

THE THERMAL AND ELECTRICAL CONDUCTIVITIES OF
SOME TRANSITION METALS AND THEIR ALLOYS.

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PREFACE

The transport properties of metals and alloys at high temperatures have attracted considerable attention in the recent years because of their technological and theoretical importance. In particular, the transition metals characterised by an incomplete d band have a different electrical and thermal behaviour compared to normal metals. The electron transport properties of transition metals are evaluated by Kolomoets using a model of two overlapping bands in which the density of states is sharply different. This results in an electronic Lorenz number L_e which is less or more than the normal Sommerfeld value L_n , depending upon the sign and magnitude of the parameter $\gamma = (E_F - E_0)/kT$. E_F and E_0 are the electron energies at the Fermi level and at the edge (top or bottom) of the d band. To check Kolomoets' predictions, measurements on the thermal and electrical conductivities of transition metals and their alloys are quite essential.

It is well known that phonons as well as electrons play an important part in the thermal and electrical transport in metals. The Wiedemann-Franz Lorenz relation $K_e r/T = L_e = \text{constant}$, can be used to separate the electronic part (K_e) and the phonon part (K_p) of thermal conductivity from the total thermal conductivity (K). However, this method failed since it yielded negative values of K_p for iron, which is hard

to understand. Though Backlund's modified formula $L_e = K_e(r+r_0)/T$ (where r_0 is the resistivity obtained on extrapolating the linear r - T curve to 0°K), was successfully applied for some metals, it failed in the case of nickel, cobalt, palladium etc. Hence there is a great need to develop a reasonable method of separating K_p and K_e . Alternative methods have also been applied in this context, employing L_0 evaluated by Makinson for a simple monovalent metal.

The present thesis is an attempt towards applying our existing concepts to derive meaningful electronic and lattice components of the thermal conductivity. The thermal and electrical conductivities of rhodium, iridium and three palladium-tungsten alloys (containing 6.5, 9.5, 12.5 atoms percent of tungsten in solid solution in palladium) have been determined in the temperature range 1200-1600 K. The total and spectral emittances are also determined in the same temperature range in the wavelength range 0.52 - 0.65 μ . For determining the thermal conductivity of the three palladium-tungsten alloys, the Jain and Krishnan method modified by Jain and Goel is used. The same method could not be used for rhodium, since the rhodium specimen was short. The parabolic law used by Jain and Krishnan for short specimens is liable to large errors as pointed out by Flynn. Hence the original expressions were used, taking care to include the higher order terms, to give accurate values of thermal conductivity. This method and also the logarithmic relation

used by Jain and Goel have been used to obtain the thermal conductivity of iridium. A new method of determining the spectral emittance of thin wires has been suggested and used to determine the spectral emittance of the palladium-tungsten alloys at 0.65μ .

Electrical resistivities of all these samples at liquid helium temperatures have also been measured for purposes of specimen characterisation. The ice point thermo-electric powers and the room temperature magnetic susceptibilities of pure palladium and the three palladium-tungsten alloys have also been measured and are included in the discussion.

The thesis has been divided into five chapters. The first chapter gives an introduction to the field including the different methods of measuring the thermal and electrical conductivities and the total and spectral emittances of metals and alloys at high temperatures.

The experimental methods used in the present investigation are described in Chapter II. The methods of calculating the thermal conductivity using both the logarithmic and parabolic regions in the Jain and Krishnan method are discussed. The modification used in calculating the thermal conductivity of short specimens is described. The higher order terms included to give accurate values of thermal conductivity are calculated and are reported in this chapter. Since the palladium-tungsten alloys are very thin (diameter ~ 0.5 mm), the method used to determine the spectral emittance in the

case of rods could not be used, because of the large errors involved. Hence a new method has been used and is described in this chapter.

The experimental results of the thermal and electrical conductivities and total and spectral emittances of rhodium and iridium in the temperature range 1200-1600 K are reported in chapter III. The separation of phonon and electronic thermal conductivities is carried out assuming that the phonon part K_p is inversely proportional to the absolute temperature and the electronic part K_e is directly proportional to the absolute temperature T , i.e. the experimental results are fitted to the equation $KT = aT^2 + b$ where $a = L_e/r$. The KT vs T^2 plots come out to be linear for these metals. From the measured values of K , L_e is calculated from 'a'. From 'b' the lattice part (K_p) at different temperatures is calculated. This simple method of separating K_p and K_e gives reasonable (positive) values of K_p and K_e for the metals discussed here. L_e obtained from this analysis for these at 1200 K is significantly less than L_n and is in conformity with Kolomoets' prediction for transition metals in which d band is nearly filled up. This method is satisfactory in the sense that we are not confronted with an awkward situation of a negative lattice conductivity.

The fourth chapter gives the experimental results of the thermal and electrical conductivities and the total and spectral emittances of the three palladium-tungsten alloys. The results are analysed by the method given in Chapter III.

The results of our low temperature resistivity measurements are also included for specimen characterisation. The electrical residual resistivity and its variation with the increase of tungsten content is discussed.

The variations of the room temperature electrical resistivity, the magnetic susceptibility and the thermo-electric power of the palladium - tungsten alloys with the tungsten content are similar to those of the palladium-uranium system studied by Catterall. The behaviour of the Pd-W system can be understood following Catterall's explanation for Pd-U alloys. The deviation from linearity of the high temperature electrical resistivity data is used in this chapter to show that γ can be considered to be positive in the Pd-W alloys and increasing with the tungsten content. On this basis a value of the electronic Lorenz number L_e larger than L_n and increasing with the tungsten content is obtained which is fully consistent with Kolomoets' predictions.

The fifth chapter deals with the ferromagnetic metals: Iron, cobalt and nickel. The experimental results on the thermal and electrical conductivities of various investigators are analysed. The KT vs T^2 plots come out to be linear for the three ferromagnetic states. Our analysis leads to an electronic Lorenz number $L_e < L_n$ in the temperature range of our analysis for all the three metals conforming to Kolomoets' predictions.

CONTENTS

	<u>Page</u>
Acknowledgements	
Pre face	i-v
Chapter I	
Introduction and a Brief Survey of the Earlier Work.	1
1.1 Introduction	1
1.2 The Electrical Resistivity	4
1.2.1 Mechanisms of Electrical Resistivity	4
1.2.2 Temperature Dependence of the Electrical Resistivity.	6
1.3 Thermal Conductivity	8
1.3.1 Introduction	8
1.3.2 Separation of the Electronic and Phonon Components	9
1.4 The Electronic Lorenz Number	11
1.5 Thermo-electric Power and Magnetic Susceptibility	13
1.6 Experimental Methods	13
1.6.1 Thermal Conductivity	13
a) Steady State Methods	14
b) Transient Methods	18
1.6.2 Measurement of Electrical Resistivity	19
1.6.3 Measurement of Total and Spectral Emittances	20
1.7 Soope of the Present Study	22
References	23

Chapter II	<u>Page</u>
Theoretical and Experimental Details	27
2.1 The Method Used in the Present Work	27
2.2 Theoretical:	
2.2.1 The Heat Conduction Equation	27
2.2.2 The Jain and Krishnan Method	28
Case I	28
Case II	31
2.3 Methods used in the Present investigation	34
2.3.1 Rhodium and Iridium	34
2.3.2 Palladium-tungsten Alloys	34
2.4 Experimental Details:	
2.4.1 The High Vacuum System	34
2.4.2 Temperature Measurement	36
2.4.3 Measurement of Spectral Emittance	36
2.4.4 Measurement of Total Emissivity and Electrical Resistivity.	40
2.4.5 Measurement of Alternating Potential and Current.	41
2.4.6 Measurement of Electrical Resistivity at low temperatures.	42
2.4.7 Measurement of Thermo-electric Power.	43
2.4.8 Measurement of Magnetic Susceptibility.	45
References	46

Chapter III

Rhodium and Iridium	47
3.1 Samples	47
3.1.1 Rhodium	47
3.1.2 Iridium	48
3.2 Spectral Emittance	49
3.2.1 Results and Discussion	49
3.2.2 Relation between Spectral Emittance and Thermal Conductivity	51
3.3 Total Emittance	52
3.3.1 Relation between Electrical Resistivity and Total Emittance	53
3.4 Electrical Resistivity	54
3.4.1 Results	54
3.4.2 Discussion	55
a) Calculation of the Correction Term due to the Temperature Variation of θ_D .	57
b) General Expressions for Transition Metals.	59
c) Comparison with the Theoretical Values of r .	64
3.5 Thermal Conductivity	66
3.5.1 Results	66
3.5.2 Method of Analysis	67
3.5.3 The Leibfried-Schlomann Relation	69
3.5.4 Theoretical Calculation of Thermal Conductivity	70
3.5.5 The Cezairliyan Correlation	72
3.6 The Lorenz Number	72
3.6.1 Results and Discussion	72
3.6.2 Kolomoets' Calculations	76
References	79

Chapter IV

Palladium-Tungsten Alloys	82
4.1 Introduction	82
4.2 Specimen Details	83
4.3 Spectral Emittance	86
4.4 Total Emittance	86
4.5 Electrical Resistivity	87
4.6 The Residual Electrical Resistivity	87
4.7 Magnetic Susceptibility	88
4.7.1 Results	88
4.7.2 Discussion	89
4.8 The Thermo-electric Power (TEP)	93
4.8.1 Results	93
4.8.2 Discussion	94
4.9 Temperature Variation of Electrical Resistivity	97
4.10 Thermal Conductivity	100
4.10.1 Results	100
4.10.2 Methods of Analysis	101
4.11 The Electronic Lorenz Number: Results and Discussion	106
4.12 Conclusions	109
References	112

Chapter V

Thermal Conductivity of the Ferromagnetic Transition Metals	114
5.1 Introduction	114
5.2 Present Method of Analysis	116
5.3 Separation of $(K-K_e)$ from K .	117
5.4 Separation of Spin Excitation and Phonon Components.	118
5.5 The Electronic Lorenz Number	119
References	121