

# Electrical Resistivity of Copper, Gold, Palladium, and Silver

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In this work, recommended values for the electrical resistivity as a function of temperature from the cryogenic region to well beyond the melting point are given for bulk pure copper, gold, palladium, and silver. In addition to the total electrical resistivity values for the solid state, intrinsic electrical resistivity values are presented from cryogenic temperatures to the melting point. The values are corrected for the change in geometry due to thermal expansion. The recommendations are based on theoretical considerations and on the experimental data found in the open literature. Those available experimental data together with information pertaining to the specimen characterization and measurement conditions are included in this work. The methods of data evaluation and other considerations used in arriving at the recommendations are described. For the solid state, an interpolation scheme is given to aid in the determination of values between those supplied in the tables; for the liquid state, equations are given.

Key words: Copper; critical evaluation; data analysis; data compilation; data evaluation; data extraction; data synthesis; electrical resistivity; elements; gold; metals; molten metals; palladium; precious metals; reference data; silver; solid state physics; transport properties.

## Contents

	Page		Page
List of Tables.....	1147	7. References.....	1290
List of Figures.....	1148	7.1. Copper.....	1291
Explanation of Symbols.....	1148	7.2. Gold.....	1293
1. Introduction.....	1148	7.3. Palladium.....	1294
2. Some Theoretical Background.....	1149	7.4. Silver.....	1295
2.1. Matthiessen's Rule.....	1149	7.5. Other References.....	1295
2.2. Bloch-Grüneisen Formula.....	1153	Appendix 1. Methods of Measuring Electrical	
2.3. Change of Resistivity on Melting.....	1153	Resistivity.....	1296
3. Evaluation and Synthesis of Data.....	1153	Appendix 2. Conversion Factors for Units of	
3.1. Extraction of Data from the		Electrical Resistivity.....	1297
Literature.....	1153		
3.2. General Procedures in the Analysis			
and Synthesis of Data.....	1153		
3.3. Fitting Functions.....	1156		
3.4. Estimation of Uncertainty.....	1156		
3.5. Types of Evaluated Data.....	1156		
4. Data and Numerical Results.....	1157		
4.1. Copper.....	1159		
4.2. Gold.....	1206		
4.3. Palladium.....	1236		
4.4. Silver.....	1257		
5. Summary.....	1290		
6. Acknowledgments.....	1290		

## List of Tables

1. Physical Characteristics of Copper, Gold, Palladium, and Silver.....	1158
2. Recommended Values for the Electrical Resistivity of Copper.....	1161
3. Measurement Information on the Electrical Resistivity of Copper.....	1164
4. Experimental Data on the Electrical Resistivity of Copper.....	1169
5. Recommended Values for the Electrical Resistivity of Gold.....	1209
6. Measurement Information on the Electrical Resistivity of Gold.....	1212

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	Page		
7. Experimental Data on the Electrical Resistivity of Gold .....	1227	$L_F$	Latent heat of fusion
8. Recommended Values for the Electrical Resistivity of Palladium .....	1239	$M$	Atomic weight; mass
9. Measurement Information on the Electrical Resistivity of Palladium .....	1242	$M$	Code for mutual inductance method
10. Experimental Data on the Electrical Resistivity of Palladium .....	1252	$P$	Power of a term in modified Bloch-Grüneisen function $G_2(T)$
11. Recommended Values for the Electrical Resistivity of Silver.....	1260	$P$	Code for van der Pauw method
12. Measurement Information on the Electrical Resistivity of Silver.....	1263	$R$	Radius; resistance
13. Experimental Data on the Electrical Resistivity of Silver.....	1281	$R$	Code for rotating magnetic field method
14. Comparison of $\rho_L/\rho_S$ at the Melting Point Between Present Results and Mott's Theory		$S$	Code for self-inductance method
A-1. Conversion Factors for Units of Electrical Resistivity.....	1296	$T$	Temperature
		$T$	Code for transient (subsecond) method
		$T_m$	Melting point
		$V$	Code for voltmeter and ammeter direct reading method
		$x$	Variable in Grüneisen function and transport integral $J_s(x = \theta/T)$
		$\Delta$	Deviation from Matthiessen's Rule
		$\Delta \ell$	Change in length
		$\theta$	Constant; electrical resistivity Debye temperature
		$\rho$	Electrical resistivity
		$\rho_0$	Residual electrical resistivity
		$\rho_i$	Intrinsic electrical resistivity
		$\rho_L$	Electrical resistivity in the liquid state at the melting point
		$\rho_s$	Electrical resistivity in the solid state at the melting point
		$\Phi(x)$	Grüneisen function $F(x)$ divided by $x$

### List of Figures

1. Intrinsic Electrical Resistivity as Given by Bloch-Grüneisen Equation (Linear Scales).....	1150
2. Intrinsic Electrical Resistivity as Given by Bloch-Grüneisen Equation (Logarithmic Scales) .....	1151
3. Illustration when Matthiessen's Rule is Valid.....	1152
4. Logarithmic Derivative of the Intrinsic Electrical Resistivity as Given by Bloch-Grüneisen Equation.....	1154
5. Electrical Resistivity of Copper (Logarithmic Scales) .....	1162
6. Electrical Resistivity of Copper (Linear Scales) ..	1163
7. Electrical Resistivity of Gold (Logarithmic Scales).....	1210
8. Electrical Resistivity of Gold (Linear Scales).....	1211
9. Electrical Resistivity of Palladium (Logarithmic Scales) .....	1240
10. Electrical Resistivity of Palladium (Linear Scales).....	1241
11. Electrical Resistivity of Silver (Logarithmic Scales) .....	1261
12. Electrical Resistivity of Silver (Linear Scales) .....	1262

### Explanation of Symbols

$A$	Area; constant
$A$	Code for dc potentiometric method
$B$	Constant
$B$	Code for dc bridge method
$c$	Concentration
$C$	Constant
$C$	Code for ac potentiometric method
$D$	Constant
$D$	Code for ac bridge method
$E$	Code for eddy current decay method
$F(x)$	Grüneisen function
$G_1(T)$	A modified Bloch-Grüneisen function
$G_2(T)$	Another modified Bloch-Grüneisen function
$I$	Code for induction method
$J_s(x)$	A transport integral
$\ell$	Length

## 1. Introduction

The central purpose of this work is to present recommended values for the electrical resistivity of bulk pure copper, gold, palladium, and silver over the full range of temperatures to the melting point and beyond. It includes also a summary of all data found in an extended search of the open literature for these metals with less than 1/2 weight percent impurities as well as a complete characterization of the materials to which the data relates, so far as it can be determined. Some original data provided by authors of recent papers have been included. In all, 621 sets of original data from 188 references are provided. It is believed that essentially all important documents in the open literature on the pure metals have been located through 1976, and that the coverage is 75% complete for materials with less than 1/2 weight percent impurities. This information has been studied, correlated, and integrated with theoretical and empirical knowledge to arrive at the recommended values for the resistivity of the pure metals, corrected for the change in geometry of samples due to thermal expansion at normal pressures.

The organization of this work is as follows. Section 2 gives a brief discussion of some items from the theory of electrical resistivity in order to establish terminology and notation and to state equations of which use is to be made. It is not intended to provide a survey of the theory. Section 3 indicates some general ideas and procedures used in judging the experimental evidence and in arriving at the recommended values for the resistivity.

Section 4, Data and Numerical Results, is the heart of this work. It is divided into subsections relating to the four elements, preceded by a discussion of items common to the four subsections. Each subsection opens with a description of the element and some of its properties. The scope of the available information on its electrical resistivity is indicated, and the selection of the sets of data used in arriving at the recommended values for the resistivity of the pure bulk material is discussed. Any special methods used in arriving at the recommended values are described, and the uncertainty to be attributed to these values is indicated. The full data are then presented. The recommended values in tabular form are followed by a graphical display of the data along with the curve of the recommended values. Then the information pertaining to the specimen characterization and measurement conditions for each set of data is provided in tabular form. Finally, tables of the original experimental data, either as stated by the original authors or as extracted from their graphs, are presented.

Section 5, Summary, contains a statement characterizing the results of this work. In addition, a brief description of the methods used in arriving at the final smoothed values of resistivity is given. Also, a comparison of the ratio of the resistivity of the liquid to that of the solid at the melting point is made between a simple theory and the results of this work.

The last two sections are for Acknowledgments and References, respectively. The latter, section 7, contains references to sources of data, as well as to other publications referred to in the text. It is arranged to bring together references to sources of information on each of the metals: first copper, then in turn gold, palladium, and silver. To avoid multiplication of references to papers that deal with more than one of these metals, the references for each metal except copper are of two types. First, there are full references, arranged alphabetically by first author, to all papers for which full references are not given elsewhere; then, following the notation "See also," are listings (again alphabetically by first author) to preceding reference numbers under which one will find full references to other papers also dealing with this metal. Each listing ends with the numbers of the data sets for that metal derived from the listed paper. The references thus provide an index to the data tables and the associated measurement information tables for each metal. Section 7 concludes with references to publications not dealing directly with these particular metals.

## 2. Some Theoretical Background

This section contains a brief discussion of some points from the theory of the electrical resistivity of metals to which later reference will be made.

### 2.1. Matthiessen's Rule

The electrical resistivity of a chemically pure metallic element with no physical defects is called its intrinsic resistivity  $\rho_i(T)$ . It is the resistivity caused by the scattering of the charge carriers (electrons or holes) by quantized vibrations of the lattice (that is, phonons) and by their

collisions with each other. The intrinsic resistivity of metals goes to zero at  $T=0$  K, roughly as some power of  $T$ . When impurities are present they also scatter the carriers, and this increases the resistivity. To the extent that the scattering from different impurity atoms is independent, the different types of impurity will make independent, additive contributions to the resistivity, each proportional to the concentration  $c$  of that impurity. The contribution of the impurities to the resistivity is to the first approximation independent of temperature and remains as the residual resistivity  $\rho_0$  at  $T=0$  K. To the approximation that the contribution of the impurities to the resistivity is additive and independent of temperature, one can write the total resistivity as

$$\rho(c, T) = \rho_0(c) + \rho_i(T). \quad (1)$$

This relation is commonly referred to as Matthiessen's Rule [219, pp. 7-8; 191, p. 433; 218]<sup>1</sup>, though this is not the form originally given by Matthiessen. The same name is often given to the more general idea of the additivity of resistivity contributions from different sources. In this form it applies to the effects of other sources of scattering, such as lattice imperfections that make contributions to the resistivity that vary with temperature, and it implies that the total added resistivity is a linear function of the concentration of each type of impurity and imperfection that may be present. Here the name Matthiessen's Rule will be applied to eq (1), supplemented by the idea that  $\rho_0$  is proportional to  $c$ .

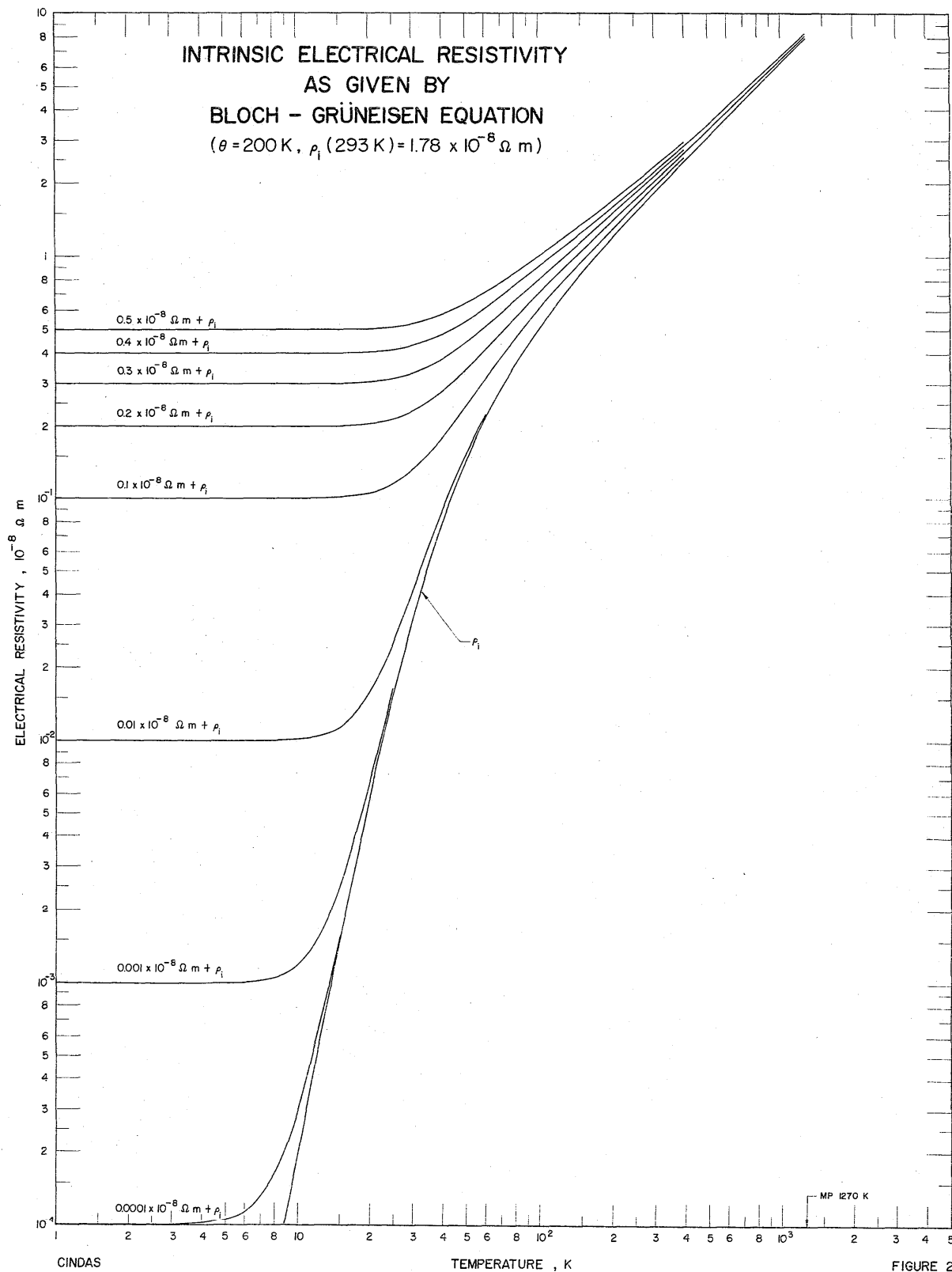
The qualitative behavior of the electrical resistivity of impure metals is illustrated in figures 1 and 2. In constructing these figures,  $\rho_i(T)$  has been taken to be given by the Bloch-Grüneisen expression (section 2.2), and  $\rho$  has been computed using Matthiessen's Rule for several values of  $\rho_0$ . Figure 1 uses linear scales, and figure 2 uses logarithmic scales, as is much preferred with nearly pure metals. For  $T$  below about 10 K the residual resistivity is essentially the total resistivity, and the plots are all nearly straight horizontal lines from which  $\rho_0$  can be read. In analyzing data on a metal containing various concentrations  $c$  of a single impurity or dopant, one can make such plots, read  $\rho_0$  from them, and then test Matthiessen's Rule in two ways:

- (a) by checking the proportionality of  $\rho_0$  to  $c$ , and
- (b) by checking that  $\rho - \rho_0$  is the same for all samples.

In fact, deviations from Matthiessen's Rule do occur and in some materials are of major interest. When a single impurity is involved, the deviations can be brought out, even when the impurity concentrations are not well known, by constructing plots such as that in figure 3. Here  $\rho - \rho_0$  for various samples at the same  $T$  is plotted against  $\log \rho_0$  as a (nonlinear) measure of the impurity concentration. If Matthiessen's Rule is strictly obeyed, such a plot will be a horizontal line corresponding to the value of  $\rho_i(T)$ ; if it is not, the curve may deviate from a straight line as is indicated in the high-concentration range in figure 3 by the dotted line. In the latter case,  $\rho_i(T)$  can be determined from the horizontal asymptote of the curve at the lowest

<sup>1</sup> Figures in brackets indicate literature references.





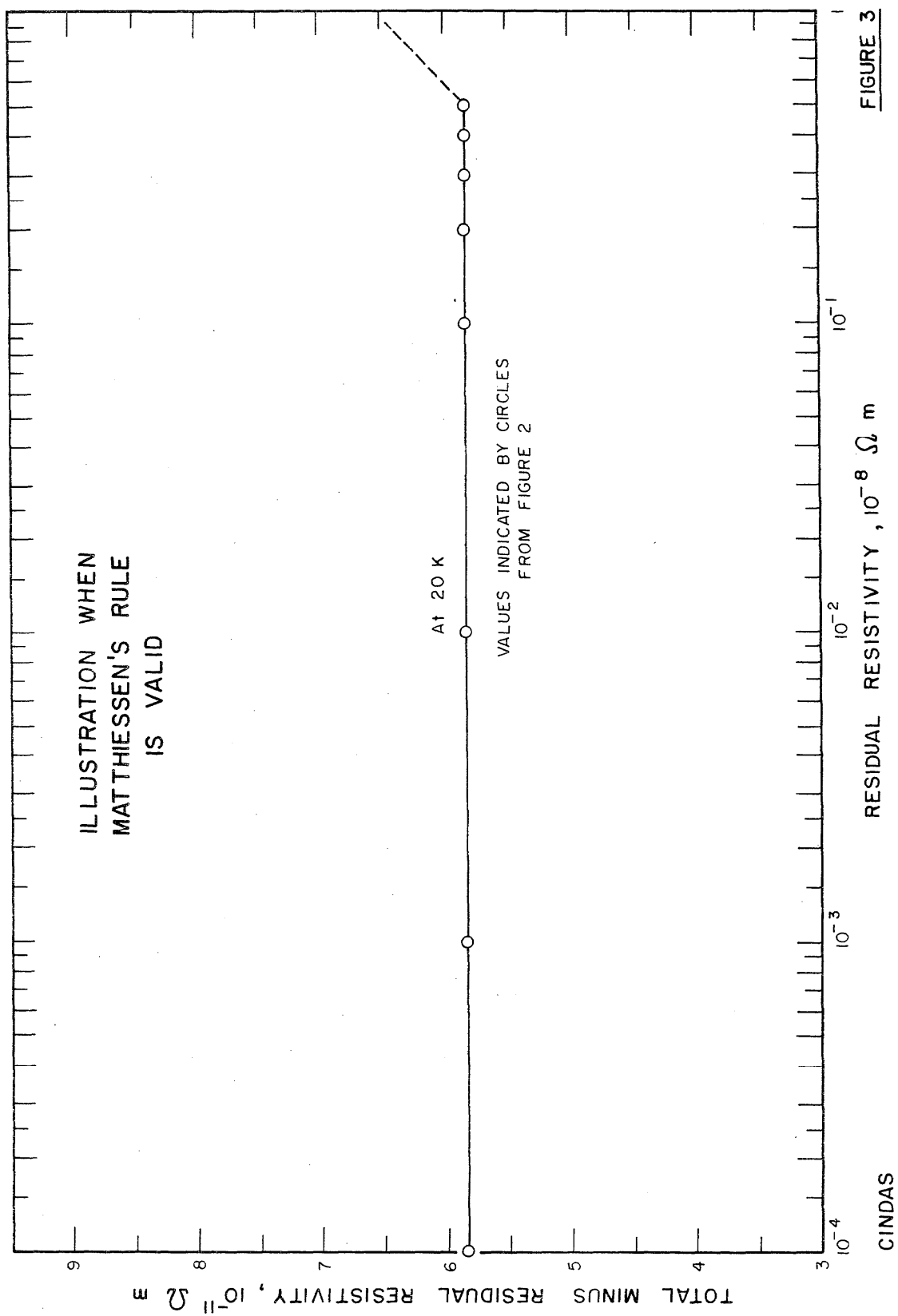


FIGURE 3

concentrations, and the "deviation from Matthiessen's Rule," defined as

$$\Delta(c, T) = [\rho(c, T) - \rho_0] - \rho_i(T), \quad (2)$$

can be determined by comparing the curve with its asymptote.

Comprehensive reviews of deviations from Matthiessen's Rule have been given by Bass [191] and Cimberle et al. [199]. The latter authors include a presentation of experimental data that is available for copper alloys [199, pp. 647-9], gold alloys [199, pp. 649-51], and silver alloys [199, pp. 651-4]. They give figures similar to figure 3, thus allowing a determination of the validity of Matthiessen's Rule for a given combination of temperature, residual resistivity, and impurity species.

## 2.2. Bloch-Grüneisen Formula

An important theoretical expression for the intrinsic resistivity of a metal is the Bloch-Grüneisen equation,

$$\rho_i(T) = \frac{C}{M\theta} \left(\frac{T}{\theta}\right)^5 \int_0^{\theta/T} \frac{z^5 e^z}{(e^z - 1)^2} dz, \quad (3)$$

which can also be written as

$$\rho_i(T) = \frac{C}{M\theta} \left(\frac{T}{\theta}\right)^5 J_5\left(\frac{\theta}{T}\right), \quad (4)$$

with  $T$  the temperature,  $\theta$  a characteristic temperature of the metal known as the electrical resistivity Debye temperature,  $M$  the atomic weight,  $C$  a constant of the metal, and  $J_5$  a transport integral [219, 223, 207, 208, 194, 195]. The Bloch-Grüneisen formula is derived for a quite special model: a monovalent metal with a spherical Fermi surface and a phonon spectrum derived from a Debye model. It is treated as having volume, Debye temperature  $\theta$ , and carrier-phonon interaction parameters all independent of temperature, and the derivation is carried through with neglect to Umklapp processes [233, chapter IX].

Despite the special assumptions made in arriving at this equation, it is quite useful to compare experimental results with it as a basis for the further elaboration of ideas. Experimental results for real materials are sometimes stated in terms of it: for instance, treating  $\theta$  as the only parameter variable with  $T$ , one can determine  $\theta$  as a function of  $T$  so as to reproduce the observed  $\rho_i(T)$ , and then discuss the variation of this  $\theta$  with  $T$  [219, section 4.3; 215; 216]. As will be seen later, its generally appropriate form can also be modified by elaborations that represent the effects of other factors acting in real metals in order to make it represent quite well the observed behaviors of real materials.

At limiting temperatures the Bloch-Grüneisen equation takes on simple forms:

$$\rho_i(T) \rightarrow 124.431 \frac{C}{M\theta} \left(\frac{T}{\theta}\right)^5, \text{ as } T \rightarrow 0, \quad (5)$$

$$\rho_i(T) \rightarrow \frac{C}{4M\theta} \left(\frac{T}{\theta}\right), \text{ as } T \rightarrow \infty. \quad (6)$$

Figures 1 and 2 were constructed for illustrative purposes using a Bloch-Grüneisen form for  $\rho_i(T)$ , with values

of the parameters generally appropriate for the metals treated in this report:  $\theta$  was taken to be 200 K, the melting point 1270 K, and  $C$  was chosen to make the intrinsic resistivity  $1.78 \times 10^{-8} \Omega \text{ m}$  at 293 K. Figure 4 gives, for this same function, a plot of the logarithmic derivative of the intrinsic resistivity,  $d \ln \rho_i / d \ln T$  or the "local power"; it shows clearly the rapid departure from the fifth-power law at low temperatures as well as the slower approach to the first-power law at higher temperatures, which is nearly complete at  $T = \theta$ .

## 2.3. Change of Resistivity on Melting

When a metal melts, the resistivity changes abruptly [202] and generally increases [203]. A theory of the ratio of the resistivity  $\rho_L$  of the liquid to the resistivity  $\rho_S$  of the solid, both at the melting point, has been given by Mott [220], who finds

$$\left(\frac{\rho_L}{\rho_S}\right)_{T_m} = \exp\left(\frac{80 L_F}{T_m}\right). \quad (7)$$

Here  $T_m$  is the melting point in kelvins and  $L_F$  is the latent heat of fusion in kilojoules per mole. In deriving this equation, Mott adopts the Einstein model for the atomic motions in a solid and a corresponding model of the liquid in which the atoms vibrate about fixed but imperfectly ordered mean positions; he then assumes that the change in resistivity on melting is primarily due to the change of the frequencies of atomic vibrations or of  $\theta$ . A comparison of the results of the present work with Mott's rough and simple theory will be found in section 5.

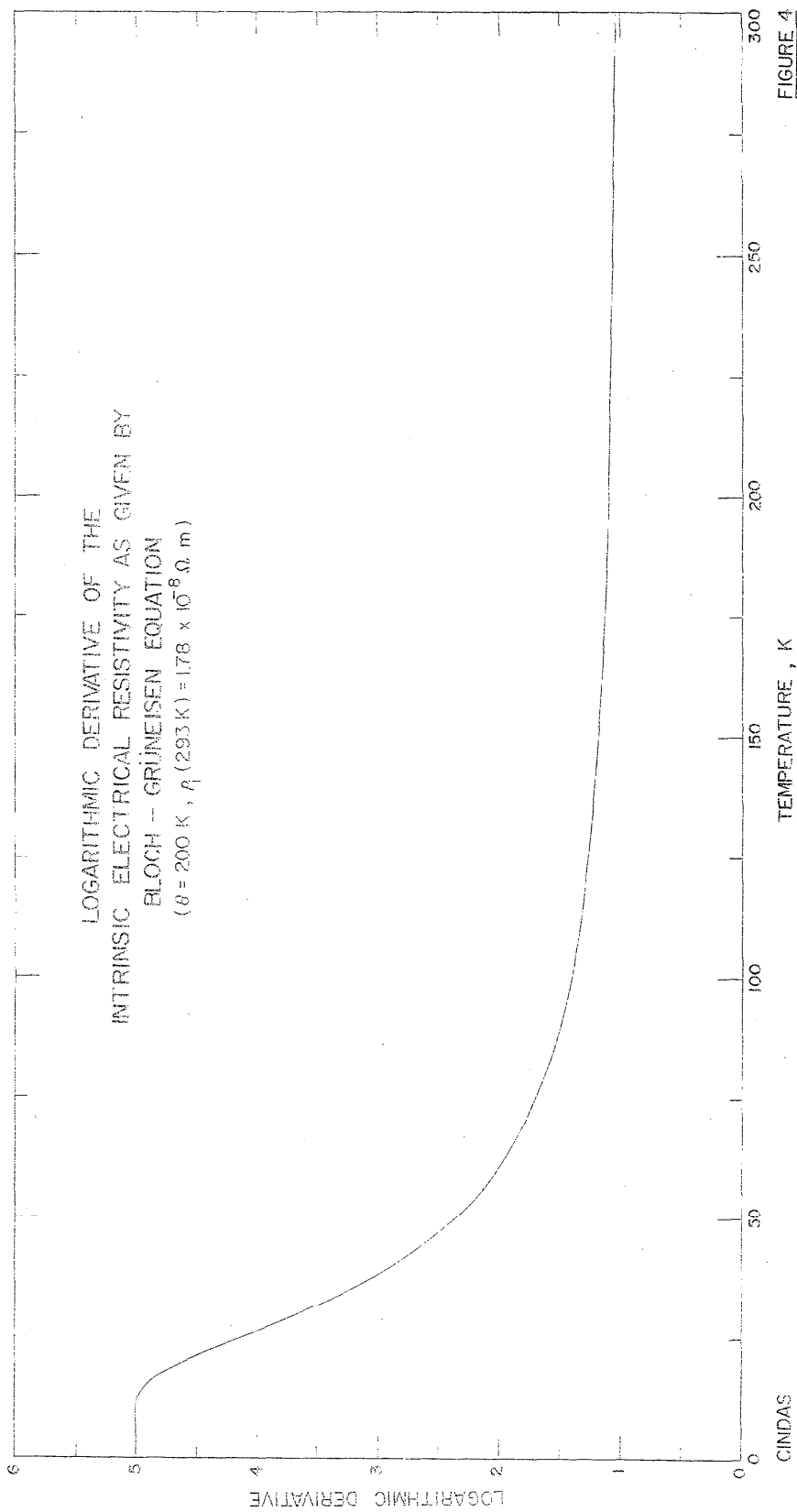
## 3. Evaluation and Synthesis of Data

### 3.1. Extraction of Data from the Literature

Extraction of data from the literature must, of course, precede its evaluation. It is important that one extract not merely the raw numerical data, reading it from graphs, if necessary, but also the fullest possible characterization of the measured samples, and an adequate characterization of the method of measurement. While the author's estimate of the accuracy of the results is essential, a comparison of the results and estimated accuracies of different authors will soon undermine any uncritical trust in their estimates. Data extraction has been carried out with the aim of minimizing the need for a second examination of a paper, but this cannot always be avoided. The results of data extraction are summarized in the Tables of Experimental Data and Tables of Measurement Information in section 4.

### 3.2. General Procedures in the Analysis and Synthesis of Data

In beginning the analysis, it is very useful to bring all data onto a single graph in order to make evident any gross discrepancies and to facilitate the recognition of subtler similarities and differences. In the present work, plots of  $\rho$





or  $\rho_i$  against  $T$  were not useful for this purpose, because  $\rho$  changes by orders of magnitude over the full range of  $T$ , while the percentage accuracy of the measurements is about constant; plots of  $\log \rho$  against  $\log T$  are required. These bring out large discrepancies that can lead to the exclusion of some work from consideration, and, in the low-temperature range, make very evident the differing purities of different samples. The general agreement or disagreement of results obtained by different observers using different methods and the fit of low-temperature to higher-temperature measurements may send one back to an examination of some of the original papers.

The preliminary selection of what data to include as the basis of the evaluated data depends on many factors including the central purpose of this work, the explicitness with which experimenters report their results, and how the data are reported. Since the central purpose of this work is to generate evaluated data for the pure bulk material, data for conditions not relevant to this central purpose were not considered in the evaluation. In addition, abnormal values were also excluded. The explicitness with which certain items are reported enhances the quality of the reported data. Such items include purity, method and procedure of fabrication, thermal history, specimen dimensions, method of measurement, and measurement environment. Data in tabular form are given higher weight than data reported in a figure, and data over an extended temperature range are given more importance than data over a limited range of temperatures. The final decision of the data to be included in the synthesis of information will include considerations such as the method of measurement and the evidence of care with which it was applied, the methodology used in sample preparation (in which there are sometimes dramatic steps forward), and the consistency of the results of different workers.

Before the final synthesis of data from different sources, one must be sure that they are as closely comparable as possible. One matter to be considered is the correction for thermal expansion of the sample made by the original author. Electrical resistivity measurements are ordinarily made at constant pressure on samples with dimensions that change with temperature. In deriving the resistivity  $\rho$  from a measured resistance  $R$  using an equation such as

$$\rho = RA/\ell, \quad (8)$$

where  $\ell$  is the length between the voltage probes on a specimen and  $A$  the cross-sectional area of the specimen, it is common to use for  $A$  and  $\ell$  the values measured at room temperature. This is not inappropriate in reporting measurements of limited accuracy over not-too-large a temperature range, but the difference between

$$\rho(T, \text{nominal}) = R(T) A(293 \text{ K})/\ell(293 \text{ K}) \quad (9)$$

and

$$\rho(T) = R(T) A(T)/\ell(T) \quad (10)$$

ought not to be ignored in other cases. Unfortunately, there is not full uniformity in the reporting of  $\rho(T, \text{nominal})$  as a substitute for  $\rho(T)$ . In the present work, it has been important to determine which quantity has been reported and to bring the results to a common basis by use of a relation such as

$$\begin{aligned} \rho(T, \text{nominal}) &= \rho(T) \left[ \frac{A(T)}{A(293 \text{ K})} \frac{\ell(293 \text{ K})}{\ell(T)} \right]^{-1} \\ &\cong \rho(T) \left[ 1 + \frac{\ell(T) - \ell(293 \text{ K})}{\ell(293 \text{ K})} \right]^{-1} \end{aligned} \quad (11)$$

before making comparisons. (It should be emphasized that not all methods of measuring  $\rho$  are equivalent to measuring  $R$ ,  $A$ , and  $\ell$ , and that the correction for dimensional changes with changing  $T$  may differ with the experimental set-up.) It has been most convenient to reduce data reported as  $\rho(T)$  to terms of  $\rho(T, \text{nominal})$  since most reported data are in terms of  $\rho(T, \text{nominal})$  and to then carry out the synthesis of all data using  $\rho(T, \text{nominal})$ . The final results have, however, been converted to and reported as the true  $\rho(T)$ .

The values of  $\rho(T, \text{nominal})$  were converted to  $\rho_i(T, \text{nominal})$  by Matthiessen's Rule using values of  $\rho_0$  provided by the authors or deduced from the low-temperature values of  $\rho(T, \text{nominal})$ . When measurements are made only above room temperature, authors commonly do not provide a value of  $\rho_0$ , and one cannot deduce it from the measurements of  $\rho$ . For the purer samples one can then appropriately neglect the difference between  $\rho$  and  $\rho_i$ , since the difference is smaller than other sources of error.

Reduction of the selected values of  $\rho_i(\text{nominal})$  to a smoothed curve must ultimately depend on a draftsman's eye supplemented by a physical understanding of the behavior to be expected. To improve on the precision attainable by smoothing on a large-scale plot of  $\log \rho_i(\text{nominal})$  against  $\log T$ , an intermediate numerical fitting to a suitable analytic function has been employed. In this connection a suitable function is one that can easily represent the general behavior of the data at high, low, and intermediate temperatures, that does not tend to misbehave seriously outside the range of the fitted data, and that involves only a small number of parameters that can be adjusted by a computer to achieve an optimum fit to the data, ordinarily in a least-squares-error sense. A plot of the fractional deviation of the data from the smooth fitted curve or of  $\log [\rho_i(\text{data, nominal})/\rho_i(\text{fitted, nominal})]$  against  $\log T$  then gives a conveniently enlarged presentation of any systematic deviations of the data from the fitted curve on which are superimposed the erratic deviations due to experimental errors. Using this, one can construct a smoothed curve from which to read fractional deviations of recommended values from the fitted curve at the  $T$ 's that are to appear in the table. Values of  $\rho_i(\text{nominal})$  as thus obtained were corrected to get values of  $\rho_i$  using eq (11) and the best available data on the thermal expansion of the material. Finally, values of  $\rho(T)$  were constructed for a material with specified  $\rho_0$  by using Matthiessen's Rule.