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

B.KRISHNAMMA REDDY

Thesis submitted to 'INDIAN INSTITUTE OF TECHNOLOGY', DELHI
for partial fulfilment of the Degree of
DOCTOR OF PHILOSOPHY
1974.

ACKNOWLEDGEMENTS

This work has been carried out under the inspiring guidance of Dr.S.C.Jain and Dr.M.S.R.Chari. The author wishes to record her heart-felt thanks for their valuable guidance and for the constant encouragement they have rendered through out the progress of the work.

The author is grateful to Dr.T.C.Goel for his help in the high temperature measurements and for the many stimulating discussions she had with him. The author is thankful to Dr.N.S.Natarajan, M/s Hari Kishan and Lakha Singh for their help in the low temperature measurements, to Mr. B.B.Sharma for his useful suggestions, to the Director, National Physical Laboratory for allowing the author to carry out the low temperature measurements and to Mr.K.P.S.Nair for supplying liquid helium.

It is a pleasure to thank all her colleagues of the optics group and other disciplines of the Indian Institute of Technology, National Physical Laboratory and her friends at the Solid State Physics Laboratory for their cooperation.

The author wishes to thank her sister-in-law and brother Mrs. and Dr.B.M.Reddy, Mrs. Sudha Jain and Dr.D.R.K.Reddy for their affectionate encouragement.

Grateful thanks are also due to Mr. S.C.Bahl for typing out the manuscript with great care.

B. Krishnamma Reddy
12/8/74.

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 $\gamma = (E_F - E_o)/kT$. E_F and E_o 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 $K_e\, r/T = L_e =$ 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 $L_e=K_e(r+r_o)/T$ (where r_o is the resistivity obtained on extrapolating the linear r-T curve to O'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_e 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 toal 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 0.65 μ.

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 $\sim$ 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 significantl 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

Chapter II

Chapter III

Chapter IV

Chapter V