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**STUDIES OF THE THERMOELECTRIC POWERS AND
RESISTIVITIES OF PRIMARY SOLID SOLUTIONS OF
Au, Cd, Zn, In, Ge, Tl, and Sb IN SILVER**

by

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A thesis submitted to the Faculty of
Graduate Studies in partial fulfilment
of the requirements for the degree of
Doctor of Philosophy

Carleton University

Ottawa, Ontario

July, 1966

To my wife

The undersigned hereby recommend to the Faculty of
Graduate Studies acceptance of this thesis, submitted by Laurie
Stuart Wright, B.Sc., in partial fulfilment of the requirements
for the degree of Doctor of Philosophy.

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ABSTRACT

The thermoelectric powers and resistivities of primary solid solutions of Cd, Zn, In, Ge, Tl, Au, and Sb in silver were measured over the temperature range 90 to 240°K. The characteristic thermoelectric powers of the impurities have been determined in the diffusion region by the Nordheim-Gorter rule. Furthermore, a method has been successfully tested for finding the characteristic thermoelectric powers of the impurities in the phonon-drag region. The phonon-drag component of the thermoelectric power has been determined at 90°K for 1 atomic percent of each impurity in silver showing that the impurities Cd, In and Sb in silver do not suppress phonon-drag whereas the impurities Zn, Tl and Au in silver are effective in suppressing phonon-drag. The characteristic thermoelectric powers of the impurities Au, In, Tl and Ge in silver, from the diffusion thermoelectric power region, are compared with the characteristic thermoelectric powers of these impurities determined in the temperature range 0.1 to 5°K by Dr. A. M. Guénault at the National Research Council. The characteristic thermoelectric powers and the resistivities are discussed in terms of a free-electron rigid band model.

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CHAPTER 1

Introduction to Thermoelectricity

1:1 Thermoelectricity from 1826-1960

In 1826 Thomas Johann Seebeck (1) discovered that a potential difference, ΔV , could be produced by purely thermal means in a circuit of two different metals A and B whose junctions are maintained at different temperatures, T and $T + \Delta T$, (see Figure 1.1). The two metals constitute a thermocouple and the potential difference produced in the circuit is called a Seebeck emf or a thermo-emf. The thermo-emf depends only on ΔT and the type of metals used; it does not depend on the dimensions of the metals A and B, nor does it depend on the type or dimension of the junction. When one of the junctions is maintained at a constant temperature and the temperature of the other junction is varied, the Seebeck emf is found to be a function of the temperature of the test junction. This fact enables the thermocouple to be used as a thermometer. The advantage of a thermocouple thermometer is that the test junction comes quite rapidly to thermal equilibrium with the system whose temperature is to be measured because the heat capacity of the test junction can be made small. The thermocouple, therefore, follows temperature changes rapidly. The Seebeck coefficient, Q , or the thermoelectric power of the thermocouple is defined as

$$Q = \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T} \quad (1.1)$$

Figure 1-1. Circuit for producing thermo-emfs.

In 1834 Jean Charles Athanase Peltier (2) discovered that when a current is passed through a junction connecting two different metals, heat is either liberated or absorbed depending on the direction of the current through the junction. Experiments have shown that the rate of heat transferred at any junction is proportional to the current passing through the junction. The proportionality constant is known as the Peltier coefficient π . In recent years much effort has gone into a search for materials exhibiting large Peltier coefficients in the hope that an efficient refrigeration unit could be produced. The advantage of such a unit would be its small size.

In 1854 William Thomson (Lord Kelvin) (3) theoretically predicted the existence of a third thermoelectric effect: If an electric current is maintained in a wire along which a temperature gradient exists, heat is either liberated or absorbed at all points along the wire. Experiments have shown that the rate of heat liberation or absorption is proportional to the product of the current density and the temperature gradient along the wire. The proportionality constant is known as the Thomson coefficient μ .

Thomson (4), in a series of papers from 1854 to 1857 gave experimental evidence that the Thomson coefficient, μ , existed and he put forward two relations known as the Kelvin relations connecting the Seebeck coefficient with the Peltier and Thomson

coefficients. The Kelvin relations are

$$\pi = TQ, \quad (1.2)$$

$$\mu = TdQ/dT, \quad (1.3a)$$

or

$$Q = \int_0^T \frac{\mu}{T} dT. \quad (1.3b)$$

Thomson's derivation of the Kelvin relations was not completely justifiable but his experiments confirmed the validity of the results obtained. H. B. Callen (5), using the reciprocal relations of Onsager (6), has provided a valid derivation of the Kelvin relations.

Much confusion exists in the literature surrounding the interpretation of the Seebeck and Peltier effects since the presence of a junction between two different metals is necessary to observe them. This led some people to assume that the Seebeck and Peltier effects are junction effects. However, the Thomson coefficient in no way depends upon a junction and since the validity of the Kelvin relations has been established this means that the Seebeck coefficient and the Peltier coefficient must be properties of the bulk material rather than being detailed features of the junction itself.

It is obvious from the Kelvin relations that if the thermoelectric power of a material can be determined as a function of temperature, then the Peltier and Thomson coefficients can easily be calculated. This is ideal from the experimentalist's point of view since the measurements of the Peltier and Thomson coefficients require complicated calorimetric techniques whereas the measurement of the thermoelectric power should be relatively easy since only a potential difference and a temperature difference

must be measured. However, one difficulty exists. The measurement of the thermoelectric power involves a circuit of two different metals (see Figure 1.1) so that the thermoelectric power of material A relative to material B is obtained rather than the absolute thermoelectric power of material A or B.

In 1927 Meissner (7) experimentally established the absence of thermoelectric effects in superconductors below their transition temperatures. Hence, a superconductor can be used as one of the materials in forming a junction and the thermoelectric effects observed will then be due to the bulk properties of the other material used in forming the junction. The experiment can only be carried out up to the transition temperature of the superconductor so that the experiment is only possible over a very limited temperature range.

In 1900 Drude (8) formulated the first concept of a metal as a framework of atoms surrounded by a free-electron gas. Drude assumed that the electrons in equilibrium were moving randomly as a gas but making frequent collisions with the atomic lattice and that after each collision any "memory" of the previous electron velocity was obliterated. Drude also assumed that in between collisions the electrons would obey Newton's equation of motion. Drude derived expressions for the electrical and thermal conductivities of metals but he did not concern himself with thermoelectricity.

In 1905 H.A. Lorentz (9) introduced two important concepts to the theory of transport phenomena. Lorentz treated the

electron gas in a metal by classical Maxwell-Boltzmann statistics and he introduced the Boltzmann equation to describe the motion of electrons in a metal under the influence of external fields.

Lorentz's treatment of transport phenomena using classical statistics was certainly a step in the right direction but it met with limited success. The Lorentz theory was applied by various authors to many of the magnetic and thermal effects associated with metallic conduction. There were a few apparent successes coupled with a large number of failures.

In 1928 Sommerfeld (10) published a paper in which he re-examined Lorentz's transport theory in the light of Fermi-Dirac statistics, developed independently by Fermi (11) and Dirac (12) in 1926, rather than classical Maxwell-Boltzmann statistics. Subsequently most of the difficulties of the Lorentz theory were reconciled using Sommerfeld's ideas.

By 1930 theoretical developments in the field of transport phenomena had surpassed experimental developments particularly in the field of thermoelectricity because of the problems of measuring thermoelectric effects. Borelius et al. measured the Thomson heat of an alloy of silver containing 0.37 atomic percent gold and the thermoelectric power of tin and lead against the silver alloy. In 1932 Borelius et al. (13), using the above data in conjunction with Equation (1.3b), established absolute scales of thermoelectricity for these metals from 4.2 to 300°K. This now meant that the thermoelectric power of any conductor could be determined

using the circuit shown in Figure 1.1 in which one of the materials used would be tin, lead or the silver alloy. The effect of this material could then be removed using the appropriate scale of thermoelectricity developed by Borelius.

In 1936 Wilson (14), on the basis of Sommerfeld's ideas, showed that the thermoelectric power of a metal should be given by

$$Q = - \frac{\pi^2 k^2 T}{3 |e|} \left[\frac{\partial}{\partial \epsilon} \ln \sigma(\epsilon) \right]_{\epsilon = \epsilon_f}, \quad (1.4)$$

where k is Boltzmann's constant, e is the electronic charge ($e = -1.6021 \times 10^{-19}$ coulombs), and $\sigma(\epsilon)$ is an electrical conductivity generating function arising from a variational solution of the Boltzmann equation. When ϵ is set equal to ϵ_f , the Fermi energy, $\sigma(\epsilon_f)$ is an approximation to the measured electrical conductivity. Wilson derived this result on the basis of elastic scattering of electrons in metals. When Wilson compared this result with experiments on the noble metals, he found that in the region of room temperature his equation correctly predicted the temperature dependence of the thermoelectric power but it gave an incorrect sign for the thermoelectric power. This problem still exists and will be mentioned again in section 1:3.

In 1945 Gurevich (15) pointed out that a "stream" of lattice waves (or phonons) could drag electrons along with it and hence could be a source of thermoelectricity. Phonon-drag thermoelectricity was first experimentally identified in semiconductors by Frederikse (16) in 1953. W.B. Pearson (17) in 1961 was the

first to establish experimentally the existence of phonon-drag thermoelectricity in the noble metals. The results of Pearson's experiments are shown in Figure 1.2 and they indicate three broad regions of interest: A high temperature region above 100°K where the thermoelectric power is directly proportional to temperature, known as the region of diffusion thermoelectricity; a region from about 15 to 100°K where the hump occurs in the curve, known as the region of phonon-drag thermoelectricity, and a very low temperature region below 15°K which has only recently been investigated. The phonon-drag hump had been observed in copper before Pearson carried out his experiments but it was not clear that the hump was due to electron-phonon collisions. A.V. Gold et al. (18) in 1960 observed unusually large thermoelectric powers in the phonon-drag region when small amounts of iron were present in copper and there was some speculation that the presence of iron would explain the hump.

Gold's paper is rather important on two counts. First, it focused attention on the effects of the transition elements as impurities in the noble metals. A further discussion of these effects will be carried out in sections 1:2 and 1:3. Second, it gave experimental confirmation of a theory proposed by Nordheim and Gorter (19) for dealing with the thermoelectric power of metals containing impurities.

In 1864 Matthiessen (20) discovered that the addition of an impurity to a metal of lattice resistivity $\rho_l(T)$ increased the

Figure 1-2. Thermoelectric power of copper, silver, and gold as a function of temperature. (After Pearson (17)).

resistivity by an amount ρ_i , which is temperature independent so that the total resistivity of the material is given by

$$\rho(T) = \rho_t(T) + \rho_i. \quad (1.5)$$

This expression is known as Matthiessen's rule.

In 1935 Nordheim and Gorter (19) proposed that the thermoelectric power of a metal to which an impurity has been added should be given by

$$Q(T) = \frac{\rho_t(T)}{\rho(T)} Q_t(T) + \frac{\rho_i}{\rho(T)} Q_i(T) \quad (1.6)$$

where Q_t is the thermoelectric power of the pure metal and Q_i is the thermoelectric power caused by the scattering of conduction electrons from the impurities. If Equation (1.5) is substituted in Equation (1.6) to eliminate ρ_i , Q is given by

$$Q(T) = Q_i(T) + (Q_t(T) - Q_i(T)) \frac{\rho_t(T)}{\rho(T)}. \quad (1.7)$$

It is obvious from this equation that if Q is plotted against $\frac{1}{\rho}$ a straight line should result and from the intercept when $\frac{1}{\rho} \rightarrow 0$ and the slope, the components Q_t and Q_i can be found. This is known as a Nordheim-Gorter plot.

A. V. Gold et al. (18) carried out a series of experiments in which they alloyed chromium, gallium, germanium, indium, and tin with copper and found the Nordheim-Gorter relation (1.7) to be true.

In a paper (21) published in 1960, Blatt et al. presented data on the thermoelectric power of dilute binary copper and silver alloys containing one atomic percent zinc, cadmium, indium, germanium,

tin, and antimony. Unfortunately, they chose to carry out their measurements against copper and silver instead of lead, for which an absolute scale of thermoelectricity existed. It was not until 1961 that Pearson (17), in the light of the work by A.V. Gold et al. (18) on the thermoelectric power of copper with an iron impurity, showed that traces of iron could radically alter the thermoelectric power of the noble metals.

In a paper in 1960, Pearson (22) illustrated the importance of cold working on silver and gold; he showed that cold working introduced scattering mechanisms which altered the thermoelectric power of silver and gold according to the Nordheim-Gorter rule (Equation (1.7)).

1:2 Important experiments on the thermoelectric power of the noble metals after 1959

Before the paper of A.V. Gold et al. (18) in 1960, experimentalists did not realize the extent to which an iron impurity in the noble metals would affect the thermoelectric power. Hence a detailed review of experimental work on the noble metals before 1960 has been omitted and only an outline of the work before 1960 has been included in section 1:1 to illustrate the phenomenological development of thermoelectricity.

As previously mentioned, the paper by A.V. Gold et al. (18) was important on two counts: first, it illustrated that the transition metals could give rise to thermoelectric powers much larger than would normally be expected particularly in the temperature range from 15 to 100°K. This is an interesting phenomenon in itself and

was investigated by MacDonald et al. (23) in 1961. They studied the thermoelectric power of dilute binary alloys of gold containing the transition metals manganese, chromium, nickel, cobalt, and iron, and showed that transition metal impurities in the noble metals give rise to so-called "giant" thermoelectric powers in the phonon-drag region.

Since iron is a naturally occurring impurity in the noble metals, this meant that extra precautions had to be taken in preparing samples of the noble metals for thermoelectric power studies.

Second, it showed that the Nordheim-Gorter relation (Equation (1.7)) could be used to separate the contributions to the thermoelectric power of the noble metals from different scattering mechanisms in the diffusion region.

From the experiments of A. V. Gold et al. (18), there was speculation that the presence of iron in the noble metals was responsible for the hump in the thermoelectric power between 15 and 100°K. Pearson's measurements (17) of the thermoelectric powers of "pure" copper, silver, and gold resolved this problem and showed that phonon-drag is responsible for the hump in the "pure" metals.

In 1963 W. G. Henry et al. (24) investigated the resistivities and thermoelectric powers of α -phase copper-zinc alloys between 4.2 and 300°K.

In 1964 R. S. Crisp et al. (25) investigated the thermoelectric powers and resistivities of primary solid solutions of zinc, gallium, germanium, and arsenic in copper from 5 to 290°K.

Also in 1964 R.S. Crisp et al. (26) investigated the temperature dependence of the characteristic thermoelectric powers of zinc, gallium, germanium, and arsenic in copper and silver at two temperatures, 290°K and 375°K .

The experimental method in the three papers just mentioned was to fix the temperature of one end of the sample and continuously raise the temperature of the other end so that a ΔV versus ΔT curve was obtained.

In order to extract the thermoelectric power from the raw data, the raw data were first interpolated linearly to equal intervals. The data were then smoothed by a least squares fitting of four points on either side of a given data point to a parabola, and then by obtaining a smoothed value of the data point from this parabola. The derivatives were obtained using Newton's forward and backward formulae for the ends and using Stirling's formula for the centre. The derivatives were again smoothed. This seems to be a very cumbersome procedure.

Furthermore the investigation of the temperature dependence of the characteristic thermoelectric powers of zinc, gallium, germanium, and arsenic in copper and silver at only the two temperatures, 290°K and 375°K , seems hardly sufficient to establish a temperature relationship.

In view of the scanty experimental data on the effects of non-transition metal impurities on the thermoelectric power of the noble metals, it was decided to investigate the thermoelectric

powers and resistivities of primary solid solutions of silver with varying concentrations of gold, indium, zinc, cadmium, germanium, thallium, and antimony between 80 and 250°K. The result of this work is the main object of this thesis. It was also hoped that some correlation could be found between these measurements and a series of measurements being carried out by Dr. A.M. Guénault at the National Research Council on similar samples between 0.1 and 5°K.

1:3 Review of the theoretical developments on the thermoelectric power of the noble metals

Wilson (14), in 1936, carried out a very comprehensive study of the transport properties of metals based on the ideas of Lorentz and Sommerfeld (see section 1:1). Generally speaking there has been very little change in the approach to transport theory. The Boltzmann equation forms the basis for discussion and various techniques have been developed for attempting its solution.

Wilson attempted a solution of the Boltzmann equation assuming the existence of a relaxation time. Expressions for the electrical resistivity and the thermoelectric power have been derived using this method (see Appendix 1). Kohler (27, 28) and Sondheimer (29) have developed a more powerful technique which depends upon the solution of a variational problem resulting in the transport coefficients such as electrical resistivity and thermoelectric power being expressed in terms of integrals of the following form

$$\int \left\{ \Phi_{\mathbf{k}} - \Phi_{\mathbf{k}'} \right\}^2 P_{\mathbf{k}}^{\mathbf{k}'} d\vec{\mathbf{k}} d\vec{\mathbf{k}'} \quad (1.8)$$

where Φ_k is a trial function and $P_k^{k'}$ is the transition probability for scattering from state $\vec{k}$ to state $\vec{k}'$. The evaluation of these integrals necessitates the development of models for the various scattering processes which can occur in a metal.

As pointed out in section 1:1, the thermoelectric power of the noble metals as a function of temperature can be broken down into three categories; the very low temperature region below about 15°K, the phonon-drag region, and the region of diffusion thermoelectricity at high temperatures.

The low temperature region: When a temperature gradient is maintained in a conductor, there is a flow of energy through the atomic lattice in the form of thermally generated lattice waves (phonons) with a net energy flow from the hotter to the colder end. If $\vec{q}$ is the phonon wave vector, and $\vec{k}$ and $\vec{k}'$, the electron wave vectors before and after the collision of an electron and a phonon, then in a "normal" phonon-electron collision, momentum must be conserved according to

$$\hbar \vec{k} - \hbar \vec{k}' - \hbar \vec{q} = 0 \quad (1.9)$$

The scattering processes involved in the very low temperature region have been treated by Klemens (30), Sondheimer (31), and Bailyn (32).

The change in momentum of the electron undergoing a normal phonon-electron collision produces an electric field and consequently a thermoelectric power.

The phonon-drag region: In a phonon-electron collision, it is also possible to have a Bragg reflection taking place in the

collision so that a large additional change of momentum takes place characterized by the vector $\vec{g}$. This is called an Umklapp process and momentum must be conserved according to

$$\hbar \vec{k} - \hbar \vec{k}' + \hbar \vec{q} = \hbar \vec{g} \quad (1.10)$$

The large change in momentum would contribute to a large electric field and consequently, a potentially large thermoelectric power. Moreover the momentum reversal implied in the Bragg reflection involves a possible change in the sign of the electric field in the conductor and hence the thermoelectric power. The frequency of Umklapp processes generally increases very rapidly with temperature so that as the temperature in a metal is raised, the phonon-drag effects may appear very rapidly and hence the thermoelectric power will increase rapidly.

The scattering processes in the phonon-drag region have been extensively discussed by Peirels (33), MacDonald (34), and Ziman (35).

The diffusion region: In the region of diffusion thermoelectricity, it has been assumed that phonon-drag effects (phonon-electron collisions) have disappeared, that is, the phonon system is assumed to be in thermal equilibrium. However electron-phonon collisions are still present giving the lattice or ideal resistance and will contribute to the thermoelectric power.

Pearson's measurements (17) on "pure" copper, silver and gold show that the thermoelectric power is positive in the region of diffusion thermoelectricity. Ziman (35, 36) has developed

theoretical expressions for the thermoelectric power of the noble metals in the diffusion region but his calculations suggest that the thermoelectric power should be negative. This is an intriguing problem and has focused attention on the possible scattering mechanisms in the diffusion region, the effect of a non-spherical Fermi surface making contact with the (111) faces of the Brillouin zone, the phonon frequency spectrum, and the energy dependence of the relaxation time of the conduction electrons. No detailed work has been done including all these effects in a realistic manner.

Contributions to the thermoelectric power of the noble metals from impurity scattering: The thermoelectric power of the noble metals when impurities are present is described by the Nordheim-Gorter rule (Equation (1.7)). Q_i is the thermoelectric power caused by the scattering of conduction electrons from impurities and can be described by (see Appendix 1)

$$Q_i = -\frac{\pi^2 k^2 T}{3|e|} \left[\frac{\partial \ln \sigma_i(\epsilon)}{\partial \epsilon} \right]_{\epsilon = \epsilon_f} \quad (1.11)$$

where $\sigma_i(\epsilon)$ is an electrical conductivity generating function resulting from a solution of the Boltzmann equation. When ϵ is set equal to ϵ_f , $\sigma_i(\epsilon_f)$ is an approximation to the measured electrical conductivity caused by impurity scattering.

The Nordheim-Gorter rule has been reformulated by A. V. Gold et al. (18) to give

$$Q = \frac{\sum W_i Q_i}{\sum W_i} \quad (1.12)$$

where W_i is the thermal resistivity caused by the i th scattering mechanism and Q_i is the contribution to the thermoelectric power due to the i th scattering mechanism assumed to be acting independently of any other scattering mechanisms. Equation (1.12) is restricted to the analysis of diffusion thermoelectric power (see A.V. Gold et al. (18)).

In the temperature range $T \geq \theta$, where θ is the Debye temperature, the electrical and thermal resistivities should obey the Wiedemann Franz law:

$$\frac{\rho}{WT} = L_0 \quad (1.13)$$

If Equation (1.13) is true for each scattering component, then Equation (1.12) becomes

$$Q = \frac{\sum \rho_i Q_i}{\sum \rho_i}$$

and Equation (1.7) can be derived from this expression.

The experiments of A.V. Gold et al. (18), W.G. Henry et al. (24), R.S. Crisp et al. (25), and R.S. Crisp et al. (26) indicate that Q_i for impurities is negative so that the term $\left[\frac{\partial \ln \sigma_i}{\partial \epsilon} \right]_{\epsilon = \epsilon_f}$ (see Equation (1.11)) should be positive. de Faget de Casteljau and Friedel (37) using a square well potential to represent the impurities have shown that $\left[\frac{\partial \ln \sigma_i}{\partial \epsilon} \right]$ is positive. Hence Equation (1.11) gives a reasonably good description of the thermoelectric power caused by impurity scattering.

If the impurities are transition metals, it is not simple to show that Equation (1.11) will describe the behaviour of the thermo-

electric power. MacDonald (34) gives a review of the various models that have been developed in attempts to explain the scattering effects of transition metals as impurities in the noble metals.

CHAPTER 2

Resistivity and Thermoelectric Power Measurements2:1 Introduction

In this section the measurement of the thermoelectric power and resistivity of samples of pure silver and silver alloyed with gold, cadmium, zinc, indium, germanium, thallium, and antimony will be discussed. The measurements were carried out over the temperature range 80 to 250°K.

In order to measure the thermoelectric power, a temperature difference, ΔT , is established across the sample (see Figure 2.1). If the circuit is completed with a second material of different thermoelectric properties (see Figure 2.2), an electric current, I , will flow. If the material marked as 2 is broken (see Figure 2.3), a potential difference, ΔV_{21} , is observed. ΔV_{21} is called a thermo-emf.

The thermoelectric power, Q_{21} , of the couple is defined as (34)

$$Q_{21} = \lim_{\Delta T \rightarrow 0} \frac{\Delta V_{21}}{\Delta T} \quad (2.1)$$

If the observed potential difference has the polarity shown in Figure 2.3, then the thermoelectric power, Q_2 , of material 2 is negative with respect to the thermoelectric power, Q_1 , of material 1, i.e.

$$Q_2 - Q_1 = \frac{dV_{21}}{dT} < 0 \quad (2.2)$$

Figure 2-1.

Figure 2-2.

Figure 2-3.

It is possible to derive the absolute thermoelectric power of a single conductor by starting from measurements of the Thomson coefficient, μ , and using the relation (34)

$$\mu = T \frac{dQ}{dT}. \quad (2.4)$$

Integrating Equation (2.4) gives

$$Q(T) - Q(0) = \int_0^T \frac{\mu}{T} dT. \quad (2.5)$$

H. B. Callen (38) has applied the Onsager theorem to thermoelectric effects and shows that the thermoelectric power can be looked on as the entropy transported per coulomb by the electron flow. Hence the third law of thermodynamics gives

$$Q(0) = 0$$

so that Equation (2.5) becomes

$$Q(T) = \int_0^T \frac{\mu}{T} dT. \quad (2.6)$$

Therefore the absolute thermoelectric power of a conductor can be determined from Thomson coefficient measurements using Equation (2.6).

Lead has been chosen as a standard reference material (see Pearson et al. (39) and Jan et al. (40)) for thermoelectric power measurements. J. W. Christian et al. (41) have determined the absolute thermoelectric power of lead from its superconducting transition temperature at 7.15°K to 18°K and they extended the scale to 300°K on the basis of work by Borelius et al. (13).

Once the thermoelectric power of a sample-lead couple,

$Q_{s,Pb}$, is measured, the thermoelectric power of the sample, Q_s , is obtained by subtracting the thermoelectric power of lead, Q_{Pb} , from $Q_{s,Pb}$.

The resistance of a sample is measured by passing a current, I , through the sample and measuring the potential difference, V , established across the sample. Since the samples used in these experiments were in the form of wires, the resistivity, ρ , is given by

$$\rho = \frac{RA}{L} \quad (2.7)$$

where A is the cross-sectional area of the sample, L is the length of the sample between the potential contacts and R is the resistance of the sample and is given by the relation

$$R = \frac{V}{I}. \quad (2.8)$$

2:2 Sample Preparation

The samples (see Table 2.1) were prepared by J.W. Fisher at the National Research Council. The pure silver sample is Tadanac high purity silver obtained from COMINCO Ltd. in Montreal. The silver was etched to remove any surface impurities imparted during handling and then drawn to wire, 0.25 mm in diameter. The wire was annealed for 18 hours at 540°C to remove any effects of cold working. The impurities to be added in forming the alloys were 99.99% pure.

Table 2.1. List of the samples used for thermoelectric power measurements. The error in the diameter is $\pm .001$ mm.

<u>Sample</u>	<u>Diameter</u>
Ag + 1 at. % Cd	0.252 mm
Ag + 0.25 at. % Au	0.252 mm
Ag + 0.5 at. % Au	0.251 mm
Ag + 1 at. % Au	0.251 mm
Ag + 1 at. % Zn	0.252 mm
Ag + 1 at. % Sb	0.254 mm
Ag + 0.2 at. % In	0.509 mm
Ag + 0.5 at. % In	0.511 mm
Ag + 1 at. % In	0.510 mm
Ag + 2 at. % In	1.023 mm
Ag + 0.2 at. % Ge	0.250 mm
Ag + 0.5 at. % Ge	0.512 mm
Ag + 1 at. % Ge	0.252 mm
Ag + 0.25 at. % Tl	0.251 mm
Ag + 0.5 at. % Tl	0.252 mm
Ag + 1 at. % Tl	0.253 mm
Pure Silver	0.252 mm

The alloys were formed by adding the proper weight of impurity to the silver in the melt. The silver was melted at 1050°C in a quartz tube that had been cleaned with hydrofluoric acid. The impurity was added and the melt was agitated. The melt was allowed to solidify and the ingot was maintained at 920°C for 3 days for homogenization. The alloy was then cooled in air and drawn to wire. The wires were annealed at 540°C for 18 hours.

2:3 Thermoelectric Power Apparatus

A general view of the cell used for both the thermoelectric power and resistivity measurements is shown in Figure 2.4.

The thermoelectric power measurements were made under vacuum for two reasons: 1) to simplify the production and measurement of a temperature difference across the sample and, 2) to allow the ambient temperature of the system to be varied in a controlled manner from 77.6 to 250°K .

The system for evacuating the cell (see Figure 2.5) consists of a fore-pump capable of producing a vacuum of approximately 10^{-4} mm of Hg, a pirani vacuum gauge, an air leak, and a controlled helium leak.

Thin-walled nickel-silver tubing is used between the inner cell and its surroundings to minimize heat flow by conduction into the inner cell.

One end of the sample is mounted in a copper block at the top of the inner cell and the other end is mounted in a bakelite block so that it is insulated both electrically and thermally from the

Figure 2-4. General view of the cell.

LEGEND

Brass

Copper

- T₁ Upper Thermocouple
- T₂ Lower Thermocouple
- 1 Sample
- 2 Lead Wires
- 3 Inner Heater
- 4 Outer Heater

Figure 2-5. Vacuum system.

LEGEND

- 1 Vacuum Pump
- 2 Pirani Gauge
- 3 Helium Leak
- 4 Air Leak
- 5 Pressure Gauge
- X Vacuum Valve

inner cell. Heating of the sample by radiation was shown to be negligible by placing the evacuated cell at room temperature into a liquid nitrogen bath. The temperature of the sample was observed to fall at a rate of about 1 K° per hour.

The outer heater has a dual purpose. It is used for varying the ambient temperature of the system as well as for helping to produce a temperature difference across the sample by heat conduction through the copper can and copper block of the inner cell to the sample. The outer heater consists of chromel wire wound non-inductively on a grooved PVC sleeve.

The inner heater is used to maintain a constant temperature difference across the sample. The inner heater is constructed of chromel wire wound on a grooved bakelite core.

The upper and lower thermocouples marked as T_1 and T_2 in Figure 2.4 are used to measure the temperature difference across a portion of the sample. The thermocouples are copper-constantan couples and are soldered to the sample with high-purity indium.

The thermocouple circuit (see Figure 2.6) consists of copper wire, 0.25 mm in diameter, welded to constantan wire, 0.25 mm in diameter, to form the measuring junction. The thermocouple is connected to a millivolt potentiometer with copper wires, 0.3 mm in diameter, which are welded to the copper and constantan wires to form reference junctions. The reference junctions are

Figure 2-6. Thermocouple circuit.

LEGEND

- 1 Measuring Junction
- 2 Constantan Wire
- 3 Copper Wire
- 4 Reference Junction

encased in glass tubes filled with Tellus oil 41 made by the Shell Oil Co. Ltd.

The reference junctions of the copper-constantan thermocouples were placed in a triple-point-of-water cell to ensure the production of a constant reproducible reference temperature. The triple-point-of-water cell (see Figure 2.7) was manufactured by the Jarret Instrument Co. of Wheaton, Maryland.

An ice mantle approximately 5 mm thick is formed by dropping crushed dry ice directly into the thermometer well. The dry ice is removed and the ice mantle is allowed to melt away from the thermometer well. The thermometer well is filled with water and the thermocouple reference junctions are inserted.

In order to maintain the ice mantle for long periods of time, the cell was placed in a dewar filled with crushed ice and water. The crushed ice was made from distilled water. The cell was made up 24 hours before an experiment to allow the temperature of the cell to stabilize. A temperature reproducible to 10^{-3}°K was obtained in the vicinity of 273°K . It was not necessary to know this temperature since the thermocouples were calibrated against it.

The millivolt potentiometer used to measure the thermocouple emf's was manufactured by the H. J. Tinsley Co. The range of the instrument used during the experiment was 0.8623 to 5.5603 mv. Measurements can be repeated within a limit of error of a quarter of a microvolt. The potentiometer was calibrated by Guildline Instruments of Smith Falls, Ont. and was rechecked

Figure 2-7. Triple-point-of-water cell.

against a standard cadmium cell at Carleton University.

Since an absolute scale of thermoelectricity has been established for lead (41), lead wire, 0.4 mm in diameter, was used to complete the measuring circuit (see Figure 2.3). The lead wires were soldered to the same point on the sample as the copper-constantan thermocouples. The lead wire, obtained from COMINCO Ltd. in Montreal, is 99.999% pure and the purity agrees with the purity of the lead used by Christian *et al.* (41).

The thermo-emf produced by the sample-lead couple was measured with a microvolt potentiometer manufactured by Guildline Instruments Ltd. in Smith Falls, Ont. The instrument has measuring ranges of -0.01 to +101.00 μv in steps of 0.01 μv and -0.1 to +1010.00 μv in steps of 0.1 μv .

The galvanometer system used with the potentiometer was manufactured by Guildline Instruments Ltd. (see Figure 2.8). The system consists of a photocell amplifier, and a galvanometer.

The photocell amplifier (42) (see Figure 2.9) consists of a galvanometer, two photocells connected in series opposition, and a feedback system. A beam of light reflected from the mirror of the galvanometer falls upon the photocells. The net current from the cells is indicated by a secondary galvanometer. A system of negative feedback of the output from the photocells is used to provide a linear correspondence between the input to the photocell amplifier and its output. The photocell amplifier has a maximum voltage sensitivity of $0.19 \times 10^{-4} \mu\text{v}/\text{mm}$ with an external circuit resistance of zero ohms.

Figure 2-8. Galvanometer system.

LEGEND

- 1 Microvolt Potentiometer**
- 2 Galvanometer Amplifier**
- 3 Galvanometer**

Figure 2-9. Photocell amplifier.

LEGEND

- 1 Primary Galvanometer
- 2 Secondary Galvanometer
- 3 Photocells

2:4 Calibration of the Thermocouples

The thermocouples were calibrated against a platinum resistance thermometer supplied by the Defence Research Telecommunications Establishment at Shirley's Bay, Ont. The resistance thermometer was calibrated by Dr. R. J. Berry at the National Research Council's Division of Applied Physics. The calibration was carried out from 10.2 to 90°K by comparing the resistance thermometer with a standard platinum resistance thermometer calibrated in terms of the N.B.S. 1955 temperature scale. The resistance of the thermometer was also determined at the ice and steam points and the calibration was completed using the resistance-temperature relationship

$$\frac{R_t}{R_{ice}} = 1 + At + Bt^2 + C(t - 100)t^3. \quad (2.9)$$

The resistance thermometer consists of platinum wire wound on a strain-free mica cross. The resistance element is encased in a platinum tube 5.5 mm O.D. and 6 cm long. The resistance element has four leads so that a four terminal measurement of its resistance can be made. The leads are brought out of the tube through a glass-to-metal seal. The resistance of the thermometer varies from 0.017130 ohms at 10°K to 47.893482 ohms at 450°K.

The resistance thermometer was mounted in a copper sleeve with a wall thickness of 0.75 mm. Silicone grease was used for thermal contact between the copper sleeve and the platinum tube. This assembly was mounted in the cell shown in Figure 2.4 in place

of the sample. The thermocouples were soldered to the sleeve with high-purity indium.

Manganin wire was used between the thermometer and a resistance bridge. Several turns of each manganin wire were made around the copper sleeve to ensure thermal stability.

The resistance bridge is a type G-2 Mueller Bridge manufactured by Leeds and Northrup. The range of the instrument is 0 to 111.111 ohms and measurements can be made within a limit of error of a few ten-thousand-ths of an ohm or a few parts per hundred thousand, whichever is larger.

The calibration of the thermocouples was carried out as follows. The cell was filled with helium gas and placed in liquid nitrogen. A temperature equilibrium was reached at 77.6°K in approximately one hour. The helium gas was pumped out of the outer cell but left in the inner cell to facilitate the production of a thermal equilibrium while the resistance of the thermometer was measured.

The outer heater was used to raise the temperature of the inner cell and calibration measurements were carried out approximately every 5 K° over the range 77.60 to 250.20°K . The order of measurements in determining a calibration was as follows: i) the emf from the thermocouple was measured with the millivolt potentiometer, ii) the resistance of the thermometer was measured with the G-2 Mueller bridge, iii) the emf from the thermocouple was rechecked, iv) a second measurement of the resistance of the

thermometer was made, v) the emf from the thermocouple was again rechecked. The two copper-constantan thermocouples were calibrated independently and the calibrations were found to be identical within the limit of error of the experiment.

2.5 Thermoelectric Power Measurement

The thermoelectric power of the sample-lead couple is given as (34)

$$Q = \lim_{\Delta T \rightarrow 0} \frac{\Delta V}{\Delta T}. \quad (2.10)$$

There are two experimental techniques which are commonly used to determine the thermoelectric power.

The first method entails keeping one end of the sample-lead couple at a fixed temperature and varying the temperature of the other junction in a controlled manner so that a graph of V versus T can be plotted. V is then found as a function of T by a curve fitting procedure and the expression is differentiated with respect to T to find the thermoelectric power at temperature T .

The second method involves varying the temperature of both ends of the sample in such a manner as to keep the temperature difference, ΔT , small. The thermo-emf, ΔV , is recorded for each temperature difference. The thermoelectric power for the sample-lead couple is given by

$$Q(T) = \frac{\Delta V(T)}{\Delta T}. \quad (2.11)$$

Suppose the ends of the sample are kept at temperatures T_1 and T_2 so that

$$\Delta T = T_2 - T_1, \quad (2.12)$$

then a voltage difference, ΔV , is measured, where

$$\Delta V = V(T_2) - V(T_1). \quad (2.13)$$

If $T_2 - T_1$ is small, then a Taylor series expansion to first order can be used, giving

$$V(T_2) - V(T_1) = (T_2 - T_1) \frac{dV \left(\frac{T_2 + T_1}{2} \right)}{dT} \quad (2.14)$$

so that

$$Q \frac{(T_2 + T_1)}{2} \approx \frac{V(T_2) - V(T_1)}{T_2 - T_1} = \frac{\Delta V(T)}{\Delta T} \quad (2.15)$$

The second method was used to avoid the complicated mathematical procedures of the first method. On the basis of Pearson's measurements (17) of the thermoelectric power of silver and the measurements of Christian et al. (41) on lead, the thermoelectric power of a silver-lead couple was computed from the relation

$$Q_{Ag, Pb} = Q_{Ag} + Q_{Pb} \quad (2.16)$$

(see Figure 2.10).

Figure 2.10 shows that between 90 and 130°K, $Q_{Ag, Pb}$ is independent of temperature so that there is justification for dropping the higher order terms in the Taylor series expansion. Above 130°K, $Q_{Ag, Pb}$ varies with temperature, therefore care must be taken to keep the temperature difference along the sample small. For example, between 225°K and 250°K, a temperature difference of 5 K° along the sample would result in an error of approximately 1% in $Q_{Ag, Pb}$.

Figure 2-10. Thermoelectric power of a silver-lead couple computed from the data of Pearson (17) and Christian et al. (41).

The experimental procedure for making the thermoelectric power measurements was as follows. The cell was filled with helium gas and placed in liquid nitrogen and an equilibrium was reached at 77.60°K in approximately one hour. The helium gas was then pumped out of both the inner and outer cells, and a vacuum of approximately 10^{-4} mm of Hg was maintained throughout the experiment.

A current of approximately 0.6 amperes was passed through the outer heater until a temperature difference of approximately 5 K° was obtained. The outer heater current was reduced to about 0.2 amperes and a current of about 0.08 amperes was passed through the inner heater to stabilize the temperature difference at about 4 K° . The temperature difference was never allowed to rise above 5 K° .

The ambient temperature of the system was allowed to increase at approximately 0.25 degrees per minute so that measurements over the temperature range 80 to 250°K could be carried out in about 12 hours.

The sequence of measurements for determining the thermoelectric power was as follows: i) the thermo-emf of the system was measured using the microvolt potentiometer, ii) the emf of the thermocouple marked T_2 in Figure 2.4 was measured with the millivolt potentiometer, iii) the emf of the thermocouple marked T_1 was measured with the millivolt potentiometer, iv) the thermo-emf of the system was rechecked.

The variation of the thermo-emf over this measuring

interval was so small as to be unmeasurable. It required approximately 10 seconds to record T_1 after T_2 so that the experimental error in the temperature difference would be about 0.04 degrees in 5 degrees which amounts to an error of 0.8%. The reading error in determining the temperature difference was about ± 0.02 degrees or $\pm 0.4\%$ hence the experimental error is about twice as large. The reading error in the thermo-emf varied from about $\pm 0.25\%$ to $\pm 0.06\%$ depending on the sample, so that the error in the thermoelectric power is about 1%.

The sequence of measurements was immediately repeated so that two measurements of the thermoelectric power within an ambient temperature change of 1 K° were easily possible. The thermoelectric power was determined at intervals of approximately 5 K° over the range 80 to 250 K° .

2.6 Electrical Resistivity Apparatus

A four-terminal measurement of the electrical resistivity of the sample can be made without making any changes in the cell used for the thermoelectric power measurements. A current can be passed through the sample using the copper wires of the thermocouples as current leads. The potential difference established across the sample can be measured using the lead wires.

The circuit for measuring the electrical resistance is shown in Figure 2. 11. S_1 is an off-on switch for supplying current from a 0-10 volt d.c. power supply. S_2 is a reversing switch for reversing the current through the sample so that thermal emfs

Figure 2-11. Circuit for measuring the electrical resistance of the sample.

LEGEND

- 1 Sample Resistance
- 2 Copper-Constantan Thermocouple
- 3 Standard Resistor

caused by a temperature difference across the sample can be averaged out. S_3 is a double pole double throw switch allowing the measurement of the voltage difference across the standard resistor in position a, and in position b, it allows the measurement of a thermocouple emf. P_{s_1} is a spring loaded switch built into the microvolt potentiometer and is normally in the open position. P_{s_2} and P_{s_3} are spring loaded switches built into the millivolt potentiometer and they are normally in the open position.

2:7 Electrical Resistivity Measurement

The cell was filled with helium and placed in liquid nitrogen and a temperature equilibrium was reached in about one hour at 77.60°K . The helium gas was pumped out of the outer cell but left in the inner cell to facilitate the production of a thermal equilibrium while the resistance of the sample was being measured.

The outer heater was used to raise the temperature of the inner cell and the resistance of the sample was measured approximately every 30 K° over the range 80 to 250°K . The procedure for determining the resistance of the sample was as follows: i) S_1 was opened so that no current was passing through the sample and S_2 was placed in the b-position, the ambient temperature of the system was measured, ii) S_1 was closed and a current of approximately 1 milliampere was passed through the sample. S_3 was placed in the a-position and the potential differences developed across the sample and the standard resistor were measured. The current was reversed through the sample with S_2 and the potential differences across the

sample and the standard resistor were remeasured. iii) S_1 was opened and S_3 was placed in the b-position and the ambient temperature of the system was remeasured.

Since the samples were in the form of wires, the resistivity of the samples is given by (see Equations (2.7) and (2.8))

$$\rho = \frac{RA}{L} . \quad (2.17)$$

The diameter, D , of each sample was measured at six different places along the length of the sample with a micrometer. An average diameter was computed for each sample and the cross-sectional area was computed from the relation

$$A = \frac{\pi D^2}{4} . \quad (2.18)$$

The errors in the cross-sectional areas of the samples varied from $\pm 0.4\%$ for the smallest diameter samples to $\pm 0.1\%$ for the largest diameter samples.

In the process of removing the samples from the cell, it was not always possible to preserve accurately the contact positions of the lead wires on the sample so that a measurement of the length of the sample became impossible. To overcome this difficulty, the resistance, R_o , of a sample of length L_o , was measured at 77.60°K so that the original length of the sample is given by

$$L = \frac{R}{R_o} L_o . \quad (2.19)$$

The length, L_0 , was measured with a travelling microscope and the error in L_0 for each sample was estimated to be $\pm 1.5\%$. The error in R and R_0 is 0.1% so that the error in the length, L , is $\pm 1.7\%$ and hence the error in the resistivity varied from $\pm 2.1\%$ for the smallest diameter samples to $\pm 1.8\%$ for the largest diameter samples.

CHAPTER 3

Experimental Results

Figure 3.1 shows the calibration curve for the thermocouples. The thermo-emf from the thermocouple, in millivolts, has been plotted against the temperature, in degrees Kelvin, of the thermocouple junction. The temperatures of the thermocouple junction have been extracted from the resistance measurements with the resistance thermometer using the calibration data on the resistance thermometer provided by the National Research Council. The calibration data on the resistance thermometer were presented in such a manner as to make a linear interpolation between calibration points possible.

In order to extract the temperature, corresponding to a thermo-emf, from the thermocouple calibration data, a Lagrangian interpolation (see Appendix 2) was carried out over five calibration points on either side of the thermo-emf. At the ends of the calibration curve where it is not possible to choose five calibration points on either side of the thermo-emf, the interpolation was carried out over ten calibration points with the thermo-emf falling at random within the calibration points. The interpolation procedure was performed with an I. B. M. 1620 computer.

The thermoelectric power of the sample-lead couple is given by

$$Q = \frac{\Delta V}{\Delta T}. \quad (3.1)$$

To find the absolute thermoelectric power of the sample, the

Figure 3-1. Calibration curve for the copper-constantan thermocouples.

thermoelectric power of lead is subtracted from the thermoelectric power of the sample-lead couple.

The thermoelectric power for lead at any temperature was extracted from the data of Christian et al. (41) using a least squares analysis to fit a second order curve to their data.

The thermoelectric power, in $\mu\text{v}/^{\circ}\text{K}$, as a function of temperature, in degrees Kelvin, has been plotted in Figures 3.2 to 3.6 for the various silver alloy systems.

The resistivity, in micro-ohm-cm, has been plotted as a function of temperature, in degrees Kelvin, in Figures 3.7 to 3.10 for the various alloy systems.

Figure 3-2. Thermoelectric power of pure silver and alloys of silver-cadmium, silver-zinc, and silver-antimony as a function of temperature.

Figure 3-3. Thermoelectric power of pure silver and silver-gold alloys as a function of temperature.

Figure 3-4. Thermoelectric power of pure silver and silver-indium alloys as a function of temperature.

Figure 3-5. Thermoelectric power of pure silver and silver-germanium alloys as a function of temperature.

Figure 3-6. Thermoelectric power of pure silver and silver-thallium alloys as a function of temperature.

Figure 3-7. Resistivity of pure silver and alloys of silver-cadmium and silver-gold as a function of temperature.

Figure 3-8. Resistivity of pure silver and silver-indium alloys as a function of temperature.

Figure 3-9. Resistivity of pure silver and silver-thallium alloys as a function of temperature.

Figure 3-10. Resistivity of pure silver and alloys of silver-antimony, silver-germanium, and silver-zinc as a function of temperature.

CHAPTER 4

Discussion of the Resistivity Results

4:1 Matthiessen's Rule

When a concentration c of an impurity (gold, cadmium, zinc, indium, thallium, germanium, antimony) is introduced into silver, the resistivity of pure silver, ρ_i , is increased by an amount ρ_i which appears to be independent of temperature but dependent on concentration (see Figures 3.7 to 3.10) and on valence (see Figure 4.1). Hence the total resistivity, ρ_T , of the alloy can be written as

$$\rho_T(T) = \rho_i(T) + \rho_i. \quad (4.1)$$

Equation (4.1) is known as Matthiessen's rule (20).

Matthiessen's rule is only true under certain special circumstances:

1) Relaxation times can be unambiguously defined for both the lattice and impurity scattering processes. Hence the total relaxation time is given by (35)

$$\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_i} \quad (4.2)$$

making the resistivities additive.

2) The electron scattering mechanisms are assumed to be operating entirely independent of one another. This means that every electron collision, whatever its cause may be, is independent of preceding or succeeding collisions. Hence when the concentration of solute is varied, ρ_i will be directly proportional to concentration.

In Figure 4.2 ρ_i has been plotted against concentration

Figure 4-1. Resistivities of the alloys containing 1 at.% of impurity as a function of temperature.

Figure 4-2. e_i as a function of concentration for the alloy systems Ag-Au, Ag-In, Ag-Tl, and Ag-Ge.

illustrating that for concentrations up to one atomic percent of gold, thallium, and germanium and two atomic percent of indium in silver, ρ_i is proportional to concentration.

3) It is assumed that variations in the concentration of a solute do not change the essential characteristics of the conduction electrons. This means that the electron density of states function is assumed to be unaffected. This is a reasonable assumption for the alloy systems used in these experiments because of the small concentrations of solutes involved.

4) It is assumed that the Fermi energy and more generally the Fermi surface as a whole is unaffected by the individual scattering mechanisms.

4:2 Linde's Rule for Monovalent Metals

For purposes of the discussion of the valence dependence of ρ_i , interest will be focused on the increase of resistance per atomic percent of impurity, $\Delta\rho$, where $\Delta\rho$ is given by

$$\Delta\rho = \frac{\partial\rho_i}{\partial c} . \quad (4.3)$$

Linde's rule (43) states that $\Delta\rho$ is approximately proportional to Z^2 , where Z is the valence difference between the solute and solvent, for impurities in the same period and to the right of the solvent. In Figure 4.3 $\Delta\rho$ has been plotted against Z^2 for the impurities cadmium, indium, and antimony in silver illustrating that $\Delta\rho$ has this valence dependence.

When an impurity is introduced into a substitutional position in the silver lattice (as is the case for the impurities used in these

experiments), the conduction electrons can be elastically scattered in three ways; 1) scattering caused by the valence difference between the solute and solvent atoms, 2) scattering caused by a change in the local ionic charge density resulting from a change in the size of the unit cell occupied by the impurity, and 3) scattering caused by the difference in the binding energies of the solute and solvent atoms.

Blatt (44) has shown that the second effect can be incorporated into a treatment of the first effect by a modification of the total charge which the conduction electron "sees" in the unit cell surrounding the impurity. This leads to an explanation of the difference in the impurity resistivities for different impurities with the same valence (from Figures 3.7 and 3.10, $\Delta\rho$ for cadmium in silver is 0.41 micro-ohm-cm per atomic percent and $\Delta\rho$ for zinc in silver is 0.56 micro-ohm-cm per atomic percent).

Dexter (45) states that there will be interference between the first two scattering effects and the third scattering effect so that $\Delta\rho$ should be of the form

$$\Delta\rho = aZ'^2 + bZ' + c \quad (4.4)$$

where Z' is the modified charge in the unit cell surrounding the impurity. Figure 4.3 distinctly shows that $\Delta\rho$ is proportional to Z^2 indicating that for the impurities cadmium, indium, and antimony in silver, the modification of Z to Z' is small and the scattering caused by the difference in the binding energies of the impurities and silver is negligible.

Figure 4-3. $\Delta\rho$ as a function of Z^2 for the alloy systems Ag-Cd, Ag-In, and Ag-Sb.

4:3 A Simple Model for the Electrical Resistivity caused by Impurity Scattering

In order to illustrate theoretically the concentration dependence of ρ_1 and the valency dependence of $\Delta\rho$, it is necessary to introduce models for the scattering of conduction electrons by impurities. The scattering of conduction electrons by impurities in substitutional positions in the lattice is normally treated as a perfectly elastic process since an impurity atom is much heavier than the electron which is scattered and moreover, the scattering centre is bound to its equilibrium position in the lattice by fairly strong elastic forces so that the change in energy of an electron during the scattering process is negligible.

Several people including Wannier (46), Tibbs (47), Peckar (48), Mott and Gurney (49) and Slater (50) have shown that the Wigner-Seitz approximation can be applied to the case where an impurity is imbedded in a regular lattice. Thus in a monovalent metal with a substitutional impurity atom, the conduction electrons may be considered as a Fermi gas of electrons with an effective mass the same as in the pure metal, scattered by the perturbing potential introduced by the impurity. Also if a rigid band model is assumed, that is, if the presence of an impurity does not change the band structure of the host material, then the Fermi energy of the alloy is the same as the Fermi energy of the host material.

From Appendix 1, ρ_i is given by

$$\rho_i = \frac{12 \pi^3 \hbar}{e^2} \left[\int v \tau_i dG \right]^{-1} \quad (4.5)$$

where G is the area of the Fermi surface and v is the velocity of the conduction electrons on the Fermi surface. The cross-section, X , for the scattering of conduction electrons by impurities is given by

$$X = \frac{1}{N_i \tau_i v} \quad (4.6)$$

where N_i is the number of impurity scattering centres per unit volume, hence

$$\rho_i = \frac{12 \pi^3 \hbar}{e^2} N_i \left[\int X^{-1} dG \right]^{-1} \quad (4.7)$$

or

$$\rho_i = \frac{12 \pi^3 \hbar n c}{100 e^2} \left[\int X^{-1} dG \right]^{-1} \quad (4.8)$$

where n is the number of silver atoms per unit volume. Equation (4.8) shows that ρ_i is directly proportional to c in agreement with the data presented in Figure 4.2

Using Equation (4.3), $\Delta\rho$ is given by

$$\Delta\rho = \frac{12 \pi^3 \hbar n}{100 e^2} \left[\int X^{-1} dG \right]^{-1} \quad (4.9)$$

and to illustrate the valency dependence of $\Delta\rho$ it is necessary to find an expression for the scattering cross-section, X .

A simplifying assumption is usually made at this point to the effect that the relaxation time for the conduction electrons is constant over the Fermi surface so that the scattering cross-section

can be taken out of the integral in Equation (4.9) giving

$$\Delta\rho = \frac{12 \pi^3 \hbar n X}{100 e^2 G}. \quad (4.10)$$

The scattering cross-section is proportional to $\left| \Psi_{k'} V(\vec{r}') \Psi_k d\vec{r}' \right|^2$ (35) where Ψ_k and $\Psi_{k'}$ are the wave functions for the conduction electrons in states k and k' and $V(r')$ is a potential energy function representing the impurity. Hence an evaluation of the scattering cross-section necessitates choosing a potential energy function $V(r')$ to represent the impurity.

The Thomas-Fermi potential: The Thomas-Fermi potential (51) given by

$$V(r) = Z e^2 \frac{e^{-qr}}{r} \quad (4.11)$$

is usually chosen as a reasonable physical representation of an impurity with a valence difference of Z from the host material. It is essentially a screened coulomb potential with a screening length q^{-1} (35).

Using the Thomas-Fermi potential, Mott and Jones (52) have calculated the cross-section for impurity scattering in a monovalent metal under the following assumptions; 1) the wave functions for the conduction electrons can be approximated by free electron wave functions, 2) the Fermi surface of the metal is spherical, and 3) the Born approximation is applicable, so that

$$X = \frac{\pi Z^2 e^4}{2 \epsilon_f^2} \left[\ln \left(1 + \frac{4 R^2}{q^2} \right) - \left(1 + \frac{q^2}{4 R^2} \right)^{-1} \right] \quad (4.12)$$

where R is the radius of the Fermi surface. Hence $\Delta\rho$ is given by

$$\Delta\rho = \frac{6\pi^4 Z^2 e^2 \hbar n}{100 G \epsilon_f^2} \left[\ln \left(1 + \frac{4R^2}{q^2} \right) - \left(1 + \frac{q^2}{4R^2} \right)^{-1} \right] \quad (4.13)$$

Equation (4.13) illustrates that $\Delta\rho$ is proportional to Z^2 in agreement with the experimental results shown in Figure 4.3

$\Delta\rho$ has been calculated from Equation (4.13) for various impurities in silver and the results are shown in Figure 4.4. The numerical agreement between theory and experiment is poor.

Friedel (53) showed that the main sources of error in this method are the use of the Born approximation and the Thomas-Fermi estimate of the screening length.

For a more reasonable evaluation of the scattering cross-section, the Schrödinger equation should be solved exactly to determine how much the phase, δ_l , of the radial function of angular momentum l differs from the no-scattering case ($\delta_l = 0$). The scattering cross-section according to Huang (54) is given by

$$X = \frac{4\pi}{R^2} \sum_{l=1}^{\infty} l \sin^2 (\delta_{l-1} - \delta_l) \quad (4.14)$$

and the phase shifts must satisfy the condition (53)

$$Z = \frac{2}{\pi} \sum_{l=1}^{\infty} (2l+1) \delta_l. \quad (4.15)$$

Equation (4.14) has been derived using a free-electron approximation for the wave functions of the conduction electrons and assuming a spherical Fermi surface.

For the Thomas-Fermi potential, the Schrödinger equation must be solved numerically to find the phase shifts. Friedel (53) has

Figure 4-4. A test of Mott and Jones' prediction of $\Delta\rho$ (52) using the Thomas-Fermi potential to represent the impurity.

carried out a calculation of this sort for impurities in copper and found good numerical agreement with experimental results.

In view of the fact that two rather serious approximations have already been made (approximating the wave functions for the conduction electrons in a monovalent metal by free electron wave functions and assuming a spherical Fermi surface) it was decided to forgo a numerical solution of the Schrödinger equation and instead investigate the square well and unscreened Coulomb potentials for which the Schrödinger equation is solvable. These calculations will then be extended in Chapter 5 to calculations of the thermoelectric power caused by impurity scattering.

The square well potential: Huang (54) has calculated $\Delta\rho$ caused by the addition of a gold impurity to silver using a square well to represent the difference in the binding energies of silver and gold (for gold in silver, $Z = 0$). Huang used approximate methods to evaluate the phase shifts for scattering from a square well and he calculated $\Delta\rho = 0.16$ micro-ohm-cm per atomic percent as opposed to a measured value of 0.43 micro-ohm-cm per atomic percent taken from Figure 3.7.

Using an exact expression for the phase shifts from the square well developed by de Faget de Casteljau and Friedel (37) and a well-depth of 2.20 eV (see Appendix 3), a value for $\Delta\rho$ of 0.33 micro-ohm-cm per atomic percent was obtained which is in much better agreement with the measured value. In Figure 4.5 $\Delta\rho$ has been plotted against the well-depth illustrating that an error of ± 0.08 eV in the

well-depth would cause $\Delta\rho$ to vary from 0.17 to 0.54 micro-ohm-cm per atomic percent.

For the impurities cadmium, zinc, indium, germanium, thallium, and antimony in silver, it is assumed that the impurity resistance arises from the scattering of conduction electrons due to the valence difference between the impurity and silver. For these impurities the well-depth was varied until the phase shifts calculated by the method of de Faget de Casteljau and Friedel (37) satisfied Equation (4.15). $\Delta\rho$ was then calculated from Equations (4.14) and (4.10) and the results are shown in Figure 4.6 giving quite a reasonable agreement with the experimental results. de Faget de Casteljau and Friedel (37) have carried out a similar analysis for impurities in copper and Blatt (44) has calculated the impurity resistance for impurities in copper and silver using a revised form of Equation (4.15) to include the effects of a change in the ionic charge density resulting from a change in the size of the unit cell occupied by the impurity. Blatt's results for impurities in silver are summarized in Table 4.1.

The Coulomb potential, $V(r) = \frac{Ze^2}{r^2}$: The expression for the phase shifts from an unscreened Coulomb potential is given by Schiff (55)

$$\delta_l = \arg \left[\left(1 + i \frac{Ze^2}{\hbar v} \right) \right] \quad (4.16)$$

From tables for the arguments of complex gamma functions (56), the phase shifts can be determined so that Equation (4.15) is approximately satisfied and $\Delta\rho$ can be calculated using Equations (4.14) and (4.10).

Figure 4-5. $\Delta\rho$ from the square well as a function of well-depth.

Figure 4-6. $\Delta\rho$ calculated using the square well and unscreened Coulomb potentials to represent the impurities.

Table 4. 1. Blatt's calculations (44) of $\Delta\rho$ for impurities in silver.

	$\Delta\rho$ (micro-ohm-cm/at. %)	
	<u>Blatt</u>	<u>Present Experiment</u>
Cd	0.74	$0.47 \pm .02$
Zn	1.18	$0.56 \pm .02$
In	2.27	$1.74 \pm .04$
Ge	5.50	$5.21 \pm .1$
Sb	6.71	$7.00 \pm .1$

The results have been plotted in Figure 4.6.

Review of the model: An expression for the contribution to the resistivity caused by impurity scattering was obtained from a solution of the Boltzmann equation assuming elastic scattering of the conduction electrons by the impurities,

$$\rho_i = \frac{12 \pi^3 \hbar n c}{100 e^2} \left[\int X^{-1} dG \right]^{-1} \quad (4.17)$$

The essential properties of Equation (4.17) are retained in the integral.

In order to evaluate the integral, it was assumed that the Fermi surface for silver is spherical and the wave functions of the conduction electrons in silver could be approximated by free electron wave functions. The cross-section for impurity scattering was calculated with three different potentials: 1) Assuming the Born approximation is applicable, $\Delta\rho$ was calculated using the Thomas-Fermi potential to represent the impurity. The correct valence dependence of $\Delta\rho$ is predicted but the numerical agreement between theory and experiment is poor. Friedel (53) showed that the main sources of error in this method are the use of the Born approximation and the Thomas-Fermi estimate of the screening parameter. 2) $\Delta\rho$ was calculated for the square well potential using exact methods to evaluate the scattering cross-section. The explicit dependence of Z is missing in the theory for the square well but the calculations are in reasonable numerical agreement with experimental results. 3) $\Delta\rho$ was calculated for the unscreened Coulomb potential using exact methods to evaluate the scattering cross-section. The numerical

agreement between theory and experiment is poor and the correct dependence of $\Delta\rho$ on Z is not predicted. The chief objection to the unscreened Coulomb potential is that it has an infinite scattering cross-section, that is, the phase shifts diverge. Hence a cut-off procedure was used in which Equation (4.15) was only approximately satisfied.

The good agreement between theory and experiment for Friedel's calculations (53) using the Thomas-Fermi potential and Blatt's (44) and the present calculations for the square well potential is rather surprising in view of the fact that two rather serious assumptions have been made (assuming free electron wave functions for the conduction electrons in copper and silver and assuming that the Fermi surface in these metals is spherical). In fact the Fermi surface in both copper and silver touches the (111) faces of the first Brillouin zone with an appreciable area of contact (see Figure 4.7) so that the conduction electrons interact with the atomic lattice and are not free. A possible explanation of this problem put forward by Ziman (36) is that most of the scattering of the conduction electrons takes place on the belly of the Fermi surface where the conduction electrons are more or less free rather than on the neck regions.

Figure 4-7. A sketch of the Fermi surface for silver taken from Ziman (36).

CHAPTER 5

Discussion of the Thermoelectric Power Results5:1 Nordheim-Gorter Rule

A.V. Gold et al. (18) have shown that the thermoelectric power of a metal, in which there is more than one mechanism scattering electrons, is given by

$$Q = \frac{\sum_i Q_i W_i}{\sum_i W_i} \quad (5.1)$$

where W_i and Q_i are the thermal resistivity and thermoelectric power corresponding to the i th scattering mechanism. In order to apply this result to a conductor with various scattering mechanisms present, the following assumptions are made (see A.V. Gold et al. (18) and MacDonald (34)):

(1) It is assumed that the electrical conduction in a conductor may be treated in terms of a single group of charge carriers (electrons). This means that the conductor should be a single band conductor.

(2) It is also assumed that the electron distribution is isotropic. Hence the matrix elements for electron scattering do not depend explicitly on the electron wave vector $\vec{k}$.

(3) The scattering mechanisms are assumed to be operating entirely independent of one another and such that any particular scattering mechanism (say the i th), if operating entirely alone, would produce a characteristic thermoelectric power, $Q_i(T)$, and a thermal resistivity due to electron scattering, $W_i(T)$. Effectively this means

that each electron collision, whatever its cause, may be considered as independent of preceding or succeeding collisions.

(4) The transport of heat (i. e., thermal conduction) in the conductor is supposed to be determined entirely (i. e., in practice predominantly) by the conduction electrons. This means that Equation (5.1) is restricted to use in the region of diffusion thermoelectricity. In the phonon-drag region when a temperature gradient is present, the phonon distribution will no longer be in thermodynamic equilibrium so that there will be a heat flow carried by the lattice vibrations.

(5) If there is a variation in the intensity of any scattering mechanism (e. g., owing to variations in the concentration of a solute or in the intensity of thermal scattering), it is assumed that the essential characteristics of the conduction electrons remain unchanged. Effectively this means that the electron density of states function is assumed to be unaffected.

(6) It is assumed that the Fermi energy, and more generally the Fermi surface as a whole, is unaffected by the individual scattering mechanisms.

As a corollary to Equation (5.1), in the temperature region $T \geq \theta$ where θ is the Debye temperature, the electrical and thermal resistivities should obey the Wiedemann-Franz law;

$$\frac{\rho}{WT} = L_o. \quad (5.2)$$

Assuming that Equation (5.2) holds for each individual scattering mechanism, Equation (5.1) can be written as

$$Q = \frac{\sum Q_i \rho_i}{\sum \rho_i} . \quad (5.3)$$

If two scattering mechanisms are present, lattice scattering and impurity scattering, then Equation (5.3) gives

$$Q = \frac{Q_l \rho_l + Q_i \rho_i}{\rho_l + \rho_i} \quad (5.4)$$

and using Matthiessen's rule (see Equation (4.1)), the total thermoelectric power is given by

$$Q = Q_i + (Q_l - Q_i) \frac{\rho_l}{\rho} . \quad (5.5)$$

Q_l and ρ_l are the contributions to the thermoelectric power and resistivity from electron-lattice collisions and Q_i and ρ_i are the contributions to the thermoelectric power and resistivity caused by the scattering of conduction electrons from impurities. If Q is plotted against $\frac{1}{\rho}$, a straight line should result with intercept Q_i and slope $(Q_l - Q_i)\rho_l$.

A.V. Gold et al. (18) showed that Equation (5.5) describes the thermoelectric power of copper with impurities of tin, indium, germanium, gallium, chromium, nickel, and iron.

Application of the Nordheim-Gorter rule to silver alloys in the diffusion thermoelectric power region: From the data presented on the thermoelectric power of silver and the silver alloys in Figures 3.2 to 3.6, the phonon-drag component of the thermoelectric power seems to have disappeared by 200°K so that Equation (5.1) should be applicable above 200°K. Furthermore since the Debye temperature for silver is approximately 210°K, the Wiedemann-Franz law should hold above 200°K so that it should be possible to describe

the thermoelectric powers of the silver alloys above 200°K with Equation (5.5), assuming the other conditions on the Nordheim-Gorter rule are satisfied.

The thermoelectric power results for the silver-gold, silver-indium, silver-germanium, and silver-thallium systems have been analysed above 200°K using Equation (5.5) and the results are shown in Figures 5.1 to 5.4. The straight line behaviour of the curves in the Nordheim-Gorter plots indicates that the conditions on the Nordheim-Gorter rule, listed at the beginning of this section, are satisfied for these alloy systems.

In the Nordheim-Gorter plot for the silver-gold alloys, Figure 5.1, the points corresponding to the alloy of silver plus 0.25 atomic percent gold are anomalous. A possible explanation of this anomaly could be the presence of a trace of iron in the gold used for making the alloys. Iron is a naturally occurring impurity in gold and is quite difficult to remove. The presence of iron in the noble metals gives rise to "giant" thermoelectric powers (23) so that a trace of iron could cause the result shown in Figure 5.1. The results of Dr. A.M. Guénault's measurements (private communication) on the thermoelectric power of silver-gold alloys from the same sample batches in the temperature range 0.1 to 5°K also indicate that a trace of iron is present.

It would seem natural to assume that if the iron impurity exists, it should be uniformly distributed throughout the gold and should affect the thermoelectric power of each silver-gold alloy in

Figure 5-1. Nordheim-Gorter plots for the Ag-Au system above 200°K.

Figure 5-2. Nordheim-Gorter plots for the Ag-In system above 200°K.

Figure 5-3. Nordheim-Gorter plots for the Ag-Ge system above 200°K.

Figure 5-4. Nordheim-Gorter plots for the Ag-Tl system above 200°K.

the same manner and not give rise to the anomalous behaviour of the 0.25 at. % gold alloy compared to the 0.5 at. % and 1 at. % gold alloys. An explanation of this behaviour is that the presence of a non-transition metal impurity (in this case gold) in sufficient abundance can reduce the effect of iron so that the alloys containing larger amounts of gold would be less affected. This is in agreement with the work of Blatt et al. (57) on the thermoelectric power of copper alloys.

The intercepts, Q_i , of the curves in the Nordheim-Gorter plots (Figures 5.1 to 5.4) have been plotted against temperature in Figure 5.5 for the various alloy systems. Figure 5.5 shows that Q_i , the contribution to the thermoelectric power from impurity scattering, has a linear temperature dependence in agreement with the prediction of Equation (1.11). A further discussion of the Q_i versus T curves will be carried out in section 5:2.

Thermoelectric power measurements were carried out on only one concentration of zinc, cadmium, and antimony in silver so that only two points were possible on the Nordheim-Gorter plots for these alloy systems, one for pure silver and one for the single concentration of the impurity. It was assumed that these alloy systems would obey the Nordheim-Gorter rule and plots were made (see Figures 5.6 to 5.8) to find the characteristic thermoelectric powers of these impurities. The Q_i versus T curves for these impurities are shown in Figure 5.9.

Application of the Nordheim-Gorter rule in the phonon-drag region: Below 200°K phonon-drag effects begin to appear in the

Figure 5-5. Q_1 plotted as a function of temperature for the impurities Ge, In, Au, and Tl in silver.

Figure 5-6. Nordheim-Gorter plots for the Ag-Zn system above 200°K.

Figure 5-7. Nordheim-Gorter plots for the Ag-Cd system above 200°K.

Figure 5-8. Nordheim-Gorter plots for the Ag-Sb system above 200°K.

Figure 5-9. Q_i plotted against temperature for the impurities Cd, Zn, and Sb in silver.

thermoelectric power of the silver-alloy systems and unless these effects can be separated from the diffusion thermoelectric power effects, the Nordheim-Gorter rule cannot be applied. A separation of the phonon-drag and diffusion components has been achieved for copper alloys by Gold et al. (18), Pearson (58), and Blatt et al. (57). Their calculations indicate that in the phonon-drag region, the total thermoelectric power of the alloy is given by

$$Q = Q_d + Q_g \quad (5.6)$$

where Q_d is the diffusion component and Q_g the phonon-drag component of the thermoelectric power. Furthermore their work indicates that the thermoelectric power of the copper alloys is a linear function of temperature in the diffusion region and a linear extrapolation of the diffusion thermoelectric power into the phonon-drag region will give the diffusion thermoelectric power in the phonon-drag region.

This technique has been applied to the silver alloys in Figures 5.10 to 5.14 to extract the diffusion component of the thermoelectric power, Q_d , in the phonon-drag region. Q_d has been plotted against $\frac{1}{\rho}$ in Figures 5.15 to 5.17 for the silver-indium, silver-germanium, and silver-thallium systems over the temperature range 190 to 140°K. In every case, the point corresponding to pure silver on the Nordheim-Gorter plots falls a considerable distance from the straight line drawn through the points for the alloys. The explanation for this behaviour is that the Wiedemann-Franz law (Equation (5.2)) no longer holds for "pure" silver in this temperature range. However

Figure 5-10. Thermoelectric power of silver and alloys of Ag-Cd, Ag-Zn, and Ag-Sb as a function of temperature illustrating the separation of the diffusion and phonon-drag components.

Figure 5-11. Thermoelectric power of the Ag-Au alloys as a function of temperature illustrating the separation of the diffusion and phonon-drag components.

Figure 5-12. Thermoelectric power of the Ag-In alloys as a function of temperature illustrating the separation of the diffusion and phonon-drag components.

Figure 5-13. Thermoelectric power of the Ag-Ge alloys as a function of temperature illustrating the separation of the diffusion and phonon-drag components.

Figure 5-14. Thermoelectric power of the Ag-Tl alloys as a function of temperature illustrating the separation of the diffusion and phonon-drag components.

Figure 5-15. Nordheim-Gorter plots for the Ag-In system below 200°K.

Figure 5-16. Nordheim-Gorter plots for the Ag-Ge system below 200°K.

Figure 5-17. Nordheim-Gorter plots for the Ag-Tl system below 200°K.

the points corresponding to the alloys lie on straight lines indicating that the Wiedemann-Franz law still holds for the alloys. Hence the impurities indium, germanium, and thallium in silver lower the Debye temperature of silver. This result is consistent with the work of Henry et al. (24) on copper-zinc alloys.

The intercepts, Q_1 , from the Nordheim-Gorter plots (Figures 5.15 to 5.17) have been plotted against temperature in Figure 5.18 along with the results from Figure 5.5. The fact that the results for Q_1 from the phonon-drag region are consistent with the results from the diffusion region indicates that this method of extracting the diffusion thermoelectric power in the phonon-drag region is valid for these silver alloys.

This technique to find Q_1 in the phonon-drag region could not be used on the silver-cadmium, silver-zinc, and silver-antimony alloys since measurements were carried out on only one concentration of these impurities in silver.

Concentration dependence of the thermoelectric power: The concentration dependence of the total thermoelectric power, Q , of the alloys in the diffusion region is shown in Figure 5.19. The Nordheim-Gorter rule, Equation 5.5, explains the concentration dependence of the thermoelectric power of the silver-gold, silver-indium, silver-germanium, and silver-thallium systems.

Differentiating Equation (5.5) with respect to concentration

Figure 5-18. Q_i plotted against temperature for the impurities Ge, In, and Tl in silver.

Figure 5-19. Thermoelectric power as a function of concentration for the alloy systems Ag-Au, Ag-In, Ag-Tl, and Ag-Ge.

$$\frac{dQ}{dc} = - (Q - Q_i) \frac{\Delta \rho}{\rho} \quad (5.7)$$

and the second derivative is

$$\frac{d^2Q}{dc^2} = 2 (Q - Q_i) \frac{\Delta \rho^2}{\rho^2} \quad (5.8)$$

and as the concentration of impurity goes to zero, Equations (5.7) and (5.8) become

$$\left. \frac{dQ}{dc} \right|_{c=0} = -(Q_t - Q_i) \frac{\Delta \rho}{\rho_t} \quad (5.9)$$

$$\left. \frac{d^2Q}{dc^2} \right|_{c=0} = 2(Q_t - Q_i) \frac{\Delta \rho}{\rho_t^2} \quad (5.10)$$

where Q_t is the thermoelectric power of pure silver.

Equation (5.9) shows that the curves of the thermoelectric power versus concentration should have an initial negative slope, as observed, since Q_i is negative and Q_t is positive. As the concentration increases, Equation (5.10) shows that the curvature will be positive until Q_t reaches $-Q_i$ when the slope will go to zero as indicated in Figure 5.19.

5:2 Discussion of the Contribution to the Thermoelectric Power caused by Impurity Scattering

The thermoelectric power caused by impurity scattering is given by (see Appendix 1)

$$Q_i = \frac{\pi^2 k^2 T}{3 |e| \epsilon_f} \left[\frac{\partial \ln \sigma_i(\epsilon)}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} \quad (5.11)$$

where $\sigma_i(\epsilon)$ is an electrical conductivity generating function for impurity scattering and when ϵ is set equal to ϵ_f , $\sigma_i(\epsilon_f)$ is an approximation to the measured electrical conductivity caused by impurity

scattering.

Figures 5.18 and 5.9 show Q_i plotted against temperature for each of the silver-alloy systems. In each case Equation (5.11) predicts the correct temperature dependence of Q_i . For the silver-gold alloys, the fact that $Q_i(0)$ is not equal to zero is attributed to the presence of iron in the gold.

It is also noted that Q_i is negative for each of the silver-alloy systems. Equation (5.11) indicates that Q_i should be negative but an analysis of the term $\left[\frac{\partial \ln \sigma_i(\epsilon)}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ is necessary to establish this fact.

The simplest general formula for $\sigma_i(\epsilon)$, based on a free-electron model, is (35)

$$\sigma_i(\epsilon) \propto \tau_i(\epsilon) G(\epsilon) v_f(\epsilon) \quad (5.12)$$

where τ_i is the relaxation time for the conduction electrons scattered by the impurities, G is the area of the Fermi surface, and v_f is the velocity of the electrons on the Fermi surface. From Equation (5.12), $\frac{\partial \ln \sigma_i}{\partial \ln \epsilon}$ is given by

$$\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} = \frac{\partial \ln \tau_i}{\partial \ln \epsilon} + \frac{\partial \ln G}{\partial \ln \epsilon} + \frac{\partial \ln v_f}{\partial \ln \epsilon}. \quad (5.13)$$

It is expected that the first term in Equation (5.13) is positive since the more energetic electrons would be less easily scattered than the slow ones and thus have longer relaxation times. In a free-electron model, G is proportional to ϵ and v_f is proportional to $\epsilon^{\frac{1}{2}}$ so that the other two terms in Equation (5.13) will be positive. Hence Equation (5.11), based on a free-electron model gives a reasonable representation of the properties of Q_i .

However silver is not a free-electron metal, in fact the Fermi surface for silver is not a sphere, it touches the (111) faces of the first Brillouin zone, so that $\frac{\partial \ln G}{\partial \ln \epsilon}$ could be negative. Therefore it would be better to write (35)

$$\sigma_i(\epsilon) \propto \int \tau_i v dG \quad (5.14)$$

and if the relaxation time of the conduction electrons is assumed to be constant over the Fermi surface, then

$$\frac{\partial \ln \sigma_i(\epsilon)}{\partial \ln \epsilon} = \frac{\partial \ln \tau_i}{\partial \ln \epsilon} + \frac{\partial}{\partial \ln \epsilon} \ln \int v dG. \quad (5.15)$$

Ziman (36) has developed a mathematical model for the Fermi surface of the noble metals and his calculations show that

$\frac{\partial \ln \int v dG}{\partial \ln \epsilon}$ remains positive.

Using Equation (5.11) and the experimental results in Figures 5.18 and 5.9, the term $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ has been calculated for each alloy system and the results are shown in Table 5.1. It is noted that $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ is different for each alloy system.

Because of the presence of the natural logarithm in the term $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$, it is expected that this term should be independent of the impurity type. Since the alloys obey the Nordheim-Gorter rule, no change should be observed in the terms $\left[\frac{\partial \ln G}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ and $\left[\frac{\partial \ln v}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ as a result of alloying. Therefore an explanation

of the dependence of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ on the impurity type must come from variations in the term $\left[\frac{\partial \ln \tau_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$. A more detailed discussion of this term will be carried out in section 5:5.

Table 5.1. Experimental values of the term $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$.

Cd	$0.44 \pm .02$
Zn	$0.52 \pm .02$
In	$0.94 \pm .02$
Ge	$0.88 \pm .02$
Tl	$1.24 \pm .02$
Sb	$1.34 \pm .02$
Ag	$-1.11 \pm .01$

5:3 The Phonon-Drag Component of the Thermoelectric Power

The phonon-drag component of the thermoelectric power has been evaluated at 90°K for silver and each of the one atomic percent alloys and the results are shown in Table 5.2.

The impurities antimony, indium, and cadmium in silver do not change the phonon-drag component of pure silver appreciably, whereas the impurities gold, zinc, and thallium considerably suppress the phonon-drag component of pure silver.

Zinc lies in the period above silver in the periodic table and gold and thallium lie in the period below silver in the periodic table so that the mass differences between silver and these impurities are large. This means that the impurities zinc, gold, and thallium are effective scattering centres for phonons in silver and thus tend to return the phonon system in silver to equilibrium with the result that phonon-drag is suppressed in these alloys. The impurities antimony, indium, and cadmium have masses which are very nearly equal to silver so that they are not very effective scattering centres for phonons in silver. Hence the phonon system remains in a non-equilibrium state with the result that phonon-drag effects are not suppressed. These results are in agreement with the results of Blatt et al. (59) on copper alloys.

5:4 Comparison of the Thermoelectric Power Results in the Diffusion Region with the Thermoelectric Powers in the Very Low Temperature Region

Dr. A.M. Guénault, at the National Research Council, has measured the thermoelectric power of the pure silver, silver-indium, silver-thallium, and silver-gold specimens from the same batches

Table 5.2. Phonon-drag components of the thermoelectric power
at 90°K for the alloys with 1 at. % of impurity

	<u>Q_g (microvolts/deg.)</u>
Ag	$0.36 \pm .02$
Cd	$0.32 \pm .02$
In	$0.32 \pm .02$
Sb	$0.27 \pm .02$
Zn	$0.18 \pm .02$
Ge	$0.29 \pm .02$
Au	$0.18 \pm .02$
Tl	$0.20 \pm .02$

as the samples reported on in this thesis over the temperature range 0.1 to 5°K (private communication).

From his measurements, Dr. Guénault determined the quantity $\left[\frac{\partial \ln \sigma_1}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ using Equation (5.11) and the results are shown in Table 5.3. The term $\left[\frac{\partial \ln \sigma_1}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ has also been determined for these alloy systems with the exception of gold, in the diffusion region and the results are also shown in Table 5.3. There is agreement in the case of indium as an impurity but $\left[\frac{\partial \ln \sigma_1}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ is larger in the diffusion region than in the very low temperature region for the impurities thallium and germanium. At the moment there is no reason to believe that impurity scattering in the low temperature region should give different results than in the diffusion thermoelectric power region. In view of the scanty amount of data available, it is impossible to attempt a correlation of the impurity scattering effects in the two temperature regions.

For the pure silver specimen, the absolute value of $\left[\frac{\partial \ln \sigma_1}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ drops by a factor of two from high temperatures to low temperatures. Ziman (35) predicts that $\left[\frac{\partial \ln \sigma_1}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ should drop by a factor of three.

5:5 A Simple Model for the Contribution to the Thermoelectric Power from Impurity Scattering

The same model will be used to describe the contribution to the thermoelectric power of silver caused by impurity scattering as was used in section 4:3 to describe the contribution to the electrical resistivity caused by impurity scattering (i. e., a free-electron rigid band model).

Table 5.3. Comparison of the values of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ at very low temperatures from Dr. A. M. Guenault's measurements with the values determined in the present experiments

	<u>Guenault's Measurements</u>	<u>Present Experiment</u>
Ag	$-0.55 \pm .1$	$-1.11 \pm .01$
In	$0.96 \pm .1$	$0.94 \pm .02$
Tl	$0.90 \pm .1$	$1.24 \pm .02$
Ge	$0.56 \pm .1$	$0.88 \pm .02$
Au	$0.78 \pm .1$	----

The contribution to the thermoelectric power from impurity scattering is given by (see Appendix 1)

$$Q_i = \frac{\pi^2 k^2 T}{3 |e| \epsilon_f} \left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} \quad (5.15)$$

and also from Appendix 1

$$\sigma_i = \frac{e^2}{12 \pi^3 \hbar} \int v \tau_i dG \quad (5.16)$$

so that $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ is given by

$$\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} = \left[\frac{\partial \ln \int v \tau_i dG}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} . \quad (5.17)$$

The cross-section, X , for impurity scattering of the conduction electrons is given by (35)

$$X = (N_i \tau v)^{-1} \quad (5.18)$$

and if the cross-section is assumed to be constant over the Fermi surface

$$\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} = \left[- \frac{\partial \ln N_i X}{\partial \ln \epsilon} + \frac{\partial \ln G}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} . \quad (5.19)$$

Assuming the Fermi surface of silver is spherical so that G is proportional to ϵ

$$\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_g} = 1 - \left[\frac{\partial \ln N_i X}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} \quad (5.20)$$

In order to evaluate $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$, it is necessary to introduce potential functions to represent the impurity. An analysis has been carried out for the same potential functions used in section 4:3.

The Thomas-Fermi potential, $V(r) = \frac{Ze^2 e^{-qr}}{r}$: Assuming the free-electron approximation for the wave functions of the conduction electrons, a spherical Fermi surface, and applying the Born approximation, Friedel (60) shows that

$$\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} = 3 - \left[\left(1 + \frac{q^2}{4R^2} \right) \left\{ \left(1 + \frac{q^2}{4R^2} \right) \ln \left(1 + \frac{4R^2}{q^2} \right) - 1 \right\} \right]^{-1}. \quad (5.21)$$

Equation (5.21) says that $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ should be independent of valence, concentration, and in general the impurity type. From Equation (5.21) $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ has a value of 1.97 for impurities in silver. The numerical agreement between this calculation and the experimental data in Table 5.3 is poor. It is believed (see section 4:3 on the Thomas-Fermi potential) that the major sources of error in this method are the application of the Born approximation and the Thomas-Fermi estimate of the screening parameter, q . To rectify these errors, a proper phase shift calculation should be carried out. In view of the difficulties involved in carrying out a proper phase shift calculation for the Thomas-Fermi potential, it was decided to investigate the square well and unscreened coulomb potentials for which exact calculations can be carried out assuming a free-electron model.

The square-well potential: Using the method of de Faget de Casteljau and Friedel (37), $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ was calculated for the impurities zinc, cadmium, indium, thallium, gold, germanium, and antimony in silver and the results are shown in Table 5.4. The correct sign of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ is predicted but the variation of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ with impurity type does not agree with the experimental results.

The Coulomb potential: An exact calculation of the electrical conductivity was carried out using the methods described in section 4:3 for the Coulomb potential and $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ was found using a method of finite differences. Again $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ varies with the impurity type but the variation does not agree with the variation in the experimental results (see Table 5.4).

Review of the model: An expression for the contribution to the thermoelectric power from impurity scattering was obtained from a solution of the Boltzmann equation assuming elastic scattering of the conduction electrons by impurities,

$$Q_i = - \frac{\pi^2 k^2 T}{3 e \epsilon_f} \left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f} \quad (5.22)$$

The essential properties of Equation (5.22) are retained in the term $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$.

In order to evaluate $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$, it was assumed that the Fermi surface for silver is spherical and the wave functions of the conduction electrons in silver could be approximated by free-electron

Table 5.4. Theoretical values of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ calculated using the square well and unscreened Coulomb potentials to represent the impurity

	<u>Square Well</u>	<u>Coulomb Potential</u>	<u>Present Experiment</u>
Cd	1.34	0.79	$0.44 \pm .02$
Zn	1.34	0.79	$0.52 \pm .02$
In	0.66	0.59	$0.94 \pm .02$
Tl	0.66	0.59	$1.24 \pm .02$
Ge	0.61	0.54	$0.88 \pm .02$
Sb	0.62	0.52	$1.34 \pm .02$

wave functions. $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ was calculated using three different potentials to represent the impurity: 1) Assuming the Born approximation is applicable, $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ was calculated using the Thomas-Fermi potential. The correct sign of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ is predicted but the numerical agreement between theory and experiment is poor. Furthermore $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ is a constant for all impurity types. Presumably the poor numerical agreement between theory and experiment is a result of the application of the Born approximation and the Thomas-Fermi estimate of the screening parameter (see section 4:3). $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ has not been calculated for the Thomas-Fermi potential using a phase shift technique.

2) $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ has been calculated for impurities in copper by de Faget de Casteljau and Friedel (37). Using their method, $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ has been calculated for impurities in silver. The proper sign of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ was predicted and the value of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ varied with impurity type but the numerical agreement between theory and experiment was poor (see Table 5.4). 3) $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ has also been calculated for the unscreened Coulomb potential using a phase shift technique. Again $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ has the proper sign but the numerical agreement between theory and experiment is poor.

The failure of the calculations for $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ in comparison to the successes for the contribution to the electrical resistivity from impurity scattering, particularly for the square well, indicate that

the free-electron approximation is not good enough. The solution to this problem must come from a more detailed analysis of $\left[\frac{\partial \ln \sigma_i}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}$ taking into account the proper wave functions for the conduction electrons in silver and a non-spherical Fermi surface.

APPENDIX 1

A typical form of the Boltzmann equation (35) is

$$-\vec{v}_k \cdot \frac{\partial f_k^0}{\partial T} \vec{\nabla} T - \vec{v}_k \cdot e \frac{\partial f_k^0}{\partial \epsilon_k} \vec{E} = \int \left\{ \left(f_k - f_k^0 \right) - \left(f_{k'} - f_{k'}^0 \right) \right\} Q_{k'}^k d\vec{k}' \quad (1)$$

When this equation has been solved for f_k , the electric current density can be calculated from the following equation

$$\vec{J} = \int e \vec{v}_k f_k d\vec{k} \quad (2)$$

The left-hand side of the Boltzmann equation can be put in a more interesting physical form by considering the properties of the Fermi-Dirac distribution f_k^0 ,

$$f_k^0 = \frac{1}{e^{(\epsilon_k - \zeta)/kT} + 1} \quad (3)$$

so that

$$\frac{\partial f_k^0}{\partial T} = - \frac{(\epsilon_k - \zeta)}{T} \frac{\partial f_k^0}{\partial \epsilon_k} - \frac{\partial \zeta}{\partial T} \frac{\partial f_k^0}{\partial \epsilon_k} \quad (4)$$

Substituting Equation (4) into the Boltzmann equation gives

$$\begin{aligned} & \vec{v}_k \cdot \frac{\epsilon_k - \zeta}{T} \frac{\partial f_k^0}{\partial \epsilon_k} \vec{\nabla} T - \vec{v}_k \cdot e \frac{\partial f_k^0}{\partial \epsilon_k} \vec{E} - \frac{1}{e} \vec{\nabla} \zeta \\ &= \int \left\{ \left(f_k - f_k^0 \right) - \left(f_{k'} - f_{k'}^0 \right) \right\} Q_{k'}^k d\vec{k}' \end{aligned} \quad (5)$$

The electric field, $\frac{1}{e} \vec{\nabla} \zeta$, is caused by the temperature gradient disturbing the equilibrium distribution of electrons in the metal. In other words, as the Fermi distribution is disturbed from equilibrium by the temperature gradient, an electric field is

established in the metal which attempts to return the electron distribution to its original equilibrium.

If a relaxation time, $\tau(\vec{k})$, exists, then the following solution of the Boltzmann equation exists (35)

$$f_k = f_k^0 - \tau(\vec{k}) \vec{v}_k \cdot (-1) \frac{(\epsilon_k - \zeta)}{T} \frac{\partial f_k^0}{\partial \epsilon_k} \vec{\nabla} T + e \frac{\partial f_k^0}{\partial \epsilon_k} \left(\vec{E} - \frac{1}{e} \vec{\nabla} \zeta \right) \quad (6)$$

and from Equation (2), the electric current density is

$$\vec{J} = - \int e^2 \vec{v}_k \vec{v}_k \tau(\vec{k}) \frac{\partial f_k^0}{\partial \epsilon_k} d\vec{k} \cdot \left(\vec{E} - \frac{1}{e} \vec{\nabla} \zeta \right) + \int e \vec{v}_k \vec{v}_k \tau(\vec{k}) \frac{(\epsilon_k - \zeta)}{T} \frac{\partial f_k^0}{\partial \epsilon_k} d\vec{k} \cdot \vec{\nabla} T. \quad (7)$$

In silver, the electron distribution is isotropic so that a simple average can be taken over terms like $\vec{v}_k \vec{v}_k \cdot \vec{E}$ and $\vec{v}_k \vec{v}_k \cdot \vec{\nabla} T$.

Hence, the electric current density is

$$\vec{J} = - \frac{1}{3} \int e^2 v_k^2 \tau(k) \frac{\partial f_k^0}{\partial \epsilon_k} d\vec{k} \left(\vec{E} - \frac{1}{e} \vec{\nabla} \zeta \right) + \frac{1}{3} \int \frac{e}{T} v_k^2 \tau(k) (\epsilon_k - \zeta) \frac{\partial f_k^0}{\partial \epsilon_k} d\vec{k} \vec{\nabla} T. \quad (8)$$

Electrical Conductivity, σ

The sample is kept at a constant temperature and an electric field gradient, $\vec{E}$, is applied. The electric current density, $\vec{J}$, is measured and σ is determined from the relation

$$\vec{J} = \sigma \vec{E}. \quad (9)$$

Setting $\vec{\nabla} T = 0$ and consequently $\vec{\nabla} f$ in Equation (8) gives

$$\vec{J} = -\frac{1}{3} \int e^2 v_k^2 \tau(k) \frac{\partial f_k^0}{\partial \epsilon_k} d\vec{k} \vec{E} \quad (10)$$

so that

$$\sigma(\epsilon) = -\frac{1}{3} \int e^2 v_k^2 \tau(k) \frac{\partial f_k^0}{\partial \epsilon_k} d\vec{k} \quad (11)$$

or

$$\sigma(\epsilon) = -\frac{e^2}{12\pi^3\hbar} \iint v_k \tau(k) \frac{\partial f_k^0}{\partial \epsilon_k} dG d\epsilon_k \quad (12)$$

where dG is an element of area on the Fermi surface. $\sigma(\epsilon)$ is an electrical conductivity generating function such that when ϵ is set equal to ϵ_f , $\sigma(\epsilon_f)$ is an approximation to the measured electrical conductivity.

The Fermi-Dirac distribution function for electrons is shown in Figure 1.

$$\int_0^\infty -\frac{\partial f_k^0}{\partial \epsilon_k} d\epsilon = -\left[f_k^0(\infty) - f_k^0(0) \right] \quad (13)$$

If the bottom of the conduction band is chosen as the origin then $f_k^0(\infty)$ is certainly zero, so that

$$\int_0^\infty -\frac{\partial f_k^0}{\partial \epsilon_k} d\epsilon = 1, \quad (14)$$

hence

$$\sigma = \frac{e^2}{12\pi^3\hbar} \int v \tau dG. \quad (15)$$

From Equation (15), the electrical resistivity is

$$\rho = \frac{12\pi^3\hbar}{e^2} \left[\int v \tau dG \right]^{-1} \quad (16)$$

Figure 1. The Fermi-Dirac distribution function and its derivative.

Thermoelectric Power, Q

When a temperature gradient is applied to a sample, the Fermi distribution is disturbed from equilibrium with the result that an electric field $\frac{1}{e} \vec{\nabla} \zeta$ is established in the metal which attempts to return the electron distribution to its original equilibrium, furthermore the action of the temperature gradient sets up a homogeneous electric field, $\vec{E}$, along the interior length of the conductor so that for zero current flow in the conductor

$$\vec{E} - \frac{1}{e} \vec{\nabla} \zeta = Q \vec{\nabla} T \quad (17)$$

Putting $\vec{J} = 0$ in Equation (8) gives

$$\vec{E} - \frac{1}{e} \vec{\nabla} \zeta = \frac{\int \frac{e}{T} v_k^2 \tau(k) (\epsilon_k - \zeta) \frac{\partial f_k^0}{\partial \epsilon_k} d\vec{k}}{\int e^2 v_k^2 \tau(k) \frac{\partial f_k^0}{\partial \epsilon_k} d\vec{k}} \vec{\nabla} T. \quad (18)$$

The denominator of this expression is simply the electrical conductivity. The numerator can be evaluated using an expansion theorem from Ziman (35), so that the thermoelectric power is given by

$$Q = -\frac{\pi^2 k^2 T}{3 |e| \epsilon_f} \left[\frac{\partial \ln \sigma}{\partial \ln \epsilon} \right]_{\epsilon = \epsilon_f}. \quad (19)$$

APPENDIX 2

Since the calibration data collected for the thermocouples was not in the form of an arithmetic progression, it is necessary to use a Lagrangian interpolation to interpolate between calibration points to find the temperature T corresponding to a thermo-emf V .

$$T = \sum_{k=0}^m \frac{T_k P_k(V)}{P_k(V_k)} \quad (1)$$

is an m th order polynomial which passes through the $m + 1$ calibration points whose coordinates are (V_i, T_i) , and

$$P_k(V) = \prod_{\substack{i=0 \\ i \neq k}}^m (V - V_i) \quad (2)$$

If V is chosen as any value in the range of the V_i , Equation (1) determines an approximate value for the corresponding T .

APPENDIX 3

The binding energy of an atom in its own lattice can be approximately evaluated using the Wigner-Seitz method (60).

Bloch's theorem states that the wave function of an electron in the k th state can be represented by a plane wave multiplied by a function exhibiting the periodicity of the lattice such that

$$\Psi_k(\vec{r} + \vec{l}) = e^{i \vec{k} \cdot \vec{l}} \Psi_k(\vec{r}) \quad (1)$$

If the state for which $k = 0$ is considered, then

$$\Psi_0(\vec{r} + \vec{l}) = \Psi_0(\vec{r}) \quad (2)$$

where $\Psi_0(\vec{r} + \vec{l})$ represents the wave function of an electron at the bottom of the conduction band. Each atom in the crystal is then surrounded by its Wigner-Seitz cell, that is the cell bounded by the perpendicular bisectors of the interatomic vectors. The shape of the cell is rather complicated so that it is convenient to replace it by a sphere containing one atomic volume of radius r_0 . If a spherically symmetric potential is chosen to represent the impurity atom, it is only necessary to solve the radial Schrodinger equation with the condition that

$$\left. \frac{\partial \Psi_0}{\partial r} \right|_{r=r_0} = 0 \quad (3)$$

The energy E_0 giving a solution of this equation should represent the energy of the bottom of the conduction band.

To deal with states of higher energy in the band, the wave function of an electron in state k can be approximately written as

$$\psi_{\mathbf{k}}(\vec{r} + \vec{t}) = e^{i\vec{k} \cdot \vec{t}} \psi_{\mathbf{o}}(\vec{r}) \quad (4)$$

and solving the Schrödinger to a first approximation, the expectation value of the energy is

$$E_{\mathbf{k}} = E_{\mathbf{o}} + \frac{\hbar^2 k^2}{2m^2} \quad (5)$$

Thus the binding energy of a metal can be written as

$$E = E_s + E_i + E_f \quad (6)$$

where E_s is the sublimation energy of the metal, E_i is the ionization potential, and E_f is the Fermi energy such that

$$E_{\mathbf{o}} = E_s + E_i \quad (7)$$

This technique for evaluating the binding energy of a metal is quite nice since the effects of exchange and correlation are taken into account in the Fermi energy.

The binding energy of silver calculated from Equation (6) is 16.04 ev and the binding energy of gold is 18.24 ev. Hence, a square well of depth 2.20 ev is used to calculate the resistivity with a gold impurity. The sublimation energies have been taken from an article by Wigner and Seitz (61) on the cohesion of metals, the ionization potentials from the Handbook of Chemistry and Physics, and the Fermi energies from Ziman (36).

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