# THERMAL AND ELECTRICAL CONDUCTIVITIES OF IRON, NICKEL, TITANIUM, AND ZIRCONIUM AT LOW TEMPERATURES

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*Summary*

Measurements are reported of the thermal and electrical conductivities of iron, nickel, titanium, and zirconium down to 2 °K. These indicate that thermal conduction in pure iron and nickel is almost completely electronic. Titanium and zirconium exhibit an appreciable lattice component of thermal conduction. In the case of titanium this lattice component varies as $T^{1.5}$.

The ideal electronic thermal resistivity below about 50 °K was found to be $10 \times 10^{-5} \, T^{2.2}$ and $11 \times 10^{-5} \, T^2$ cm deg W$^{-1}$ for iron and nickel respectively. The ideal electrical resistivity was found to vary as $T^3$ at low temperatures for all four metals.

## I. INTRODUCTION

Rosenberg (1955) has described the results of a comprehensive investigation of the low temperature thermal conductivity of a large number of metallic elements. These results confirm the generally accepted view that the thermal conductivity of those metals which are good electrical conductors is principally electronic. The electronic thermal conductivity, $\varkappa_e$, can be expressed as

$$1/\varkappa_e = W_e = W_i + W_0, \quad \dots\dots\dots\dots\dots\dots (1)$$

where $W_i$, the ideal or intrinsic thermal resistivity, arises from scattering by lattice waves and $W_0$, the residual thermal resistivity, is due to scattering by static imperfections. One would expect from theory, irrespective of the details of the electronic band structure, that

$$W_0 = \rho_0/L_0 T, \quad \dots\dots\dots\dots\dots\dots (2)$$

and, for $T \ll \theta$,

$$W_i = BT^n, \quad \dots\dots\dots\dots\dots\dots (3)$$

where $n \simeq 2$, $\rho_0$ is the residual electrical resistivity, and $L_0 = 2 \cdot 45 \times 10^{-8}$ W Ω deg$^{-2}$, the Sommerfeld value of the Lorenz ratio (see, for example, Klemens 1956).

In the absence of an appreciable lattice component of thermal conduction the Lorenz ratio $L = \rho/WT$ should tend to the value $L_0$ at those temperatures at which $\rho$ becomes constant, since the electrical and thermal resistivities are then $\rho_0$ and $W_0$ respectively. Rosenberg, however, found that in the cases of iron, titanium, and zirconium $L$ deviated markedly from $L_0$ even at liquid helium temperatures, the observed thermal conductivity being larger than

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would be expected from the substitution of the observed value of $\rho_0$ into equation (2). He found for titanium and zirconium that the thermal resistance was inversely proportional to temperature and concluded from this that for these metals the observed discrepancy could not be attributed to the presence of an appreciable lattice component of thermal conductivity ($\varkappa_g$) but must be due to a failure of the Lorenz law (2).

In view of the very general theoretical validity of (2), its failure would be very disturbing. It thus seemed worth while to reinvestigate these materials and to check that any deviations from (2) cannot, in fact, be attributed to lattice conduction, especially as recent measurements on silver alloys (Kemp *et al.* 1954, 1956) and on beryllium and copper (White and Woods 1955), as well as theoretical studies (Klemens 1955), indicate that $\varkappa_g$ may be appreciable and show various types of temperature variation, depending upon the nature of the principal lattice imperfections.

The thermal and electrical conductivities of iron and nickel were investigated as an extension of the work on transition metals previously reported (Kemp *et al.* 1955).

## II. Experimental Procedure and Specimens

The thermal conductivity measurements were made in a cryostat described previously (White 1953) and the electrical conductivity was measured simul-

TABLE 1

PURITY AND PHYSICAL STATE OF SPECIMENS

| Element | Source Material | Nominal Purity (%) | Analysis | Specimen |
|---|---|---|---|---|
| Iron.. .. | JM5092 | 99·99 | Ni (0·005%), Cu (0·0002%), Ag (0·0001%), Mn, Mg (barely visible lines) | 2 mm dia. rod annealed 750 °C for 4 hr *in vacuo* |
| Nickel .. | JM4497 | >99·99 | Si, Ca, Al, Ag, Cu (faint lines) Mg, Na, Li (very faint lines) | 2 mm dia. rod annealed 750 °C for 4 hr *in vacuo* |
| Zirconium | JM5000 | 99·99 | Fe (all sensitive lines) Hf, Ni (all sensitive lines faintly) Si, Ti (some sensitive lines) Cr, Al, Cu, Mg (faintly visible) | 3 mm dia. rod annealed 950 °C for 5 hr *in vacuo* |
| Titanium .. | JM4233 | 98 | Mg (0·024%), Si (0·13%), Fe (0·05%), Ni (0·081%), C (0·14%), $O_2$ (1·63%) | 3 mm dia. rod annealed 950 °C for 5 hr *in vacuo* |

taneously in the same cryostat with the aid of a galvanometer amplifier (MacDonald 1947). The specimens were supplied by Messrs. Johnson, Matthey and Co. Ltd.; Table 1 gives details of their physical state and purity.

Connections to the iron and nickel specimens were made with a zinc-cadmium eutectic solder which is not superconducting down to 2 °K, the temperature range of the measurements.

Initially the specimens of zirconium and titanium were mounted in the cryostat by means of copper fittings, into which the specimens were a push fit, and were sealed with baked " Araldite " cement. These were designated Zr1a and Ti1a. However, as the electrical resistance measurements were not reproducible, and on examination the contacts provided by the copper rings were found to be unsatisfactory, an alternative mounting was adopted for subsequent measurements. Holes were drilled and tapped in the zirconium and titanium specimen rods and current and potential connections (both electrical and thermal) made by means of 10 B.A. screws, which were tightly screwed into the specimens (designated Zr1c and Ti1b).

After the initial measurements on Zr1a were completed, it was thought that the current lead used for the measurements of electrical resistance may have affected the apparent thermal conductivity, as this lead was a 44 S.W.G. copper wire (later replaced by 34 S.W.G. constantan). The thermal conductivity was therefore measured again with the current lead removed (Zr1b); the values obtained nowhere differed by more than 3 per cent. from those for Zr1a.

### III. RESULTS

#### (a) Iron

While the values of the thermal conductivity (Fig. 1) appear to agree quite well with those found by Rosenberg (1955) on his first run, values of $WT$ and $\rho$
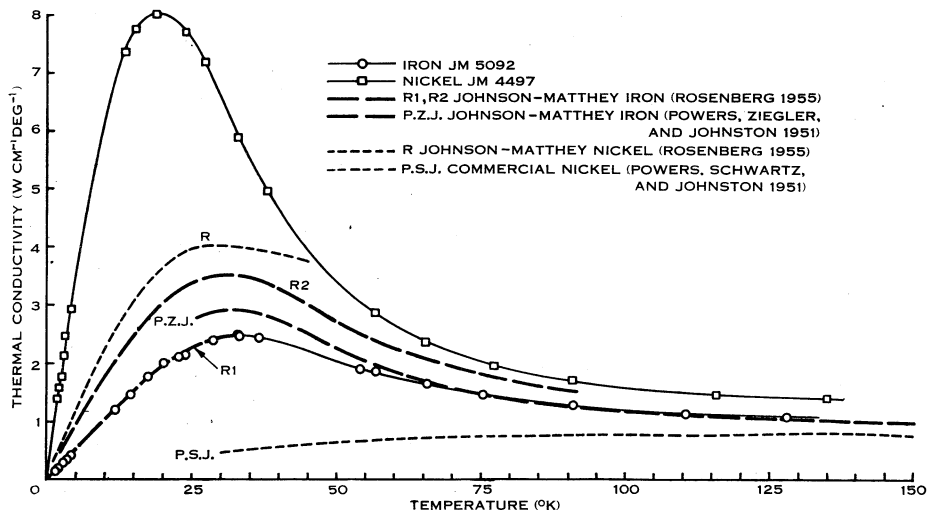


Fig. 1.—Thermal conductivity of iron and nickel at low temperatures.

are both constant to within 2 per cent. below 15 °K. Rosenberg found on his second run, in which he measured both electrical and thermal conductivities, a small anomaly in $WT$ below 10 °K and a sharp drop in $\rho$ of about 10 per cent.

around 8 °K ; his Lorenz ratio has a sharp peak at about 8 °K, and below this it falls from $2\cdot6$ to $2\cdot3\times10^{-8}$ W $\Omega$ deg$^{-2}$, whereas our specimen (Fig. 2) has
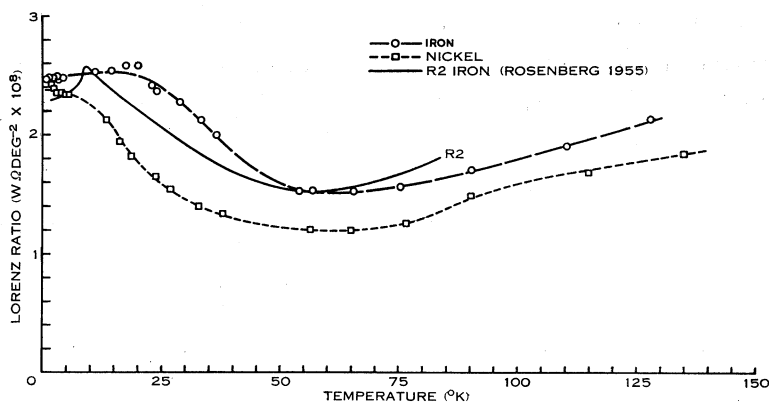


Fig. 2.—Variation of Lorentz ratio $\rho\varkappa/T$ with temperature.


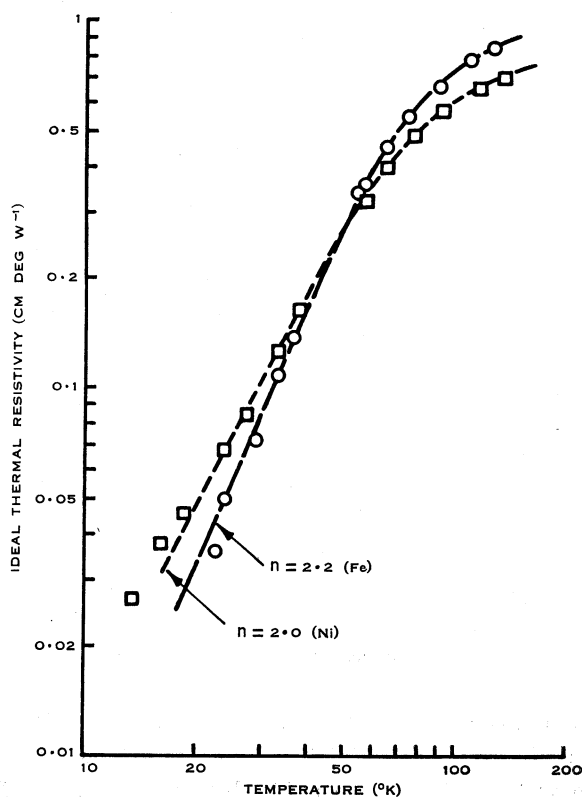
Fig. 3.—Ideal thermal resistivity of iron and nickel at low temperatures.

a value of $L=\rho/WT$ which is fairly constant (about $2\cdot5\times10^{-8}$) from 20 °K down.

B

It seems possible that the anomaly in the electrical resistance of Rosenberg's iron specimen was due to the solder (Wood's metal or soft solder) becoming superconducting below about 8 °K.

The values of the ideal thermal resistivity $W_i$, obtained from (1) by assuming the experimental figure $W_0 T = 10 \cdot 0$ cm deg$^{-2}$ W$^{-1}$, are plotted in Figure 3
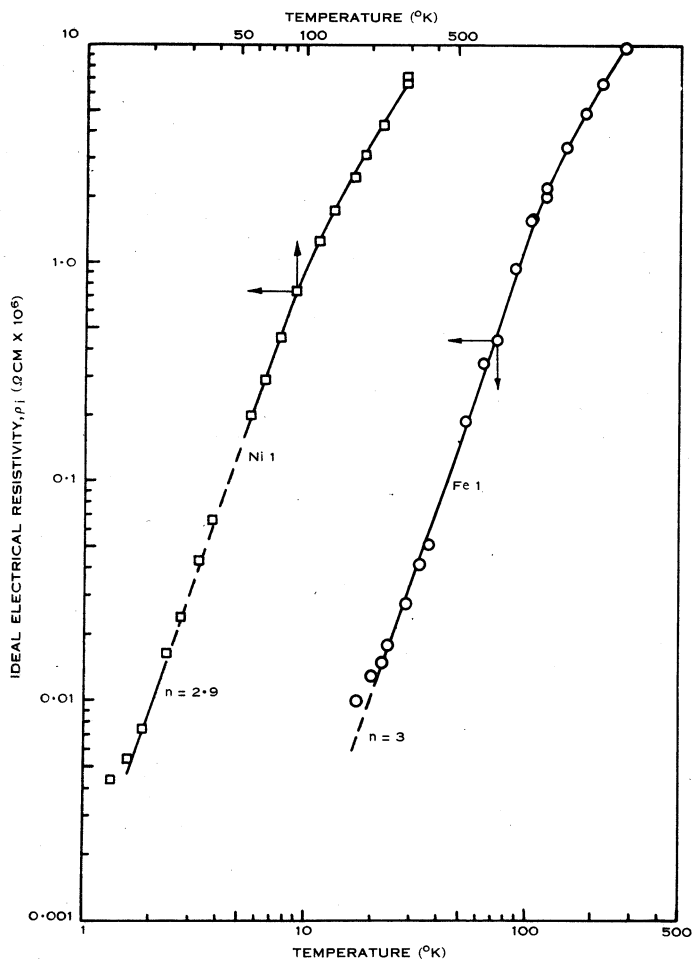


Fig. 4.—Ideal electrical resistivity of iron and nickel.

and indicate that equation (3) is satisfied below 40 °K ($\theta/10$) with $n \simeq 2 \cdot 2$. If we assume $n = 2$ and calculate $B$ at 30 °K, the value $10 \times 10^{-5}$ cm deg$^{-1}$ W$^{-1}$ is obtained, in close agreement with Rosenberg's values of $10 \cdot 2$ (R1) and $9 \cdot 5$ (R2).

The electrical resistivities at 20 °C and at helium temperatures are respectively $10 \cdot 0 \times 10^{-6}$ and $0 \cdot 248 \times 10^{-6}$ $\Omega$ cm, so that $\rho_0/\rho_{293} = 2 \cdot 48 \times 10^{-2}$. The ideal electrical resistivity $\rho_i = \rho - \rho_0$ is shown in Figure 4. Below 90 °K $\rho_i \simeq 1 \cdot 25 \times 10^{-12} T^3$ $\Omega$ cm.

### (b) Nickel

The thermal conductivity, Lorenz ratio, and ideal thermal and electrical resistivities of Ni1 are shown in Figures 1–4. Both $\rho$ and $WT$ are sensibly constant in the liquid helium region, and the Lorenz ratio $L$ has a value of $2 \cdot 38 \times 10^{-8}$, which is not inconsistent with the theoretical value, since the possible errors in the electrical and thermal measurements are both in the vicinity of 1 per cent. The values of $\rho_{293}$ and $\rho_0$ are $7 \cdot 22 \times 10^{-6}$ and $0 \cdot 0347 \times 10^{-6} \, \Omega$ cm respectively, and the low value of $\rho_0/\rho_{293} \simeq 4 \cdot 8 \times 10^{-3}$ indicates the high purity of the specimen. Below about 40 °K, $W_i = 11 \times 10^{-5} T^2$ deg cm W$^{-1}$ (see Fig. 3), as compared with Rosenberg's value of $10 \cdot 4 \times 10^{-5}$ for $B$; Figure 4 indicates that $\rho_i = 1 \cdot 19 \times 10^{-12} T^3 \, \Omega$ cm below about 90 °K.

### (c) Titanium

The thermal conductivities and electrical resistivities of titanium and zirconium are shown in Figures 5 and 6. The relatively impure titanium specimen has a smaller thermal conductivity than Rosenberg's specimens. The values of $\rho_{293}$ and $\rho_0$ are $70 \times 10^{-6}$ and $23 \cdot 6 \times 10^{-6} \, \Omega$ cm respectively. Below 50 °K ($\sim\theta/5$), $\rho_i \simeq 17 \times 10^{-12} T^3 \, \Omega$ cm; however, the ideal resistance is not determined accurately, since for such an impure specimen $\rho_0 \gg \rho_i$ at low temperatures.

This high residual resistance also makes it impossible to deduce values of $W_i$ at low temperatures. The value of $4 \cdot 5 \times 10^{-3} T^2$ for $W_i$, obtained by Rosenberg (1955) for a pure single crystal of titanium ($\rho_0 = 2 \cdot 4 \times 10^{-6}$), confirms that $W_i$ will be negligible in comparison with $W_0$ below 40 °K for the present specimen. If the lattice component of thermal conductivity were negligible at these temperatures, $\varkappa/T$ should be constant and, from (2), equal to $L_0/\rho_0$. The measurements indicate that $\varkappa/T$ is not constant, and is larger than $L_0/\rho_0$. This suggests that there is an appreciable heat transport by the lattice. If this is so, then the lattice thermal conductivity should be given by

$$\varkappa_g = \varkappa - \varkappa_e = \varkappa - L_0 T/\rho_0, \quad \ldots\ldots\ldots\ldots\ldots \; (4)$$

and, when thus obtained, can be expressed as $\varkappa_g = 1 \cdot 8 \times 10^{-4} T^{1 \cdot 5}$ W cm$^{-1}$ deg$^{-1}$ between 2 and 30 °K.

### (d) Zirconium

Figure 5 illustrates the thermal conductivity of the zirconium samples 1a, 1b, and 1c. The conductivity of 1c is about 10 per cent. lower, apparently due to strains induced by drilling and tapping to insert the connectors for mounting. In the case of titanium this produced no noticeable change because its residual resistivity was already very high.

Equations (1), (2), and (3) seem reasonably well obeyed, and it is found that in (3) $n \simeq 2$ and $B = 1 \cdot 3 \times 10^{-3}$ cm deg$^{-1}$ W$^{-1}$. The value for $B$ is in good agreement with the values obtained by Rosenberg. The electrical resistivities $\rho_{293}$ and $\rho_0$ are $48 \times 10^{-6}$ and $1 \cdot 98 \times 10^{-6} \, \Omega$ cm respectively and $\rho_i$ varies approximately as $T^3$ below 40 °K. In contrast to Rosenberg's result, the Lorenz ratio
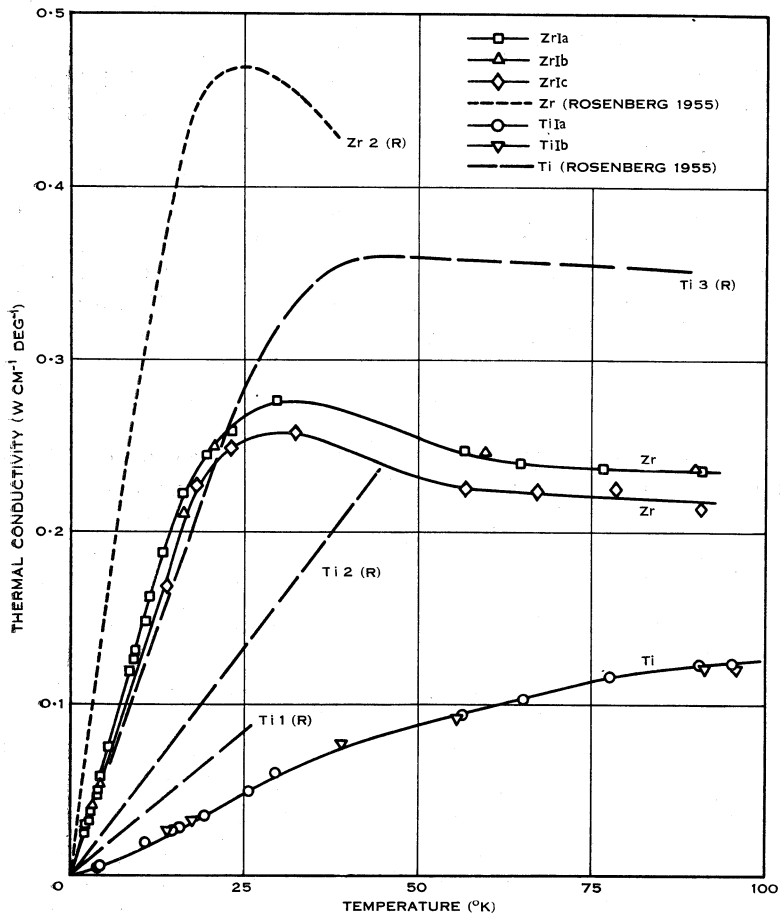
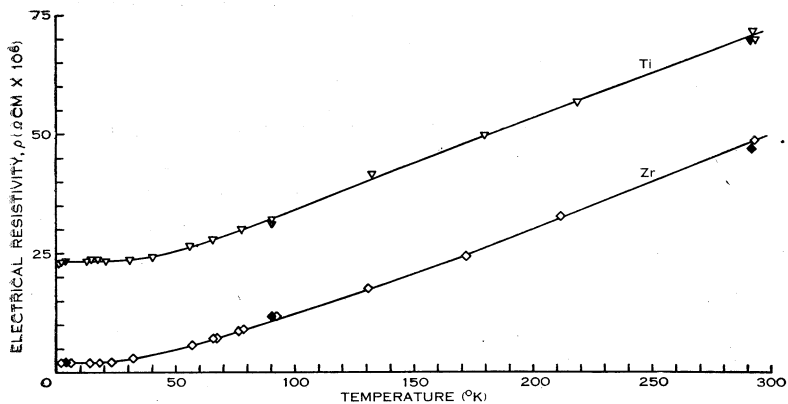Fig. 5.—Thermal conductivity of titanium and zirconium at low
temperatures.

Fig. 6.—Electrical resistivity of titanium and zirconium.

has a sensibly constant value of $2 \cdot 4 \times 10^{-8}$ W $\Omega$ deg$^{-2}$ below 25 °K (see Fig. 7). It falls to a slightly lower value at about 40 °K and then increases again with increasing temperature to well above $L_0$. Such behaviour is consistent with the presence of an appreciable lattice component of thermal conductivity; however, it is not possible to deduce its value from these results.
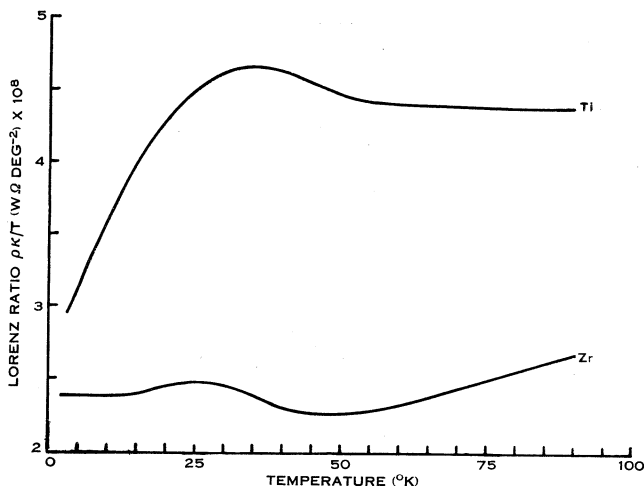


Fig. 7.—Lorenz ratio $\rho \varkappa /T$ for titanium and zirconium.

## IV. DISCUSSION

It appears that the electronic conduction properties of iron and nickel can be interpreted along the same lines as those of palladium (Kemp *et al.* 1955). The conductivities are mainly due to electrons in the $s$-band, and are limited by $(s-s)$ and $(s-d)$ transitions. The resistances due to $(s-s)$ transitions are described by the Bloch single-band theory, so that at low temperatures their contribution to the ideal electrical and thermal resistivities, $\rho(s,s)$ and $W(s,s)$, vary as $T^5$ and $T^2$ respectively. The $(s-d)$ transitions can be described by a relaxation time, so that $\rho(s,d)/TW(s,d)=L_0$; it can also be shown that $\rho(s,d) \propto T^3$, since the resistance arises from single-step phonon processes, instead of multiple-step diffusion over the Fermi surface; similarly $W(s,d) \propto T^2$. Thus $L_i=\rho_i/W_iT$ tends to a constant value at lowest temperatures, and in the limit $L_i/L_0=W(s,d)/[W(s,d)+W(s,s)]$. The present results indicate that for iron and nickel $W(s,d)/W(s,s) \simeq 0 \cdot 8$, while for palladium this ratio had been found to be about $0 \cdot 5$.

The electronic conduction properties of titanium and zirconium may also be interpreted similarly, even though the band structure is probably different and more complicated. One can distinguish between transitions within a band (type I) and transitions from one band to another (type II). It again appears that one band only contributes appreciably to the conduction properties. At sufficiently low temperatures $\rho(\text{I}) \propto T^5$, $\rho(\text{II}) \propto T^3$, $W(\text{I})$ and $W(\text{II})$ both vary as $T^2$ and $\rho(\text{II})/TW(\text{II})=L_0$. Thus $L_i/L_0=W(\text{II})/[W(\text{I})+W(\text{II})]<1$. In the case of titanium, using Rosenberg's value of $W_i$ and the present results for $\rho_i$, $L_i/L_0$

tends to a limit of $\sim 0 \cdot 15$, while for zirconium in the limit of lowest temperatures $L_i/L_0 \sim 0 \cdot 75$.

The present results on titanium and zirconium can, we believe, be explained in terms of an appreciable lattice component of thermal conductivity. They also reveal that the features which led Rosenberg (1955) to reject lattice thermal conduction as responsible for his large values of $\rho/WT$ are not a general property of these substances. He found the values of $\rho/WT$ in the residual resistance region to be (a) temperature independent, (b) greater than $L_0$, and (c) apparently independent of $\rho_0$; none of these findings is confirmed by the present results.

Rosenberg's results also can be interpreted in terms of an appreciable lattice component $\varkappa_g$. In his case $\varkappa_g$ would be larger than in the present specimens ; this is not unlikely in view of the known sensitivity of $\varkappa_g$ to some lattice imperfections, especially dislocation arrays. In the present titanium specimen the high oxygen content could easily be responsible for a reduction in $\varkappa_g$. In Rosenberg's specimens $\varkappa_g$ would need to be proportional to $T$. Such a temperature dependence is by no means impossible ; it would, for example, result from the scattering of lattice waves by thin sheets of disordered material embedded in a crystal of fixed orientation (Klemens 1956). The apparent independence of $\rho/WT$ of $\rho_0$ would indicate that the same imperfections which limit $\varkappa_g$ are also responsible for the major part of the residual resistance.

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