Electrical and Thermal Conductivities

of Elemental Metals below 300 K[1]

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ABSTRACT

New equations correlating the electrical resistivity and thermal conductivity of elemental metals for all temperatures up to room temperature are described. The equations require input of a single parameter, the residual resistance ratio "RRR", which essentially specifies the impurity and/or dislocation content of the user's sample. Two adjustable parameters for each non-magnetic metal are then required in order to predict electrical resistivity to a general accuracy of a few percent, usually comparable to the accuracy of available experimental data. From a known or calculated electrical resistivity, a three-parameter Lorenz equation is then used to calculate thermal conductivity to an accuracy usually comparable with that of experimental data. The resistivity correlation gives inaccurate results for magnetic metals, but the thermal conductivity correlation is satisfactory for magnetic metals provided that independent knowledge of their electrical resistivity is known. Correlation parameters have been developed for aluminum, copper, gold, iron, lead, nickel, niobium, platinum, palladium, silver, tantalum, titanium, and tungsten.

KEY WORDS: resistivity, conductivity, thermal conductivity, metals, residual resistance, aluminum, copper, gold, iron, lead, nickel, niobium, platinum, palladium, silver, tantalum, titanium, tungsten

1. INTRODUCTION

At low temperatures the electrical and thermal conductivities of elemental metals are governed by the impurity and/or lattice dislocation content of any given sample. At room temperature and above these properties can be simply specified as a function of temperature for any element. These properties have been documented for selected samples through tabular and graphical reference data as a function of temperature, but equations to predict these properties for a user-specified sample are generally unavailable. The NIST Office of Scientific Reference Data offers no summary publications or computer programs in this field.

Here new equations for correlating these transport properties are described. The equations require user input of a single parameter “RRR”, described below, which essentially specifies the impurity and/or dislocation content of the user’s sample. A correlation between the electrical resistivity and the thermal conductivity of a given sample provides the framework for this analysis. The electrical resistivity is discussed in section 2. The derived thermal conductivity is discussed in section 3. Summary and conclusions are given in section 4.

2. ELECTRICAL RESISTIVITY

The resistivity of a metal may be written as the sum of 3 terms [1],

$$\rho(T) = \rho_0 + \rho_{ph} + \alpha\, \rho_{ph}\rho_0 / (\rho_{ph} + \rho_0) \qquad \text{(eq. 1)}$$

where ρ_0 is the temperature independent resistivity (due to impurities and lattice defects), $\rho_{ph}(T)$ is the temperature dependent resistivity (discussed in section 2.2 below), and α is a positive number of O(1), the "interactive" coefficient. Both $\rho_{ph}(T)$ and α are unique for a given metal. When $\alpha = 0$, equation (1) is known as Matthiessen’s Rule, and has been the

basis for many correlations of electrical resistivity. Theory says that α should be (zero or) positive; in practice α is observable only in a fairly narrow temperature range where $\rho_{ph}(T)$ and ρ_0 are comparable in magnitude.

2.1 Sample purity

Impurities and lattice imperfections determine the residual resistivity ρ_0. For a given metal, ρ_0 is most easily determined by measuring the ratio of the electrical resistance at room temperature to the electrical resistance in liquid helium, for any (arbitrary) sample geometry. This ratio is known as the residual resistivity ratio, RRR

$$\text{RRR} = \rho(T_{ref})/\rho(T_{He}). \qquad \text{(eq. 2)}$$

T_{ref} in equation 2 is “room temperature”, not always precisely defined. Provided that RRR >> 1, $\rho(T_{ref})$ is almost independent of impurity/dislocation content, and so usually can be obtained at "room temperature" from the literature. Except in extremely pure metals, ρ_0 is the only measurable term at liquid helium temperature, 4.2K. Typical values of RRR for nominally pure, annealed metals lie in the approximate range from 20 to 200. RRR values up to 3000 or above can be found for samples of exceptional purity. Values of RRR less than about 10 typify alloys, for which the correlations developed here are of dubious accuracy.

2.2 The "phonon" resistivity, $\rho_{ph}(T)$

In this paper the temperature dependent component of the electrical resistivity, written as $\rho_{ph}(T)$ in equation 1 is denoted the "phonon" term. It is so named because the scattering of conduction electrons by phonons is the dominant resistivity mechanism, at least at higher temperatures. At lower temperatures, typically below liquid nitrogen temperature,

reduced phonon scattering allows other possible temperature dependent electron scattering mechanisms to be detected. Thus in the low temperature limit, $\rho_{ph}(T)$ may depend on the type of impurity or dislocation as well as on temperature. In practice, the residual resistivity ρ_0 so dominates equation 1 at low temperature that an empirical assignment of $\rho_{ph}(T)$ at low temperatures is satisfactory for analysis of all but the highest purity samples.

2.3 A scaling equation for $\rho_{ph}(T)$.

When closely spaced resistivity data are not available for a given metal, it is important in this work to find a theoretical or empirical equation to span widely spaced reference data. An equation by Gruneisen [2] is often cited for this purpose. However, we have found the following empirical scaling equation for $\rho_{ph}(T)$ offers generally higher accuracy:

$$\rho_{ph}(T) = b\ T\ C_P(T)\ F_R(T/\theta_R), \qquad \text{(eq. 3)}$$

where b = a scale factor evaluated at one temperature (ca. room temperature) where all other terms in equation 3 are known, $C_P(T)$ is the <u>measured</u> specific heat for the metal, θ_R is a constant for each element, and $F_R(x)$ is defined

$$F_R(x) = F_1 = 1. - 1.783 \exp(-x/0.15) + 0.783 \exp(-x/0.20) \text{ when } x \leq 0.18$$

$$= \text{linearly weighted mean of } F_1 \text{ and } F_2 \text{ when } 0.18 < x < 0.22$$

$$= F_2 = 1.043 - 0.02 /x^{1.5} \quad \text{when } 0.22 \leq x < 0.6$$

$$= 1.0 \text{ when } x \geq 0.6$$

2.4 Resistivity data

Figure 1 shows the percentage deviation of equation 3 with θ_R = 333 K (the solid line) and of high qualtiy CINDAS tabular reference data [3] (plotted points) from a comprehensive NIST correlation [1] for copper. The NIST and CINDAS $\rho_{ph}(T)$ data agree within about 1.5% down to 80 K, diverging to about 25% at 40 K. This figure illustrates the difficulty of obtaining truly accurate $\rho_{ph}(T)$ below about 50 K. Equation 3 turns out to agree better with the CINDAS copper data than with the NIST copper data which were used as a reference during the equation 3 development.

Further in this work we find that equation 3 provides accuracies generally to 2 % or better, for temperatures above 50 K, for copper, silver[3], gold[3], aluminum[1], lead[4], platinum[5], tungsten[1,6], titanium[7,8], niobium[9], and one sample of polycrystalline beryllium[4]. It is not satisfactory for the magnetic metals iron[1], nickel[9], and chromium[9]. Space does not permit showing all graphical figures in this paper.

3 THERMAL CONDUCTIVITY

In this work the thermal conductivity K is calculated from the electrical resistivity via the Lorenz relationship, i.e,

$$K = K_e + K_{ph} = LT/\rho + K_{ph} \qquad \text{(eq.4)}$$

where K_e is the thermal conductivity associated with the conduction electrons, $\rho(T)$ is the electrical resistivity (eq. 1 above), L is a Lorenz function which is described below in some detail, and K_{ph} is lattice conductivity which would exist in the absence of conduction electrons. K_{ph} is generally small compared to K_e and will be ignored in this discussion, though it has been included in supporting calculations.

3.1 The Lorenz function

A new equation for the Lorenz function has been developed, based on two observations discussed by Hust and Sparks [10]

(a) When $\rho_0 >> \rho_{ph}(T)$, in eq. 1, the Lorenz function appears to approach its classical value, L_0 = 2.443e-10 W-Ω/K^2, for nominally pure metals in a majority of experiments. This is the low temperature limit.

(b) When $\rho_0 << \rho_{ph}(T)$, the Lorenz function seems to follow a Debye-like curve as a function of temperature. This curve approaches zero in the low temperature limit and the classical value (given above) in the high temperature limit.

A basic assumption of this work is that observation (a) above is true for all cases, i.e., that reported failures to reach the classical Lorenz number in the low temperature limit are due to experimental errors. Such errors, of 20 to 40 % or less, are not totally unreasonable for simultaneous measurements of resistivity and conductivity on high purity samples.

An empirical expression for the Debye-like Lorenz curve, observation (b) above, is

$$L_D = 1.2306\ (1 - \exp(-x/0.15)) + 1.2227\ (1 - \exp(-x/0.46))$$

where $x = T/\theta_L$ and θ_L is a constant for each element. The complete Lorenz function becomes

$$L = (1-w)*L_0 + w*L_D(T/\theta_L), \quad w = (\rho(T) / \rho_0)^n, \quad n = g_1 + g_2 \log_e (\rho_0).$$

In practice, there are not many metals for which sufficient conductivity data exists that a non-zero value of g_2 can be determined.

3.2 Thermal Conductivity data.

Hust and Langford [1] give a comprehensive review and least squares analysis of the

thermal conductivity of copper, leading to tabular recommended values for 5 different purities. Figure 2 shows generally excellent agreement between the NIST tabulation and calculated values from equations 3 and 4. The same publication also includes iron data. Figure 3 shows excellent agreement of equation 4 with the iron conductivity data using the NIST equation for $\rho_{ph}(T)$, but unsatisfactory agreement if the "best" fit of equation 3 is used for $\rho_{ph}(T)$. Similar curves have been obtained, showing good agreement with available conductivity data, for aluminum[1], gold[11], lead[11], nickel[7], niobium[7], palladium[7], silver[12], tantalum[7,13], titanium[7,8], and tungsten[1,7]; however, space does not permit their inclusion in this paper. A recent review paper by White and Mingus [14] summarizes the current state of knowledge for many of these reference data.

4 SUMMARY and CONCLUSIONS

Fitted parameters in equations 1, 3, and 4 are listed in table I, for 13 metals, with θ_R and θ_L normalized by the Debye temperature θ_D (from C_P data). Values of θ_R/θ_D in parentheses are somewhere near an optimum, but yield an unacceptable or questionable fit of equation 3 to experimental data; for platinum the fit is within 3 percent, but platinum thermometer calibration data [5] are selected for further work. Individual resistivity reference data rather than equation 3 have been used to calculate thermal conductivity for these metals.

It is notable that the (normalized) parameters θ_R and θ_L tend to cluster at about 0.9±0.2 and 1.0±0.2 respectively and that the parameters g_1 cluster around 0.6±0.1. The fact that there is no major variation in these parameters from metal to metal gives some confidence in the use of the correlating equations even where supporting reference data are

relatively scarce or of uncertain accuracy. Certainly the data for titanium should be reviewed for possible error. Further, it is encouraging to note that the Lorenz correlation works satisfactorily for magnetic metals provided that accurate resistivity data are available.

The parameter α is generally difficult to determine with confidence. It affects both the electrical resistivity and the thermal conductivity data correlation, but in a relatively narrow temperature range. It would not be surprising to find sizeable changes in α resulting from future, more detailed, work on individual metals.

This work can be further developed in four directions: (1) Additional reference data for the listed metals would allow more sophisticated statistical measures to be used for optimizing the parameters. (2) As a basic reference data program it would be useful extend the work to a wider range of metals. (3) It would be useful to extend the work to temperatures above 300 K. For reasonably pure metals, the resistivity and conductivity become independent of RRR at high temperature, so that this extension would be a relatively simple step. (4) It would be useful to explore the accuracy of these equations for less pure samples or dilute alloys of technological interest, e.g., for RRR in the 2 to 10 range.

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Table I. Fitted parameters for 13 metals. Values in parentheses are approximate, and unused in further calculations.

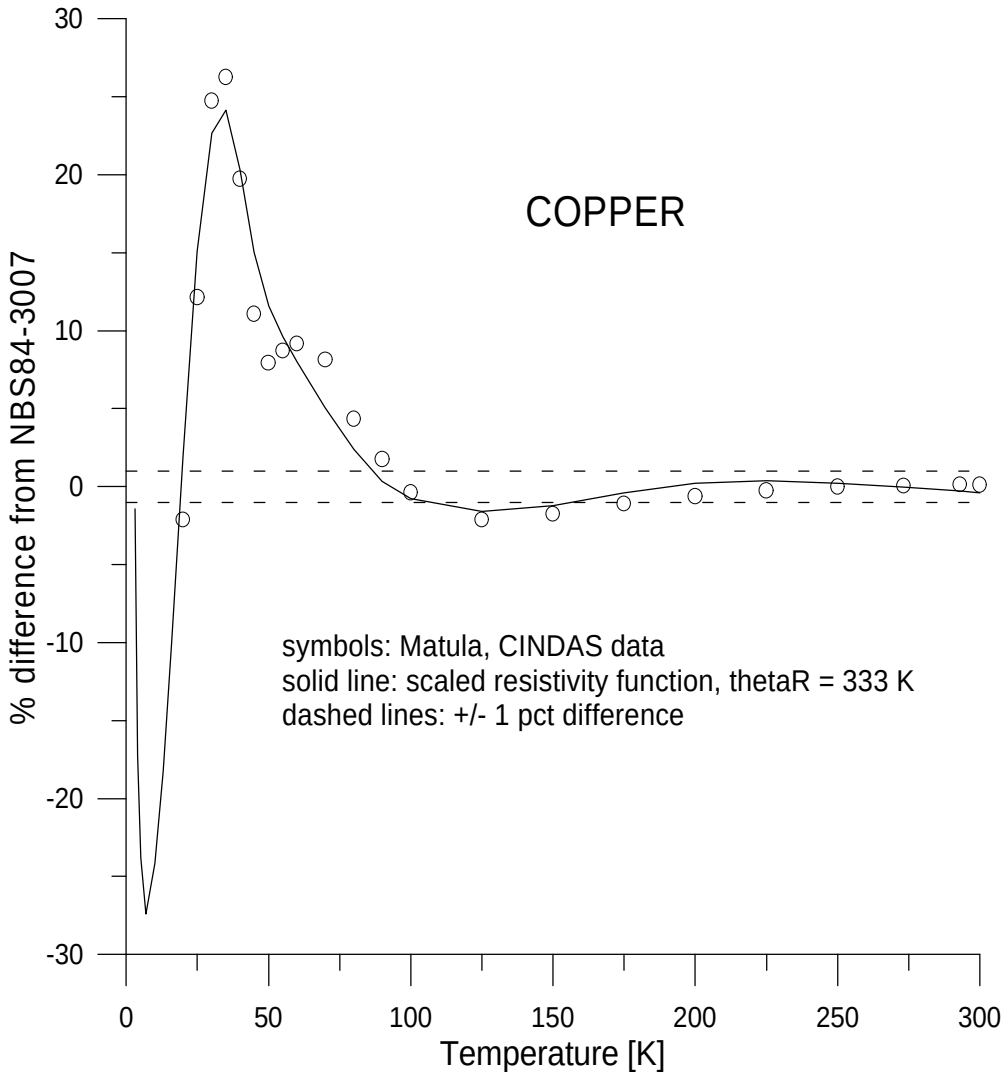
	θ_D	θ_R/θ_D	α	θ_L/θ_D	g_1	g_2
AL	426	(0.90)	0.73	1.127	0.57	0.048
CU	344.5	0.967	0.45	0.929	0.68	0.08
AU	165	0.921	0.12	0.836	0.67	0.10
FE	464	(1.27)	0.19	0.891	0.68	0.
PB	96	0.885	0.80	1.000	0.69	0.10
NI	440	(1.30)	0	0.818	0.58	0.
NB	251	0.797	1.10	1.036	0.45	0.
PT	240	(0.47)	0.84	0.783	0.46	0.
PD	274	(.365)	0.85	1.040	0.70	0.06
AG	226	1.049	0.15	1.000	0.65	0.056
TA	250	0.920	0.90	0.980	0.51	0.
TI	420	0.500	0.50	0.143	0.50	0.
W	382.5	(1.06)	0.60	0.837	0.60	0.

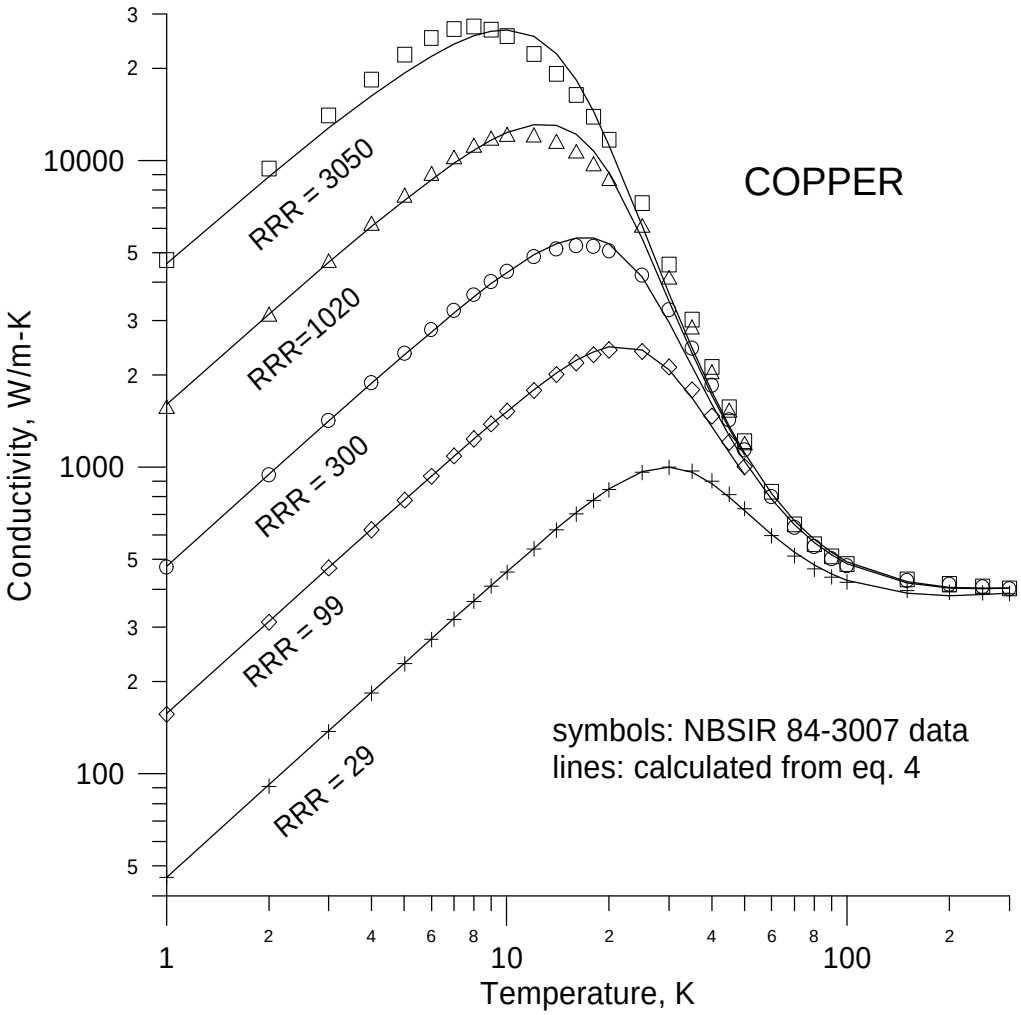
FIGURE CAPTIONS

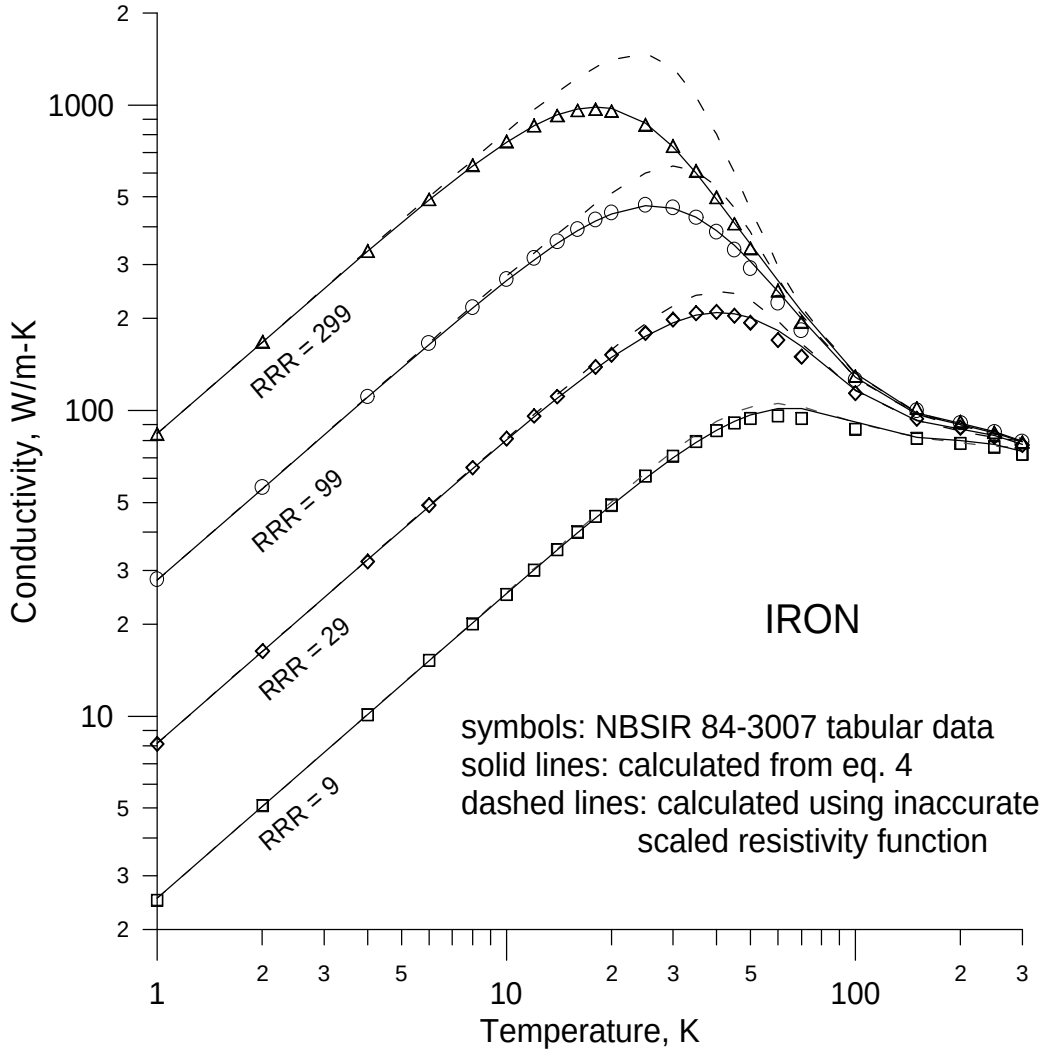
Fig 1. Percent deviation of CINDAS reference data[3] (points) and the equation 3 prediction (solid line) from $\rho_{ph}(T)$ as calculated in a NIST publication[1], for copper.

Fig. 2. Calculated thermal conductivity of copper, for 5 different sample purities. The symbols are from a tabular NIST correlation[1], and the lines are calculated from equation 4, using resistivity data calculated from equation 3.

Fig. 3. Calculated thermal conductivity data for iron, for 4 different sample purities. The symbols are from a tabular NIST correlation[1]. The solid lines are calculated from equation 4 using $\rho_{ph}(T)$ as calculated by NIST. The dashed lines are calculated from equation 4 using $\rho_{ph}(T)$ as calculated by an ill-fitting equation 3 for this magnetic metal.


COPPER
% difference from NBS84-3007
Temperature [K]
30
20
10
0
-10
-20
-30
0
50
100
150
200
250
300
symbols: Matula, CINDAS data
solid line: scaled resistivity function, thetaR = 333 K
dashed lines: +/- 1 pct difference


COPPER
RRR = 3050
RRR=1020
RRR = 300
RRR = 99
RRR = 29
symbols: NBSIR 84-3007 data
lines: calculated from eq. 4
Conductivity, W/m-K
Temperature, K
10000
1000
100
1
10
100


Conductivity, W/m-K
Temperature, K
RRR = 299
RRR = 99
RRR = 29
RRR = 9
IRON
symbols: NBSIR 84-3007 tabular data
solid lines: calculated from eq. 4
dashed lines: calculated using inaccurate
scaled resistivity function