Experimental Determinations of the Lorenz Number

3 authors:

Gobburu S Kumar
Osmania University
152 PUBLICATIONS   1,512 CITATIONS

SEE PROFILE

Guduru Prasad
Osmania University
149 PUBLICATIONS   1,186 CITATIONS

SEE PROFILE

Robert Otto Pohl
Cornell University
301 PUBLICATIONS   9,216 CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project — Effect of Different Halide substitution on conduction mechanism in Potassiun halide solid solutions View project

Project — M E Composites View project

Review

Experimental determinations of the Lorenz number

G. S. KUMAR, G. PRASAD
Department of Physics, Osmania University, Hyderabad 500007, India

R. O. POHL
LASSP Cornell University, Ithaca, NY 14853, USA

The Lorenz number, which was assumed to be a universal factor, was later found to be deviating from its theoretical Sommerfeld value. Our understanding of the physics of the Weidemann–Franz–Lorenz law is based on a large number of investigations. In view of its importance in the understanding of thermal and electrical conductivity (particularly the electronic contribution), an attempt has been made to review the experimental determination of Lorenz number in metals, semi-metals, alloys and degenerate semiconductors.

1. Introduction

In 1853, Wiedemann and Franz reported an observation which has had far-reaching consequences for the understanding of metallic conduction [1]. In an investigation of the thermal conductivity of several metals at room temperature, they noted that it was proportional to the electrical conductivity. The results they reported are shown graphically in Fig. 1 which shows a plot of the thermal conductivities Λ, relative to that of silver, Λ_{Ag}, versus the electrical conductivities, σ, also relative to that of silver, σ_{Ag}. The electrical conductivities were taken from the works of Riess, Becquerel, and Lenz, without, however, any references (amazingly, the entire paper contains not a single reference). From their finding, written in the form of an equation

$$\frac{\Lambda}{\sigma} = \text{constant (at room temperature)} \quad (1)$$

the authors concluded that "the conductivities of metals for electricity and heat are very closely related to each other, and are probably both functions of the same quantity".

The first investigation of the temperature dependence of Λ/σ was published by Lorenz in 1872 [2]. By comparing measurements of the thermal conductivity of metals performed by Angstrom and other unreferenced investigators, with those of the electrical conductivity by Matthiessen and v. Bose, Lorenz concluded that "the ratio of the conductivities for heat and electricity of pure metals is proportional to the absolute temperature", in the form of the equation

$$\frac{\Lambda}{\sigma} = LT \quad (2)$$

Following modern use, we have written the proportionality constant as L, the Lorenz number. Equation 2 is usually called the Wiedemann–Franz law; in recognition of the very important contribution made by Lorenz in its discovery, it is also called as the Wiedemann–Franz–Lorenz law.

In 1881, Lorenz published his own measurements of both Λ and σ of metals at two different temperatures [3, 4], and thus demonstrated the validity of Equation 2. No further tests of Equation 2 were published until 1899 [5]. At about the same time, Riecke [6, 7] used a free-electron model to explain the temperature dependence, and Drude [8] derived the theoretical value of the Lorenz number, which was very close to the experimental value. Using Fermi–Dirac statistics, Sommerfeld [9–12] showed in 1927 the value of the theoretical Lorenz number to be

$$L_0 = \frac{\pi^2 (K_B)^2}{3 \ e^2} = 2.44 \times 10^{-8} \text{W K}^{-2} \quad (3)$$

where K_B is Boltzmann's constant, and e the electron charge. L_0 is called the Sommerfeld value of the Lorenz number.

It had been noticed already by Lorenz, [3, 4] and by Jaegar and Diesselhorst [5], that L was not a universal factor, but depended on the metal. Later work also showed that (Λ/σ) was not always strictly proportional to T; for a review of the experimental situation in 1935, see Meissner [13].

The Lorenz number, L, would be equal to L_0 if the electron gas is highly degenerate and also if the electron mean free path, l_e, is the same for electrical and thermal conductivities. The condition for high degeneracy is almost always satisfied at low temperatures. The equality of the mean free paths for electrical and thermal conductivities, however, depends on the nature of the scattering process. In general, l_E, the mean free path for electrical conduction, is not equal to l_T, the mean free path for thermal conduction, and

hence the Lorenz ratio, L, departs from the Sommerfeld value, L_0

$$L = \frac{\Lambda}{\sigma T} = L_0 \left(\frac{l_T}{l_E}\right) \qquad (4)$$

The important scattering processes in thermal and electrical conduction are: (i) elastic scattering by solute atoms, impurities and lattice defects, (ii) scattering of the electrons by phonons, and (iii) electron–electron interactions. In the elastic scattering region, i.e. at very low temperature, $l_E = l_T$ and hence $L = L_0$. At higher temperatures, electron–electron scattering and electron–phonon scattering dominate and the collisions are inelastic. Then $l_E \neq l_T$ and hence L deviates from L_0.

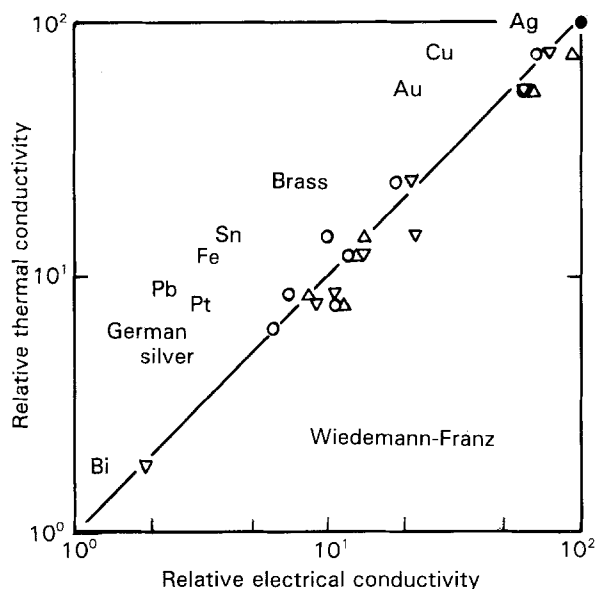Deviations from the Sommerfeld value of the Lorenz number are due to various reasons. In metals,

at low temperatures the deviations are due to the inelastic nature of electron–phonon interactions. In some cases, a higher Lorenz number is due to the presence of impurities. The phonon contribution to thermal conductivity sometimes increases the Lorenz number, and this contribution, when phonon Umklapp scattering is present, is inversely proportional to the temperature. The deviations in Lorenz number can also be due to the changes in band structure. In magnetic materials, the presence of magnons also can change the Lorenz number at low temperatures. In the presence of a magnetic field, the Lorenz number varies directly with magnetic field. Changes in Lorenz number are sometimes due to structural phase transitions. In recent years, the Lorenz number has also been investigated at higher temperatures and has been found to deviate from the Sommerfeld value [14–20] and it is sometimes attributed to the incomplete degeneracy (Fermi smearing) [21] of electron gas. The Lorenz number has also been found to vary with pressure [22, 23].

In alloys, the thermal conductivity and hence the Lorenz number have contributions from the electronic and lattice parts at low temperatures. The apparent Lorenz ratio (L/L_0) for many alloys has a peak at low temperatures. At higher temperatures the apparent Lorenz ratio is constant for each sample and approaches L_0 as the percentage of alloying, x, increases. In certain alloys at high temperatures, the ordering causes a peak in L/L_0.

The Lorenz number of degenerate semiconductors also shows a similar deviation to that observed in metals and alloys. Up to a certain temperature, inelastic scattering determines the Lorenz number value, and below this the scattering is elastic which is due to impurities. Supression of the electronic contribution to thermal conductivity and hence the separation of the lattice and electronic parts of conductivity can be done by application of a transverse magnetic field and hence the Lorenz number can be evaluated. The deviation of the Lorenz number in some degenerate semiconductors is attributed to phonon drag. In some

Figure 1 Relative thermal conductivities, Λ, measured by Wiedemann and Franz (Λ_{Ag} assumed to be = 100) and relative electrical conductivities, σ, measured by (○) Riess, (△) Becquerel, and (▽) Lorenz. σ_{Ag} assumed to be = 100. After Wiedemann and Franz [1].
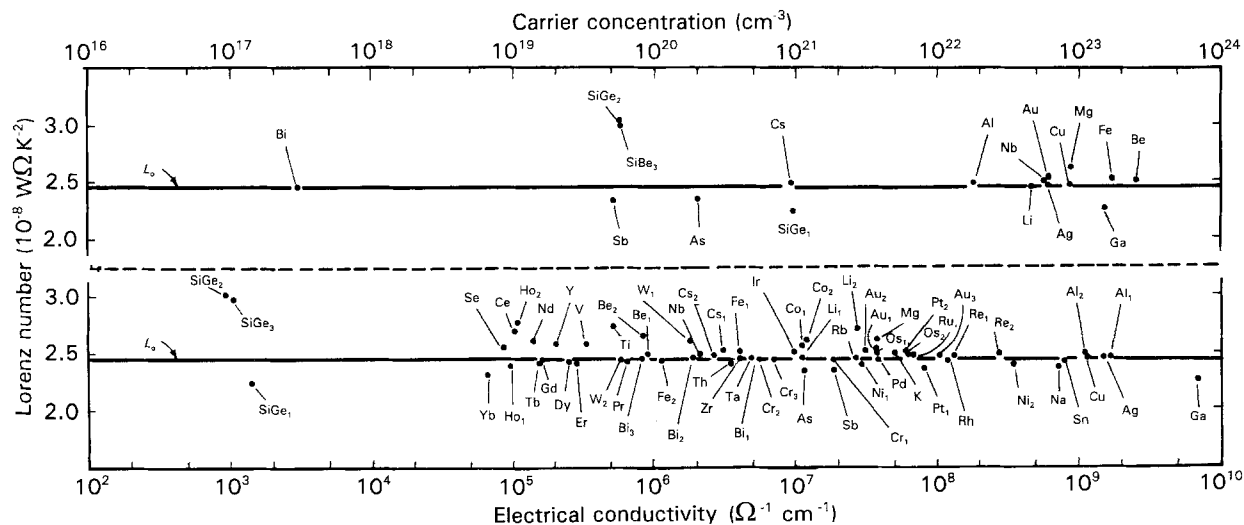

Figure 2 Experimental Lorenz number of elemental metals in the low-temperature residual resistance regime, see Table I. Also shown are our own data points on a doped, degenerate semiconductor (Table III). Data are plotted versus electrical conductivity and also versus carrier concentration, taken from Ashcroft and Mermin [24] except for the semiconductors.

cases, when the mobility of the carriers is not high, it is necessary to go to very low temperatures to separate their lattice and electronic thermal conductivities and hence to determine the Lorenz number.

Our understanding of the physics of the Wiedemann–Franz–Lorenz law is based on a large number of investigations. When we became interested in this subject during an investigation of the thermal conductivity of doped degenerate semiconductors, we were amazed by the very large number of publications dealing with the Wiedemann–Franz–Lorenz law, and by the absence of a recent review of this subject on metals, alloys and semiconductors. While we do not intend here to give such a review, we nonetheless believe that a listing of the experiments reported to date and a mention of the interpretation of these experimental results may be of some use for anyone

interested in this subject. We have aimed at completeness; however, we do not vouch for our success. All we can hope is that our work will make the next person's work a little easier.

As a graphical demonstration of the vast body of published information, we show in Fig. 2 the experimental low-temperature limits of the Lorenz number for all the metallic elements we have collected (and also for one degenerate semiconductor, observed in our own work).

2. Description of tables

The information is presented in Tables I-III: elemental metals and semi-metals, metallic alloys, and degenerate semiconductors.

TABLE I Elemental metals and semi-metals

Element	Temperature range (K)	σ_0 (Ω^{-1} cm^{-1})	L in residual resistivity range, (10^{-8} WΩ K^{-2})	Notes	Reference
Aluminium	2–30	1.76×10^9 1.11×10^9	2.46(1) 2.48(2)	1	[28]
	1.4–4.2	210(RRR) 3490(RRR)	2.44 (2.5 K) 2.44(1.5 K)	2	[26]
Antimony	2–150	1.85×10^7	2.33	3	[28]
Arsenic	2–300	3.3×10^9 (Binary direction)	1.81	4	[29]
	0.3–8	1.16×10^7 (Binary direction)	2.34 (below 2 K)	5	[30]
	2–300	1450(RRR) (Trigonal) 5310(RRR) (Trigonal)	1.8 (at 3 K) 1.4 (at 3 K)	6	[31]
Beryllium	2–300	9×10^5 8.3×10^5	2.48(1) 2.64(2)		[32]
Bismuth	35–140		2.4 (50 K)	7	[33]
	0.1–1	5.41×10^6 1.85×10^6 8.24×10^5	2.45(1) 2.45(2) 2.45(3)	8	[34]
Cerium	2–20	1×10^5 (4.2 K)	2.68 (4.2 K)	9	[35]
Caesium	2–16	2.99×10^6 2.58×10^6	2.51(1) 2.47(2)	10	[36]
Chromium	5–130 1.5–300 323–1300	1.82×10^7 5.45×10^6	2.44(1) 2.44(2)	11 12	[37] [38] [39]
Cobalt	2–120 1.2–6	1.1×10^7 1.15×10^7	2.55(1) 2.59(2)		[40] [41]
Copper	2–90 2–60 (Low temp)	1.5×10^8 1.15×10^9 1.11×10^8	2.49 2.45 ± 0.05 2.4 1.8 (with magnetic field)	13 14 15	[42] [43] [44]
Dysprosium	0.3–4.2	4.95×10^5 2.47×10^5 1.86×10^5 (annealed)	2.59 2.43 2.56	16	[45]
	5–300	1.66×10^6 (c-axis)	5.3	17	[47]
Erbium	0.3–4.2	1.16×10^5 2.84×10^5	2.40 2.41	16	[45]
	5–300	2.15×10^5 (b-axis) 1.25×10^5 (c-axis)	4.5 4.5	17	[47]

TABLE I Continued

Element	Temperature range (K)	σ_0 (Ω^{-1} cm^{-1})	L in residual resistivity range, (10^{-8} WΩ K^{-2})	Notes	Reference
Gallium	1.4–4.2	6.94×10^9	2.25		[48]
	303		2.4		[49]
Gadolinium	0.3–4.2	2.97×10^5	2.53	16	[45]
		1.55×10^5	2.44		
	5–300		3.5 (c-axis)	18	[50]
			4.5 (a-axis)		
Gold	2–30	1.06×10^8	2.47(3)	19	[25]
		3.04×10^7	2.50(2)		
		3.559×10^7	2.51(1)		
	300–1200	7.31×10^7	2.42		[51]
Hafnium	2–90	2.36×10^5	3.47	20	[52]
Holmium		9.43×10^4	2.38(1)		[45]
	0.3–4.2	1.03×10^5	2.76(2)		
	5–300	3.33×10^5	5.3 (c-axis)	18	[50]
		2.5×10^5	4.0 (a-axis)		
Iridium	4–130	9.67×10^6	2.5		[53]
Iron	2–77	2.45×10^7	2.55		[54]
	2–90	1.09×10^6	2.44(2)		[55]
	2–100	4.03×10^6	2.5(1)	21	[56]
Lead	100–200	1×10^6	2.5(200 K)		[57]
Lithium	2–100	1.45×10^7	2.49	22	[36]
		2.69×10^7	2.70(2)		
	2–90	1.124×10^7	2.45(1)		[58]
		2.136×10^7	2.49		
Lutetium	5–300	1.43×10^6	3.4 (c-axis)	17	[47]
		3.7×10^5	4.3 (b-axis)		
Magnesium	2–35	3.70×10^7	2.6		[59]
Neodymium	2–40	3.33×10^5	3.3	23	[60]
		2.17×10^5	4.5		
	2–20	1.33×10^5	2.65	24	[61]
Nickel	5–150	3.43×10^8	2.38	21	[62]
	2–100	2.88×10^7	2.38		[56]
Niobium	2–90	2.13×10^6	2.49	20	[53]
Osmium	2–20	3.60×10^7	2.49(1)		[63]
		6.01×10^7	2.48(2)		
	2–300	1.0×10^7	2.60		[64]
		1.15×10^7	2.61		
Palladium	2–30	5.50×10^7	2.45		[65]
	2.5–19	3.73×10^7	2.45		[66, 67]
Platinum	0.1–1.2	8×10^7	2.50(2)	25	[68]
	3–130	8×10^7	2.35(1)		[53]
Potassium	2–90	7.5×10^7	2.55		
		4.59×10^7	2.49	22	[36]
Praseodymium	2–40	1.67×10^6	3.2 (2K)	26	[70]
	2–20	6.25×10^5	2.44	24	[61]
Rhenium	2–120	7.69×10^7	2.43		[40]
		1.27×10^6	2.56 (unannealed)		
	2–20	1.33×10^8	2.46(1)		[20]
		2.73×10^8	2.49(2)		
Rhodium	4–120	1.19×10^8	2.41		[53]
	2–90	1.19×10^8	2.44		[55]
Rubidium	2–70	2.60×10^7	2.45	22	[36]
	40–300		2.45 (at 300 K)		[71]
Ruthenium	2–300	4.35×10^6	2.40		[64]
		6.67×10^7	2.46		
Scandium	2–20	8.3×10^4	2.55 (4.2)	27	[35]
Silver	2–30	1.49×10^9	2.45	1	[25]
		1.25×10^9	2.48		
	0.3–1.2	4.93×10^8	2.53	28	[68]
	300–1100	4.09×10^8	2.42 (700 K)		[51]

TABLE I Continued

Element	Temperature range (K)	σ_0 (Ω^{-1} cm^{-1})	L in residual resistivity range, (10^{-8} WΩ K^{-2})	Notes	Reference
Sodium	2–16	7.06×10^8	2.36	22	[36]
		6.0×10^8	2.31		
Tantalum	2–140	4.81×10^6	2.45		[72]
Terbium	0.3–4.2	1.51×10^5	2.41	16	[45, 46]
	5–300	5×10^5	4.4 (a-axis)	18	[50]
		5×10^5	5.5 (c-axis)		
Thorium	3–300	3.45×10^7	2.4 (2 K)	29	[73]
		9.88×10^6	2.8 (2 K)		
		2.13×10^6	2.6 (2 K)		
	4–100	1.5×10^6	3.0 (100 K)		[74]
Thulium	5–300	5.78×10^5	4.1 (b-axis)	30	[75]
		2.74×10^5	8.8 (c-axis)		
Tin	4.5–77	8.06×10^8	2.44 (6 K with tetragonal axis)		[76]
		1.16×10^9	2.43 (72 K with tetragonal axis)		
	5–70	4.35×10^6	1.78 (5 K)	31	[77]
Titanium	2–140	5.09×10^5	2.74 2,78 (β-phase)		[72]
	2–100	4.24×10^4	2.9		[56]
	200–1900		3.02 (α-phase)	21	[78]
Tungsten	2–120	3.22×10^7	2.65		[40]
	1.5–6.0	1.767×10^6	2.64(1)		[79]
		5.72×10^5	2.44(2)		
Vanadium	2–90	3.23×10^5	2.57	20	[52]
Ytterbium	0.3–4.2	6.35×10^4	2.30	16	[45, 46]
Yttrium	2–20	2×10^5	2.58	32	[35]
	3–300	4.3×10^5	3.02 (3 K)		[80]
Zirconium	2–80	3.96×10^6	2.4	21	[56]

Notes

1. Lorenz number at low temperatures, in the range of impurity scattering, is very close to Sommerfeld value. No electron–electron scattering was noticed.

2. As impurity content increases, L approached L_0 faster, i.e. at higher temperatures, than in pure. The maximum phonon contribution at these low temperatures cannot be more than 3% according to calculations and could not be detected in the present experiment. This experiment was performed to verify the fact that there is additional phonon contribution reported by [27] and $L_0 = 2.5 \times 10^{-8}$ WΩ K^{-2} (RRR = residual resistivity ratio).

3. For pure antimony the two components of conductivity (electron and phonon) are comparable except at very low or high temperatures. The electronic component behaves very much like that in a simple monovalent metal. The electronic component of thermal conductivity is separated, by suppressing it by applying a magnetic field and measuring only the lattice part and subtracting this from the total conductivity.

4. The Lorenz number obtained from the thermal conductivity data is smaller than the Sommerfeld value (as in bismuth), and may be due to inelastic scattering of the carriers by phonons or carrier–carrier scattering.

5. Below 2 K, the Lorenz number is within 4% of the Sommerfeld value, but above that the value decreases and is 1.85×10^{-8} WΩ K^{-2} at 7 K, where inelastic scattering of charge carriers becomes important.

6. The Lorenz number for both crystallographic orientations (binary and trigonal) is well below the Sommerfeld value showing clearly that the carrier scattering is highly inelastic between 3 and 80 K. There is a tendency to reach the Sommerfeld value at still lower temperature, where the scattering may be purely due to impurities and elastic. The Lorenz number is smaller in purer samples (RRR = residual resistivity ratio).

7. In the temperature range investigated, electronic thermal conductivity is nearly constant, and at low temperatures is only a small fraction of the total thermal conductivity. The Lorenz number at 50 K is equal to the Sommerfeld value like any other degenerate conductor, but starts decreasing with decreasing temperature, which may be due to inelastic scattering. The electronic term is separated from the total thermal conductivity by the method of applying strong magnetic fields and suppressing the electronic part. At around 140 K, about 30% of the electronic thermal conductivity is due to the bipolar flow of carriers.

8. The Lorenz number obtained is equal to the Sommerfeld value. The thermal conductivity varies linearly with temperature between 1.5 and 3 K, but below 1 K, it deviates from this fit. This is due to reduction in phonon mean free path below 1 K.

TABLE I (*Notes continued*)

9. Cerium has a slightly higher L compared to L_0 and in the present range of measurement, it is not sure whether the residual resistivity range has been reached. With increase of temperature, the Lorenz number also increases, which indicates that there is enough phonon contribution to thermal conductivity even at these low temperatures. The Lorenz number at 20 K is 3.83×10^{-8} WΩ K^{-2}.

10. As the normal melting point for caesium is 28 °C, it is spontaneously inflammable on exposure to air and has a rather smaller thermal conductivity than the other alkali metals. It also frequently contains dissolved oxygen, due to which one of the samples showed considerable hysteresis in the experimental value of thermal conductivity. A very small coefficient for the phonon term is present at low temperature.

11. The Lorenz number obtained at low temperatures is very close to the Sommerfeld value in all the chromium samples studied.

12. At low temperatures, the Lorenz number obtained for all the samples is equal to that of the Sommerfeld value. But as the temperature increases, the Lorenz number decreases due to inelastic scattering of carriers. At 90 K, the Lorenz number is higher than L_0 which is due to the band structure of chromium and not due to the phonon contribution. This type of behavior has been reported by Powell and Tye [39] in the temperature range 323–1300 K.

13. Below 4 K, an additional electrical resistance was observed and due to this, there is an increase in Lorenz number to 2.56×10^{-8} WΩ K^{-2}. The resistance observed is more in electrical resistance than in thermal resistance, and if any process is responsible for this, it is more effective on electrical resistivity.

14. This paper clarifies the discrepancy about the increase in the Lorenz number at low temperatures, and it was found that the Wiedemann–Franz–Lorenz law is well obeyed at low temperatures and L is equal to L_0 within 2%.

15. The effect of magnetic fields on the variation of Lorenz number was studied in copper at low temperatures. The Lorenz number without magnetic field at low temperature was equal to L_0. But, with transverse magnetic field applied, L varies directly with the strength of the field. When applied longitudinally, L remains constant ($= 1.8 \times 10^{-8}$ WΩ K^{-2}) irrespective of the strength of the field.

16. In all the heavy rare-earth metals studied, the thermal conductivity has an electronic term which becomes linear with temperature, and another quadratic term, which is due to the phonon contribution. The Lorenz numbers evaluated from the linear terms are very close to the Sommerfeld value.

The ideal resistivity increases in the elements with increasing atomic number, irrespective of whether they are magnetic or non-magnetic, indicating that the dominant effect on the ideal resistivity arises from phonons rather than magnons.

17. In all the samples studied, the Lorenz number was always higher than the Sommerfeld value throughout the temperature range, except in lutetium sample (*c*-axis). The reason for the higher Lorenz number may be due to the contribution of phonons and magnons to thermal conductivity, which is common in heavy rare-earth elements.

18. The Lorenz numbers obtained in gadolinium, terbium and holmium are all higher than the Sommerfeld value, implying that an appreciable amount of heat is conducted by phonons and magnons in rare-earth metals.

An attempt was made to determine the dominant scattering mechanisms at low temperatures. For gadolinium, a plot of T/K ($K = $ thermal conductivity) versus T^3 was fairly linear for 8–16 K, but in terbium and holmium data did not fit this dependence very well. In addition to impurities and phonons, magnons can also scatter electrons. Thus, it is surprising that measured thermal conductivities do not follow the equation $1/K_e = A/T + BT^2$, very well.

19. Higher Lorenz number may be due to more impurities in the gold samples, but further experiments are required to establish the fact.

20. In the case of vanadium and niobium, the Lorenz numbers obtained are very close to the Sommerfeld value. For one of the vanadium samples, which has a higher impurity concentration, L is slightly greater, suggesting that the impurities reduce the conductivity due to the free electrons to such an extent that the lattice thermal conductivity becomes significant. In the case of hafnium, for which the experimental Lorenz number is higher, it appears probable that lattice conductivity is quite appreciable.

21. Iron and nickel show a variation characteristic of metals in Lorenz number at low temperatures and are close to the Sommerfeld value. In the case of zirconium, at low temperatures, the Lorenz number is almost equal to that of L_0, but at higher temperatures, L reduces below L_0, and then rises above L_0, indicating that a considerable fraction of the heat is carried by the phonons. In the case of titanium, the Lorenz number is always higher than L_0 and approaches the Sommerfeld value around 2 K.

22. For thermal conductivity at low temperatures ($T \ll \theta$), $1/K = (A/T) + BT^2$ ($K = $ thermal conductivity) is well obeyed in all the alkali metals studied. At low temperatures where impurity scattering is dominant, the experimental Lorenz numbers lie in the range $(2.45 \pm 0.15) \times 10^{-8}$ WΩ K^{-2} which is within the experimental error compared to that of Sommerfeld value.

23. In all the samples of neodymium studied, the Lorenz number obtained was always higher and with annealing the Lorenz number decreased. The extra thermal conductivity observed is not solely due to phonons. If it was due to phonons only, after annealing, one should get a higher number of phonons and hence higher thermal conductivity. This effect may be due to the presence of two structures (d h c p and f c c) initially and change of structure after annealing.

24. In the temperature range studied, the Lorenz number of praseodymium varies very much as in a metal and reaches a Sommerfeld value at 2 K but rises slightly above it, possibly due to some phonon contribution there. With increase of temperature, the Lorenz number decreases due to inelastic scattering of carriers. In the case of neodymium, the Lorenz number is always higher than L_0, and approaches the Sommerfeld value below 4 K. The extra thermal conductivity may be due to phonons.

25. In platinum, in the range 0.3–1.2 K, the Lorenz number is higher than L_0, and this is definitely due to the phonon contribution. This work has provided further evidence that the details of electron–electron scattering in the transition metals vary greatly from metal to metal, i.e. the simple Lorenz ratio is not applicable.

26. The Lorenz number of praseodymium has a metallic-like variation with temperature; but the L obtained at low as well as high temperature are higher than L_0. After annealing the sample, the L value dropped but still remained higher than the Sommerfeld value. As in neodymium, L decreased after annealing and shows that the additional thermal conductivity observed is not completely due to phonons, and may be due to presence of two structures.

27. In scandium, the higher Lorenz number 2.64×10^{-8} WΩ K^{-2}, obtained at 4.2 K, is due to the presence of phonon contribution to the thermal conductivity. After separating the linear term from the T^2 term, L obtained is close to L_0. The Lorenz number increases with temperature, indicating the increase of lattice conductivity with temperature. The Lorenz number at 20 K is 2.98×10^{-8} WΩ K^{-2}.

28. The anomalous oscillatory behaviour cannot be found in these data as reported by Sharma [69]. The Lorenz number is larger compared to L_0. This was attributed to the phonon contribution in aluminium by Willott [27]. In this experiment, there was no evidence of a decrease in the phonon contribution, even at 0.35 K.

29. The three samples studied had different impurities. The purest showed the usual behaviour of a metal at low temperatures, but L increased to a value of 3×10^{-8} WΩ K^{-2}, at 200 K. This cannot be due to phonons, because at these temperatures the phonon contribution is very small because of Umklapp processes; Therefore, this excess Lorenz number is probably related to the band structure of thorium and represents a deviation from the free electron model. The other two impure samples show an increase of Lorenz number at low temperature over the Sommerfeld value and then fall back to the Sommerfeld value around 2 K. This may be due to the phonon contribution to thermal conductivity, which shows up as a quadratic term in addition to the linear term (due to electrons).

TABLE I (*Notes continued*)

30. At low temperatures thulium becomes ferrimagnetic, and magnons contribute to enhancement of specific heat: the large deviation of total Lorenz number measured from the Sommerfeld value shows that magnons also contribute to thermal conductivity in addition to electrons at low temperatures.

31. Three single crystals of tin with different orientations and impurity contents were studied to understand the elastic and the inelastic scattering mechanism. An attempt has been made to separate the vertical and horizontal components of thermal conductivity, where the vertical component is due to the inelastic scattering of electrons. Its variation with temperature is studied in the range 5–10 K. At higher temperatures, the Lorenz number reaches the Sommerfeld value and with decreasing temperature, because of the inelastic scattering (vertical component), L shows a dip and again rises. The temperature at which the dip occurs, depends upon the impurity content.

32. Like other rare-earth metals, yttrium also shows the presence of a phonon contribution to thermal conductivity at low temperatures. The total Lorenz number at 4.2 K obtained is higher than L_0 and is 2.64×10^{-8} WΩ K^{-2}, but after subtracting the phonon term, the Lorenz number is close to L_0. At higher temperatures, the phonon conductivity increases, which can be seen by the increase of the total Lorenz number.

TABLE II Metallic alloys and compounds

Alloy	Temperature range (K)	$\sigma_0(\Omega^{-1}\text{cm}^{-1})$	$L(10^{-8}$ WΩ K$^{-2})$	Notes	Reference
Copper + 0.02% Ge	2–300	1.19×10^7	2.68	1	[32]
+ 0.0043% Fe		2.43×10^7	2.70		
+ 0.056% Fe		1.88×10^6	2.45		
Cu–7.5% Au	2–90	2.83×10^5	2.40		[81]
Cu–16.5% Au		1.42×10^5	2.52		
Cu–2% Zn		1.78×10^6	2.39		
Cu–5% Zn		8.33×10^5	2.37		
Cu–10% Zn		5.15×10^5	2.42		
Cu–0.9% Pt	2–90	4.90×10^5			[82, 83]
Cu–1.1% Pt		4.41×10^5			
Cu–2.0% Pt		2.49×10^5	≈ 2.45		
Cu–0.35% As		3.69×10^5			[82, 84]
Cu–1.0% Sb		1.89×10^5			[82, 85]
Copper + 0.056% Fe	2–90	1.79×10^6			[82, 86]
+ 0.12% Fe		8.13×10^5	≈ 2.44		
+ 0.31% Fe		3.18×10^5			
+ 2.2% Si		1.39×10^5	≈ 2.44		[82, 83]
Copper + 50 p.p.m. Cr	1.6–4	1.61×10^6	2.44	Unannealed	
		3.33×10^7	3.23	Long annealed	[87, 88]
		2.09×10^6	2.45	Partially annealed	
+ 36 p.p.m. Cr		5.05×10^6		Unannealed	
		8.13×10^6	2.85	Partially annealed	
		5.88×10^7	3.39	Long annealed	
Cr–4.57% V	4–300	7.40×10^5	≈ 2.5 (at 4.2 K)	2	[89]
Cr–3.89% Mo		4.12×10^5			
Cr–9.35% Mo		2.39×10^5			
Silver + 29.97% Cd	2–300	2.72×10^5	2.24	Rod annealed	[90]
+ 19.21% Cd		3.03×10^5	2.40	Rod recast	
+ 9.51% Cd		4.42×10^5	2.41	Rod annealed	
+ 4.91% Cd		7.25×10^5	2.34	Rod annealed	
+ 1.96% Cd		1.59×10^6	2.38	Rod strained	
+ 2.08% Pd		1.12×10^6	2.38	Rod annealed	
+ 20.08% Pd		1.21×10^5	2.04	Rod annealed	
+ 29.62% Pd		7.82×10^4	2.10	Rod annealed	
+ 50% Pd		3.61×10^4	4.76	Rod annealed	

TABLE II Continued

Alloy	Temperature range (K)	$\sigma_0(\Omega^{-1}\mathrm{cm}^{-1})$	$L(10^{-8}\ \mathrm{W}\Omega\ \mathrm{K}^{-2})$	Notes	Reference
+ 70% Pd		2.81×10^4	5.4	Rod annealed	
+ 95% Pd		1.72×10^5	2.35	Rod annealed	
Silver					
+ 0.55% Mn	1.6–4.5	1.09×10^6	≈ 2.45 (at 1 K)	Minimum in L occurs at above 4 K	[91]
+ 0.32% Mn		2×10^6	≈ 2.45 (at 1 K)	Minimum in L occurs at 3.5 K	
+ 0.14% Mn		3.8×10^6	≈ 2.45 (at 1 K)	Minimum in L occurs at 2.5 K	
Silver	2–90	3.82×10^5	≈ 2.4		[82, 83]
+ 1.8% Pt		2.83×10^5	≈ 2.4		
+ 1.6% Al					
Ag + Cr					
Tin	7–300	4.41×10^6	≈ 2.3 (at 7 K)	3	[92]
+ 15% lead					
+ 30% lead		4.13×10^6	2.4 (at 7 K)		
+ 50% lead		3.85×10^6	2.5 (at 7 K)		
+ 70% lead		3.92×10^6	2.2 (at 7 K)		
Sodium tungsten bronzes	4.2–300	2.92×10^5 ($x = 0.86$)	2.5	4	[93]
$\mathrm{Na}_x\mathrm{WO}_3$		3.28×10^4 ($x = 0.51$)			
$0.5 \leqslant x \leqslant 0.86$		1.26×10^5 ($x = 0.75$)			
		9.17×10^4 ($x = 0.70$)			
		5.18×10^4 ($x = 0.63$)			
Zinc					
+ 4.1% Al	Measured at 4.2 and 77	6.67×10^5	3.14 (4.2 K)	Lorenz number at 4.2 K is higher than L_0 because of lattice contribution due to alloying	[94]
+ 3.1% Cu			3.08 (77 K)		
+ 0.05% Mg					
NbO	100–660	5.88×10^5	2.6	5	[95]
RuO_2	2–47	7.58×10^6	2.49		[96, 97]
		9.61×10^6	2.49		
	10–100		2.60		[98]
$\mathrm{V}_3\mathrm{Si}$	4.2–80	4.0×10^5	1.97 (18–55 K)	6	[99, 100]
Uranium mononitride	2–85	1.32×10^5	2.47 (2 K)	7	[101, 102]
	80–400				
$\mathrm{VO}_{0.79}$ to $\mathrm{VO}_{1.29}$	100–1000		≈ 2.6		[96, 103]
TiO	123–1000		≈ 2.6		[96, 104]
$\mathrm{TiO}_{1.4}$	123–1000		≈ 2.6		[96, 105]
UC	500–1800		2.21		[106, 107]
WSi_2	1000–1500		3.01		[106, 107]
TiC	800–2300		4.0		[106, 108]
ZrC	900–2300		2.07		[106, 109, 110]
LaS *	400		3.37		[106, 111]
$\mathrm{Pd}_{77.5}\,\mathrm{Si}_{16.5}\,\mathrm{Cu}_6$	273	1.42×10^4	2.4		[112]
$\mathrm{Fe}_{73}\,\mathrm{Mo}_{10}\,\mathrm{B}_{17}$	273	8.2×10^3	3.2		[112]
$\mathrm{Fe}_{80}\,\mathrm{B}_{20}$	273	8.2×10^3	2.9		[112]

TABLE II Continued

Alloy	Temperature range (K)	$\sigma_0(\Omega^{-1}cm^{-1})$	$L(10^{-8}\ W\Omega\ K^{-2})$	Notes	Reference
$Zr_{70}\ Co_{30}$	273	6.5×10^3	2.9		[112]
$Zr_{70}\ Ni_{30}$	273	6.3×10^3	2.2		[112]
$Ti_{50}\ Be_{40}\ Zr_{10}$	273	4.7×10^3	2.8		[112]
$(La_{0.9}\ Pr_{0.1})\ Sn_3$	0.3–12	1.33×10^6	1.42 (0.5 K)	8	[113]

Notes

1. In copper + 0.02% germanium, and copper + 0.0043% iron, the electronic component of thermal conductivity, K_e, appears to be the dominant part of the thermal conductivity and is similar to that observed in pure copper. In copper + 0.056% Fe, K_e and K_g (lattice part of thermal conductivity) are comparable at low temperatures. The maximum value of K_g of copper appears to be about 1 W cm^{-1} K^{-1} at 30 K.

2. Alloys of chromium with molybdenum and vanadium also behave like pure chromium showing anomolous increase of L below 100 K and again above 200 K. Below 100 K it is due to phonons but above 200 K, it is due to the electronic band structure of chromium.

3. In all the compositions of tin–lead alloys studied, the total Lorenz number is higher at low temperatures and tends to decrease at high temperatures. The maximum total Lorenz number observed at low temperatures is in 50–50 alloy, where one expects maximum phonon conductivity contribution. This system behaves like any other alloy system.

4. The apparent Lorenz ratio for the samples studied have a peak at low temperatures caused by lattice conduction. At higher temperatures the apparent Lorenz ratio is constant for each sample and approaches L_0 as x increases. At low temperatures lattice conductivity calculated using the Callaway theory, correlated well with that obtained by subtracting $L_0\sigma T$ from the measured thermal conductivity. Large deviations occurred at high temperatures indicating that the high-temperature Lorenz ratio for smaller values of x is considerably larger than L_0, but approaches L_0 at low temperatures. The ordering of the sodium atoms enhances the low-temperature lattice conductivity, and at high temperatures the ordering causes a peak in L/L_0 at $x = 0.75$. The higher values of L observed at high temperatures cannot be attributed to the lattice, but are due to the narrow d-type conduction band. This type of anomaly was observed in thorium, chromium and hafnium.

5. The Wiedemann–Franz–Lorenz law is rather well obeyed; however, as in chromium, there is a positive deviation from theoretical Lorenz number, L_0. This deviation is maximum of 30% from L_0 at approximately 250 K. Following chromium, this positive deviation is attributed to the multi-energy band-structure of NbO and not to the lattice component of thermal conductivity.

6. In the range from 16.9–9 K, thermal conductivity is determined by electrons being scattered at the imperfections. The phonon contribution may be neglected in this range. Below 9 K, the quantity of the normal electrons is reduced to such a degree by the formation of Cooper pairs that the phonon contribution becomes noticeable, which with decreasing temperature, rises greatly until the mean free path of phonons approaches the crystal dimensions.

7. Measurement of thermal conductivity in the range 80–400 K indicates that the lattice conductivity peaks in the range 250–300 K, and that the high-temperature limit of the Lorenz number may be greater than the Sommerfeld value. Thermal conductivity measurements in the range 2–85 K indicate that the heat is carried by electrons exclusively below 10 K. The electronic term diminishes around the Neel temperature, and the lattice term becomes prominent.

8. The results obtained in this investigation on the sample (Pr = 0.1) show deviations in Lorenz number at low temperatures from that of Sommerfeld value, L_0. It becomes larger than L at 7 K and above. With decreasing temperature, the Lorenz number drops very rapidly to a minimum value of 0.976 and then rises again at still lower temperatures and reaches a value 1.42 × 10^{-8} WΩ K^{-2} around 0.5 K, which is still smaller than L_0. This lowering of the Lorenz number is due to inelastic scattering present due to the crystal field splitting of Pr^{3+}.

TABLE III Degenerate semiconductors

Alloy	Temperature range (K)	$\sigma_0(\Omega^{-1}\ cm^{-1})$	Carrier concentration (cm^{-3})	$L\ (10^{-8}W\Omega\ K^{-2})$	Notes	Reference
n-HgTe	20–200	7.1×10^3	3×10^{18}	≈ 2.4	1	[114]
p-PbTe	20–100	–	3×10^{18}	1.7 (at 80 K)	2	[115]
	3–100	–	2.6×10^{18}	2.3 (10 K)	4	[116, 117]
n-PbTe	20–100	–	5×10^{18}	1.7 (at 20 K)	2	[115]
			2×10^{18}	1.59 (at 20 K)		
	80–250	–	6.3×10^{18}	2.07 (at 250 K) 1.59 (at 100 K)	3	[118]
	80–200		8.9×10^{18}	2.07	3	[118]
	3–100	6×10^4	1.3×10^{19}	2.4 (at 18 K)	4	[116, 117]
5% PbSe + 95% PbTe	80–300	–	$\approx 10^{18}$	2.20 (at 260 K) 1.6 (at 100 K)	3	[118, 119]

4269

TABLE III Degenerate semiconductors

	Temperature range (K)	$\sigma_0(\Omega^{-1}\,cm^{-1})$	Carrier concentration (cm^{-3})	$L\,(10^{-8}W\Omega\,K^{-2})$	Notes	Reference
40% PbSe + 60% PbTe	80–300	–	$\approx 10^{18}$	2.4 (200 K and above) 2.2 (at 100 K)	3	[118, 119]
p-PbSe	3–100	8×10^4	7×10^{18}	2.4 (15 K)	4	[116, 117]
n-PbS	3–100	6.5×10^4	6.7×10^{18}	2.4 (15 K)	4	[116–117]
PbTe + 5% SnTe	80		2.1×10^{19}	1.73	–	[119]
PbTe + 5% PbS	80		2.4×10^{18}	1.95	–	[119]
PbTe + 10% PbS	80		7.9×10^{18}	1.61	–	[119]
HgSe	2–200		6×10^{18}	2.5 (35 K) 0.98 (80 K)	5	[120]
n-HgSe	80–400		1×10^{18}	2.32 (at 400 K)		[121]
n-Ag₂Te	80–230	$5.5. \times 10^3$ (80 K) 6×10^3 (80 K)	1.55×10^{18} 3.14×10^{18}	1.46 1.46	6	[122]
	80–300	–	1.23×10^{19} 4.32×10^{18} 1.55×10^{18}	2.4 (80 K) 1.68 1.49	6	[123]
n-InSb	100–500	1.2×10^4 (150 K)	1×10^{19}	1.83 (100 K)	7	[124, 125]
n-Cd₃As₂	15–100	1.9×10^4	2×10^{18} 2×10^{18}	1.66 (115 K) 3.09 (310 K)	8	[126] [127]
Si₇₈Ge₂₂ p	0.07–100	1.42×10^3	9.1×10^{19}	2.22	9	[128]
Si₇₈Ge₂₂ p	0.3–100	8.77×10^2	5.6×10^{19}	3.04		
Si₇₈Ge₂₂ n	0.07–100	1.01×10^3	7.1×10^{19}	2.74		

Notes

1. The Lorenz number studied in the temperature range 20–200 K shows a qualitatively similar deviation as observed in metals, but above 40 K, L is lower than the Sommerfeld value, L_0. The maximum deviation observed was at 200 K, with L equal to 1.95×10^{-8} WΩ K^{-2}. This shows that below 40 K the scattering of carriers is elastic and above, inelastic. The separation of electronic conductivity from the total conductivity was done by suppressing the electronic thermal conductivity by applying magnetic field (Maggi–Righi–Leduc effect). This can be done only in some compounds where the following conditions are satisfied: (1) high mobility of the carriers ($\mu H/c \gg 1$); (2) the electronic part of thermal conductivity should be an appreciable fraction of the total thermal conductivity.

2. All the samples measured show a lower Lorenz number even at 20 K, which shows that scattering of the carriers by optical vibrations is inelastic.

3. (a) The role of the inelastic carrier scattering in n-type PbTe has been investigated over a wider range of carrier densities and at high temperatures than ever before.

(b) From theoretical calculations (for low temperatures) and experimental data for $T > 20$ K, $L \approx L_0$ at 4 K for samples with $n \approx 10^{18}$ cm^{-3}, but with increasing temperature L decreases, passes through a minimum value of about 1.7×10^{-8} WΩ K^{-2} at 77 K, and then again becomes equal to L_0 at $T = 300$ K.

(c) When the carrier density increase, L tends to equal L_0; when $n > 10^{19}$ cm^{-3} $L = L_0$ at all investigated temperatures (80–300 K).

(d) L of PbT–PbSe, solid solution, behaves like PbTe, with small concentrations of PbSe; when the content of PbSe is increased $L = L_0$ at all temperatures, with a small dip around 80 K.

(e) The value, the temperature dependence, and the carrier density dependence of L can be explained theoretically by electron–electron collisions.

4. The most interesting result in this investigation was that the Lorenz number of all three degenerate semiconductors (PbTe, PbSe, and Pbs) measured at $T > 20$ K differs considerably from its theoretical value for the elastic scattering mechanism. The Lorenz number is smaller in the inelastic scattering case. These results can be explained by assuming that the scattering of carriers in PbTe, PbSe and Pbs crystals is, to a considerable degree, inelastic. When the temperature is lowered ($T < 30$ K), impurity scattering becomes more important and this scattering is elastic. Consequently, the Lorenz numbers obtained from all three investigated compounds approach the theoretical value.

5. The variation of the Lorenz number in degenerate samples of HgSe indicates that elastic scattering becomes important only below 40 K. L is larger than L_0 around 30 K, which might be due to the phonon drag, which is also observed in thermoelectric measurements. Above 40 K, carrier scattering becomes inelastic and the Lorenz number decreases and reaches the lowest value (0.98×10^{-8} WΩ K^{-2}) at 200 K and again reaches L_0 above 400 K. Thus, it may be concluded that in the range 40–400 K electron scattering in HgSe inelastic.

6. The Lorenz number obtained in the present investigation, in both samples is lower than the Sommerfeld value, L_0, in the temperature range investigated, indicating that the scattering of electrons is inelastic. The Lorenz number obtained at 80 K shows that it is also dependent

TABLE III (Notes continued)

on the carrier density. The inelasticity observed in Ag_2Te in mainly due to electron–electron interaction rather than optical phonon interaction which is 1%–2% only.

7. The limitations in the method of applying transverse magnetic fields in order to suppress the electronic contribution of the thermal conductivity and then estimating the lattice part are: (1) material should have high carrier mobility throughout the range of measurement; (2) lattice thermal conductivity should not be very high; examples for high conductivities are germanium, silicon n-InSb and n-InAs.

In the case of n-InSb, the range was chosen so that the mobilities were still high, and thermal conductivity not large. L is smaller than L_0 in the range 100–500 K and only has a tendency to approach L_0 at low temperatures and above 500 K. The reason for this may be inelastic scattering of electrons by electrons or by optical phonons. In the range where mobilities are small, the method to evaluate Λ_e was to calculate L from L_{th}, by $L = L_{th} - \alpha^2$, where α is the Seebeck coefficient.

8. n-Cd_3As_2 also exhibits elastic scattering of carriers below 35 K, but the Lorenz number rises above L_0 below 30 K, the reason for which is not understood. Above 40 K, L decreases with decreasing temperature and is equal to 1.96×10^{-8} $W\Omega K^{-2}$ around 100 K. This decrease of the Lorenz number may be attributed to inelastic electron–electron scattering.

9. In all degenerate semiconductors, except $Si_{78}Ge_{22}$, the electronic thermal conductivity was separated from the total conductivity by subtracting the lattice contribution, obtained by supressing the electronic term by applying a transverse magnetic field. This technique requires many conditions to be satisfied: (1) high mobility of the carriers; (2) the electronic term should be greater than $\approx 5\%$ of the total thermal conductivity; (3) high magnetic fields to suppress the electronic contribution. This technique cannot be applied in the case of $Si_{78}Ge_{22}$ because of the high lattice thermal conductivity and a relatively small electronic contribution at elevated temperatures (10–100 K). Therefore, in order to separate the electronic term, the phonon conductivity was intentionally lowered by choosing polycrystalline samples of few micrometres grain size, and measuring the thermal conductivity below 1 K, where the phonon contribution decreases as T^3 and is limited by the size of the grains. Then by plotting a graph, Λ/T versus T^2, we estimated the electronic term from the $T = 0$ intercept of the straight line. The Lorenz number at low temperatures was evaluated from the electronic term and the electrical conductivity which remained constant below liquid nitrogen temperatures. We believe that the deviation of the Lorenz value obtained in this work is due to experimental error in the measurement of thermal conductivity at very low temperatures rather than elastic electron scattering.

The first column lists the materials, in alphabetical order, except for the semiconductors; the second row lists the temperature range of the investigation, the third column lists the low-temperature residual electrical conductivity $\sigma_0 = \rho_0^{-1}$, if available, otherwise the residual resistivity ratio (RRR), which is the ratio of resistivity, ρ, at a given temperature to that of residual resistivity, ρ_0, and the fourth column the Lorenz number, L. For metals and alloys, L is the value measured in the residual resistance range. For metals, a number in parentheses after the value of L refers to the data point shown in Fig. 2. The last two columns refer to notes and references. An additional column in Table III lists the number density of charge carriers in the semiconductors.

Acknowledgements

References

1. G. WIEDEMANN and R. FRANZ, Ann. Phys. Chem. 89 (1853) 497.
2. L. LORENZ, Ann. Phys. 147 (1872) 429.
3. Idem, ibid. 13 (1881) 422.
4. Idem, ibid. 13 (1881) 582.
5. W. JAEGER and H. DIESSELHORST, Sitzungsber. Koenig. Preussischen Akad. Wissen. Berlin 38 (1899, part II) 719.
6. E. RIECKE, Ann. Physik 66 (1898) 353.
7. Idem. ibid. 66 (1898) 545.
8. P. DRUDE, ibid. 1 (1900) 566.
9. A. SOMMERFELD, Naturwissenschaften 15 (1927) 825.
10. Idem, ibid. 16 (1928) 374.
11. Idem, Z. Phys. 47 (1928) 1.
12. Idem, ibid. 47 (1928) 43.
13. W. MEISSNER, in "Handbuch der Experimentalphysik", Vol. II, part 2 (Akademische Verlagsgesellschaft, Leipzig 1935) pp. 188–204.
14. L. BINKELE, High temp.-High Pressures 17 (1985) 437.
15. Idem, ibid. 18 (1986) 599.
16. J. MUCHA, K. GALUSZEWSKI, A. JEZOWSKI and J. RAFALOWICZ, Phys. Status. Solidi (b) 142 (1987) K-57.
17. M. S. R. CHARI and M. V. N. CHARI, Phys. Lett. A. 136 (1989) 149.
18. M. S. R. CHARI and R. G. SHARMA, Phys. Status Solidi (a) 116 (1989) 377.
19. M. S. R. CHARI and M. V. N. CHARI, J. Phys. Condens. Matter 2 (1990) 631.
20. J. T. SCHRIEMPF, J. Phys. Chem. Solids 28 (1967) 2581.
21. P. G. KLEMENS and R. K. WILLIAMS, Int. Mater. Rev. 31 (1986) 197.
22. P. JACOBSSON and B. SUNDQUIST, High temp.-High Pressures 17 (1985) 103.
23. Idem, Int. J. Thermo phys. 9 (1988) 577.
24. N. W. ASHCROFT and N. D. MERMIN, "Solid State Physics" (Holt, Rinehart and Winston, New York, 1976).
25. E. W. FENTON, J. S. ROGERS and S. B. WOODS, Can. J. Phys. 41 (1963) 2026.
26. T. AMUNDSEN, A. MYHRE and J.A.M. SALTER, Philos. Mag. 25 (1972) 513.
27. W. B. WILLOTT, ibid. 16 (1967) 691.
28. G. K. WHITE and S. B. WOODS, ibid. 3 (1958) 342.
29. J. HEREMANS, J. P. ISSI, A. A. M. RASHID and G. A. SAUNDERS, J. Phys. C 10 (1977) 4511.
30. C. UHER, J. Phys. F 8 (1978) 2559.
31. D. T. MORELLI and C. UHER, Phys. Rev. B 28 (1983) 4242.
32. G. K. WHITE and S. B. WOODS, Can. J. Phys. 33 (1955) 58.
33. C. UHER and H. J. GOLDSMID, Phys. Status Solidi (b) 65 (1974) 765.
34. W. P. PRATT Jr and C. UHER, Phys. Lett. A 68 (1978) 74.
35. M. A. CAMPOS TOME, J. Low Temp. Phys. 20 (1975) 691.
36. D. K. C. MacDONALD, G. K. WHITE and S. B. WOODS, Proc. R. Soc. Lond. 235 (1956) 358.
37. A. F. A. HARPER, W. R. G. KEMP, P. G. KLEMENS, R. J. TAINSH and G. K. WHITE, Philos. Mag. 8 (1957) 577.
38. J. F. GOFF, Phys. Rev. B 1 (1970) 1351.
39. R. W. POWELL and R. P. TYE, J. Inst. Met. 85 (1956) 185.
40. G. K. WHITE and S. B. WOODS, Can. J. Phys. 35 (1957) 656.
41. P. RADHAKRISHNA and M. NIELSEN, Phys. Status Solidi 11 (1965) 111.
42. R. BERMAN and D. K. C. MacDONALD, Proc. R. Soc. Lond. 211 (1952) 122.
43. G. K. WHITE and R. J. TAINSH, Phys. Rev. 119 (1960) 1869.
44. R. W. ARENZ, C. F. CLARK and W. N. LAWLESS, Phys. B 26 (1982) 2727.

45. R. RATNALINGAM and J. B. SOUSA, *J. Low Temp. Phys.* **4** (1971) 401.

46. *Idem, Phys. Lett. A* **30** (1969) 8.

47. D. W. BOYS and S. LEGVOLD, *Phys. Rev.* **174** (1968) 377.

48. D. L. WALDORF, R. I. BOUGHTON, M. YAQUB and D. ZYCH, *J. Low Temp. Phys.* **9** (1972) 435.

49. G. BUSCH, H. J. GÜNTHERODT and P. WYSSMANN, *Phys. Lett. A* **39** (1972) 89.

50. W. J. NELLIS and S. LEGVOLD, *Phys. Rev.* **180** (1969) 581.

51. M. J. LAUBITZ, *Can. J. Phys.* **47** (1969) 2633.

52. G. K. WHITE and S. B. WOODS, *ibid.* **35** (1957) 892.

53. *Idem, ibid.* **35** (1957) 248.

54. J. B. BIETCHMAN, C. W. TRUSSEL and R. V. COLE-MAN, *Phys. Rev. Lett.* **25** (1970) 1291.

55. W. R. G. KEMP, P. G. KLEMENS and R. J. TAINSH, *Ann. Phys.* **7** (1959) 35.

56. W. R. G. KEMP, P. G. KLEMENS and G. K. WHITE, *Aust. J. Phys.* **9** (1956) 180.

57. F. W. KUS, *J. Phys. F* **11** (1981) 1879.

58. H. M. ROSENBERG, *Philos. Mag.* **8** (1956) 738.

59. *Idem, ibid.* **45** (1954) 73.

60. K. T. TEE, K. V. RAO and G. T. MEADEN, *J. Less-Common Metals* **31** (1973) 181.

61. M. A. CAMPOS TOME, *J. Low. Temp. Phys.* **20** (1975) 677.

62. G. K. WHITE and R. J. TAINSH, *Phys. Rev. Lett.* **19** (1967) 165.

63. J. T. SCHRIEMPF, *Solid State Commun.* **6** (1968) 873.

64. G. K. WHITE and S. B. WOODS, *Can. J. Phys.* **36** (1958) 875.

65. W. R. G. KEMP, P. G. KLEMENS, A. K. SREEDHAR and G. K. WHITE, *Philos. Mag.* **46** (1955) 811.

66. J. T. SCHRIEMPF, *Phys. Rev. Lett.* **19** (1967) 1131.

67. *Idem, ibid.* **20** (1968) 1034.

68. A. C. ANDERSON, R. E. PETERSON and J. E. ROBI-CHUX, *ibid.* **20** (1968) 459.

69. B. SHARMA, *Cryogenics* **7** (1967) 141.

70. K. T. TEE and G. T. MEADEN, *J. Low Temp. Phys.* **9** (1972) 447.

71. J. G. COOK, *Can. J. Phys.* **57** (1979) 871.

72. G. K. WHITE and S. B. WOODS, *Phil. Trans. R. Soc.* **251** (1959) 273.

73. H. G. SCHETTLER, J. J. MARTIN, F. A. SCHMIDT and G. C. DANIELSON, *Phys. Rev.* **187** (1969) 801.

74. P. HAEN and G. T. MEADEN, *Cryogenics* **5** (1965) 194.

75. L. R. EDWARDS and S. LEGVOLD, *Phys. Rev.* **176** (1968) 753.

76. M. C. KARAMARGIN, C. A. REYNOLDS, F. P. LIP-SCHULTZ and P. G. KLEMENS, *Phys. Rev. B* **5** (1972) 2856.

77. K. BARTKOWSKI, D. WLOSEWICZ and J. RAFALO-WICZ (Eds), *Phys. Status Solidi (a)* **52** (1979) 397.

78. V. E. PELETSKII, *High temp.-High Pressures* **17** (1985) 111.

79. S. K. WAGNER, J. C. GARLAND and R. BOWERS, *Phys. Rev. B* **3** (1971) 3141.

80. P. V. TAMARIN, B. E. CHUPRIKOV and S. SHALYT, *Sov. Phys. JEPT* **28** (1969) 836.

81. W. R. G. KEMP, P. G. KLEMENS and R. J. TAINSH, *Aust. J. Phys.* **10** (1957) 454.

82. R. J. TAINSH and G. K. WHITE, *J. Phys. Chem. Solids* **23** (1962) 1329.

83. P. G. KLEMENS, R. J. TAINSH and G. K. WHITE, in "Proceedings of the VII International Conference on Low Temperature Physics" (University Press, Toronto, 1960) p. 273.

84. W. R. G. KEMP, P. G. KLEMENS and R. J. TAINSH, *Philos Mag.* **4** (1959) 845.

85. P. G. KLEMENS, R. G. TAINSH and G. K. WHITE, *Phys. Rev.* **118** (1960) 654.

86. G. K. WHITE and S. B. WOODS, *Philos. Mag.* **45** (1954) 1343.

87. R. G. SHARMA and M. S. R. CHARI, *J. Low Temp. Phys.* **15** (1974) 79.

88. *Idem. ibid.* **14** (1974) 365.

89. M. A. MITCHELL and J. F. GOFF, *Phys. Rev. B* **12** (1975) 1858.

90. W. R. G. KEMP, P. G. KLEMENS, A. K. SREEDHAR and G. K. WHITE, *Proc. R. Soc. Lond.* **233** (1955) 480.

91. M. S. R. CHARI, *Proc. Phys. Soc.* **78** (1961) 1361.

92. D. G. S. CHUAH, R. RATNALINGAM and R. J. SE-WARD, *J. Low Temp. Phys.* **31** (1978) 153.

93. A. E. WHITEMAN, J. J. MARTIN and H. R. SHANKS, *J. Phys. Chem. Solids* **32** (1971) 2223.

94. K. MORI and Y. SAITO, *Jpn. J. Appl. Phys.* **15** (1976) 1997.

95. N. HSIEH and M. E. FINE, *J. Appl. Phys.* **52** (1981) 2876.

96. M. E. FINE and N. HSIEH, *J. Am. Ceram. Soc.* **57** (1974) 508.

97. A. GLADUN, C. GLADUN, A. HOFMANN and B. PEI-TRASS, *Phys. Status Solidi (a)* **58** (1980) 149.

98. J. MILLSTEIN, *J. Phys. Chem. Solids* **31** (1969) 886.

99. E. HEGENBARTH and B. SCHMIDT, *Phys. Status Solidi (b)* **76** (1976) 307.

100. L. F. LOU, *Phys. Rev. B* **14** (1976) 3914.

101. L. G. RADOSEVICH and W. S. WILLIAMS, *J. Am. Ceram. Soc.* **52** (1969) 9.

102. J. P. MOORE, W. FULKERSON and D. L. McELROY, *ibid.* **53** (1970) 76.

103. M. I. AIVAZOV, A. Kh. MURANEVICH, I. A. DOMA-SHNEV and A. G. SARKISYAN, *High Temp. (USSR)* **9** (1971) 1086.

104. *Idem, ibid.* **8** (1970) 512.

105. *Idem, ibid.* **9** (1971) 74.

106. P. E. D. MORGAN, *J. Am. Ceram. Soc.* **58** (1975) 349.

107. J. L. HENRY, R. BLICKENSDERFER and D. PAULSON, *J. Am. Ceram. Soc.* **53** (1970) 335.

108. R. E. TAYLOR, *J. Am. Soc.* **44** (1961) 525.

109. G. V. SAMSONOV and V. S. SINEL'NIKOVA, *Sov. Powder Metall. Met. Ceram.* **4** (1962) 272.

110. J. F. LYNCH, C. G. RUDERER and W. H. DUCKWORTH (Eds), in "Engineering Properties of Selected Ceramic Materials", (American Ceramic Society, New York, 1966) p. 420.

111. A. V. GOLUBKOV, E. D. DEVYATKOVA, B. P. ZHUZE, V. M. SERGEEVA and I. A. SMIRNOV, *Sov. Phys. Solid State* **8** (1966) 1403.

112. T. MIZOGUCHI, T. KUDO and S. TAKAYAMA, *J. Phys. Coll. C 8* **41** (1980) 501.

113. P. SÜTSCH and E. UMLAUF, *J. Low Temp. Phys.* **42** (1981) 11.

114. V. M. MUZHDABA, V. K. OGORODNIKOV, S. A. ALI-EV, and S. S. SHALYT. *Sov. Phys. Solid State* **11** (1969) 442.

115. V. M. MUZHDABA and S. S. SHALYT, *ibid.* **8** (1967) 2997.

116. S. S. SHALYT, V. M. MUZHDABA and A. D. GALET-SKAYA, *ibid.* **10** (1968) 1018.

117. V. I. TAMARCHENKO, YU. I. RAVICH, L. YA. MOR-GOVSKII, and I. N. DUBROVSKAYA, *ibid.* **11** (1970) 2599.

118. YU. I. RAVICH, I. A. SMIRNOV and V. V. TIKHONOV, *Sov. Phys. Semicondc.* **1** (1967) 163.

119. G. T. ALEKSEEVA, I. N. DUBROVSKAYA and B. A. EFIMOVA. *ibid.* **7** (1973) 157.

120. S. A. ALIEV, L. L. KORENBLIT and S. S. SHALYT, *Sov. Phys. Solid State* **8** (1966) 565.

121. I. A. SMIRNOV and S. A. ALIEV, *ibid.* **10** (1969) 2080.

122. S. A. ALIEV, U. KH. SUYUNOV and M. I. ALIEV, *ibid.* **10** (1968) 1018.

123. S. A. ALIEV, U. KH. SUYUNOV, D. G. ARASLY and M. I. ALIEV, *Sov. Phys. Semicond.* **7** (1973) 737.

124. M. A. ALIEV, S. A. ALIEV and M. I. ALIEV, *ibid.* **3** (1970) 1331.

125. C. M. BHANDARI and D. M. ROWE, *High temp.-High Pressures* **17** (1985) 97.

126. M. A. GORYUNOVA, V. M. MUZHDABA, M. SER-GINOV and S. S. SHALYT, *Sov. Phys. Solid State* **11** (1969) 225.

127. F. A. P. BLOM and A. HUYSER, *Solid State Commun.* **7** (1969) 1299.

128. G. S. KUMAR, J. W. VANDERSANDE, T. KLITSNER, R. O. POHL and G. A. SLACK, *Phys. Rev. B* **31** (1985) 2157.