperatures and  $\beta = 95.3$ . The more exact solutions of the transport equation by Sondheimer (1950) and Klemens (1954), give values of  $\beta$  nearer to 70 but leave a small maximum (but see also Ziman 1954) in  $W_i$  (at or near  $T \simeq \theta/4$ ) which is not observed experimentally. Analysis of the experimental results assuming  $\theta = \theta_D$  (the Debye specific heat  $\theta$ ) leads to  $\beta$  values in the range 10 to 25; the exponent  $n$  (for  $T \leq \theta/10$ ) lies close to the theoretical value of 2.0 for the alkali metals but may reach 2.3 or 2.4 for some other elements.

Apart from this variation in index  $n$ , experimental values of  $W_i/W_\infty$  seem better represented by an empirical expression (see MacDonald, White & Woods 1956)

$$\frac{W_i}{W_\infty} = 2(T/\theta)^2 J_3(\theta/T) \quad (10)$$

$$\simeq 14.4(T/\theta)^2 \quad \text{for } T \leq \theta/10. \quad (11)$$

Finally, it is expected theoretically that at high temperatures, where elastic scattering predominates, the electrical resistivity and thermal resistivity (or thermal conductivity,  $\lambda$ ) should be related, as they are at very low temperatures by equation (2). That is

$$\rho\lambda/T \equiv \rho/WT \simeq \rho_i/W_\infty T = L \quad \text{for } T > \theta.$$

*General**1.3. Previous experimental work*

The principal measurements of electrical resistivity of the elements in the transition metal group have been those of Meissner & Voigt (1930) and of Potter (1941); the former authors measured the resistance at the ice-point, near 90 and 80 °K, at 20.4 °K and at liquid-helium temperature on specimens of nearly all the transition elements. Potter's measurements on nine transition elements were done at 14, 20, 77 and 90 °K and at numerous temperatures from 100 °K upwards. Values of room-temperature or ice-point resistance and some isolated low-temperature values are listed in reviews by Grüneisen (1928), Gerritsen (1956) and by van Arkel (1939) among others. However, most earlier measurements do not allow a detailed examination of the ideal electrical resistivity over the continuous temperature range from the neighbourhood of  $\theta_D$  down to temperatures of  $\theta/20$  or less, because of (a) insufficient measurements, (b) lack of purity of specimens, or (c) lack of knowledge of the absolute resistivity values.

For thermal conductivity, the experimental data obtained by Rosenberg and Mendelssohn (see Rosenberg 1955) for a number of the transition elements enable us to examine their low-temperature behaviour. This and other data, are listed in the reviews of R. L. Powell & Blanpied (1954), R. W. Powell (1955); Klemens (1956) and in some original references listed below. The *Rare metals handbook* (Hampel 1954) is also a useful source of data and original references.

*Ti, Zr and Hf*

de Haas & Voogd (1928) examined the electrical resistance of hafnium at some temperatures between 1 and 98 °K. Higher purity specimens of zirconium and hafnium were measured at 90 °K and above by Adenstedt (1952). The metallurgical monographs of McQuillan & McQuillan (1956) on titanium and Miller (1954) and Lustman & Kerze (1955) on zirconium provide a useful record of data obtained at normal temperatures. Values of electrical resistivity at room temperature (295 °K) for Ti, Zr (see Treco 1953 in particular) and Hf are about 42, 42.2 and 30  $\mu\Omega\text{cm}$ , respectively.

The thermal conductivities of titanium and zirconium were measured by Rosenberg (1955) below 40 °K; of titanium by Silverman (1953) above room temperature, and by Rigney & Bockstahler (1951) at 0 °C, their ice-point value being  $\lambda = 0.20 \text{ W cm}^{-1} \text{ deg}^{-1}$ . For zirconium Bing, Fink & Thompson (1951) and also Deem (1953*a*) found  $\lambda$  near room temperature was  $0.21 \text{ W cm}^{-1} \text{ deg}^{-1}$  and for hafnium plus 2 wt. % zirconium, Deem (1953*b*) gives  $\lambda = 0.22$ .

*V, Nb and Ta*

The vanadium and niobium specimens used by Meissner & Voigt (1930) and Potter (1941) were extremely impure. However, from these sources and from Gerritsen (1956) and van Arkel (1939), it seems that room temperature values of electrical resistivity for V, Nb, and Ta are 20 to 21, about 14, and 13.5  $\mu\Omega\text{cm}$ , respectively.

The thermal conductivities of these elements, which become electrically superconducting at sufficiently low temperatures have been studied in some detail below 10 °K by various experimenters; however, between 10 and 100 °K, the work of Rosenberg (1955) appears to



be the only source of data and his specimens were not generally of sufficiently high purity to provide unambiguous information about the ideal thermal resistivity in this temperature region. For tantalum, a room temperature value of  $\lambda = 0.54 \text{ W cm}^{-1} \text{ deg}^{-1}$  was obtained by Barratt & Winter (1925); recently Weeks & Smith (1955) found for vanadium with  $< 0.4\%$  impurities that  $\lambda = 0.357 \text{ W cm}^{-1} \text{ deg}^{-1}$  at  $70^\circ\text{C}$ ; for niobium, Tottle (1957) has found  $\lambda = 0.523 \text{ W cm}^{-1} \text{ deg}^{-1}$  at  $0^\circ\text{C}$  and  $\lambda = 0.543$  at  $100^\circ\text{C}$ .

#### Cr, Mo and W

For these three elements measurements of electrical resistivity have been made by Meissner & Voigt and by Potter; also Van den Berg (1938) made measurements on tungsten below  $20^\circ\text{K}$  and data are given in the monographs of Sully (1954) for chromium and of Northcott (1956) for molybdenum. Reliable room-temperature values of electrical resistivity for Cr, Mo and W are 13 to 14, about  $5.5$ , and  $5.4 \mu\Omega \text{ cm}$ , respectively.

The compilation of Powell & Blanpied (1954) shows that a number of measurements of heat conductivity have been made for both tungsten and molybdenum below room temperature. We have made no measurements on molybdenum but used those of Rosenberg (1955) below  $100^\circ\text{K}$  and Kannuluik (1933) above  $90^\circ\text{K}$  to obtain values of  $W_i$ , the ideal thermal resistivity. For tungsten, the ranges covered by Rosenberg and by Kannuluik do not overlap, but with our measurements and data of Grüneisen & Goens (1927) and de Haas & de Nobel (1938), they provide a continuous record of  $W_i$ . For chromium considerable data on the effect of heat treatment at normal and elevated temperatures has been given by Powell & Tye (1956). Their work indicates that for high-purity Cr,  $\lambda_{295} \simeq 0.86$ ; for Mo and W previous work indicates that  $\lambda_{295}$  has approximate values of  $1.45$  and  $1.7 \text{ W cm}^{-1} \text{ deg}^{-1}$ , respectively.

#### Mn, Tc and Re

The monograph of Sully (1955) on manganese, gives room temperature values for the electrical resistivity of  $\alpha$ -manganese varying from  $150$  to  $720 \mu\Omega \text{ cm}$ , the most probable value lying in the range  $150$  to  $250$ . For technetium we are unaware of any measurements. Data for rhenium are given by Meissner & Voigt (1930) and by Hulm & Goodman (1957) below room temperature. These indicate that for rhenium  $\rho_{295} \simeq 19$  to  $20 \mu\Omega \text{ cm}$ .

The only thermal conductivity measurements appear to be those of Rosenberg on  $\alpha$ -manganese below  $35^\circ\text{K}$ , and for  $\beta$ -manganese a value of  $\lambda \simeq 0.05 \text{ W cm}^{-1} \text{ deg}^{-1}$  obtained by Reddemann (1935) at  $83^\circ\text{K}$ .

#### Fe, Ru and Os

Isolated values of electrical resistivity have been obtained for iron below room temperature by Holborn (see, for example, the review of Grüneisen 1928) and by Meissner & Voigt and others; below  $20^\circ\text{K}$  by Olsen-Bär (1956). Some measurements on sintered rods of ruthenium at low temperatures have been made by Meissner & Voigt and by Justi (1949). For osmium the only apparent measurement is an approximate room temperature value of  $9.5 \mu\Omega \text{ cm}$  (Blau 1905); earlier work on Fe and Ru suggests that the values of  $\rho_{295}$  for these elements in a pure form are respectively  $9.9$  and about  $7.4 \mu\Omega \text{ cm}$ .

For iron, data have been obtained below  $90^\circ\text{K}$  by Rosenberg (1955), from  $20$  to  $90^\circ\text{K}$  by Grüneisen & Goens (1927) and by Powers, Ziegler & Johnston (1951) from  $20^\circ\text{K}$  to room

temperature. At room temperature the work of Powers *et al.* and R. W. Powell (1955) indicates that  $\lambda_{295} \simeq 0.82 \text{ W cm}^{-1} \text{ deg}^{-1}$ .

#### Co, Rh and Ir

As well as isolated values of electrical resistivity given by Grüneisen (1928), Meissner & Voigt (1930) and, for rhodium and iridium, by Potter (1941), more complete data for cobalt and rhodium below 20 °K have been given by Olsen-Bär (1956) and for rhodium and iridium above 80 °K by Powell & Tye (1955). Probable values of  $\rho_{295}$  for pure Co, Rh and Ir are about 5.9, 4.8 and 5.1  $\mu\Omega\text{cm}$ , respectively.

Only below 50 °K are there data for the thermal conductivity of pure cobalt (Rosenberg 1955). Rosenberg's measurements for rhodium and iridium ranged from 2 to about 30 °K, and those of Powell & Tye (1955) from 80 °K up to room temperature; these latter measurements gave  $\lambda_{295} \simeq 1.51$  (Rh) and 1.46 (Ir)  $\text{W cm}^{-1} \text{ deg}^{-1}$ .

#### Ni, Pd and Pt

Olsen-Bär (1956) has examined the temperature variation of electrical resistivity of each of these elements below 20 °K. The importance of platinum as a resistance thermometer element has led to publication of considerable data, for example, by de Haas & de Boer (1933), by Los & Morrison (1951) and Hoge & Brickwedde (1939). The room-temperature resistivities of Ni, Pd and Pt appear to be 7.2, 10.7 and 10.7  $\mu\Omega\text{cm}$ , respectively. Rosenberg's thermal conductivity data for nickel, palladium and platinum extend from 2 to about 40 °K. For nickel, values above 30 °K were obtained by Powers *et al.* (1951) and de Nobel (1951) with rather impure specimens and do not give us information about the temperature variation of the ideal thermal resistivity. For palladium, values near 20 °K and near 80 °K were reported by Grüneisen & Reddemann (1934). Meissner (1915) has given values for platinum at a few points from 20 °K up to room temperature. From values listed by R. W. Powell (1955) and by R. L. Powell & Blanpied (1954),  $\lambda_{295}$  for pure Ni, Pd and Pt appears to be about 0.9, 0.7 and 0.7  $\text{W cm}^{-1} \text{ deg}^{-1}$ .

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Cryostat and associated equipment

Usually the determinations of both electrical and thermal conductivity are made on the same specimen, in rod form, mounted in a cryostat similar to that described previously (White & Woods 1955). One end of the specimen is soldered to a copper post in the cryostat and a specimen heater is attached to the other end. Copper wires are soldered (or otherwise attached) to intermediate points on the rod to act as both thermal and electrical potential leads, to which the gas thermometer bulbs and fine electrical potential lead-wires are in turn soldered. However, in some cases (notably using fine-wire specimens), only the electrical resistivity has been measured and in these cases, the wires are surrounded by a small pressure of helium exchange gas to preserve temperature equilibrium between the specimens and the temperature-controlled surroundings.

The results for Cr and some of those described below for Pd, Fe, Ni, Ti and Zr were done by one of us with colleagues at the C.S.I.R.O. Division of Physics (Sydney, Australia) and were performed in a rather similar cryostat (White 1953*a*).

Measurements of thermal conductivity were carried out over the range of temperatures from 1.8 to about 150 °K, above which radiation corrections and the time required to establish thermal equilibrium become intolerably large with the specimens and cryostats used. However, electrical resistance measurements were generally made from about 1.2 °K up to room temperature, cooled alcohol baths being used generally for temperature control above 160 °K.

### 2.2. Accuracy of results

The ratio of the length,  $l$ , to the cross-sectional area,  $A$ , of the specimens enters directly into determinations of the absolute resistivity values. This factor could be measured within a few parts in a thousand for regularly shaped specimens and the effective  $l/A$  for specimens of irregular shape was obtained by normalizing the ideal resistivity at room temperature (or at the ice point) to that for a uniform specimen. Thus the probable error in  $l/A$  seldom exceeded 1%, but may have reached 2% in one or two cases. For a single specimen, since  $l/A$  is involved in the same way in the calculation of electrical and thermal resistivities, values obtained for the Lorenz ratio, for example, are independent of  $l/A$  as are comparative values of resistivity.

#### *Electrical resistivity*

Relative errors arise chiefly in the determination of the potential difference across the specimen. For this a galvanometer amplifier (MacDonald 1947) was used which could normally be read to about one part in 400, but with specimens of relatively small  $l/A$  and low resistivity, smaller deflexions and therefore somewhat larger relative errors had to be tolerated. Errors in  $\rho_i = \rho - \rho_0$  could have been substantially larger at low temperatures due to (a) the difference  $\rho_i$  being small in comparison with  $\rho$  or  $\rho_0$ , (b) rapid variation in  $\rho_i$  with temperature so that small errors in the temperature measurement cause much larger apparent errors in  $\rho_i$ , (c) Matthiessen's rule  $\rho = \rho_0 + \rho_i$ , not being strictly valid.

#### *Thermal resistivity*

The major uncertainty in determining the temperature variation of thermal conductivity lies in the measurement of the difference in temperature of the gas thermometers,  $\Delta T$ , or more precisely, of their pressure difference,  $\Delta P$ . This latter quantity (5 to 10 mm oil) was measured with an accuracy of about  $\pm 0.02$  mm. A slow drift in the temperature of the cryostat will affect  $\Delta T$  and hence  $\Delta P$  markedly, but our methods of temperature control seem to avoid this. The electrical power dissipated in the specimen heater is measured to considerably better than 1/10%, but the radiation heat losses were sometimes appreciable at around 100 °K. When calculating the thermal conductivity a radiation correction was applied which often amounted to 2 or 3% at 100 °K, but was itself not very accurately known. Errors in the radiation correction are probably most serious in poor conductors to which end contacts are made only with some difficulty, because then there is considerable uncertainty in the temperature of the heater. Conduction losses through the vacuum and along the thermometer and electrical connexions to the specimen were kept well below 1% of the heat flow along the specimen at all temperatures. Altogether the errors in  $\lambda$  should not be more than 1% below 100 °K but may be 2 or 3% at 150 °K.



TABLE 1. DETAILS OF SPECIMENS

no.	source	purity (%)	diam. (mm)	$10^3 \rho_0$ $\rho_{295}$	$\rho_{i(295)}$ ( $\mu\Omega$ cm)	$10^8 L_0$ ( $W\Omega$ deg $^{-2}$ )	treatment	ref.
Ti1	JM4233	98	3	330	47	3	ann. vac. 950 °C	A
Ti2	Heraeus	high	2.6 × 0.1	68.5	42.7	—	ann. vac. 700 °C	—
Ti3	Winegard	99.99	1.6 × 3.1	45.6	43.1	2.7 <sub>4</sub>	ann. vac. (10 <sup>-6</sup> , 60 h) 800 °C	—
Ti4	Winegard	99.99	1.6 × 3.1	60.9	43.8	2.8 <sub>1</sub>	as rolled	—
Ti5	Winegard	99.99	4.9 × 3.1	54.7	43.2	3.1 <sub>4</sub>	ann. vac. (10 <sup>-6</sup> , 60 h) 800 °C	—
Zr1	JM5000	99.99	3	50	45	2.4	ann. vac. 750 °C	A
Zr2	Mackay	iodide bar	3.8 × 1.9	45.3	47	—	as received and cut	—
Zr3	Betterton	99.9 <sub>5</sub>	0.6	5.96	42.4	—	ann. vac. (10 <sup>-6</sup> )	—
Zr4	Betterton	99.9 <sub>5</sub>	0.6 (× 4)	see text	—	2.45*	ann. vac. (10 <sup>-6</sup> )	—
Zr4a	Betterton	99.9 <sub>5</sub>	0.6 (× 4)	see text	—	2.45*	ann. vac. (10 <sup>-6</sup> )	—
Hf1	Footc	see below	1.5 × 5	116.5	32.3	3.4	ann. vac. 750 °C	B
Hf2	Betterton	99.9	0.4	52.7	30.9	—	ann. vac. 1000 °C	—
Hf3	Betterton	96 + 4 wt % Zr	0.64	85.2	34.0	—	ann. vac. 1000 °C	—
V1	Mackay	99.7	see below	129	(20.8)†	—	as received and rolled	B
V2	Electro	99.9	3.55	135	19.8 <sub>5</sub>	2.57	as received	B
V4	Electro	99.9	3.55	196	18.9	2.85	ann. vac. 1300 °C	B
Nb1	Mackay	?	3 × 1.5	156	(13.9)†	—	as received	B
Nb2	JM10230	99.7 + 0.3 % Ta	4.7	350	14.5	—	as received	B
Nb3	Fansteel	99.9	0.5	30	14.5 <sub>6</sub>	—	drawn, ann. vac. (to m.p.)	B
Nb5	Fansteel	99.9	1.59	31.7	14.4 <sub>4</sub>	2.49	drawn	B
Ta1	Heraeus	high	2.9 × 0.11	65	13.2	—	ann. vac. 700 °C	—
Ta2	Fansteel	99.9	0.56	13	12.9	—	ann. vac. 2500 °C	—
Ta3	Fansteel	99.9	1.5 (× 4)	16.1	12.9 <sub>5</sub>	2.45	ann. vac. 2500 °C	—
Cr1	A.R.L.	99.99 <sub>8</sub>	3	19.7	—	2.35	cold worked (ductile)	C
Cr2	A.R.L.	99.99 <sub>8</sub>	3	14.0	—	2.44	no. 1 ann. vac. 1050 °C	C
Cr3	A.R.L.	99.99 <sub>8</sub>	3	9.65	12.9	2.53	partially recryst.	C
Cr4	A.R.L.	99.99 <sub>8</sub>	3	6.95	—	2.48	no. 3 ann. vac. 1050 °C	C
Cr5	A.R.L.	99.99 <sub>8</sub>	3	4.24	12.9 <sub>5</sub>	2.44	fully recryst.	C
Mo1	Mackay	99.9	0.77	36	(5.55)†	—	ann. vac. 1350 °C	—
Mo2	Mackay	99.9	0.77	45.1	5.3 <sub>2</sub>	—	as received	—
Mo3	Mackay	99.9	1.33	40.2	5.3 <sub>4</sub>	—	as received	—
W1a	JM3610	99.98	4	5.5	5.35	—	ann. vac. 1350 °C	D
W1b	JM3610	99.98	4	5.9	5.31	2.65	ann. vac. 1350 °C	D
W2	JM3610	99.98	1	8.6	(5.58)†	—	electropol., ann. 1350 °C vac.	D
Mn1	Mackay	99.99	~ 3 × 0.7	112	137‡	—	ann. vac. 600 °C	E
Mn2	JM10792	99.99	~ 3 × 1.1	870	$\rho = 378‡$	30	as received	E
Mn3	JM10792	99.99	~ 3.3 × 1.4	73	144‡	3	ann. vac. 600 °C	E
Tc	—	—	—	—	—	—	—	—
Re1	Mackay	99.5	10 × 0.75	40.1	18.8	2.56	as rolled	C
Re2	Mackay	99.5	10 × 0.75	24.6	18.65	2.63	ann. vac. 700 °C	C
Re3	Mackay	99.5	2 × 0.7	27	(19.5)†	—	ann. vac. 700 °C	C
Re4	Hulm	99.99	6	0.737	(18.9)†	2.43	arc melted	C
Re5	Chase	?	0.25	2.77	18.6	—	ann. vac. to m.p.	—
Fe1	JM5092	99.99	2	24.6	9.85	2.50	ann. vac. 750 °C	A
Fe2	Vacuum	> 99.97	1 × 0.5	9.61	9.82	—	ann. see below	—
Ru2	Baker	~ 99.99	~ 6	27.7	(8.27)§	2.40	arc melting	F
Ru3	Baker	~ 99.99	~ 5	2.14	(7.37)§	2.46	arc melting	F
Os2	JM	~ 99.99	6	10.8	(9.13)§	2.60	arc melting	F
Os3	Baker	~ 99.99	1.88	9.46	9.13	2.61	arc melting	F

## RESISTIVITY OF TRANSITION ELEMENTS

281

TABLE 1 (*cont.*)

no.	source	purity (%)	diam. (mm)	$\frac{10^3 \rho_0}{\rho_{295}}$	$\rho_{i(295)}$ ( $\mu\Omega$ cm)	$10^8 L_0$ ( $W\Omega \text{ deg}^{-2}$ )	treatment	ref.
Co 1a	JM9484	99.999	2	15.3	5.82	—	ann. vac. 700 °C	D
Co 1b	JM9484	99.999	2	15.5	5.78	2.55	ann. vac. 700 °C	D
Co 2	JM9484	99.999	0.5	11.0	(5.67)†	—	ann. vac. 800 °C	—
Rh 1	Baker	> 99.9	1.5	83	4.80	2.73	ann. vac. 1050 °C	H
Rh 2	JM8208	99.997	1.5	1.75	4.78	2.41	ann. vac. 1050 °C	H
Ir 2	JM	99.98	2.0	20.2	5.01	2.50	ann. vac. 1300 °C	H
Ni 1	JM4497	> 99.99	2	4.81	7.30	2.38	ann. vac. 750 °C	A
Ni 2	JM10389	99.997	2	3.23	7.04	—	ann. vac. 800 °C	—
Ni 3	JM10389	99.997	0.63	4.51	(7.33)†	—	ann. vac. 800 °C	—
Pd 6	JM2928	99.995	2	1.75	10.6	2.48	ann. vac. 450 °C	G
Pd 7	JM2928	99.995	0.19	4.0	10.6	—	ann. vac. 450 °C	—
Pd 8	JM2928	99.995	0.19	15.7	(10.34)†	—	ann. vac. 500 °C	—
Pd 9	JM9401	99.999	0.28	1.73	(10.84)†	—	ann. vac. 900 °C	—
Pt 1	Baker	99.99	1.5	1.20	(10.3)†	2.35	ann. vac. 1050 °C	H
Pt 2	Baker	99.99	0.5	5.45	(10.8)†	—	ann. vac. 1050 °C	H
Pt-T 4	Morrison	?	~0.1	0.406	(?)†	—	thermometer	—
Pt 3	Baker	99.99	0.8	1.73	10.42	—	ann. vac. 1050 °C	—
Compare								
Cu 2	JM	99.999	2	~3	—	—	ann. vac. 550 °C	I
Cu A	ASARCO	99.999	0.1	1.62	1.55	—	ann. vac. 530 °C	—
Ag 2	JM	99.999	2	~0.5	—	—	ann. vac. 650 °C	J
Ag 4	JM	99.999	1.16	~1	—	—	ann. vac. 650 °C	J
Ag A	JM	99.999	0.2	3.83	1.47	—	ann. vac. 530 °C	—
Au A	JM	99.999	0.13	3.17	2.01	—	ann. vac. 530 °C	—
Au 4	JM	99.999	1.5	~3	—	—	ann. vac. 700 °C	K
Na	See Macdonald, White & Woods 1956; Berman & MacDonald 1951; Powell & Blanpied 1954; Bradshaw & Pearson 1956							

\* As values of  $\rho$  taken for Zr4, 4a were unreproducible,  $\rho_0$  was taken for Zr3 and  $\lambda_0/T$  for Zr4 and Zr4a (both the same to within 1%) and thus  $L = \rho_0 \lambda_0 / T$  obtained. Later Zr4a was unclamped and measurements of  $\rho_0$  on individual wires were found to be within 2% of values for Zr3.

† Owing to slight uncertainty  $l/A$ , resistivity values were later normalized assuming a value of  $\rho_{i(295)}$  from the other specimens of more accurately known cross-section and length.

‡ Absolute values are very uncertain, see text.

§ Absolute values obtained by subsequent grinding of specimen to regular shape and redetermining  $\rho(295)$ ,  $\rho(4.2)$ .

|| Owing to uncertainty in the diameter of these very fine wires, resistivity values were normalized using values of  $\rho_{i(273)}$  from review by Gerritsen (1956).

Under 'source' the commercial suppliers listed are: 'JM' for Johnson Matthey Ltd (London), 'Mackay' for A.D. MacKay Inc. (New York), 'Electro' for Electro Metallurgical Company (Niagara Falls, N.Y.), 'Fansteel' for Fansteel Metallurgical Corporation (Illinois), 'Chase' for Chase Brass and Copper Company (Connecticut), 'Vacuum' for Vacuum Metals Company (Massachusetts), 'Baker' for Baker Platinum Company (New Jersey), ASARCO for American Smelting and Refining Company (New York).

References: (A) Kemp, Klemens & White (1956); (B) White & Woods (1957d); (C) Harper, Kemp, Klemens, Tainsh & White (1957); (D) White & Woods (1957c); (E) White & Woods (1957b); (F) White & Woods (1958); (G) Kemp, Klemens, Sreedhar & White (1955); (H) White & Woods (1957a); (I) White (1953c); (J) White (1953b); (K) White (1953a).

## 2.3. Specimens

The specimens are listed in table 1 together with details of source, purity, dimensions, ratio of residual electrical resistance to room-temperature resistance, the 'ideal' electrical resistivity at room temperature, the value of the Lorenz ratio,  $L_0 = \rho_0 / W_0 T$ , obtained at very low temperatures, treatment and references to any earlier reports of these measurements.

In addition to the sources listed in table 1, others to whom we are particularly grateful for their kind gifts or loans of samples are:

W. C. Heraeus GmbH of Hanau, West Germany; Dr W. C. Winegard of the Metallurgy Department of the University of Toronto; Dr J. O. Betterton Jr of the Oak Ridge National Laboratory (Tennessee); Foote Mineral Company of Pennsylvania (gift of hafnium arranged through the kindness of the Pittsburgh area office of the United States A.E.C.); Dr J. K. Hulm of the Westinghouse Research Laboratories; Dr J. A. Morrison of the Division of Pure Chemistry, N.R.C. (Ottawa) and finally the Aeronautical Research Laboratories (A.R.L.) of the Commonwealth of Australia, who through the kindness of Dr H. L. Wain supplied high purity chromium to one of the authors (G. K. W.) and his colleagues at the C.S.I.R.O. Division of Physics, Sydney.

Specimens were generally about 6 to 8 cm long, although some manganese, zirconium and titanium specimens were shorter. Lateral dimensions, i.e. diameter or lengths of sides of rectangular section specimens, are listed in the table. Specimens Zr 4 and Ta 3 were each composed of four wires, placed side by side to form rods.

Copper end-pieces and potential leads (usually 0.030 in. diam. copper wires) were attached to the specimens with a non-superconducting solder, i.e. Zn + Cd eutectic or Bi + Cd eutectic solders, except where otherwise stated below. These solders were used so that small changes in the effective point of contact of the potential leads did not occur due to a superconducting layer on the specimen surface when the specimen was cooled to liquid-helium temperatures.

Further details of purity and method of mounting are given in the appendix for those specimens not adequately represented by the brief details in table 1 and not previously reported in the references listed there.

### 3. EXPERIMENTAL RESULTS

#### 3.1. *Electrical resistivity*

The measured resistivity,  $\rho$ , increases approximately linearly with temperature above about 100 °K except for the elements V, Cr, Mn and Fe, Ni, Co. At low temperature it approaches a constant value  $\rho_0$ .

In so far as the analysis of our results is concerned, we shall assume Matthiessen's rule is valid and that therefore

$$\rho_i = \rho - \rho_0$$

represents adequately the ideal resistivity due to scattering by thermal vibrations. Only in the case of niobium, owing to its high superconducting transition temperature ( $T_c \simeq 9.2$  °K), is there appreciable uncertainty in the value of  $\rho_0$ .

In table 1 values are given of  $\rho_i$  at room temperature and also of the ratio  $\rho_0/\rho_{295}$ . This ratio is a measure of the purity of the sample; in most instances we have been able to secure specimens for which  $\rho_0$  is 100 to 1000 times smaller than  $\rho_{295}$ . Low values of  $\rho_0$  make it possible to study the temperature variation of  $\rho$  down to fairly low temperatures while the component  $\rho_i$  still remains an appreciable fraction of  $\rho$ .

Figures 1, 2 and 3 illustrate the behaviour of the resistivity of nine elements from the transition group over part of the temperature range below about 300 °K. The curve for

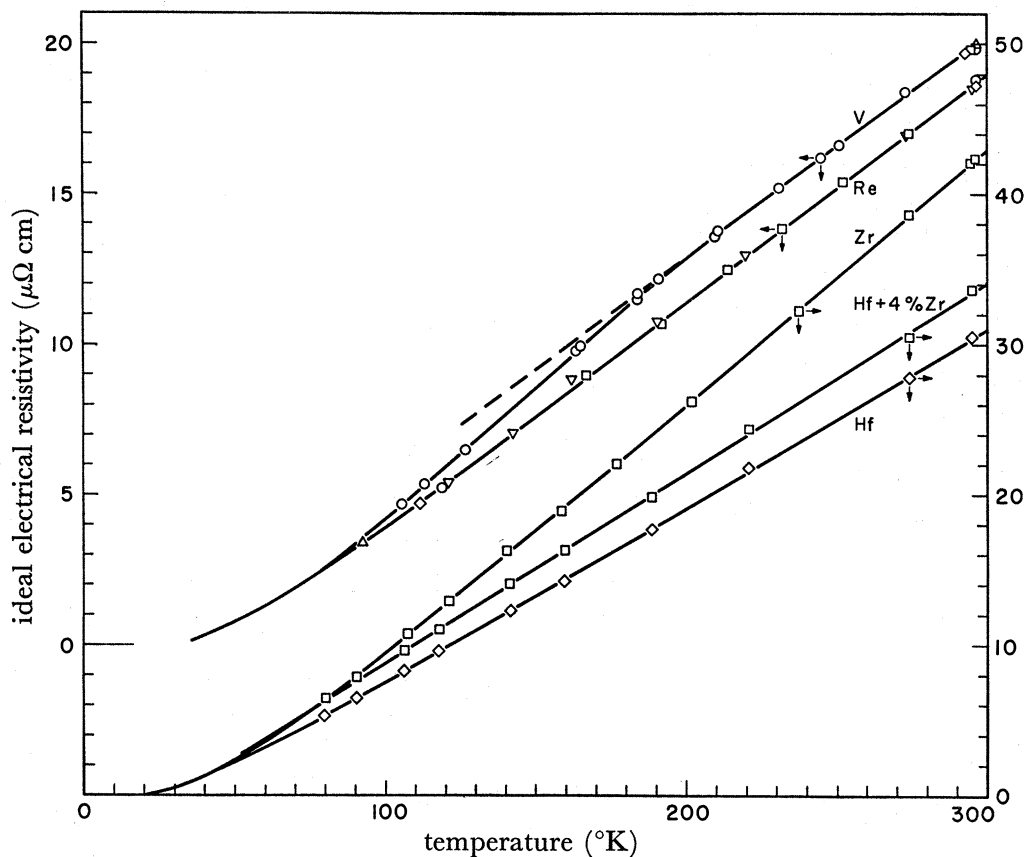


FIGURE 1. Ideal electrical resistivity of rhenium, vanadium, zirconium, hafnium and hafnium + 4 wt. % Zr. Specimens:  $\circ$ , 1;  $\diamond$ , 2;  $\square$ , 3;  $\triangle$ , 4;  $\nabla$ , 5.

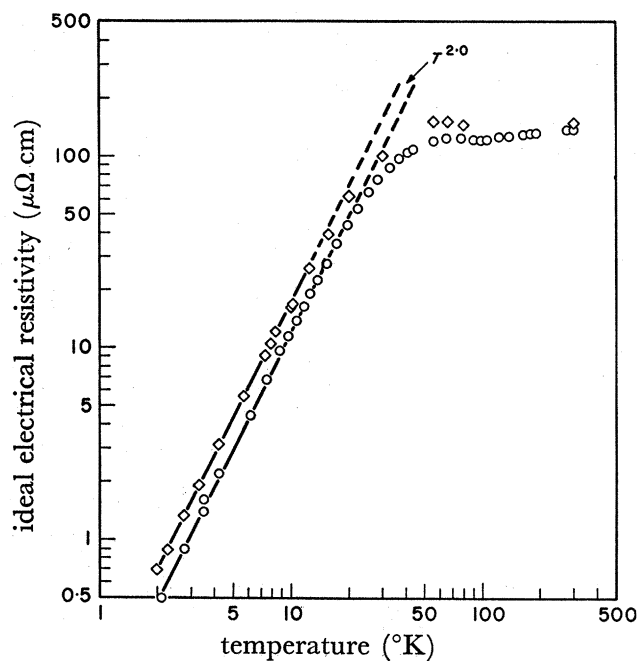


FIGURE 2. Ideal electrical resistivity of  $\alpha$ -manganese.  $\circ$ , Mn 1 ( $\rho_0 \approx 16.8 \times 10^{-6} \Omega \text{ cm}$ );  $\diamond$ , Mn 2 ( $\rho_0 \approx 11.3 \times 10^{-6} \Omega \text{ cm}$ ).



rhodium included in figure 1 is, superficially at least, typical of those obtained for the other transition metals and also for copper, silver and gold. The other curves shown here exhibit features peculiar to the metals for which they are drawn. For vanadium a change in slope occurs below about 200 °K. We observed that for both hafnium and zirconium the values of  $\rho_i$  for high-purity samples appeared to be noticeably less than for some earlier impure specimens. This apparent departure from Matthiessen's rule is illustrated in figure 1 by hafnium (pure) and hafnium plus 4 wt. % zirconium (Hf+8 at. % Zr) specimens.

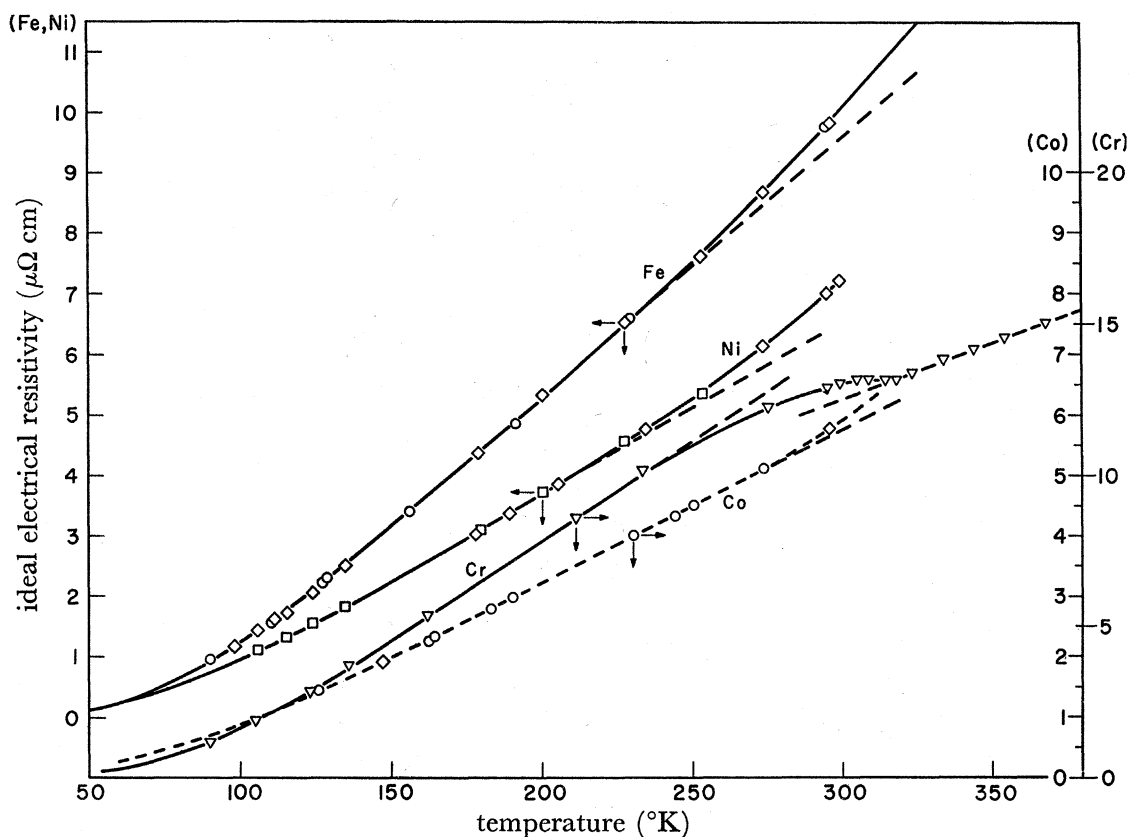


FIGURE 3. Ideal electrical resistivity of chromium, iron, nickel and cobalt.  $\circ$ , 1;  $\diamond$ , 2;  $\square$ , 3;  $\nabla$ , 5.

In figure 2 values of  $\rho_i$  for  $\alpha$ -manganese are shown on a logarithmic plot; in figure 3,  $\rho_i$  is shown for chromium with its peculiar flattening (see Sully (1955) for previous observations of this) at room temperature and for the three ferromagnetic elements for each of which  $\rho_i$  rises faster than linearly with temperature at normal temperatures.

For these and other elements, we have obtained smoothed values (from large-scale graphs) of  $\rho_i$  at various temperatures and recorded them in table 2. This table also includes values of  $\theta_D$ , the electrical resistivity at  $T = \theta_D$  (involving in some cases extrapolation of our data with the aid of earlier measurements, e.g. those of Potter (1941)) and some reduced resistivities, i.e. values of the ratio  $\rho_i/\rho_{\theta}$ , which may be compared with values derived from equations (3) and (7) (see discussion below);  $\rho_{\theta}$  here is the value of the ideal resistivity at a characteristic temperature,  $\theta$ . The values of the Debye characteristic temperature,  $\theta_D$ , calculated from specific heat measurements made in the approximate range  $\theta/2$  to  $\theta$ , i.e. high-temperature values of  $\theta_D$ , have been used here. They were chosen from a study of review articles and compilations of data by Shiffman (1952), Blackman (1955), Keesom &



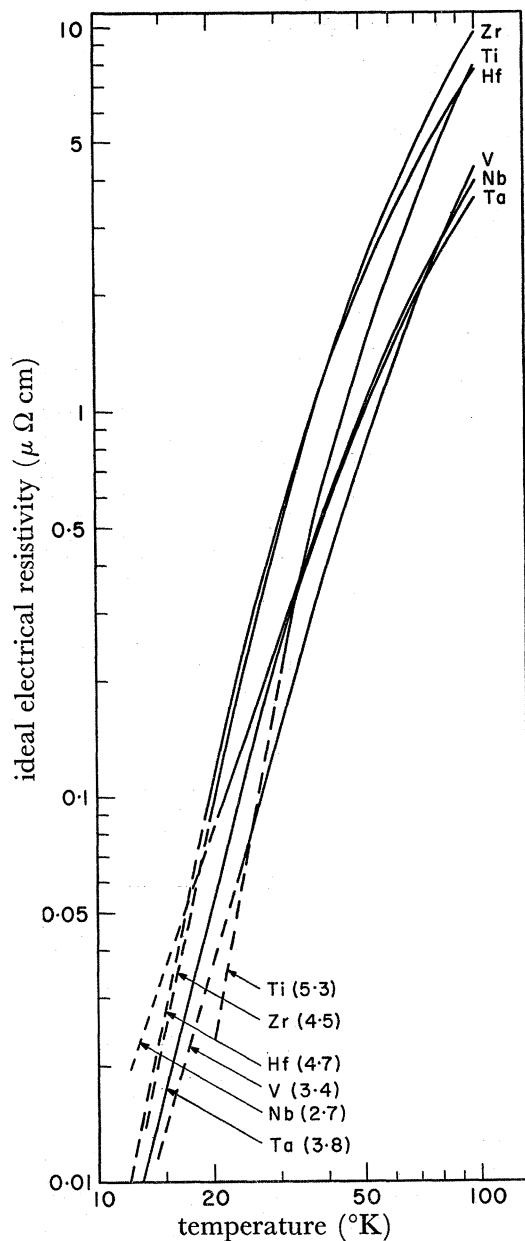


FIGURE 4. Ideal electrical resistivity below 100 °K, of Ti, Zr, Hf, V, Nb, Ta.

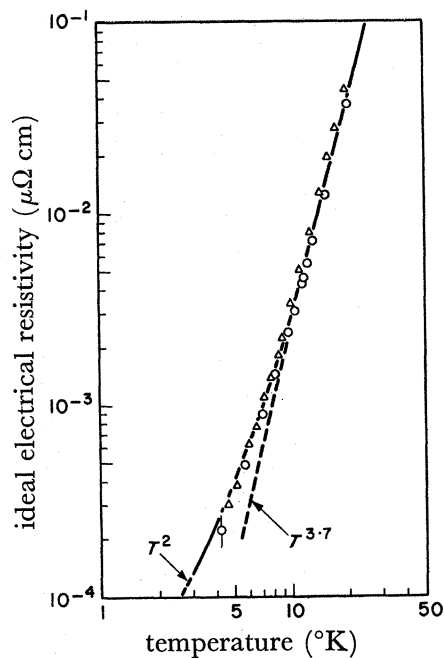


FIGURE 6. Ideal electrical resistivity of platinum below 20 °K: —, de Haas & de Boer (1933);  $\Delta$ , Pt 2;  $\circ$ , Pt-T4.

TABLE 3. INDEX OF  $T$  (IN EXPRESSION  $\rho_i \propto T^m$ ) FOR RANGE  $\theta/20 < T < \theta/10$ , AND APPROXIMATE LOWER LIMIT OF OBSERVATION IN BRACKETS

Ti	5.3 (> 15 °K)	Zr	4.5 (> 13 °K)	Hf	4.7 (> 10 °K)
V	3.4 (> 12 °K)	Nb	2.7 (figure 5)	Ta	3.8 (> 8 °K)
Cr	3.2 (> 15 °K)	Mo	5.1 (> 20 °K)	W	4.0 (figure 5)
Mn	2.0 (figure 2)	Tc	—	Re	4.6 (> 10 °K)
Fe	3.3 (figure 5)	Ru	4.7 (> 25 °K)	Os	4.7 (> 25 °K)
Co	3.3 (figure 5)	Rh	4.6 (> 20 °K)	Ir	4.7 (> 12 °K)
Ni	3.1 (figure 5)	Pd	3.2 (figure 5)	Pt	3.7 (figure 6)
Cu	5.1 (> 10 °K)	Ag	4.7 (> 10 °K)	Au	5.1 (> 10 °K)
Na	5.0 for $T > 8$ °K, 6.0 for $T < 8$ °K (See Woods 1956)				

Pearlman (1956), Bijl (1957) and some of the original references listed by these authors. Unfortunately, there is a dearth of specific heat data for niobium, ruthenium and osmium at other than very low temperatures and we believe the values of  $\theta_D$  for these elements are least reliable.

In each column of table 2, the numbers printed in italics represent the region where the residual resistivity for the purest specimen examined is comparable with the ideal resistivity, thus below this entry,  $\rho_i < \rho_0$ .

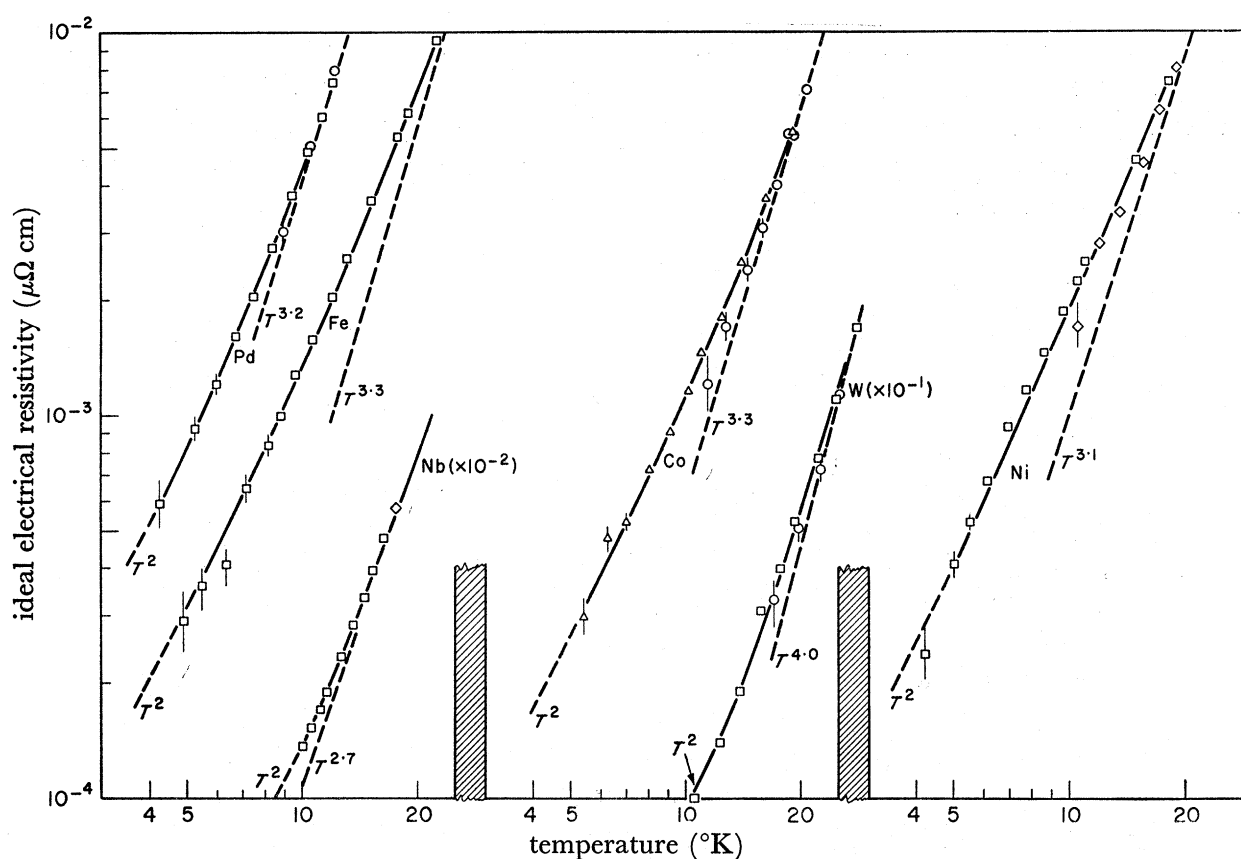


FIGURE 5. Ideal electrical resistivities below 20 °K for those elements (excepting Pt, Mn) for which  $\rho$  appears to follow a  $T^2$  law at very low temperatures, namely, Nb ( $\square$ , 3); W ( $\circ$ , 1;  $\square$ , 2); Fe ( $\square$ , 2); Co ( $\circ$ , 1;  $\triangle$ , 2); Ni ( $\diamond$ , 2;  $\square$ , 3); Pd ( $\circ$ , 8;  $\square$ , 9).

Examples of the differing behaviour of  $\rho_i$  below 100 °K for some of the elements are shown in figure 4; bracketed numbers beside the symbols for the elements denote the index of  $T$  or power law which  $\rho_i$  appears to follow in the region from about  $\theta_D/10$  to  $\theta_D/20$ . These indices are summarized in table 3. In some instances, notably Mn, Fe, Co, Ni, Pd, W, Pt and perhaps Nb, there is evidence that at the lowest temperatures this index decreases. Thus it appears that  $\rho_i$  may be proportional to  $T^2$  at the lowest temperatures in these elements. The case of niobium is most doubtful as no very precise figure for  $\rho_0$  can be obtained, since niobium becomes superconducting at about 9.2 °K and the measured resistivity has not become quite constant at this temperature. Analyses of the electrical resistivity of niobium below 15 °K show that it may be represented quite well by either an expression  $A + BT^2 + CT^5$  or  $A + BT^3$ , the values of  $A$  (and hence  $\rho_0$ ) differing slightly in the two cases. If we assume



an  $A + BT^2 + CT^5$  analysis is correct, then  $\rho_i$  for Nb is shown in figure 5. The ideal electrical resistivity below 25 °K for the other elements which exhibit this tendency to a  $T^2$  behaviour is shown in figures 5 and 6.

The approximate magnitudes of the  $T^2$  term in  $\mu\Omega\text{cm}$  units are as follows:

$$\begin{array}{lll} \text{Mn } (0.15 T^2), & \text{Nb } (140 \times 10^{-6} T^2), & \text{W } (10 \times 10^{-6} T^2), \\ \text{Fe } (13 \times 10^{-6} T^2), & \text{Co } (13 \times 10^{-6} T^2), & \text{Ni } (16 \times 10^{-6} T^2), \\ \text{Pd } (33 \times 10^{-6} T^2), & \text{Pt } (14 \times 10^{-6} T^2). \end{array}$$

Whether this apparent  $T^2$  dependence does exist in other elements is difficult to say, as many of them were not of ideal geometrical form, i.e. were not fine wires, nor of sufficiently high purity to allow accurate observations of  $\rho_i$  at very low temperatures. However, in pure zirconium and pure rhenium, such a dependence should have been observed if it was as large as that in the above metals.

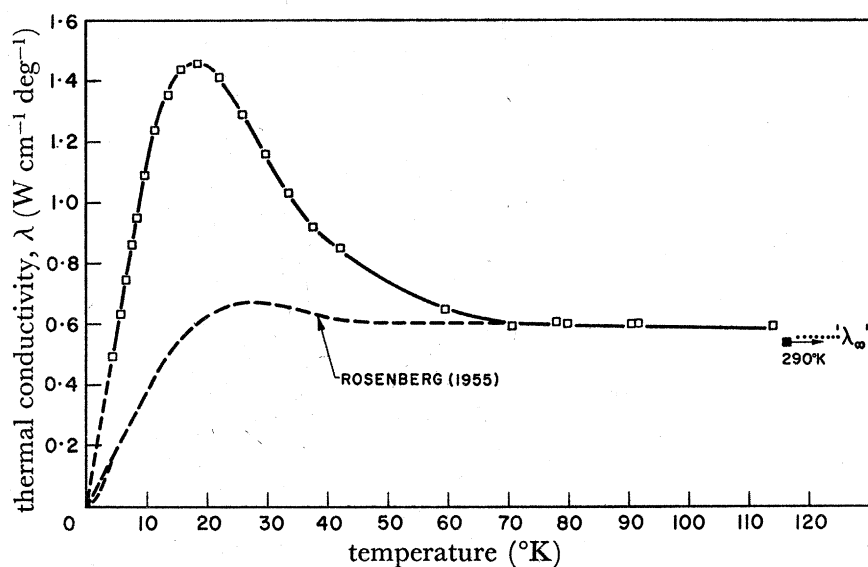


FIGURE 7. Thermal conductivity of tantalum: □, Ta 3; ■, Barratt & Winter (1925); ..., ' $\lambda_\infty$ ' =  $LT/\rho$ .

### 3.2. Thermal resistivity

The thermal conductivity,  $\lambda$ , of metallic elements generally follows a familiar pattern; it rises linearly with temperature at the lowest temperatures, passes through a maximum and becomes fairly constant above about 100 °K. The behaviour for tantalum (figure 7) is rather typical although the maximum is much smaller in magnitude than those observed (see figures in earlier reports of this work) in the higher purity specimens—Cr, W, Re, Ru, Rh, Ni, etc. At the lowest temperatures  $\rho\lambda/T$  is constant and has the values indicated by  $L_0$  in table 1. Experimental values of  $L_0 = \rho_0\lambda_0/T \equiv \rho_0/W_0T$  (equation (2)) appear to be quite close to the theoretical Lorenz ratio of  $2.45 \times 10^{-8} \text{W}\Omega\text{deg}^{-2}$  except in rather impure specimens—Ti, Hf, V and Mn—for which the ratio is appreciably greater.

The variation of thermal conductivity with temperature is shown in figure 8 for titanium and zirconium (not previously published), and the more unusual behaviour for manganese is illustrated in figure 9.

As in the electrical case, we may assume that Matthiessen's rule is valid and deduce values from experimental data for

$$W_i(T) = W(T) - W_0(T),$$

where

$$W_0 = A/T \quad \text{and} \quad W(T) = 1/\lambda(T).$$

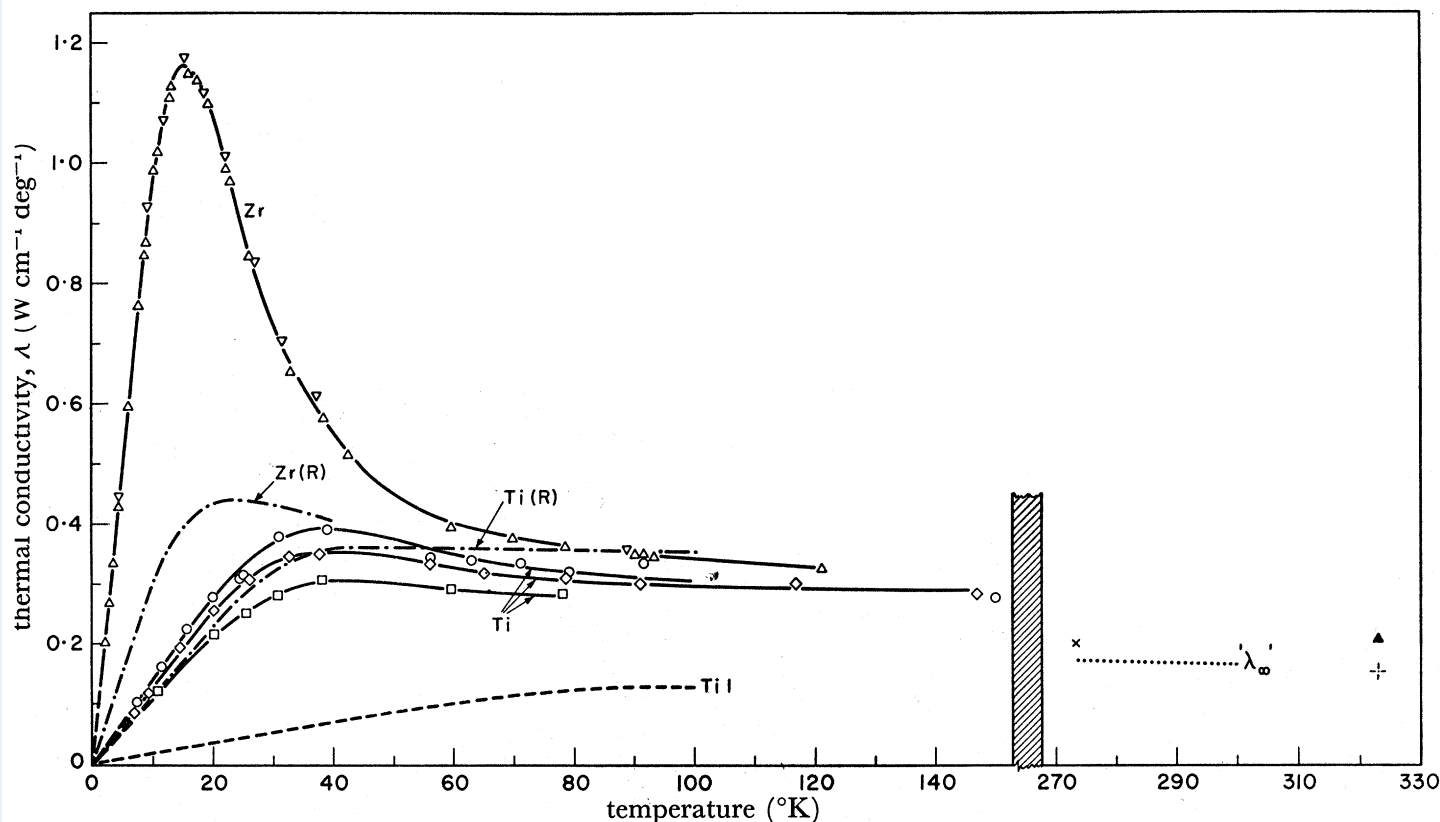


FIGURE 8. Thermal conductivity of titanium and zirconium. (R) signifies Rosenberg (1955) and ' $\lambda_{\infty} = LT/\rho$ '.  $\circ$ , Ti 3;  $\square$ , Ti 4;  $\diamond$ , Ti 5;  $\triangle$ , Zr 4;  $\nabla$ , Zr 4a;  $+$ , Ti (Silverman 1953);  $\times$ , Ti (Rigney & Bockstahler 1951);  $\blacktriangle$ , Zr (Deem 1953a, also Bing *et al.* 1951).

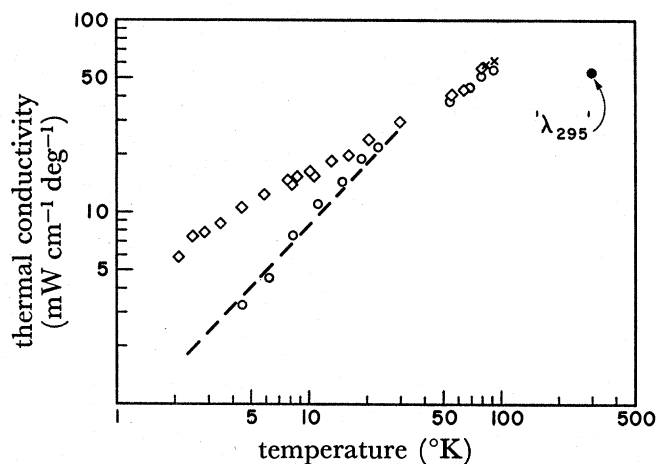


FIGURE 9. Thermal conductivity of manganese.  $\circ$ , Mn 2; —, Rosenberg (1955);  $\diamond$ , Mn 3;  $\times$ , Reddemann 1935 ( $\beta$ -Mn);  $\bullet$ , ' $\lambda_{295} = LT/\rho$ '.

Typical behaviour of  $W_i(T)$  is shown by curves in figure 10, the data for these being taken from our low-temperature values of thermal conductivity and extrapolated (usually from above 100 or 150 °K) to room temperature using data given by Powell & Blanpied (1954). For most metallic elements which are relatively good electrical conductors, such as Na, Cu,

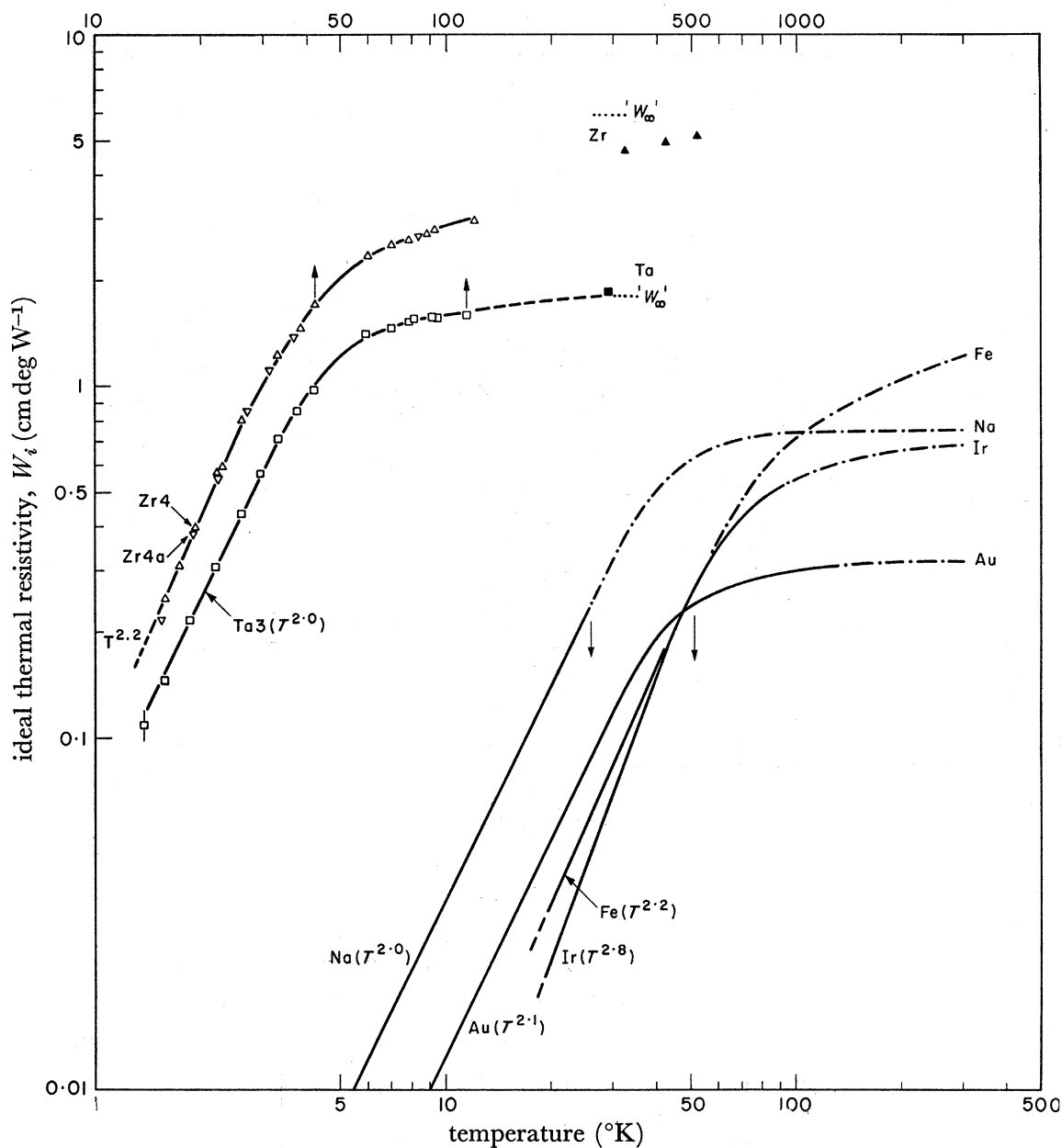


FIGURE 10. Ideal thermal resistivity of Fe, Ir, Na, Au, Ta and Zr. ' $W_\infty$ ' =  $\rho/LT$ . ■, Ta (Barratt & Winter 1925); ▲, Zr (from Deem 1953*a*, or Bing *et al.* 1951); —·—, extrapolation using experimental data of earlier workers (see Powell & Blanpied 1954).

Au and also Pt, Pd, Ir and Mo, the ideal resistivity  $W_i$  becomes fairly constant for  $T \geq \theta/2$ , appearing to approach an asymptotic value,  $W_\infty$ .  $W_\infty$  generally lies close (see table 5) to the value given by the W.-F.-L. relation

$$\rho/W_\infty T = 2.45 \times 10^{-8} \text{ W } \Omega \text{ deg}^{-2} \quad \text{for } T \geq \theta_D.$$

## RESISTIVITY OF TRANSITION ELEMENTS

291

For ferromagnetic elements, however,  $W_i$  continues to increase with temperature at higher temperatures; the curve for iron, shown in figure 10, illustrates this.

Also for elements which are rather poor conductors, e.g. titanium and zirconium, values of  $W_i$  obtained at temperatures near  $\theta_D/2$  are still much smaller than the values of  $W_\infty$  given by the W.-F.-L. law or than those obtained from the few measurements of heat conductivity at and above room temperature. We suggest below that lattice heat conduction may make an appreciable contribution at 100 °K or less which would result in the values deduced for  $W_i$  being appreciably lower than if only electronic conduction was present.

TABLE 4. IDEAL THERMAL RESISTIVITIES (CM DEG/W)

element	$W_\infty = W_{295}$	$W_{140}$	$W_{110}$	$W_{80}$	$W_{60}$	$W_{40}$	$W_{30}$	$W_{20}$	$W_{10}$	$C^\dagger$	$C$ (Rosenberg)	$n$ (index)
Ti	5.0	3.0	2.6 <sub>5</sub>	2.3	1.8*	0.9 <sub>6</sub>	0.4 <sub>9</sub>	—	—	≈ 15	~ 100	≈ 2.3
Zr	4.8	—	2.9 <sub>5</sub>	2.6 <sub>5</sub>	2.3 <sub>5</sub>	1.6 <sub>0</sub>	1.0*	0.43	—	14.8	16.4	2.2
Hf	4.5	—	—	2.5	2.0*	1.2	0.7 <sub>5</sub>	—	—	9	—	—
V	2.8	—	2.3	2.0	1.6*	0.75	0.36	—	—	24	~ 60	2.4
Nb	1.9	—	1.7 <sub>5</sub>	1.6	1.3 <sub>5</sub>	0.8 <sub>2</sub> *	0.4 <sub>7</sub>	0.2 <sub>2</sub>	—	18	16.5	1.9
Ta	1.8 <sub>5</sub>	—	1.6	1.5 <sub>4</sub>	1.4 <sub>0</sub>	0.9 <sub>4</sub>	0.5 <sub>8</sub> *	0.25 <sub>5</sub>	—	18.4	22.6	2.0
Cr	1.1 <sub>6</sub>	0.7 <sub>1</sub>	0.6 <sub>2</sub>	0.4 <sub>3</sub>	0.3 <sub>5</sub>	0.1 <sub>6</sub>	0.0 <sub>3</sub>	0.04 <sub>5</sub> *	—	20	—	1.8
Mo	0.69	0.63	0.55	0.40	0.27*	0.11 <sub>5</sub>	0.06	—	—	15.2	15.7	2
W	0.59 <sub>5</sub>	0.5 <sub>0</sub>	0.47	0.40	0.32	0.13 <sub>5</sub>	0.06 <sub>4</sub> *	0.02 <sub>2</sub>	—	11.9	15.5	2.6
Mn, Tc	—	—	—	—	—	—	—	—	—	—	—	—
Re	2.6	—	1.7	1.5	1.2	0.65	0.34	0.09*	—	10	—	3.0
Fe	1.2 <sub>2</sub>	0.9 <sub>3</sub>	0.80	0.60	0.38*	0.16	0.08 <sub>6</sub>	0.03 <sub>5</sub>	—	13.1	13	2.2
Ru	1.0	0.7 <sub>8</sub>	0.71	0.55	0.33	0.09 <sub>5</sub>	0.03 <sub>7</sub> *	0.01	—	20	—	3.3
Os	1.2 <sub>5</sub>	0.9 <sub>0</sub>	0.86	0.70	0.50	0.18 <sub>5</sub> *	0.08 <sub>5</sub> *	—	—	14.8	—	2.7
Co	0.8	0.66	0.60	0.47	0.34	0.16 <sub>5</sub>	0.09 <sub>4</sub> *	0.04 <sub>2</sub>	—	18.8	19	2.0
Rh	0.66	0.62	0.57	0.42	0.26	0.08 <sub>5</sub>	0.035*	0.01	—	9	19.8	3.0
Ir	0.68 <sub>5</sub>	0.62	0.57	0.48	0.36	0.15*	0.07 <sub>1</sub>	0.02 <sub>2</sub>	—	9.3	6	2.8
Ni	1.1	0.74	0.65	0.50	0.36	0.18	0.10 <sub>5</sub> *	0.04 <sub>7</sub>	—	15.9	14.4	2.0
Pd	1.4	1.35	1.3	1.2	1.0	0.57	0.33	0.14 <sub>5</sub> *	0.03 <sub>6</sub>	22	25	2.0
Pt	1.4	—	1.3	1.2	1.0 <sub>5</sub>	0.70	0.45	0.19 <sub>5</sub> *	0.04 <sub>5</sub>	17.8	15.6	2.1
compare												
Cu	0.24	0.22	0.20 <sub>5</sub>	0.17	0.11 <sub>5</sub>	0.050	0.026	0.010*	0.002	11.3	10	2.4
Ag	0.23	0.22	0.22	0.21	0.17 <sub>5</sub>	0.095	0.05 <sub>0</sub>	0.019*	0.003 <sub>5</sub>	10	11.5	2.4
Au	0.32	0.31	0.30	0.29	0.26	0.19 <sub>5</sub>	0.12	0.053*	0.013	14.1	20	2.1
Na	0.75	0.75	0.75	0.73	0.68	0.51	0.33	0.145	0.036*	12.5	—	2.0

$$\dagger C = \frac{W_i}{W_\infty} \left( \frac{\theta}{T} \right)^2 \text{ at } \theta/10.$$

$\bar{C} \approx 15$        $\bar{C} \approx 16$  (omitting Ti, V)

In table 4 values are listed for  $W_i(T)$  at various temperatures from 140 down to 20 °K; these are taken from curves (for example, figure 10) of our experimental results supplemented by other data (Powell & Blanpied 1954) where available. For molybdenum we have used data from Rosenberg (1955) and Kannuluik (1933). Asterisks in the rows of table 4 locate the temperature regions where the impurity thermal resistivity  $W_0$  ( $\approx A/T$ ) in the purest samples was comparable with  $W_i$ . It may be seen from figure 10 that for  $T \leq \theta_D/10$ , the ideal thermal resistivity may be represented by  $W_i \approx BT^n$  and values of the index  $n$  obtained in the range  $\theta_D/20$  to  $\theta_D/10$  are given in table 4. Generally,  $1.9 \leq n \leq 3.0$  although for ruthenium it appears that  $n \approx 3.3$ . Also values for  $W_\infty$  which are generally taken from heat conductivity measurements made near room temperature on pure samples (see § 1.3) appear in table 4. For Re, Ru, Os and Co we have been obliged to assume that  $W_\infty$  is given by

$$W_\infty \approx \rho/LT \approx \rho_i(295)/2.4_5 \times 10^{-8} \times 295.$$

As we mentioned earlier it is expected theoretically that  $W_i \propto T^{2.0}$  for  $T \leq \theta_D/10$  and there is interest in the relation of the reduced resistivity  $W_i/W_\infty$  to  $T/\theta_D$ . Values for

$$C = \frac{W_i}{W_\infty} \left( \frac{\theta_D}{T} \right)^2 \text{ at a temperature } T = \theta_D/10$$



appear in table 4 as well as values deduced for the temperature region  $T \leq \theta_D/10$  from values of  $B = W_i/T^2$  given by Rosenberg (1955) for a number of these elements. Rosenberg assumed that to a first approximation  $W_i \approx T^2$  at very low temperature, plotted  $WT$  against  $T^3$  and obtained values for  $B$  from the slope of these lines. In cases where we find  $n \approx 2$ , his values of  $C$  lie fairly close to ours, but for materials such as titanium and vanadium, with a high impurity resistivity, the lattice conduction is not negligible compared to the electronic conduction at very low temperatures, and it will strongly affect the temperature dependence of the resistivity and lead to erroneous estimates of the ideal thermal resistivity made in this region.

TABLE 5. PHYSICAL DATA

element	structure	$M$	$\theta_D$ (°K)	$\frac{\rho M \theta \Omega^\dagger}{T}$	$\lambda_{295}$ (expt.) ( $W \text{ cm}^{-1}$ $\text{deg}^{-1}$ )	' $\lambda_{295}$ ' $= LT/\rho$	$\gamma$ ( $10^{-3} \text{ J/mole deg}^2$ )
Ti	h.c.p.	47.9	360	2.3	0.20	0.16 <sub>8</sub>	3.3
Zr	h.c.p.	91.2	250	2.3	0.21	0.17 <sub>1</sub>	3.0
Hf	h.c.p.	178.6	210	2.3	0.22	0.23 <sub>6</sub>	2.6
V	b.c.c.	50.95	390	1.2*	0.36	0.36 <sub>3</sub>	9.0
Nb	b.c.c.	92.9	250	0.8	0.53	0.49 <sub>9</sub>	9.2
Ta	b.c.c.	180.9	230	1.1	0.54	0.55 <sub>2</sub>	5.9
Cr	b.c.c.	52.0	480	1.2*	0.8 <sub>6</sub>	0.56 <sub>0</sub>	1.5
Mo	b.c.c.	95.95	380	0.6	1.4 <sub>5</sub>	1.36	2.1
W	b.c.c.	183.9	315	0.8	1.7	1.36	1.2
Mn	cubic complex	54.9	410	10.7†	—	0.05 <sub>3</sub>	14
Tc	—	(99)	—	—	—	—	—
Re	h.c.p.	186.3	280	2.2	—	0.38 <sub>9</sub>	2
Fe	b.c.c.	55.85	400	0.7‡	0.82	0.73 <sub>8</sub>	5.0
Ru	h.c.p.	101.7	500	1.5	—	0.98 <sub>1</sub>	3.3
Os	h.c.p.	190.2	400	2.2	—	0.79 <sub>2</sub>	2.3
Co	h.c.p.	58.9	380	0.3 <sub>5</sub> ‡	—	1.25	5.0
Rh	f.c.c.	102.9	350	0.5‡	1.51	1.51	4.9
Ir	f.c.c.	193.1	290	0.65	1.46	1.43	3.1
Ni	f.c.c.	58.7	390	0.45‡	0.91	1.03	7.0
Pd	f.c.c.	106.7	295	0.8	0.7	0.68 <sub>5</sub>	9.9
Pt	f.c.c.	195.2	225	0.8 <sub>5</sub>	0.7	0.69 <sub>4</sub>	6.7
Cu	f.c.c.	63.5	310	0.08	4.1	4.25	0.8
Ag	f.c.c.	107.9	220	0.07	4.2	4.49	0.7
Au	f.c.c.	197.2	185	0.12	3.1	3.29	0.7
Na	b.c.c.	23.0	160	0.03	1.3 <sub>5</sub>	1.54	1.4

\* Anomaly in resistivity.

† If a spin disorder term ( $\rho_s \approx 112 \times 10^{-6} \Omega \text{ cm}$ ) is subtracted from  $\rho_i$ , then the parameter has a value of about 1.7.

‡ Ferromagnetic elements.

We have not been able to deduce  $W_i$  values for manganese; and those for titanium, hafnium and vanadium are probably unreliable as the samples were rather impure and the results may be influenced by the presence of lattice conduction.

#### 4. DISCUSSION

##### 4.1. Electrical resistivity

With a few exceptions which we may call *anomalous*, the transition elements exhibit an electrical resistivity which is almost a linear function of temperature from 295 down to  $\sim 100$  °K. Below this  $\rho_i$  falls more rapidly and in the range  $\theta_D/10$  to  $\theta_D/20$ ,  $\rho_i \propto T^m$ , where

$m$  has values in the range 3 to 5, the index 5 being expected if  $\rho_i$  follows a Bloch–Grüneisen relation. The extent to which this relation is obeyed may be judged from the reduced resistivity values in table 2. These show that with the exception of Mn, Co, Ni, Fe, Cr and V (the *anomalous* elements),  $\rho_i$  follows the Bloch–Grüneisen law (using  $\theta = \theta_D$ ) quite well down to about  $\theta_D/3$  and tolerably well to below  $\theta_D/5$ ; marked departures occur below about  $\theta_D/10$  and these are reflected in the variety of values for the index  $m$ . Except perhaps for palladium the  $J_3$  function of equation (7) does not fit the experimental values. In table 2 the values of the reduced resistivity,  $\rho_i/\rho_\theta$ , may be compared with those predicted by the Bloch–Grüneisen (equation (3)) and the Wilson (equation (7)) functions. For  $T/\theta_D = 0.4$ , these predict  $\rho_i/\rho_\theta$  should be 0.30<sub>4</sub> and 0.33, respectively, whereas the mean for all elements listed in table 2 is 0.291 with a mean deviation of  $\pm 0.026$  and the mean for those transition elements which are not *anomalous* is  $0.297 \pm 0.016$ .

For  $T/\theta_D = 0.2$  equations (3) and (7) give 0.068 and 0.094, respectively, whereas the experimental means (all elements) are  $0.066 \pm 0.011$  and (restricted number)  $0.070 \pm 0.009$ .

For  $T/\theta_D = 0.1$ , equations (3) and (7) give 0.0049 and 0.0149, respectively, whereas the experimental means are  $0.0069 \pm 0.0020$  and  $0.0072 \pm 0.0018$ . Values of ideal or intrinsic resistivity at room temperature are believed to be correct to within 1% (excepting manganese for which the irregular form of the flakes did not allow reliable estimates of the geometrical form); generally these agree well with values listed earlier in § 1.3 from previous work, although in some cases earlier values are higher by a small percentage, reflecting the presence of an appreciable impurity resistance in these values. It may be pointed out that many values quoted and reproduced in standard tables, handbooks and textbooks are quite different from those listed in § 1.3 or from those found by us and such values presumably date back to measurements on very impure samples for which there was no knowledge of the impurity resistance.

Turning to the behaviour at temperatures less than  $\theta_D/20$ , the data in table 3 and figures 5 and 6 indicate that  $m$  approaches 2 in the region  $T \leq 10^\circ\text{K}$  for the elements Fe, Co, Ni, Pt, Pd, W and perhaps Nb. de Haas & de Boer (1933) observed this phenomenon for platinum and it was ascribed (Baber 1937) to the effect of electron-electron interactions. Olsen–Bär (1956, see also Mendelsohn 1956) has examined  $\rho_i$  for the elements Fe, Co, Ni, Pt, Pd and Rh below  $25^\circ\text{K}$  and her experimental results also suggest that the index  $m$  has a value close to 2 at sufficiently low temperatures. It may be significant that it is those elements with a high electronic specific heat that exhibit  $\rho_i \propto T^2$  below about  $10^\circ\text{K}$ ; possible exceptions are vanadium and tantalum, but our specimens of these elements did not have suitable purity or dimensions for accurate examination below 15 or  $20^\circ\text{K}$ . Two elements of high room temperature resistivity, zirconium and rhenium, were both examined down to about  $10^\circ\text{K}$ , but showed no evidence of a  $T^2$  term in  $\rho_i$  and it is interesting that neither of these elements have a particularly large electronic specific heat (see values of  $\gamma$  in table 5, taken largely from reviews by Keesom & Pearlman (1956), Bijl (1957) and from Horowitz & Daunt (1953) and Wolcott (1955)). Values of electronic specific heat give direct information concerning the density of states  $N(E)$ , since  $C_{el.} = \gamma T = \text{constant} \times N(E) T$ , where  $N(E)$  is number of electron energy states per unit energy range at the Fermi surface. The differing density of states at the Fermi surface for the overlapping *s*- and *d*-bands should also affect the influence of electron-electron interaction on resistivity and could account for the correlation

between the behaviour of the resistivity at low temperatures and the electronic specific heats.

A similarity of the values of  $\rho_i M\theta^2 \Omega^{\frac{3}{2}}/T$  (see § 1.2) for elements within each group warrants attention. At room temperature iron, cobalt and nickel are well below their ferromagnetic Curie temperatures so that it may be assumed that the *d*-band states with one spin direction are all filled and only about half the *s*-electrons (those with spins parallel to the spins of the empty *d*-band states) may make *s-d* transitions. Hence, we expect  $\rho_i$  at 273 °K for these elements to have only about half the value it would have if they were paramagnetic. Taking account of this and neglecting manganese because of its anomalous behaviour it appears that the values shown in table 5 for  $\rho_i M\theta^2 \Omega^{\frac{3}{2}} T^{-1}$  at 273 °K are approximately the same for the elements within a group. Unfortunately, these data do not give unambiguous information about the number of conduction electrons or the electron energy density functions for these elements, but may be a guide in this direction.

#### *Anomalous elements*

*Vanadium.* Our vanadium specimens were more impure than any of the other specimens we used and it is possible that the change in slope of the curve of  $\rho_i$  against *T* at about 200 °K (figure 2) may be connected with an appreciable oxygen content. While investigating the vanadium-oxygen phase diagram, Rostoker & Yamamoto (1955) measured the resistance of a vanadium bar in the range  $-60$  to  $+20$  °C and observed a small anomaly (similar in form to that in figure 2) at about 240 °K. They suggest that at low temperatures the stable structure may be body centred tetragonal, this being the  $\beta$ -phase which occurs in the *V+O* system at room temperature. It is hoped that high-purity specimens will become available or that we may further purify some rods by electron-bombardment zone-melting and then re-examine this minor anomaly.

*Chromium.* The anomaly previously observed in the electrical resistance at room temperature persists in this high-purity ductile chromium and must be assumed to be associated with the anomalies found in thermoelectric power, expansion coefficient, Young's modulus and in internal friction at 35 to 40 °C (see the book by Sully 1955 on chromium). Recently a very detailed X-ray examination by Straumanis & Weng (1955) has revealed a change in the variation of the lattice constant with temperature at 32.5 °C, corresponding to an expansion coefficient of  $4.4 \times 10^{-6}/^\circ\text{C}$  below 32.5 °C and of  $7.47 \times 10^{-6}/^\circ\text{C}$  above 32.5 °C. Bridgman (1932-33) observed that the resistance anomaly (a plateau with a very shallow minimum at 37 °C in our specimens) shifted to lower temperatures with increase in pressure. Magnetic susceptibility measurements (again see Sully's book) have shown no peculiarity and the weak antiferromagnetic transition observed by Shull & Wilkinson (1953) was at 450 °K.\* Detailed specific heat studies, perhaps a re-examination of magnetic susceptibility of high purity chromium and nuclear resonance studies giving the Knight shift over the range 10 to 50 °C might each help to clarify the situation.

*Manganese.* In comparison with other metals, the resistivity-temperature relation in  $\alpha$ -manganese (see figure 2) appears most peculiar; the resistivity above 100 °K is more than

\* *Note added in proof* (17 December 1958): Dr R. J. Weiss of the Ordnance Materials Research Laboratory, Watertown, Mass. has shown (private communication 1958) that the antiferromagnetic transition occurs in solid chromium (a single crystal) at 38.5 °C.

100  $\mu\Omega\text{cm}$  and decreases quite slowly with temperature, but appears to have a slight minimum at the temperature of the reported antiferromagnetic transition (100 °K by Shull & Wilkinson 1953) and falls rapidly below about 60 °K, finally decreasing as  $T^2$  below about 30 °K. Recently a paper by Mott & Stevens (1957) and a review by Coles (1958) have pointed out that in manganese and in some rare-earth elements a large spin-disorder term may arise in the resistance above the Curie temperature and be temperature independent. According to their arguments the unpaired electrons must be regarded as being localized on particular atoms causing them to possess localized, but randomly oriented spins which may interact with the conduction electrons giving an additional term in the electrical resistance. Below the Curie temperature, ordering of the spins should decrease this resistance term markedly. If the  $\rho$ - $T$  curve above 100 °K be extrapolated to  $T = 0$  °K a spin disorder resistivity of about 112  $\mu\Omega\text{cm}$  is deduced for  $\alpha$ -manganese which if subtracted (together with  $\rho_0$ ) from  $\rho_{273}$  gives a value for  $\rho_{i(273)}$  of 24  $\mu\Omega\text{cm}$ . The value of  $\rho_i M\theta^2 \Omega^{\frac{1}{2}}/T$  would then be about 1.7, similar to that for rhenium.

*Iron, cobalt and nickel.* The ferromagnetic Curie temperatures of these elements are 1043, 1400 and 631 °K, respectively. The rapid filling of the  $d$ -band states with one spin direction (5 of the 10 states per atom) as the material is cooled below the Curie temperature is the suggested explanation of the rather rapid decrease in electrical resistivity in this temperature region (see, for example, Mott & Jones 1936) and the subsequent tendency to a linear variation with temperature at about 100 to 200 °K when only electrons of one spin can make  $s$ - $d$  transitions. This behaviour is illustrated in figure 3 although only a short portion of the rapid change is shown near room temperature.

#### 4.2. Thermal resistivity

Despite differing band structures and effective numbers of free electrons, the ideal thermal resistivities follow much the same pattern for the transition elements (excepting manganese) as for the monovalent elements with a few exceptions, namely:

(a) A tendency for the index  $n$  in the expression  $W_i = BT^n$  ( $T \leq \theta_D/10$ ) to have rather larger values (see table 4 where  $n > 2.5$  for W, Re, Rh, Os and Ir). In Cu and Ag,  $n$  is observed to be about 2.4 rather than the value 2.0 predicted by theory, and it has been suggested that this is due to a decreasing probability of Umklapp processes in this temperature range. For the transition elements there is the added possibility of an exponential decrease in the probability of  $s$ - $d$  transitions, lowering their contribution to the thermal resistance as the temperature is lowered. The mere presence of  $s$ - $d$  transitions does not affect the temperature dependence as both  $W_i(ss)$  and  $W_i(sd)$  should vary as  $T^2$  (for  $T \ll \theta$ ) in contrast to the electrical case where  $\rho_i(ss) \propto T^5$  and  $\rho_i(sd) \propto T^3$  (see, for example, Klemens 1956).

(b) In the ferromagnetic elements, Fe, Co and Ni, the ideal resistivity  $W_i$  continues to increase with  $T$  at normal temperatures rather than to approach a constant value  $W_\infty$ , as it is observed to do for the alkali metals, for Cu, Ag, Au and also for Pt, Rh, Ir and Pd, for example. Presumably this is another effect of the band structure believed to be responsible for the electrical resistance peculiar to ferromagnetic elements (see § 4.1).

(c) In table 5 values are given for the thermal conductivity observed at or near 295 °K and also values calculated from the electrical resistivity at 295 °K using the Wiedemann–Franz



law. For those elements which have a particularly high resistivity and for which quite pure specimens were available for the thermal conductivity measurements (e.g. Ti, Zr, Hf, Nb and Cr), the measured value,  $\lambda_{295}$ , appears to be appreciably greater than  $LT/\rho$ . This suggests the presence of an appreciable lattice component in the thermal conductivity which would be most noticeable in these elements with high resistivity. Also for these elements  $W_i$  shows the greatest change between our highest temperature readings (110 or 140 °K in table 4) and those obtained near room temperature by previous workers. The values shown

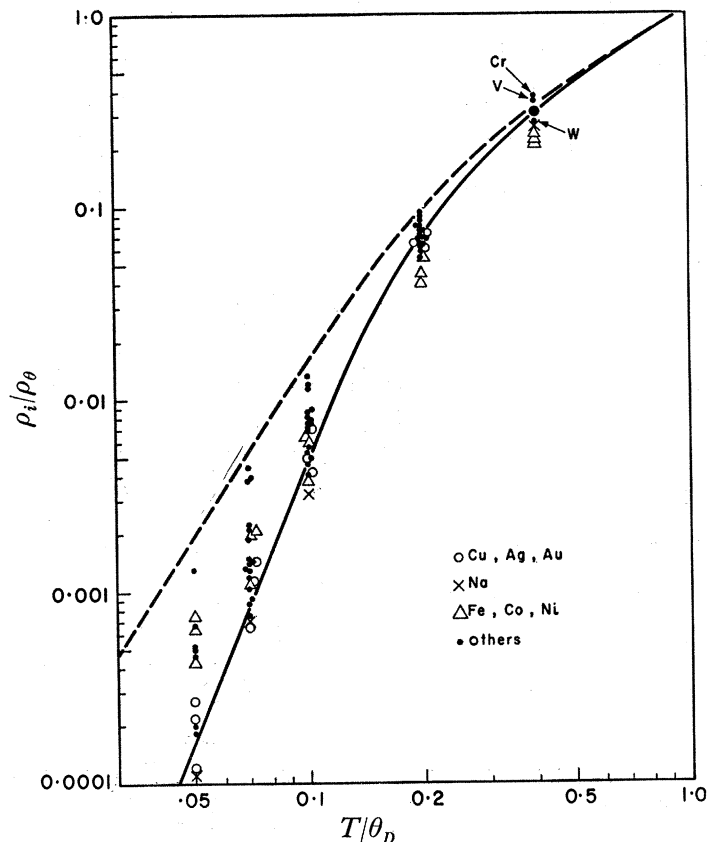


FIGURE 11. Reduced values of ideal electrical resistivity  $\rho_i/\rho_\theta$  as function of  $T/\theta_D$  for transition elements, and Cu, Ag, Au, Na. —, represents  $\rho_i/\rho_\theta = 4.226(T/\theta_D)^5 \int_0^{\theta/T} \frac{x^5 dx}{(e^x - 1)(1 - e^{-x})}$ ; ---,  $\rho_i/\rho_\theta = 2.084(T/\theta_D)^3 \int_0^{\theta/T} \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})}$ .

in table 5 confirm that in Ti, Zr, Cr, Re and perhaps in Hf,  $W_i$  must increase substantially between 100 and 295 °K in contrast with the behaviour in other elements with comparable  $\theta_D$  (e.g. Cu, Ag, Au).

The lattice component of conductivity,  $\lambda_g$ , should vary as  $1/T$  in the region  $T \geq \theta$ , where anharmonic coupling between lattice vibrations is the major limitation on  $\lambda_g$ . From table 5 it might appear that  $\lambda_g(295)$  is of the order of 0.03 to 0.05 W cm<sup>-1</sup> deg<sup>-1</sup> in Ti, Zr, Nb, ~0.1 in Mo and ~0.3 in Cr and W (assuming  $\lambda_g(295) \simeq \lambda_{295}(\text{expt.}) - LT/\rho$ ).

There is no direct method of measuring  $\lambda_g$  in good metallic conductors and the theoretical treatments (for example, Leibfried & Schlömann 1954; Dugdale & MacDonald 1955)

have been based on models of simple cubic crystals. These treatments produce equivalent results of which a convenient form is

$$\lambda_g \simeq 3.6 \frac{MA_0 \theta_D^3}{\gamma^2 T} \text{ W cm}^{-1} \text{ deg}^{-1}, \quad (12)$$

where  $A_0$  is lattice constant and  $\gamma$  the Grüneisen parameter. For Ag and Cu approximate experimental values of  $\lambda_g$  (see work on dilute alloys by Kemp, Klemens, Sreedhar & White 1956; White & Woods 1954) are found to be somewhat smaller but comparable with those predicted by the equation above. Assuming  $\gamma \simeq 2$ , (12) gives values of  $\lambda_g$  at 295 °K of about

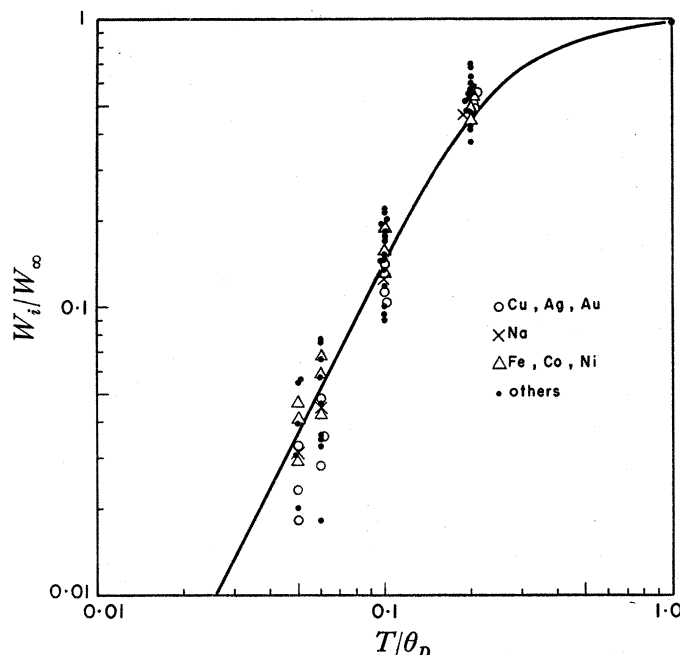


FIGURE 12. Reduced values of ideal thermal resistivity,  $W_i/W_\infty$  as function of  $T/\theta_D$  for transition elements and Cu, Ag, Au, Na. —, represents function  $W_i/W_\infty = 2(T/\theta_D)^2 \int_0^{\theta/T} \frac{x^3 dx}{(e^x - 1)(1 - e^{-x})}$ .

0.5 for Cr and W, 0.2 for Fe, Mo, Pt and Cu and 0.1<sub>5</sub> for Ti, Zr, Hf and Nb. These seem rather large in comparison with the values deduced from table 5, but in our experience this equation appears to overestimate  $\lambda_g$  and also future measurements of  $\lambda_{295}$  on very high-purity materials may give somewhat higher experimental values. In any case it seems not improbable that the lattice component,  $\lambda_g$ , is the major cause of departures from the Wiedemann–Franz law in these elements.

(d) The extent to which  $W_i/W_\infty$  departs from the function  $(T/\theta)^2 J_3(\theta/T)$  is illustrated in figure 12 and in table 4 by the values of  $(W_i/W_\infty)(\theta/T)^2 \simeq C$  at  $T = \theta/10$ , which for this function has the value 14.4.

## 5. CONCLUSIONS

By measuring the electrical resistance and thermal conductivity of specimens of the transition elements over a fairly wide range of low temperatures, we have deduced and tabulated values for the intrinsic or ideal electrical resistivity,  $\rho_i$ , from 295 °K to about 10 °K and for the ideal thermal resistivity,  $W_i$ , from above 100 °K to about 20 °K.

With certain exceptions (notably manganese),  $\rho_i$  follows approximately a Bloch–Grüneisen type of relation from room temperature down to about  $0.2\theta$ , but for  $T \leq \theta/10$  the index  $m$  (in  $\rho_i \propto T^m$ ) ranges from 3 to 5 and in some elements (e.g. Pt, Pd, Fe, Co and Ni) there appears to be a  $T^2$  region (possibly characteristic of electron-electron interaction) at or below  $10^\circ\text{K}$ . Values of the resistivity parameter,  $\rho_i M\theta^2 \Omega^{\frac{1}{2}}/T$ , appear to be greatest for group IV A and VII A elements and least for metals in groups VI A and some in group VIII (Co to Pt).

The reduced thermal resistivity  $W_i/W_\infty$  can be approximated by a function  $(T/\theta)^2 J_3(\theta/T)$ , although in many elements  $W_i$  falls more rapidly than  $T^2$  for  $T \leq \theta/10$ . In the elements of highest resistivity (e.g. Ti, Zr, etc.) a lattice component of thermal conductivity is probably significant and makes it likely that values of  $W_i$  deduced from  $W_i = W - W_0$  are not truly representative of an electronic process.

Measurements on higher purity samples, particularly of Ti, Mn and V would be of interest. Also for many of these elements measurements of heat conduction in pure samples at temperatures of 200 to  $400^\circ\text{K}$  would be useful.

We are very grateful to Mr F. Anglin and Dr M. T. Elford for their help with many of the measurements, to our colleagues Drs D. K. C. MacDonald, W. B. Pearson, Z. S. Basinski for discussions and metallurgical advice, to Mr W. Stockdale for some spectroscopic analyses and finally to Messrs F. Richardson and J. Broome for keeping us supplied with liquid helium.

#### APPENDIX

Notes are given below regarding purity, etc., of the specimens. These elaborate the brief details in table 1 for specimens concerning which we have made no previous report.

##### *Titanium*

Ti 2 (stated by Heraeus to be ‘...as pure as can be obtained by us...’) had the copper leads welded to it.

For Ti 3, 4, 5 spectroscopic and gas analyses supplied by Dr Winegard showed  $0.002\%$   $\text{N}_2$ ,  $0.002\%$   $\text{O}_2$ ,  $0.005\%$  Si,  $0.001\%$  C and less than  $0.01\%$  total of Mn, Cr, Mg, Cu and Fe. After chemically cleaning the rods in dilute acid, end sections were copper plated in a cyanide bath and leads attached to this with soft solder.

##### *Zirconium*

Zr 2, cut from an iodide-bar had copper leads welded to it. For Zr 3, Dr Betterton supplied analyses showing 132 p.p.m. Hf, 79 p.p.m. C, 24 p.p.m. Fe, 11 p.p.m. Ni, 21 to 50 p.p.m.  $\text{O}_2$ , 3 to 50 p.p.m.  $\text{N}_2$ ,  $<100$  p.p.m. of Zn and P, 2 to 7 p.p.m. each of Ca, Cr, Mo, Si,  $\text{H}_2$  and a total of less than 10 p.p.m. of 18 other elements. Vickers Hardness was 58. It was arc cast, annealed 4 h at  $1100^\circ\text{C}$ , swaged at room temperature, annealed for 15 min at  $1000^\circ\text{C}$  and finally for 15 min at  $800^\circ\text{C}$  in a vacuum of  $(1 \text{ to } 2) \times 10^{-6}$  mm Hg. Fine copper leads were twisted round the wire and held by a conducting silver paste (Silverprint of General Cement Manufacturing Company, Illinois). Zr 3 was later cut into four lengths and these were held together by small clamps to form Zr 4. These small copper clamps had copper leads attached to them and good contact to the rods was ensured by a film of conducting silver paste between the clamp surface and the zirconium. As electrical resistance measurements were

not reproducible (in contrast to measurements of  $\lambda$ ), Zr 4 was removed, the Silverprint was dissolved away and the clamps were tightened again. The specimen was then called Zr 4a and was remounted in the cryostat.

### *Hafnium*

No analysis for Hf 1 was available, but it is believed to be rather similar to those specimens used by Adenstedt (1952) containing about 0.8 wt. % ( $\sim 1.6$  at. %) Zr as the major impurity. The rod was electropolished, end sections were copper plated in a cyanide bath and leads attached with Zn + Cd solder.

For Hf 2 and 3, analyses were supplied by Dr Betterton. Spectroscopic and neutron activation analyses showed 0.05 wt. % Zr in Hf 2, plus Ca (10 p.p.m.), Fe (61 p.p.m.), Ni (18 p.p.m.), Si (17 p.p.m.), Ti (30 p.p.m.), Zn and P (each  $< 100$  p.p.m.); combustion analysis gave 0.03 wt. % C, while vacuum fusion indicated O<sub>2</sub> (7 p.p.m.), H<sub>2</sub> (10 p.p.m.), and N<sub>2</sub> ( $< 5$  p.p.m.). The iron content may have risen as much as 400 p.p.m. during swaging of the crystal bar. The minor impurities in Hf 3 were similar but 3.8 to 4.2 wt. % ( $\sim 8$  at. %) Zr and 100 p.p.m. of O<sub>2</sub> were also present. Both specimens were mounted in an alumina tube with four small brass screws in pressure contact with points near the extremities and only  $\rho$  was measured.

### *Tantalum*

Ta 1, stated by Heraeus to be 'as pure as can be obtained by us' was annealed and leads spot-welded to it.

Ta 2 and Ta 3 were each annealed by passing large electric currents through them in a vacuum ( $\sim 10^{-5}$  mm Hg), first outgassing them and later raising their temperature almost to the melting point of tantalum for a minute or two. Ta 2 was afterwards mounted in an alumina tube (see Hf 2 and 3) and Ta 3 was fitted with copper clamps (see Zr 4).

### *Molybdenum*

Leads were attached to Mo 1 with silver solder. Owing to a slight uncertainty in the shape factor ( $l/A$ ) two other wires—one of larger diameter—were later mounted in a clamping device, in which a more accurate estimate of the length  $l$  could be made. Then measurement of length, cross-section and electrical resistance at 295, 77.6 and 4.2 °K gave a reliable value of  $\rho_{i(295)}$  with which the values of  $\rho$  for Mo 1 could be normalized.

### *Rhenium*

Re 5, for which we have no analysis, was cut from a wire that had been electrically annealed close to its melting point (see Ta 2 and 3).

### *Iron*

Fe 2 was prepared by Dr Z. S. Basinski of this laboratory, from the original (Vacuum Metals Co.) rod, by zone-melting in wet hydrogen gas to produce large crystals and later electrical annealing in high vacuum at about 600 °C to remove hydrogen. Spectrographic analyses done here indicated lines of Si ( $\sim 0.004$  %), Mo ( $\sim 0.003$  %), Mn ( $\sim 0.003$  %), Cu, Ni, Co (each  $< 0.004$  %), Sn ( $< 0.0001$  %) and minute traces of Pb and Zr.

*Cobalt*

The cobalt wires were prepared by Johnson, Matthey and Co. from sponge for which spectrographic analyses indicated lines of Si (estimated 2 p.p.m.), Fe (5 p.p.m.), Al ( $\sim 1$  p.p.m.), Mg, Cu ( $< 1$  p.p.m.).

*Nickel*

Supplier's analyses for rods from which Ni 2 and Ni 3 were drawn lists the following impurities: 10 p.p.m. Fe; 10 p.p.m. Si; 3 p.p.m. Cr and Mg; 2 p.p.m. Cu, Mn and Ca; 1 p.p.m. Ag.

*Palladium*

Pd 9 was drawn from JM 9401 for which the supplier's analysis lists: about 2 p.p.m. Cu; 1 p.p.m. each of Fe, Ca and Na; less than 1 p.p.m. of Ag, Mg and Si. Earlier specimens were made from JM 2928 for which analysis gave strong Ag lines and faint Ca, Cu, Si and Mg lines.

*Platinum*

Pt-T4 was a resistance thermometer, one of six whose calibrations above 11 °K are described in detail by Los & Morrison (1951). We used this thermometer to check our gas thermometry from 12 to 295 °K and also checked its resistance at the ice and oxygen points, finding them in agreement with the 1951 calibration to within a few thousandths of a degree. We also measured its residual resistance  $R_0$  at about 1.2 to 2 °K and then measured  $R$  from 3 to 12 °K, later converting values of  $R$  to  $\rho$  with the aid of measurements on a length of thicker platinum wire, Pt 3.

*Copper, silver, gold*

The fine wires on which measurements of electrical resistance were made, and the rods on which one of us (G. K. W.) had earlier made thermal conductivity measurements were annealed specimens of very high purity.

## REFERENCES

- Adenstedt, H. K. 1952 *Trans. Amer. Soc. Metals*, **44**, 949.  
 van Arkel, A. E. 1939 *Reine Metalle*. Berlin: Springer Verlag.  
 Baber, W. G. 1937 *Proc. Roy. Soc. A*, **158**, 383.  
 Barratt, T. & Winter, R. M. 1925 *Ann. Phys., Lpz.*, **77**, 1.  
 Berman, R. 1951 *Proc. Roy. Soc. A*, **208**, 90.  
 Berman, R. & MacDonald, D. K. C. 1951 *Proc. Roy. Soc. A*, **209**, 368.  
 Bijl, D. 1957 *Progress in low temperature physics*, **2**, 395. Amsterdam: North-Holland.  
 Bing, G., Fink, F. W. & Thompson, H. B. 1951 Report, United States Atomic Energy Commission-BMI-65.  
 Blackman, M. 1955 *Handb. Phys.* **7**, 325.  
 Blau, F. 1905 *Elektrotech. Z.* **25**, 198.  
 Bradshaw, F. J. & Pearson, S. 1956 *Proc. Phys. Soc. B*, **69**, 441.  
 Bridgman, P. W. 1932-33 *Proc. Amer. Acad. Arts Sci.* **68**, 27.  
 Coles, B. R. 1958 *Phil. Mag. Suppl.* **7**, 40.  
 Deem, H. W. 1953a Report United States Atomic Energy Commission-BMI-849.



- Deem, H. W. 1953*b* Report United States Atomic Energy Commission-BMI-853.
- Dugdale, J. S. & MacDonald, D. K. C. 1955 *Phys. Rev.* **98**, 1751.
- Gerritsen, A. N. 1956 *Handb. Phys.* **19**, 137.
- Grüneisen, E. 1928 *Handb. Phys.* **13**, 1.
- Grüneisen, E. & Goens, E. 1927 *Z. Phys.* **44**, 615.
- Grüneisen, E. & Reddemann, H. 1934 *Ann. Phys., Lpz.*, **20**, 843.
- de Haas, W. J. & de Boer, J. 1933 *Physica*, **1**, 609.
- de Haas, W. J. & de Nobel, J. 1938 *Physica*, **5**, 449.
- de Haas, W. J. & Voogd, J. 1928 *Commun. Phys. Lab. Univ. Leiden*, No. 194*c*.
- Hampel, C. A. 1954 *Rare metals handbook*. New York: Reinhold.
- Harper, A. F. A., Kemp, W. R. G., Klemens, P. G., Tainsh, R. J. & White, G. K. 1957 *Phil. Mag.* **2**, 577.
- Hoge, H. J. & Brickwedde, F. G. 1939 *J. Res. Nat. Bur. Stand. Wash.* **22**, 351.
- Horowitz, M. & Daunt, J. G. 1953 *Phys. Rev.* **91**, 1099.
- Hulm, J. K. & Goodman, B. B. 1957 *Phys. Rev.* **106**, 659.
- Jones, H. 1956 *Handb. Phys.* **19**, 227.
- Justi, E. 1949 *Z. Naturf.* **4a**, 472.
- Kannuluik, W. G. 1933 *Proc. Roy. Soc. A*, **141**, 159.
- Keesom, P. H. & Pearlman, N. 1956 *Handb. Phys.* **14**, 282.
- Kemp, W. R. G., Klemens, P. G., Sreedhar, A. K. & White, G. K. 1955 *Phil. Mag.* **46**, 811.
- Kemp, W. R. G., Klemens, P. G. & White, G. K. 1956 *Austral. J. Phys.* **9**, 180.
- Kemp, W. R. G., Klemens, P. G., Sreedhar, A. K. & White, G. K. 1956 *Proc. Roy. Soc. A*, **233**, 480.
- Klemens, P. G. 1954 *Austral. J. Phys.* **7**, 64.
- Klemens, P. G. 1956 *Handb. Phys.* **14**, 198.
- Leibfried, G. & Schlömann, E. 1954 *Nachr. Ges. Wiss. Göttingen*, II*a*, 71.
- Los, J. M. & Morrison, J. A. 1951 *Canad. J. Phys.* **29**, 142.
- Lustman, B. & Kerze, F. 1955 *The Metallurgy of zirconium*. New York: McGraw-Hill.
- MacDonald, D. K. C. 1947 *J. Sci. Instrum.* **24**, 232.
- MacDonald, D. K. C., White, G. K. & Woods, S. B. 1956 *Proc. Roy. Soc. A*, **235**, 358.
- McQuillan, A. D. & McQuillan, M. K. 1956 *Titanium*. London: Butterworths.
- Meissner, W. 1915 *Ann. Phys., Lpz.*, **47**, 1001.
- Meissner, W. & Voigt, B. 1930 *Ann. Phys. Lpz.*, **7**, 892.
- Mendelssohn, K. 1956 *Canad. J. Phys.* **34**, 1315.
- Miller, G. L. 1954 *Zirconium*. London: Butterworths.
- Mott, N. F. 1936 *Proc. Roy. Soc. A*, **153**, 699.
- Mott, N. F. & Jones, H. 1936 *Theory of the properties of metals and alloys*. Oxford University Press.
- Mott, N. F. & Stevens, K. W. H. 1957 *Phil. Mag.* **2**, 1364.
- de Nobel, J. 1951 *Physica*, **17**, 551.
- Northcott, L. 1956 *Molybdenum*. London: Butterworths.
- Olsen-Bär, M. 1956 Thesis, University of Oxford.
- Pines, D. 1955 *Solid state physics*, **1**, 368. New York: Academic Press.
- Pines, D. 1956 *Canad. J. Phys.* **34**, 1379.
- Potter, H. H. 1941 *Proc. Phys. Soc.* **53**, 695.
- Powell, R. L. & Blanpied, W. A. 1954 *Nat. Bureau Stand. Circular* 556. Washington, D.C.: U.S. Govt. printing office.
- Powell, R. W. 1955 *Bull. Inst. Int. Froid*, Annexe 1955-2, p. 115. Paris.
- Powell, R. W. & Tye, R. P. 1956 *J. Inst. Metals*, **85**, 185.
- Powell, R. W. & Tye, R. P. 1955 *Proc. IXth Int. Congr. Refrig. Paris*, Commission 2, p. 083.
- Powers, R. W., Schwartz, D. & Johnston, H. L. 1951 *Tech. Rep.* 264-5 *Cryogenics Lab., Ohio State Univ.*
- Powers, R. W., Ziegler, J. B. & Johnston, H. L. 1951 *Tech. Rep.* 264-6, *Cryogenics Lab., Ohio State Univ.*
- Reddemann, H. 1935 *Ann. Phys., Lpz.*, **22**, 28.

- Rosenberg, H. M. 1955 *Phil. Trans. A*, **247**, 441.
- Rostoker, W. & Yamamoto, A. S. 1955 *Trans. Amer. Soc. Metals*, **47**, 1002.
- Rigney, C. J. & Bockstahler, L. I. 1951 *Phys. Rev.* **83**, 220 (A).
- Shiffman, C. A. 1952 *Heat capacities of the elements below room temperature*. Schenectady, New York: G.E.C. Research Publication Services.
- Shull, C. G. & Wilkinson, M. K. 1953 *Rev. Mod. Phys.* **25**, 100.
- Silverman, L. 1953 *J. Metals*, **5**, 631.
- Sondheimer, E. H. 1950 *Proc. Roy. Soc. A*, **203**, 75.
- Sondheimer, E. H. 1957 *Progress in low temperature physics*, **2**, 151. Amsterdam: North-Holland.
- Straumanis, M. E. & Weng, C. C. 1955 *Acta Cryst.* **8**, 367.
- Sully, A. H. 1954 *Chromium*. London: Butterworths.
- Sully, A. H. 1955 *Manganese*. London: Butterworths.
- Treco, R. M. 1953 *Trans. Amer. Soc. Metals*, **45**, 872.
- Tottle, C. R. 1957 *J. Inst. Metals*, **85**, 375.
- Van den Berg, G. J. 1938 Thesis, University of Leiden.
- Weeks, J. L. & Smith, K. F. 1955 *J. Metals*, **7**, 1010.
- White, G. K. 1953*a* *Proc. Phys. Soc. A*, **66**, 559.
- White, G. K. 1953*b* *Proc. Phys. Soc. A*, **66**, 884.
- White, G. K. 1953*c* *Austral. J. Phys.* **6**, 397.
- White, G. K. & Woods, S. B. 1954 *Phil. Mag.* **45**, 1343.
- White, G. K. & Woods, S. B. 1955 *Canad. J. Phys.* **33**, 58.
- White, G. K. & Woods, S. B. 1957*a* *Canad. J. Phys.* **35**, 248.
- White, G. K. & Woods, S. B. 1957*b* *Canad. J. Phys.* **35**, 346.
- White, G. K. & Woods, S. B. 1957*c* *Canad. J. Phys.* **35**, 656.
- White, G. K. & Woods, S. B. 1957*d* *Canad. J. Phys.* **35**, 892.
- White, G. K. & Woods, S. B. 1958 *Canad. J. Phys.* **36**, 875.
- Wilson, A. H. 1938 *Proc. Roy. Soc. A*, **167**, 580.
- Wilson, A. H. 1953 *The theory of metals*. Cambridge University Press.
- Woods, S. B. 1956 *Canad. J. Phys.* **34**, 223.
- Wolcott, N. M. 1955 *Conférence de physique des basses températures, Paris 1955*, p. 286. Annexe 1955-3. *Bull. Inst. Int. Froid, Paris*.
- Ziman, J. M. 1954 *Proc. Roy. Soc. A*, **226**, 436.