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Thermal Properties on Metals at Cryogenic Temperatures

Cemil Koyunoğlu

Abstract

The thermophysical and some other properties of solids are of great importance for the use in the chemical, military, and even aerospace industries and for the design of efficient cryogenic equipment. Considering the heat loads, cooling, thermal fluctuations, or stresses or cryogenic fluids in boilers, the thermophysical properties should be considered. There is a considerable literature on the mechanical and structural properties of solids at cryogenic temperatures, but unfortunately there is not enough literature available for thermophysical properties. This chapter is recommended to close this gap. This chapter basically states: thermophysical properties of metals at cryogenic temperatures, specific heats, and thermal conductivity.

Keywords: cryogenic temperature, specific heat, thermal conductivity, advanced aviation technology

1. Thermophysical properties of metals at cryogenic temperatures

The mechanical and fabrication properties of solids are of paramount importance for the design of efficient cryogenic equipment for the chemical, military, and aerospace industries. The thermophysical properties are also important whenever heat loads, refrigeration, thermal fluctuations, or stresses or boiling cryogenic fluids must be considered. There is a relatively large amount of information available on the mechanical and structural properties of solids at cryogenic temperatures, but unfortunately the opposite is true for thermophysical properties.

The solid materials for which there are complete thermophysical data are only a minor fraction of the total number that are important and commercially available. This dearth of information will undoubtedly continue in the future, in spite of increased interest, activity, and financial support for cryogenic research, because of the considerable difficulty and expense of the actual experimental measurements. It is, therefore, of the utmost importance that a design or materials engineer must be able to estimate accurate values for new or untested materials. Unlike many mechanical or fabrication properties, the thermophysical properties (except thermoelectricity) for a given material may often be predicted from theoretical or semiempirical knowledge combined with data on similar materials.

This presentation stresses the basic phenomena and the fundamental concepts and assumptions. Each property is discussed with emphasis on temperature dependences and contributions to the total observed effect.

Also noted are the interrelations between the various properties and the value of those interrelations as aids in prediction. Besides the usual references to articles and

books, information is given on useful compilations and sources of specialized up-to-date bibliographies and data collections.

Because of the breadth of subject and limitations of space, it is impractical to give in this chapter either a complete review of the data on various thermophysical properties of solids or a detailed explanation of the underlying assumptions and theories. To make the following discussions more manageable, the solid materials are limited to metals, and the thermophysical properties are limited to specific heat and thermal conductivity. As this is a review article, the subjects will not be confined to our own experimental programs and results.

2. Specific heats

The specific heats of metals and alloys are fitted very well by existing theories, at least as far as engineering data are concerned. Therefore, it is common either to tabulate experimental values or to represent them on a common, reduced temperature graph. **Figure 1** shows a graph, but without specific metals or temperatures represented. The essential experimental problem is to ascertain the characteristic temperature, Θ . Conversely, given the values of the characteristic temperatures, values for specific heat are easily obtained. The specific heat at constant volume of a metal may be defined as $C_v = (\frac{\partial U}{\partial T})_v$, where U is the total internal energy of the metal or alloy system and T is the absolute temperature. It is important to determine the theoretical problem of energy transformation. The first of these is that the energy and indirectly the specific heat are slowly changing temperature functions as shown in **Figure 1**. For example, the energy of an ionic lattice structure of a metal and electrons in its free or conductive behavior can be given. Secondly, it can be said that a particular type of internal energy will change significantly only in a limited temperature range. The transformation energies for phase changes and magnetic order are the examples given for the second type. The effect of the specific heat for these processes can only be observed in the same limited temperature range as the energy change. Although the limited temperature range or abnormal specific temperatures are of

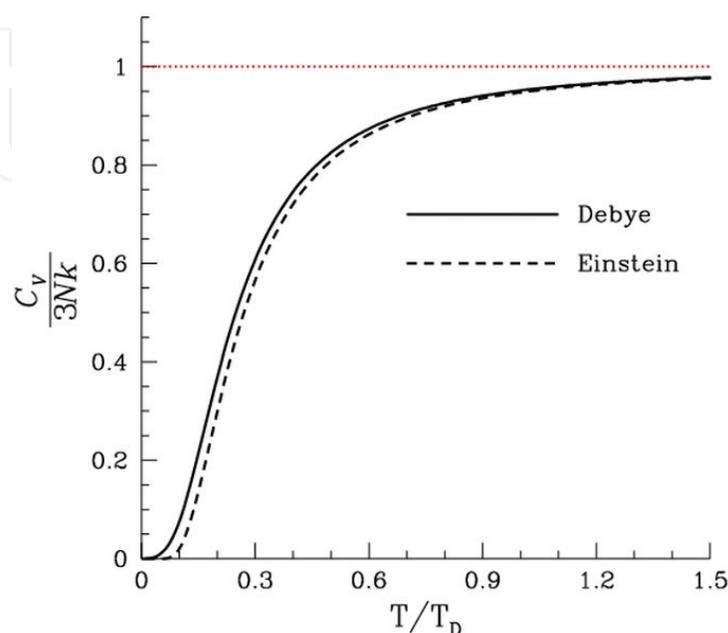


Figure 1.
Typical internal energy and specific heat curve for metals [5].

great importance for academic research in physics and chemistry, it can often be said that they are not of great importance in commercial materials [1–4].

The lattice specific heat is much larger than the electronic specific heat at most temperatures. It will be discussed first. Einstein's representation of the ionic lattice as a system of independent oscillators led to the equation $C_v = 3RE(\Theta/T)$, where Θ is a characteristic temperature, R is the gas constant, and E is the Einstein function as defined by $E(\Theta/T) = (\Theta/T)^2 e^{\Theta/T} / (e^{\Theta/T} - 1)^2$. This gives a good fit and above room temperatures, approximating the earlier observed Dulong-Petit universal value for heat capacity at high temperatures. It does not fit well at low temperatures, however. The lattice of ions is known to interact. When this is taken into consideration and some simplifying approximations are made for the distributions of energies, the Debye theory is obtained. This theory is almost too good; Its predictive ability was so successful that theoretical refinements were not considered seriously for many years [1, 2]. The Debye specific heat (for the lattice) is $C_v = 3RD(\Theta/T)$, where the Debye function, D , is defined as

$$D \frac{\Theta}{T} = 3 \left(\frac{T}{\Theta} \right)^3 \int_0^{\Theta/T} \frac{x^4 e^x}{(e^x - 1)^2} dx$$

The Einstein and Debye specific heat and energy curves are shown in **Figure 1**.

The main characteristics of the Debye curve are easily seen. At low temperatures the specific heat varies as T^3 ; at high temperatures it is approximately constant. The theory was developed for isotropic, homogeneous porous metals; how does it apply to alloys?

In near room temperature, the specific heat of an alloy is obtained quite well by the Kapp-Joule rule: the total specific heat is a linear combination of the specific heats of the constituents, each weighted according to its relative abundance. At low temperatures, one can either combine additively the actual specific heats of the constituents or take a weighted average of the characteristic temperatures. Either of the procedures will give approximately correct results [6–8].

The electronic specific heat is small compared to the lattice contribution at high temperatures, but it is linear in its temperature variation. Since the lattice term decreases as T^3 , the electronic term will become significant only at the lowest temperatures. It is usually not significant for engineering applications [5, 9].

3. Thermal conductivity

The thermal conductivities of several solids, values for metals, and their alloys are represented in **Figures 2–4**. Even within those restrictions, there is considerable variation. Is it possible to make order out of this variety; Is it possible to be able to predict reasonably well the thermal conductivity for new or untested materials? It is, if one utilizes knowledge of the fundamental phenomena [10, 11].

Two parallel mechanisms connected at low temperatures are primarily responsible for transporting heat from a metal. First one is the thermal energy transmission with the transmission electrons movement, and the most important is the transmission of electronic heat. The second is the thermal energy transport by the lattice thermal conduction, the movement of conductive electrons. The mesh is the thermal conduction; the thermally induced interactive lattice ions are carried by directional cooperative quantitative vibration (phonons). These are the same phonons which are responsible for the specific warming and thermal expansion observed in metals. Mesh thermal conductivity is insignificantly compared with electronic thermal conductivity, for pure metals and dilute alloys. For alloys

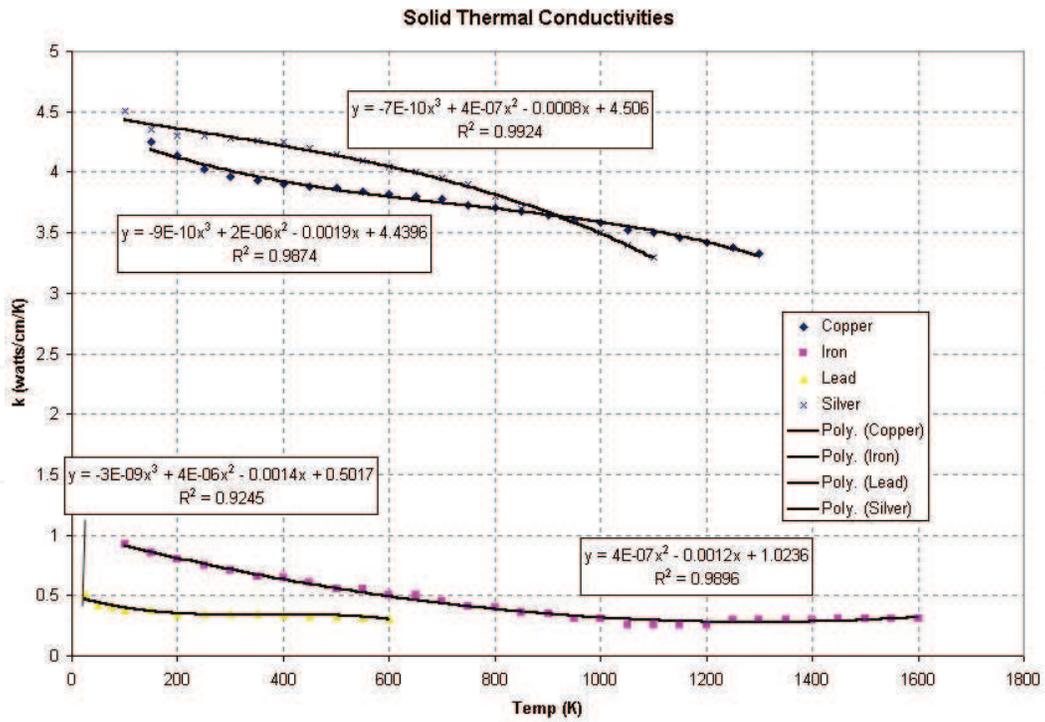


Figure 2.
Thermal conductivity of some solids [12].

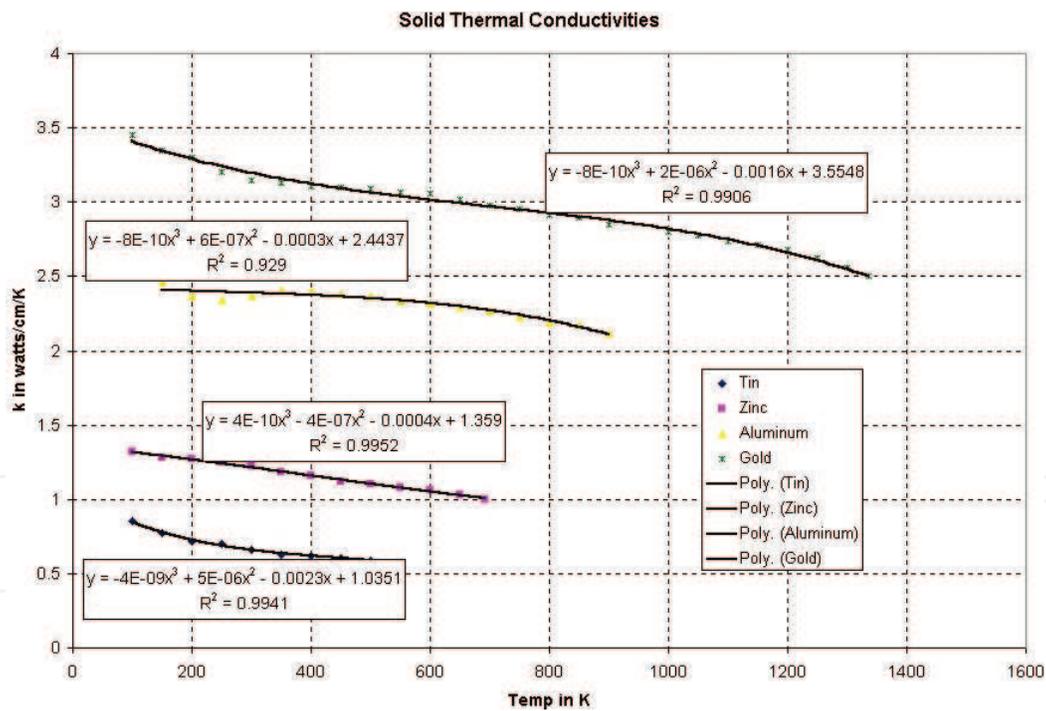


Figure 3.
Thermal conductivity of some solids [12].

containing several or more percent additives, decreasing electronic thermal conductivity ensures that the lattice additives are still small, but still small compared to the electronic additive. For most metals and alloys, total conductivity means K_g (g refers to Gitter, German word for cage), $K = K_e + K_g$. This equation is the same as the two conductors used for total conductivity in parallel in electrical circuit theory. Both conductive mechanisms, K_e and K_g , are limited to various scattering processes that limit electronic conductivity in the above statement [12–14]. A sample of the analog is presented in **Figure 5**.

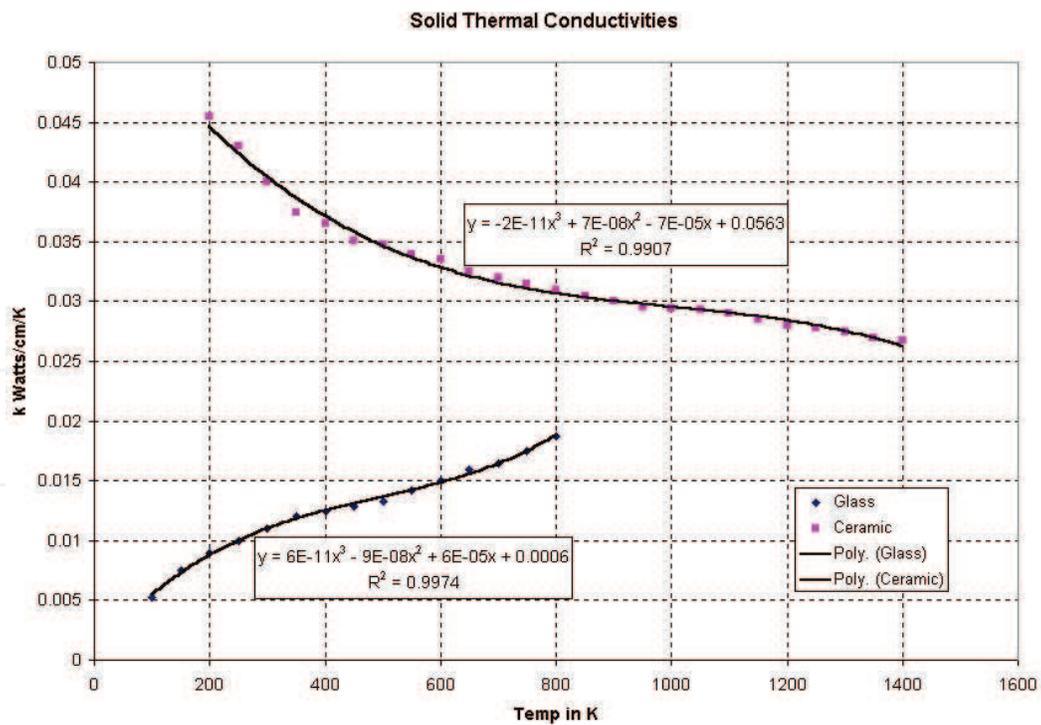


Figure 4.
 Thermal conductivity of some solids [12].

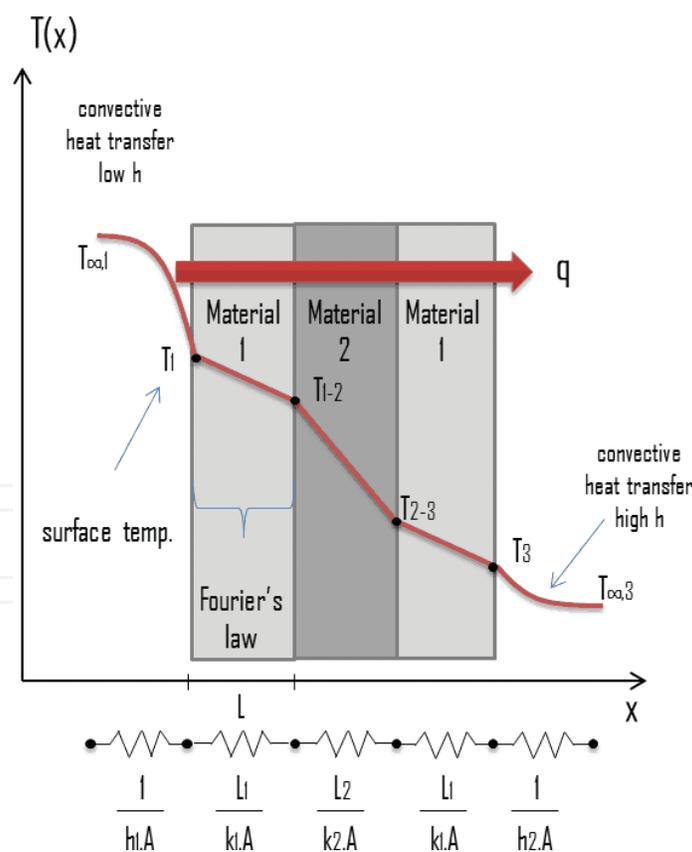


Figure 5.
 Thermal conduction's sample electrical analog [15].

The first of these is the diffusion of the electrons that are represented as a characteristic feature for a given metal to the electron-phonon resistance (W_L). This spreading is most important at higher intermediate temperatures (about 40–80 K) and at higher temperatures. The second process is the conductive electron

propagation by defects (both lattice defects and impurity atoms) as represented by electron-defect resistance W_o . This scattering is more important at low temperatures. K_e , which is the total electronic thermal conductivity equivalent, also gives the total electronic heat resistance. The resistances W_L and W_D are treated as the default of the sum of W_{Lo} , that is, plus a small deviation term, $1/K_e$. And $1/K_e = W_e = W_L + W_o + W_{Lo}$. This equation is similar in the electrical circuit theory to the equation used for the total resistance of the resistors in the series. $W_{Lo} = \alpha W_L W_o / (\beta W_L + (W_o))$. Here, α , β , and γ are constants and can be determined experimentally. Although theoretically meaningful, these terms are only numerically important for very pure metals [12–14].

When the interaction term W_{Lo} is negligible, the Matthiessen's electrical resistance rule for thermal equivalent is roughly as accurate as $W_e = W_L + W_o$. A graph for this relationship and its equivalent for conductivity is given in **Figure 6**. The estimation of total electronic thermal resistance can be done by two separate components [12–14].

Both theoretical and empirical researches are defined by different expressions for the magnitude of electron-phonon and electron-defect resistance and temperature dependencies: $W_L = AT^n$ ($n = 2-3$, $T < 40$ K); $W_L = a$ is constant (near room temperature); $W_o = B/T$ (at all temperatures). The term constant A in the term electron-phonon resistance refers to the specific characteristics (or characteristic temperature) of a given metal and will not change for the small chemical additive addition or physical defects and the specific sample for residual electrical resistance. At all temperatures above 40 K, often labeled $W_\infty = B/T$, the electron-phonon resistivity approaches a constant value. The constant A in the electron-phonon resistivity term is related to a given metal intrinsic properties (including the characteristic temperature, Θ) and will not change for chemical impurities for minor additions or physical imperfections; B in the electron-defect resistivity term is related to the given imperfections amount and the specific specimen's residual electrical resistivity. Above 40 K, the electron-phonon resistivity approaches a constant value, often labeled W_∞ .

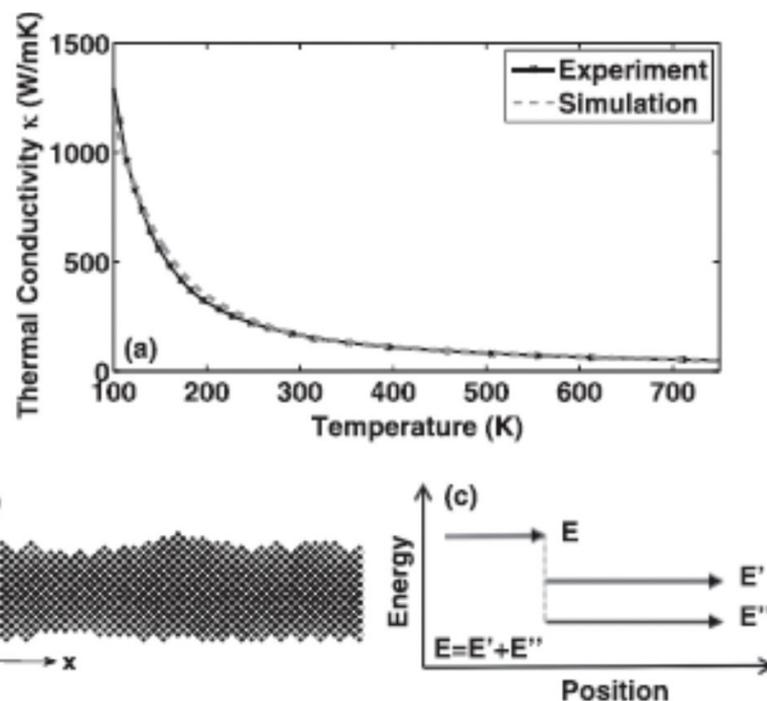


Figure 6.

A sample graph explaining Matthiessen's rule for electrical resistivity (a) thermal conductivity of bulk Si, (b) Si nanowire's surface roughness and (c) anharmonic phonon-phonon scattering process [15].

In a detailed analysis, the term electron-phonon will show that W_L is unchanged, that is, it is really specific to aluminum. **Figures 3** and **4** clearly illustrate adding more impurities effects to a given metal, thus increasing W_0 . At low temperatures, when the curves are parallel, the high impurity alloy is low. When the curves approach each other, the differences are reduced by approximately $1/T$, at high temperatures.

The curve shapes for the aluminum given in **Figure 3** are specific to pure metals: electronic conductivity is predominant and mesh conductivity is insignificant. For a metal sample with physical defects or without chemical impurities, the electron-phonon scattering component caused by the thermally induced ionic cage W_L directs its dependence on the temperature of the conductivity. As the temperature is lowered, the resistivity decreases in approximate proportion to T^2 ; the conductivity rises equivalently. Superimposed on this decreasing ideal of electron-phonon resistivity is the electron-defect resistivity which increases as the temperature is decreased. The maximum heat conduction resistance at the minimum temperature in the two temperature-spreading mechanisms is considered to be approximately the same. However, at high temperatures, electron-phonon scatter is dominant; at low temperatures, heat loss from electron defect is dominant. On the other hand, the conductivity-limiting defects at low temperatures can be quite diverse: chemical impurities, residues, gaps, inter-atoms, dislocations, particle boundaries, outer surface boundaries, etc. The waste heat dissipation resistance, except for the final defect for almost every situation, has the same temperature dependency B/T as previously mentioned. At very low temperatures, boundary scattering is difficult to investigate and can only be observed in extremely pure metals [12–14].

Today, it is not possible to accurately estimate the thermal conductivity of pure metals on the basis of chemical or physical properties because every kind of chemical impurity is specific to that substance. It also depends on the magnetic interactions of matter and the differences between the ionic mass, ion volume, and the host and impurity in the valance electrons. Much work has been done on the specific effects of impurities in electrical resistance, but little has been done about thermal conductivity. Sometimes a chemical analysis in this regard can hardly be helpful, given that a given impurity is much more effective as a scattering agent in the form of a solid solution, rather than leaving the test boundaries or residues. This decomposition effect is very pronounced in copper. Similar interpretive difficulties arise for physical defects in test items [15, 16].

Thermal conductivity changes are caused by relatively physical defects or small chemical impurities in contrast to losses in thermal expansion or specific temperatures. Successful estimation of thermal conductivity depends on an ingenious analysis of possible propagation mechanisms of about 10–20% and obtaining experimental results on a very similar metal or alloy. As will be shown later, the low temperature electrical resistance data are also very valuable for predicting thermal conductivity [15, 16].

In many low-conductivity alloys, the lattice structure of the material's thermal conductivity can be measured in K_0 , and separate propagation components can be observed for this. For most alloys, there are three main processes that limit the lattice structure conductivity. The first operation is the conductive electrons scattering, as represented by phonon-electron resistance. This is electron equivalent scattered by phonons. The second process is the W_p distribution from the phonon-scattering resistance, resulting from construction defects. At low temperatures, the first two processes limit the lattice structure's conductivity of the material; the third condition is the limitation at higher temperatures [17, 18].

The phonon-loss and phonon-electron resistors have the same temperature dependence. Thus, for a sample metal or alloy, two scattering mechanisms cannot

be clearly distinguished. For annealed samples, the two resistances are approximately the same size; for non-annealed samples, loss resistance is heavier than phonon-electron resistance. The conductivity of the metal lattice structure below the temperature of about 40 K can be represented by the following formula:

$1/K_g = W_g = W_e + W_d + W_p = ((E + D) T^{-2} + PT)$. Due to the effect of the phonon-electron and phonon-loss resistors, T^{-2} dependence is expected to be dominant at low temperatures and negligible at high temperatures. The maximum conductivity in the cage structure conductivity is generally in the range of 50–100 K for most alloys. However, above these temperatures, the lattice structure's heat conduction cannot be readily separated from the electronic conductivity experimentally because the electronic conductivity has a much larger magnitude [19, 20].

For the aluminum alloys of **Figure 4**, there are special shapes of curves; for example, electronic conductivity is dominant, but the conductivity of the metal lattice structure can be observed. In addition, the effects of impurities are obvious. For aluminum alloys, the lattice conduction may be about the total's 10%; for some iron or nickel alloys, it may be much higher [21, 22].

Due to the Wiedemann-Franz-Lorenz law, $\rho = LW_eT$, where L is the Lorenz ratio, it is assumed to be a fundamental constant given by the Sommerfeld value $L = (\pi^2/3)(K/e)^2 = 2.44 \times 10^{-8}$ [watt-ohm/(deg K)²], whether there is no direct information on the metal thermal conductivity; after that data on the electrical resistivity may be related to the electronic thermal resistivity [23, 24].

The separation and scattering of components for electrical conductivity is almost the same as described above on electronic thermal conductivity. Total electrical resistance, ρ , is considered to be about two separate resistances, electron-phonon or total resistances, ρ_L and electron, or residual defective resistance, ρ_o . Alternatively, Matthiessen is estimated to be close to the principle of electrical resistance expressed by $\rho = \rho_L + \rho_o$ [25, 26].

The above-described internal system and residual terms have temperature statements of approximately $\rho_L = \alpha T^n$ ($n = 4-5$, $T < 40$ K); $\rho_L = \alpha'T$ (300 K close to T); $\rho_o = \beta$ (constant). For a general metal, a separation graph of the electrical resistance components is shown in **Figure 6** [25, 26]. The experimental results for a typical series of alloys are given in **Figure 7**.

For the aluminums and aluminum alloys, calculated Lorenz ratios are given in **Figures 2, 3, and 7**. The numbers calculated and shown in **Figure 8** express the ratios of the electrical resistivities. At the lowest temperatures, the extrapolated values L_o , however, should in electronic terms only represent ratios since the lattice contribution to the total thermal conductivity is greatly reduced [23]. A graph for Lorenz ratios for a general metal is given in **Figure 8**.

The ratios of Lorenz for high-conductivity materials are extrapolated to roughly Sommerfeld at 0 K, but at lower temperatures, that falls considerably below this value. However, the low-conductivity alloy behavior is different: the conductivity value is higher than the values between about 10 and 60 K, while the conductivity value is lower than 60 K value. In the case of where the ratios are above the Sommerfeld value, the temperature ranges in which the metal lattice structure conductivity is important are shown in [24, 25].

In metal structure, the Lorenz ratio should be constant in the conduction electrons' elastic distribution. This is almost the case when the thermal vibration at the high temperatures causing the large electron-phonon scatter is maximum, and the residual term expressed in the above equation is dominant in the electrical resistance at low temperatures. It can be said that the Lorenz ratios are significantly reduced from Sommerfeld in the case of medium temperatures where there is a large thermal vibration amount causing large electron-phonon scattering and in low temperatures where the term is dominant in the elasticity and the thermal

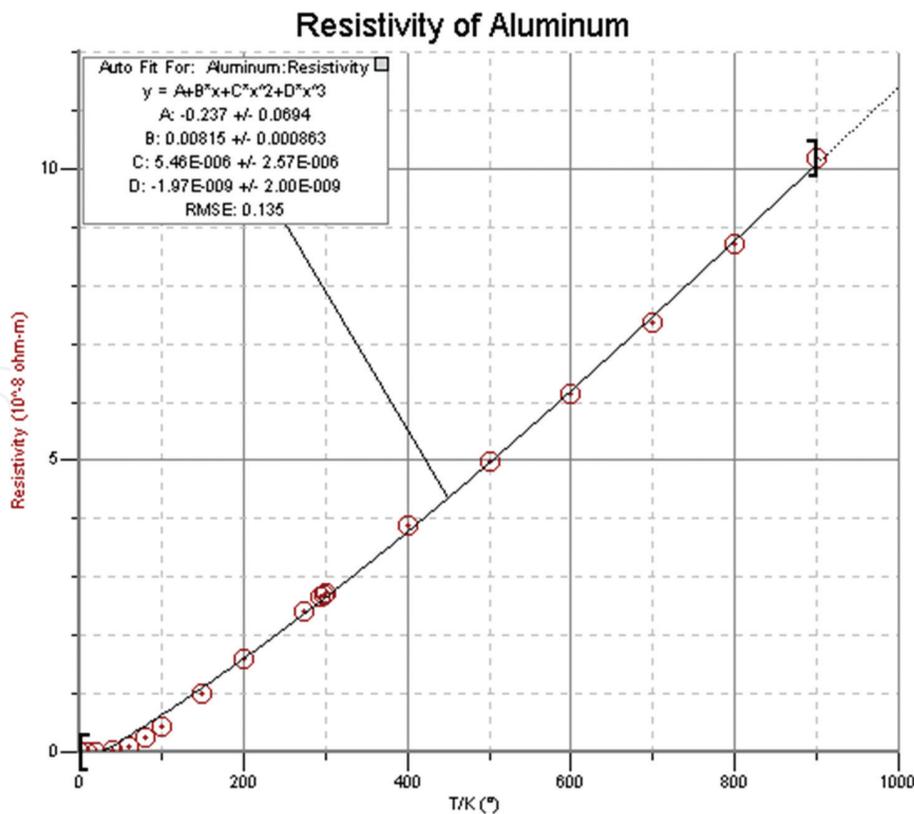


Figure 7.
 Thermal resistivity of aluminum [23].

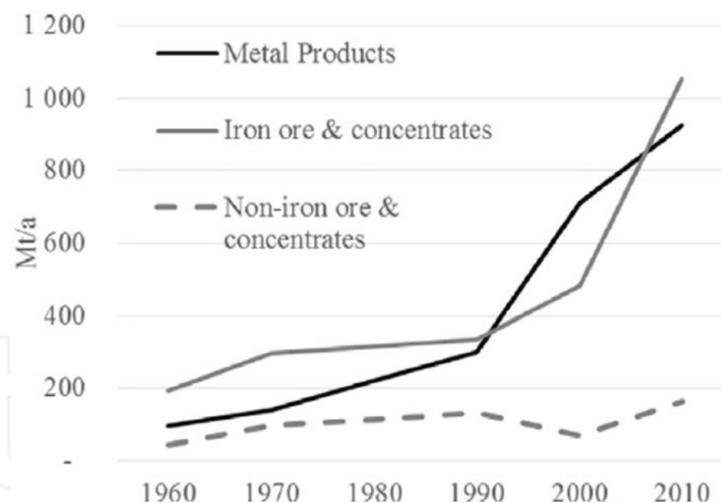


Figure 8.
 Lorenz curve of waste rock and metal extraction primary y-axis, by area x-axis in 2010 [24].

conductivity of the metal cage structure is insignificant. For situations where a significant lattice thermal conductivity amount is present, the increase in the Lorenz ratio can only be said to be above the value of the electronic term in the thermal conductivity formula [24, 25].

Up to now, on the commercial alloys' Lorenz ratio, very little research has been reported. Whenever Lorenz ratios for the general class of materials and electrical resistivities for a special material are available, reasonable predictions for thermal conductivity can be obtained [23, 26].

It has been shown that at the present time, it is not possible to accurately predict thermal conductivities for metals and alloys from the fundamentals. It is possible to

make adequate predictions, however, if there are data on the thermal or electrical resistivities of similar materials and if one uses proper interpolation formulas and a knowledge of the effects of minor changes in the chemical impurities or physical imperfections. It is imperative, of course, that good compendiums of experimental data exist. Fortunately, they do [23, 26].

Nomenclature

C_v	Specific heat at constant volume, J/(kg·°C)
U	Total internal energy, kg/ms ²
T	Absolute temperature, K
Θ	Characteristic temperature, K
R	Gas constant, J/mol·K
E	Einstein function
D	Debye function
x	length, m
K	Total conductivity, S/m
W	Electron-phonon resistivity
A	Intrinsic properties
B	Physical imperfections
P	Point imperfections
ρ	Total electrical resistivity, (Ω m)
L	Lorentz ratio, (watt-ohm/(K) ²)
e	electron charge, Coulomb

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