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ELECTRICAL RESISTIVITIES OF DILUTE ALLOYS AND DEVIATIONS FROM MATTHIESSEN'S RULE

by

© RAJINDER S. SETH

A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "ELECTRICAL RESISTIVITIES OF DILUTE ALLOYS AND DEVIATIONS FROM MATTHIESSEN'S RULE", submitted by Rajinder S. Seth in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

The electrical resistivity of polycrystalline silver, aluminum, cadmium and magnesium and over twenty dilute alloys of these metals with different solute concentrations has been measured from 1.5°K to 300°K. From the resistivity data, deviations from Matthiessen's rule in these alloys have been evaluated. Deviations with positive as well as negative sign have been observed.

A recent theoretical prediction by Bhatia and Gupta (1969) shows that if the interference between the scattering of electrons by lattice vibrations of the host atoms and the excess potential due to the impurities is considered, this leads to significant deviations Δ from Matthiessen's rule of either sign in the temperature range $T \gtrsim \theta_D$. In complementary alloys in which the solute and the solvent atoms exchange roles, they have predicted that $d\Delta/dT$ should have opposite sign for the two alloys of the system. This feature of the reversal of slope $d\Delta/dT$ at high temperatures in complementary alloys has been examined for the data obtained experimentally here. A comparison has been carried out between the experimental results and the theoretical prediction and qualitative agreement has been established. The precise results in this thesis obtained over a wide temperature range considerably extend the experimental data available on Matthiessen's rule but the comparison with theory particularly at lower temperatures is made difficult by the complexity of the scattering processes. Where possible these comparisons have been made.

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INTRODUCTION

Soon after the discovery of the electron, it was recognized that high electrical conductivity of metals is due to the presence of large numbers of quasi-free electrons. Under the influence of an applied electric field, these electrons, because of their wave nature, can move through a perfectly periodic lattice without being scattered. Electrical resistance arises from scattering by the aperiodicity of the lattice potential caused by static imperfections - either chemical impurities or physical defects - and the thermal vibrations of the atoms of the crystal. To a first approximation, scattering by impurities and the thermal vibrations (phonons) is additive.

The electrical resistivity ρ of a metal may be considered as being due to two contributions: (i) the temperature-dependent 'ideal' resistivity ρ_i which is characteristic of the pure metal and arises because of the scattering of electrons by the thermal vibrations of the lattice, and (ii) the resistivity ρ_o due to the

scattering of electrons from impurities*, which one would not expect to depend on the temperature. As the temperature approaches zero, the ideal resistivity ρ_i goes rapidly to zero, whereas ρ_o, which is a function of the type and concentration of the impurity, persists and is usually called the 'residual' resistivity. This separation of the total resistivity $\rho(T)$ into two independent components $\rho_i(T)$ and ρ_o is known as Matthiessen's rule (Matthiessen, 1862), which may be written

$$\rho(T) = \rho_o + \rho_i(T) \ . \qquad (1)$$

This rule is not strictly accurate but it is a useful first approximation.

Matthiessen's rule was originally given as an empirical rule deduced from experimental results. It was first stated in a slightly different but equivalent form, that the increase in resistivity of a metal due to small concentration of another metal in solid solution is in general independent of temperature. In other words $d\rho/dT$ is independent of the impurity and its concentration.

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* In this thesis, we shall be concerned only with the chemical impurities of non-magnetic nature.

On the basis of certain simplifying assumptions, theoretical justification for Matthiessen's rule has been given (Jones, 1956). It is assumed that unique times of relaxation can be defined for both the scattering processes leading to the ideal and the residual resistivity and that the ratio of the two times is independent of the direction of motion of the electron. In real metals deviations from this rule, defined as

$$\Delta = \rho - (\rho_o + \rho_i) \quad , \tag{2}$$

are expected at all temperatures and have, indeed, been observed. They are appreciable in magnitude and can have either sign. These deviations were first observed by Grüneisen (1933) up to 90°K in copper and Linde (1939) at higher temperatures in some dilute alloys. The dependence of deviations on temperature and on the type and concentration of the impurities in dilute alloys has been experimentally investigated, among others, by Krautz and Schultz (1957), Alley and Serin (1959), Das and Gerritsen (1964), Hedgcock and Muir (1964), Damon and Klemens (1964, 1965), Seth (1967), Dugdale and Basinski (1967), Panova, Zhernov and Kutaitsev (1968) and Damon, Mathur and Klemens (1968).

From a theoretical point of view, the problem of electrical resistivity of a pure metal itself is quite

complicated. A treatment of the problem of deviations from Matthiessen's rule, as one might expect, is very difficult. No satisfactory quantitative theory which could explain the entire temperature and concentration dependence exists as yet.

Several earlier theoretical investigations have predicted some qualitative features of the deviations. Using the variational method, Kohler (1949) solved the Boltzmann equation when two scattering mechanisms (phonons and impurities) act on electrons in a single conduction band. He obtained an expression according to which Δ is always positive, proportional to ρ_i in the low-temperature limit and to ρ_o at the high-temperature limit. Sondheimer and Wilson (1947), using a different model in which there is two-band conduction in the metal, obtained an expression quite similar to that of Kohler, particularly in the low- and high-temperature limits. Assuming that the relaxation time for the impurity scattering is independent of the electron wave number while that for the lattice scattering is not, MacDonald (1956) derived an expression for Δ which again has the same limits. Sondheimer (1950) using a one-band, free-electron model has calculated a correction to Matthiessen's rule. These deviations are zero at high and low temperatures and rise to a maximum when $\rho_i \simeq \rho_o$, but are much

too small to explain the experimental results. Unfortunately, none of the above theories is adequate to explain the observed deviations in dilute alloys.

Koshino (1960) suggested that the inelastic scattering of conduction electrons, which arises from the thermal vibrations of the impurity potential, may explain some of the deviations from Matthiessen's rule. However, this work has been criticized by Taylor (1962), who showed that Koshino had neglected a set of terms the effect of which is precisely to cancel the terms on the basis of which Koshino had obtained the deviations. It was found by Taylor (1964) that this cancellation is complete at high temperatures and partial at low temperatures. Therefore the effect due to inelastic scattering processes is too small to explain the observed deviations.

A slightly different mechanism for phonon-assisted impurity scattering was proposed by Klemens and coworkers (Klemens, 1963; Damon and Klemens, 1964; Damon, Mathur and Klemens, 1968). They have considered a contribution to deviations arising from the deformation of the impurity potential caused by the thermal vibrations. According to this theory, the impurity potential does not move rigidly with the thermal vibrations of the host but changes

slightly owing to the strain of the surrounding lattice. The additional resistivity due to this effect varies as T^4 at low temperatures and T at high temperatures.

Bhatia (1965), Bhatia and Gupta (1969) and Gupta (1969a) have pointed out that the failure of the earlier theories to give a satisfactory account of the deviations from Matthiessen's rule was due to the fact that there, the scattering due to the vibrations of the host atoms and the excess potential due to impurities had been treated separately. In this way, the contribution of the interference term has been omitted. On evaluating the interference term under the assumption that the thermal motion of the impurity is similar to that of the host atoms, it was found that it leads to significant deviations which can have either sign and at high temperatures have the linear dependence on temperature observed in practice. An interesting consequence of their calculation is that in complementary alloy pairs, that is, alloys in which the solute and the solvent atoms exchange roles, the deviation versus temperature curves for the two alloys are expected to have opposite slopes. Independently, Kagan and Zhernov (1966), using a different formalism, arrived at the same result but underestimated the contribution of the interference term. These authors take into account the deformation of the phonon spectrum due to the mass difference between

the impurity and the host atoms and its contribution to the deviations from Matthiessen's rule. While certainly broad in scope, this theory remains qualitative because of the nature of the approximations made.

The purpose of this thesis is to report measurement of electrical resistivity of pure polycrystalline silver, aluminum, cadmium and magnesium and a number of dilute alloys of these metals. The measurements have been made over a temperature range from 1.5°K to 300°K. The choice of these metals was influenced by the consideration that complementary homogeneous solid solutions such as A-B and B-A could be formed. From the resistivity measurements, deviations from Matthiessen's rule in these alloys have been calculated and the results compared with the predictions of Bhatia and Gupta (1969). Some preliminary measurements on aluminum-magnesium alloys have been reported earlier by this author in an M.Sc. thesis in 1967.

This thesis essentially contains three chapters. In the first chapter, relevant theories regarding the deviations from Matthiessen's rule are discussed in some detail. The second chapter contains the description of the apparatus, preparation of specimens and the experimental technique for measurement of deviations. In the third chapter, the experimental results are presented and discussed in the light of the existing theoretical information.

CHAPTER I

THEORY

CALCULATION OF ELECTRICAL RESISTIVITY DUE TO IMPURITIES AND DEVIATIONS FROM MATTHIESSEN'S RULE

1.1 General

The electrical resistivity of a metal containing a small amount of impurity is usually written in the form

$$\rho(T) = \rho_i(T) + \rho_o \quad , \tag{1.1}$$

where ρ_i is the resistivity caused by thermal vibrations of the lattice, and ρ_o is the resistivity due to the scattering of electrons by impurities. This statement is known as Matthiessen's rule.

The standard procedure for the calculation of electrical resistivity of a metal involves solution of the Boltzmann transport equation. This requires, first of all, the calculation of an expression for $P(\vec{k},\vec{k}')$, the probability of scattering of an electron from a state $\vec{k}$ to a state $\vec{k}'$. In a metal containing impurities (or a dilute alloy), the contributions to P come from two scattering mechanisms, namely the lattice vibrations or phonons and the impurities. Once the probability of scattering is known, one has to proceed to obtain a solution for the Boltzmann equation.

The derivation of Matthiessen's rule employs two assumptions. Firstly, the contributions to the probability of scattering P from impurity and lattice vibrations are additive, i.e.,

$$P = P_i + P_o \quad , \tag{1.2}$$

where P_i and P_o are, respectively, the probabilities of scattering due to the host lattice and the impurities. In other words, the two scattering mechanisms act independently of each other. Secondly, when P is known and the Boltzmann equation is solved, it is assumed that the solution ϕ of this equation with P_i alone is the same, apart from a constant multiplier, as that for P_o alone. This assumption means that

$$\phi = c_1 \phi_i = c_2 \phi_o \quad , \tag{1.3}$$

where ϕ, ϕ_i, and ϕ_o are the solutions corresponding to P, P_i, and P_o respectively. c_1 and c_2 are constants independent of $\vec{k}$. In particular (1.3) is valid if times of relaxation can be defined for both P_i and P_o and if their ratio is independent of $\vec{k}$ (Wilson, 1953).

Deviations from Matthiessen's rule occur when one or both of the above assumptions are violated. Let us define the deviations by

$$\Delta(T) = \rho(T) - \rho_i(T) - \rho_o \quad . \tag{1.4}$$

If the first assumption is violated, Δ can have either sign depending upon which of the two sides of (1.2) is greater. But when the second assumption is violated, we shall see from the variational principle that Δ will always be positive. To a first approximation, the effects due to violation of the two assumptions are expected to be additive.

Before we discuss the violation of these assumptions and the deviations from Matthiessen's rule therefrom, we shall first describe the Boltzmann equation and its approximate solutions for the problem of electrical resistivity.

1.2 The Mechanism of Conductivity

1.2.1 The Boltzmann Equation

Boltzmann equation is a statistical approach to the theory of electron transport in metals. There are detailed discussions of this equation in the literature (Ziman, 1960; Blatt, 1968) but only a brief description will be given here.

Let us define for electrons in a metal a distribution function $f_{\vec{k}}$ such that

$$1/4\pi^3 \, f_{\vec{k}} \, d\vec{k} \tag{1.5}$$

is the number of electrons per unit volume with wave

vector $\vec{k}$ in the element $d\vec{k}$. $f_{\vec{k}}$ represents the probability that the electron state designated by $\vec{k}$ will be occupied. At equilibrium, $f_{\vec{k}}$ reduces to $f^{o}_{\vec{k}}$, the Fermi distribution function. We are primarily interested in the change with time of the distribution function due to the disturbing influence of an electric field $\vec{\varepsilon}$ balanced by the change as a result of collisions. In a steady state, the Boltzmann equation is

$$\left.\frac{\partial f}{\partial t}\right]_{field} + \left.\frac{\partial f}{\partial t}\right]_{coll.} = 0 \quad . \tag{1.6}$$

The first term in (1.6) which arises from the drift of electrons due to the electric field $\vec{\varepsilon}$ is given by

$$\left.\frac{\partial f}{\partial t}\right]_{field} = - \frac{e\vec{\varepsilon}}{\hbar} \frac{\partial f_{\vec{k}}}{\partial \vec{k}} \quad . \tag{1.7}$$

For the second term, introduce $Q(\vec{k},\vec{k}')$ which is the probability per unit time that an electron in state $\vec{k}$ is scattered into the state $\vec{k}'$. The collision term becomes

$$\left.\frac{\partial f}{\partial t}\right]_{coll.} = \int [Q(\vec{k}',\vec{k}) f_{\vec{k}'}(1 - f_{\vec{k}}) - Q(\vec{k},\vec{k}') f_{\vec{k}} (1 - f_{\vec{k}'})]\, d\vec{k}' \quad . \tag{1.8}$$

It is assumed that $Q(\vec{k},\vec{k}')$ does not depend on $\vec{\varepsilon}$. In equilibrium when $f_{\vec{k}} = f^{o}_{\vec{k}}$, detailed balance exists.

Therefore $\left.\frac{\partial f}{\partial t}\right]_{\text{coll.}} = 0$, which means that the integrand in (1.8) vanishes. This gives

$$\left.\frac{\partial f}{\partial t}\right]_{\text{coll.}} = \int Q(\vec{k},\vec{k}')f^{o}_{\vec{k}}(1 - f^{o}_{\vec{k}'})\left[\frac{f_{\vec{k}'}(1-f_{\vec{k}})}{f^{o}_{\vec{k}'}(1-f^{o}_{\vec{k}})} - \frac{f_{\vec{k}}(1-f_{\vec{k}'})}{f^{o}_{\vec{k}}(1-f^{o}_{\vec{k}'})}\right]d\vec{k}' \quad . \tag{1.9}$$

Let us define $\phi_{\vec{k}}$ by

$$f_{\vec{k}} = f^{o}_{\vec{k}} - \phi_{\vec{k}}\frac{\partial f^{o}_{\vec{k}}}{\partial E_{\vec{k}}} \quad . \tag{1.10}$$

$f^{!}_{\vec{k}} = -\phi_{\vec{k}}\frac{\partial f^{o}_{\vec{k}}}{\partial E_{\vec{k}}}$ measures the small deviation of the true distribution function from the equilibrium. Substitution of (1.10) into (1.9) gives, to first order of f',

$$\left.\frac{\partial f}{\partial t}\right]_{\text{coll.}} = \frac{1}{k_B T}\int Q(\vec{k},\vec{k}')f^{o}_{\vec{k}}(1-f^{o}_{\vec{k}'})(\phi_{\vec{k}'} - \phi_{\vec{k}})d\vec{k}' \quad , \tag{1.11}$$

where k_B is the Boltzmann constant and we have used

$$f^{o}_{\vec{k}}(1 - f^{o}_{\vec{k}}) = -k_B T\frac{\partial f^{o}_{\vec{k}}}{\partial E_{\vec{k}}} \quad . \tag{1.12}$$

The linearized Boltzmann equation which is also known as the Bloch equation now becomes

$$-\frac{e\vec{\mathcal{E}}}{\hbar}\frac{\partial f^{o}_{k}}{\partial \vec{k}} = \frac{1}{k_B T}\int Q(\vec{k},\vec{k}')f^{o}_{\vec{k}}(1 - f^{o}_{\vec{k}'})(\phi_{\vec{k}} - \phi_{\vec{k}'})d\vec{k}' \quad . \tag{1.13}$$

1.2.2 Relaxation-Time Approximation

In general, the Boltzmann equation cannot be solved exactly. One way of getting a solution is by using the relaxation-time approximation according to which the collision term can be expressed in the form

$$\left[\frac{\partial f}{\partial t}\right]_{\text{coll.}} = -\frac{f_{\vec{k}} - f^{o}_{\vec{k}}}{\tau_{\vec{k}}} \quad . \tag{1.14}$$

$\tau_{\vec{k}}$ is the relaxation time; it is the time constant associated with the rate of return to equilibrium of the electron distribution when the external field is switched off. $\tau_{\vec{k}}$ is a meaningful parameter only if it is independent of the nature of the external influence. It is a useful approximation for scattering from impurities and phonon scattering at high temperatures in metals. From (1.11), (1.12) and (1.14), we get

$$\frac{1}{\tau_{\vec{k}}} = \int Q(\vec{k},\vec{k}') \left[\frac{1 - f^{o}_{\vec{k}'}}{1 - f^{o}_{\vec{k}}}\right] \left[1 - \frac{\phi_{\vec{k}'}}{\phi_{\vec{k}}}\right] d\vec{k}' \quad . \tag{1.15}$$

For elastic processes, $E_{\vec{k}} \simeq E_{\vec{k}'}$, (1.15) becomes

$$\frac{1}{\tau_{\vec{k}}} = \int Q(\vec{k},\vec{k}') \left[1 - \frac{\phi_{\vec{k}'}}{\phi_{\vec{k}}}\right] d\vec{k}' \ ,$$

$$= \int Q(\vec{k},\vec{k}) \left[1 - \frac{\tau_{\vec{k}} \vec{\varepsilon}.V_{\vec{k}'}}{\tau_{\vec{k}} \vec{\varepsilon}.V_{\vec{k}}}\right] d\vec{k}' \ .$$

For a spherical Fermi surface,

$$\frac{1}{\tau_{\vec{k}}} = \int Q(\vec{k},\vec{k}')\left[1 - \frac{\tau_{\vec{k}'}\vec{\epsilon}.\vec{k}'}{\tau_{\vec{k}}\vec{\epsilon}.\vec{k}}\right] d\vec{k}' \quad . \tag{1.16}$$

If $Q(\vec{k},\vec{k}')$ depends only on the angle θ between $\vec{k}$ and $\vec{k}'$ and not their absolute orientations, $Q(\vec{k},\vec{k}')=Q(|\vec{k}-\vec{k}'|)$. Therefore,

$$\frac{1}{\tau_k} = \int Q(|\vec{k}-\vec{k}'|)(1 - \cos\theta)\, d\vec{k}' \quad , \tag{1.17}$$

independent of the direction of $\vec{k}$.

The current density $\vec{J}$ is defined to be

$$\vec{J} = \frac{e}{4\pi^3} \int f_{\vec{k}}\, V_{\vec{k}}\, d\vec{k} \quad ,$$

$$= \frac{-e^2}{4\pi^3} \int \tau_{\vec{k}}\, V_{\vec{k}}\, (V_{\vec{k}}.\vec{\epsilon})\, \frac{\partial f^0_{\vec{k}}}{\partial E_{\vec{k}}}\, d\vec{k} \quad . \tag{1.18}$$

The first term on the right hand side of (1.10) does not contribute to the current. The conductivity tensor σ_{ij} can now be written as

$$\sigma_{ij} = \frac{-e^2}{4\pi^3} \int \tau\, v_i v_j\, \frac{\partial f^0_{\vec{k}}}{\partial E_{\vec{k}}}\, d\vec{k} \quad .$$

A simple explicit expression for σ for metals with cubic symmetry, quadratic E-k relationship and spherical Fermi surface is

$$\sigma = \frac{ne^2\tau_{k_F}}{m^*} \quad , \tag{1.19}$$

where n is the number of electrons per unit volume and m^* is the effective mass of the electron.

In the general case, $Q(\vec{k},\vec{k}')$ depends on the direction of $\vec{k}$ and $\vec{k}'$ separately and the Fermi surface is not spherical. $\tau_{\vec{k}}$ could therefore depend on $\vec{k}$ and the Boltzmann equation has to be solved for each specific case.

1.2.3 Variational Solution

An alternative method of solving the Boltzmann equation is by the variational technique. The application of this procedure (which is valid for both elastic and inelastic scattering) requires the selection of a suitable trial function for $\phi_{\vec{k}}$ containing parameters which are adjusted in accordance with the variational principle.

The linearized Boltzmann equation (1.13) can be written as

$$-\frac{e\vec{\mathcal{E}}}{\hbar}\frac{\partial f_k^o}{\partial \vec{k}} = \frac{1}{k_B T}\int P(\vec{k},\vec{k}')(\phi_{\vec{k}}-\phi_{\vec{k}'})\,d\vec{k}' \quad , \tag{1.20}$$

where $P(\vec{k},\vec{k}') = f_{\vec{k}}^o(1-f_{\vec{k}}^o)Q(\vec{k},\vec{k}')$. This equation can further be expressed as an operator equation (Ziman, 1960)

$$X = P\phi \quad , \tag{1.21}$$

where P is the scattering operator. The variational principle requires that the solution of the integral equation

(1.20) be chosen so that it gives

$$\rho = \frac{\Pi}{J^2} = \frac{\langle \phi, P\phi \rangle}{[\langle \phi, X \rangle]^2} \quad , \tag{1.22}$$

a minimum value. J is given by (1.18) for unit electric field and

$$\Pi = \frac{1}{2k_B T} \iint P(\vec{k},\vec{k}')(\phi_{\vec{k}} - \phi_{\vec{k}'})^2 \, d\vec{k} \, d\vec{k}' \quad . \tag{1.23}$$

Therefore, in order to calculate the electrical resistivity of a metal, one has first to find an expression for $P(\vec{k},\vec{k}')$ and then select a suitable trial function for $\phi_{\vec{k}}$. The simplest trial function could be of the form

$$\phi_{\vec{k}} = \alpha \, \vec{k} \cdot \vec{u} \quad , \tag{1.24}$$

where $\vec{u}$ is a unit vector parallel to the electric field and α is a constant whose value does not matter as it cancels out in the equation (1.22).

1.3 Deviations from Matthiessen's Rule

1.3.1 Violation of the First Assumption

A. Calculation of Electrical Resistivity of an Alloy and contribution of the Interference Term (Bhatia and Gupta, 1969). From the time dependent perturbation theory, the probability per unit time $Q(\vec{k},\vec{k}')$ that an

electron is scattered from state $\vec{k}$ to $\vec{k}'$ is

$$Q(\vec{k},\vec{k}') = \frac{2\pi}{\hbar}\left|<\vec{k}'|W|\vec{k}>\right|^2 \delta(E_{\vec{k}} - E_{\vec{k}'} + \hbar\omega) \ , \tag{1.25}$$

where $\hbar\omega$ is the energy transferred during the scattering and W is the appropriate pseudopotential. The matrix element of W can be written as

$$<\vec{k}'|W|\vec{k}> = \frac{1}{N}\sum_i e^{-i\vec{q}.\vec{r}_i} (\vec{k}'|w_i|\vec{k}) \ , \tag{1.26}$$

where $\vec{q} = \vec{k}' - \vec{k}$, the states $|\vec{k})$ and $|\vec{k}')$ are normalized to unity over Ω_o, the volume per unit atom. N is the total number of atoms in the crystal and $\vec{r}_i$ is the position of the atom i. The matrix elements $(\vec{k}'|w_i|\vec{k})$ are the pseudopotential form factors. From (1.25) and (1.26), one gets

$$P(\vec{k},\vec{k}') = \frac{2\pi}{\hbar^2 N} f^o_{\vec{k}}(1 - f^o_{\vec{k}'})\Gamma(\vec{q},\omega) \ , \tag{1.27}$$

where $\Gamma(\vec{q},\omega)$ is the Van Hove scattering correlation function given by

$$\Gamma(\vec{q},\omega) = \int \frac{dt}{2\pi N} e^{-i\omega t} < \sum_{i,j=1}^{N} w_i(q)w_j(q)\, e^{-i\vec{q}.\vec{r}_i(o)} e^{i\vec{q}.\vec{r}_j(t)} > \ , \tag{1.28}$$

where w_j is the pseudopotential matrix element of the atom j <u>in the alloy</u> and <.....> denotes ensemble average.

Restoring the factors $\Omega(=\Omega_o N)$ and using (1.27), (1.23) becomes

$$\Pi = \frac{\Omega_o \pi}{\hbar^2 k_B T} \int (\phi_{\vec{k}} - \phi_{\vec{k}'})^2 f^o_{\vec{k}}(1 - f^o_{\vec{k}'})\Gamma(\vec{q},\omega)d\vec{k}\, d\vec{k}' \quad . \qquad (1.29)$$

Define $\varepsilon_{\vec{k}} = E_{\vec{k}} - E_F$, where E_F is the Fermi energy. Therefore

$$\int d\vec{k}' = \int \frac{d\varepsilon_{\vec{k}'}}{8\pi^3 |\text{grad}_{\vec{k}} E|} \int_{FS} dS_{\vec{k}'} \quad ,$$

$$= \int \frac{\hbar\, d\omega}{8\pi^3 |\text{grad}_{\vec{k}} E|} \int_{FS} dS_{\vec{k}'} \quad ,$$

where $\hbar\omega = E_{\vec{k}'} - E_{\vec{k}}$, and the surface integral is taken on the Fermi surface when $\hbar\omega \ll E_F$. Further

$$\int d\vec{k}\, f^o_{\vec{k}}(1-f^o_{\vec{k}'}) = \int \frac{d\varepsilon_{\vec{k}}}{4\pi^3 |\text{grad}_{\vec{k}} E|} \frac{1}{(e^{\varepsilon_{\vec{k}}/k_B T} + 1)(1 + e^{-(\varepsilon_{\vec{k}}+\hbar\omega)/k_B T})}$$

$$\int dS_{\vec{k}}$$

$$= \frac{1}{4\pi^3 |\text{grad}_{\vec{k}} E|} \frac{1}{1 - e^{-\hbar\omega/k_B T}} \int dS_{\vec{k}} \quad .$$

With these relations, one gets

$$\Pi = \frac{\Omega_o}{32\pi^5 \hbar} \iint_{FS} \frac{dS_{\vec{k}'}}{|\text{grad}_{\vec{k}} E|} \frac{dS_{\vec{k}}}{|\text{grad}_{\vec{k}} E|} (\phi_{\vec{k}} - \phi_{\vec{k}'})^2 \gamma(\vec{q}) \quad , \qquad (1.30)$$

where

$$\gamma(\vec{q}) = \int \frac{\beta\omega\Gamma(\vec{q},\omega)d\omega}{1 - e^{-\beta\omega}} \quad , \tag{1.31}$$

β being $\hbar/k_B T$.

For cubic symmetry and spherical Fermi surface and also using the simple trial function of the type (1.24), the variational expression for ρ becomes

$$\rho = D \int_0^2 \gamma_{av}(x)\, x^3\, dx \quad , \tag{1.32}$$

where

$$x = \frac{q}{k_F} \quad , \qquad D = \frac{3\pi\, m^{*2}\, \Omega_o}{4\, \hbar^3\, e^2\, k_F^2} \quad ,$$

and $\gamma_{av}(x)$ is the average of $\gamma(\vec{q})$ over all the directions of $\vec{q}$ in the crystal.

In order to calculate $\gamma(\vec{q})$ or $\gamma(\vec{q},\omega)$ for an alloy, make the simplifying assumptions that (i) the alloy is of substitutional type and that the two types of atoms A (host) and B(impurity) in it are distributed at random, and (ii) the atoms A and B have roughly the same volume, mass and force constants so that the effect of local strain and of changes in vibration frequency spectrum can be neglected. Then in (1.28) one can replace $w_i w_j$ by its configurational average $\overline{w_i w_j}$ before taking the thermal

average. For a random alloy, when $i \neq j$,

$$\overline{w_i w_j} = \overline{w_i}\ \overline{w_j} = (\bar{w})^2$$

$$= [c\ w_B + (1-c)\ w_A]^2 \quad ,$$

and for $i=j$,

$$\overline{w_i w_j} = \overline{w_i^2} \quad ,$$

$$= c\ w_B^2 + (1-c)\ w_A^2 \quad .$$

Therefore

$$\overline{w_i w_j} = (\bar{w})^2 + \delta_{ij}[\overline{w^2} - (\bar{w})^2] \quad ,$$

c is the concentration of the impurity atoms B in host atoms A. This gives

$$\overline{w_i w_j} = ((1-c)w_A + c\ w_B)^2 + \delta_{ij}\ c(1-c)(w_A - w_B)^2 \quad . \tag{1.33}$$

Substituting (1.33) in $\Gamma(\vec{q},\omega)$ and using (1.31), $\gamma(\vec{q})$ becomes

$$\gamma(\vec{q}) = [(1-c)w_A + cw_B]^2\ S(\vec{q}) + c(1-c)(w_A - w_B)^2\ S_{inc}(\vec{q}) \quad , \tag{1.34}$$

where

$$S(\vec{q}) = \int \frac{\beta\omega \, d\omega}{1-e^{-\beta\omega}} \int \frac{dt}{2\pi N} e^{-i\omega t} < \sum_{i,j} e^{-i\vec{q}.\vec{r}_i(o)} e^{i\vec{q}.\vec{r}_j(t)} > , \quad (1.35)$$

and

$$S_{inc}(\vec{q}) = \int \frac{\beta\omega \, d\omega}{1-e^{-\beta\omega}} \int \frac{dt}{2\pi N} e^{-i\omega t} < \sum_{i} e^{-i\vec{q}.\vec{r}_i(o)} e^{i\vec{q}.\vec{r}_i(t)} > . \quad (1.36)$$

Retaining only the terms linear in c, one gets

$$\gamma(\vec{q}) = [w_A^2 + 2cw_A(w_B - w_A)]S(\vec{q}) + c(w_A - w_B)^2 S_{inc}(\vec{q}). \quad (1.37)$$

Rearranging terms in(1.37) gives

$$\gamma(\vec{q}) = w_A^2 S(\vec{q}) + c(w_A - w_B)^2 S_{inc}(\vec{q}) + 2cw_A(w_B - w_A)S(\vec{q}) . \quad (1.38)$$

The first term in (1.38) is the (statistical average) square of the scattering amplitude due to host ion and is responsible for the ideal resistivity ρ_i of the host metal. The second term is due to the excess potential of the vibrating impurities. The third term is the interference between the two scattering amplitudes. The second and the third terms constitute the impurity resistivity of the alloy.

From (1.38), the only possibility of satisfying the first assumption for the validity of Matthiessen's rule is if somehow the three terms on the right hand side add up to give $\gamma_{host}(\vec{q})$ plus $\gamma_{imp}(\vec{q})$, this being evaluated for the rest position of the impurities. This can be expected if the thermal vibrations of the impurities give the same scattering as those of the host ions (Mott and Jones, 1936). If this condition is not satisfied, $\gamma_{\Delta}(\vec{q})$ defined by

$$\gamma_{\Delta}(\vec{q}) = \gamma_{alloy}(\vec{q}) - \gamma_{host}(\vec{q}) - \gamma_{imp}(\vec{q})$$

gives rise to deviations from Matthiessen's rule. The value of Δ corresponding to a given $\gamma_{\Delta}(\vec{q})$ can be obtained from

$$\Delta = D \int_0^2 \gamma_{\Delta}^{av}(x)\, x^3\, dx \quad ,$$

as in (1.32).

The Interference Term. Consider the relation (1.38) again. Writing $S_{inc}(\vec{q}) = 1 + \theta(\vec{q})$, one gets

$$\gamma(\vec{q}) = w_A^2\, S(\vec{q}) + c(w_A - w_B)^2 + 2w_A(w_B - w_A)c$$

$$S(\vec{q}) + c(w_A - w_B)^2\, \theta(\vec{q}) \quad . \qquad (1.39)$$

The second term in (1.39) is now the residual resitivity ρ_o of the alloy. One can verify that at high temperatures

$\beta\omega \ll 1$, $S_{inc}(\vec{q}) = 1$ and therefore $\theta(\vec{q}) = 0$. At low temperatures, $T \ll \theta_D$, $\theta(\vec{q})$ gives rise to a term in the resistivity (call it Δ_1) which is proportional to T^2 (Taylor, 1964) and can dominate over the contribution from the third term in (1.39) (call it Δ_2) which will be proportional to T^5 through $S(\vec{q})$. Koshino (1960) ascribed the deviations from Matthiessen's rule to a term similar to the last term in (1.39) but with $\theta(\vec{q})$ replaced essentially by $S(\vec{q})$ and thus he wrongly estimated its importance especially at high temperatures. The error in Koshino's work was pointed out by Taylor (1962).

For $T \gtrsim \theta_D$, the third term which is the interference term makes the dominant contribution Δ_2 to the deviations from Matthiessen's rule. This is

$$\Delta_2 \simeq D\, 2c \int_0^2 w_A(w_B - w_A) S_{av}(x) x^3 dx \ . \qquad (1.40)$$

For comparison

$$\rho_o \simeq Dc \int_0^2 (w_A - w_B)^2 x^3 \, dx \ .$$

Because of the presence of $S(\vec{q})$, Δ_2 has a temperature dependence similar to that of the ideal resistivity ρ_i, that is, T^5 at low temperatures and T at high temperatures. Further, because of the Umklapp collisions, $S_{av}(x)$ is

strongly peaked in the backward direction (x=2). For example, whereas $S_{av}(0) \simeq 10^{-2}$, $S_{av}(2) \simeq 0.4$ at 273°K for sodium (Greene and Kohn, 1963). Thus for $T \gtrsim \theta_D$, one expects from (1.40) that Δ_2/ρ_o will, in general, be of the order of a few percent or more and $\Delta_2 \propto T$, which is actually observed.

An interesting point about the expression (1.40) is the combination $w_A(w_B - w_A)$ in which the pseudopotential matrix elements w_A and w_B occur. This is in contrast to the expressions for Δ given by Koshino (1960), Taylor (1964) and Damon, Mathur and Klemens (1968)where w_A and w_B essentially occur in the combination $(w_A - w_B)^2$. A consequence of (1.40) is that Δ_2 can be of either sign. Note that because of the factor $S_{av}(x)x^3$, the sign of Δ_2 would largely depend on the sign of $w_A(w_B - w_A)$ in the neighbourhood of x=2. In other words, one could expect that in a complementary alloy pair, $d\Delta_2/dT$ should have opposite signs for the two alloys.

B. Effects due to Deformation of the Phonon Spectrum and Strain at the Impurity Potential. In the above discussion the thermal vibrations of the impurities were assumed to be similar to those of the host atoms. However because of the difference in the force constants and the masses of the host and the impurity atoms, this

assumption is not valid. Neglecting the effect due to force constants, and attributing the change in the phonon spectrum entirely to the mass difference, Kagan and Zhernov (1966) have studied the deviations from Matthiessen's rule. It is shown that in the low temperature range, electron scattering by an oscillating impurity atom leads to the appearance of a term proportional to T^2, interference between the scattering by an impurity ion and a deformed phonon spectrum to a term proportional to T^4 and scattering by a deformed phonon spectrum to a term proportional to T^5. For low impurity concentration, c, all these terms are proportional to c. The total effect is that in addition to Δ_1 and Δ_2 discussed above, the deformed phonon spectrum contributes a term Δ_3 to the deviations. The sign of this term is positive if $\Delta M(=M_B - M_A)$ is positive and negative if ΔM is negative. Further, Δ_3 depends on w_A and when $|\Delta M|/M_A \gg 1$, Δ_3 as a function of temperature passes through a maximum at a temperature $T < \hbar\omega^*/k_B$. ω^* corresponds to the frequency of the quasi-local mode associated with the impurity atom and is given by

$$\omega^* \simeq w_D \left[3\left|\frac{M_B - M_A}{M_A}\right|\right]^{-\frac{1}{2}} \quad . \tag{1.41}$$

Here w_D is the Debye frequency. For $T > \frac{1}{2} T^*$, Δ_3 is proportional to T while ρ_i is still proportional to T^5.

At high temperatures, for $T > \theta_D/2$, it is shown that all contributions to Δ vanish except the interference term Δ_2 which varies as T. Kagan and Zhernov have underestimated the contribution of the interference term because in their work, this term is taken essentially proportional to S(o) (neglect of Umklapp processes).

In addition to the deviations discussed above, Klemens and coworkers [Klemens (1963), Damon, Mathur and Klemens (1968)] have considered another contribution Δ_4 to the deviations. They assume that the perturbation Hamiltonian representing the interaction of conduction electrons with a vibrating impurity is expressed not in terms of the displacement of the impurity atom from its mean position (as considered by Koshino, 1960) but in terms of the change of form of the impurity potential owing to the strain of the surrounding lattice. This leads to an additional temperature-dependent electrical resistivity of the form

$$\Delta_4 = A\, \rho_o\, \langle \varepsilon^2 \rangle \quad , \tag{1.42}$$

where A is a numerical constant, ρ_o is the residual resistivity and $\langle \varepsilon^2 \rangle$ is the mean square thermal strain about the impurity and can be expressed as

$$\langle \varepsilon^2 \rangle = \frac{4E(T)}{Mv^2} \quad ,$$

E(T) being the thermal energy per atom, M the atomic mass and v the sound velocity. The component Δ_4 is expected to vary as T^4 at very low temperatures ($<20^{\circ}K$) and has been measured by them in gold alloys containing copper, platinum and indium as impurities.

We have now completed the discussion of deviations from Matthiessen's rule which arise due to the violation of the first assumption, or in other words, due to the difference between P and $P_o + P_1$. Let us call these deviations Δ_A. To summarize, the various contributions to Δ_A could be due to: (1) modification of the incoherent term by thermal vibrations, (2) interference between the impurity and the thermal scattering, (3) the deformation of the phonon spectrum and (4) strain at the impurity potential due to thermal vibrations. For small concentration of the impurity, all these contributions are proportional to c. As one can see, the situation at low temperature is quite complicated and it is difficult to sort out the various effects. Fortunately, at high temperatures the dominant contribution to Δ_A comes from Δ_2, the deviation due to the interference term. Therefore, it should be possible to make comparisons of the experimental results with quantitative estimates of this term and the

slope $d\Delta/dT$, the sign of which at high temperatures is of special interest in complementary alloy pairs.

1.3.2 Violation of the Second Assumption

Let us suppose that for the two scattering mechanisms in an alloy, we know the transition probabilities P_i and P_o and $P = P_i + P_o$. Then from the variational expression for resistivity (1.18), we have (Ziman, 1960)

$$\rho = \frac{\langle \phi, P_i \phi \rangle + \langle \phi, P_o \phi \rangle}{[\langle \phi, X \rangle]^2} \quad , \tag{1.43}$$

where ϕ is the exact solution of the Boltzmann equation for P. But, by the variational principle,

$$\frac{\langle \phi, P_i \phi \rangle}{[\langle \phi, X \rangle]^2} \geq \rho_i \quad ,$$

where ρ_i is the exact value when P_i is present alone, for ϕ is not necessarily a solution of the Boltzmann equation for P_i, and similarly for ρ_o. Therefore

$$\rho \geq \rho_i + \rho_o \quad .$$

The equality sign will hold only if $\phi = c_1\phi_i = c_2\phi_o$, where c_1 and c_2 are constants. This will be true only if unique times of relaxation can be defined for both the

mechanisms and if their ratio is independent of $\vec{k}$. In other words,

$$\frac{1}{\tau} = \frac{1}{\tau_i} + \frac{1}{\tau_o} \quad . \tag{1.44}$$

A. Kohler's Calculation of Δ. Kohler (1949) has calculated an upper limit to Δ by choosing a trial function for P of the form

$$\phi = \eta \ \phi_i + (1-\eta)\ \phi_o \ ,$$

where ϕ_i and ϕ_o are the exact solutions for P_i and P_o respectively and η is a variational parameter. Δ in this case is given by

$$\Delta = \frac{\beta\gamma\rho_o\rho_i}{\beta\rho_o+\gamma\rho_i} \quad . \tag{1.45}$$

This Δ which we can call Δ_B is the difference of the actual resistivities ρ_i and ρ_o from the resistivity calculated using the wrong distribution function ϕ. β and γ here are small positive constants. The nature of Δ given by (1.45) is quite complicated except only in the low-temperature limit where

$$\Delta \propto \rho_i \qquad \text{for} \quad \rho_o >> \rho_i \quad ,$$

and in the high-temperature limit where

$$\Delta \propto \rho_o \qquad \text{for} \quad \rho_i >> \rho_o \quad .$$

In general, it is difficult to make any quantitative estimates because nothing is known about the temperature and concentration dependence of parameters β and γ.

B. Two-Band Model. We have seen that Matthiessen's rule is exact if a single unique time of relaxation can be defined for each of the two mechanisms (phonons and impurities) at all parts of the Fermi surface. This would be true if the Fermi surface were spherical. But if the Fermi surface is not spherical or if it has regions in different Brillouin zones, then the time of relaxation will vary over the Fermi surface. The two-band model of Sondheimer and Wilson (1947) provides an example of such a case. We assume, for this model, that in each zone the Fermi surface forms a simply connected closed surface and there are no inter-zone transitions. In other words, each zone behaves independently of the other. Thus we have τ_1 and τ_2 for each zone and the two times will not, in general, be equal. The metal will thus behave like two independent conductors connected in parallel.

When a metal contains impurities, the relaxation time τ_1 of a single zone is made up of two parts:

$$\frac{1}{\tau_1} = \frac{1}{\tau_{i1}} + \frac{1}{\tau_{o1}} \quad ,$$

and similarly for τ_2. This means that Matthiessen's rule applies separately to each zone:

$$\rho_1 = \rho_{i1} + \rho_{o1} \quad ,$$

$$\rho_2 = \rho_{i2} + \rho_{o2} \quad .$$

However, when the total conductivity, which is the sum of the conductivities of the two zones, is evaluated, deviations from Matthiessen's rule will occur. Δ in this case is given by the expression

$$\Delta_{SW} = \frac{\rho_o \rho_i (\lambda-\mu)^2}{\mu\rho_o(1+\lambda)^2 + \lambda\rho_i(1+\mu)^2} \qquad (1.46)$$

where

$$\lambda = \frac{\sigma_{o1}}{\sigma_{o2}} = \frac{\rho_{o2}}{\rho_{o1}} \quad ,$$

and

$$\mu = \frac{\sigma_{i1}}{\sigma_{i2}} = \frac{\rho_{i2}}{\rho_{i1}} \quad .$$

Δ_{SW} is always positive and its temperature dependence comes from two factors. The first is through ρ_i and the second through the temperature dependence of μ. λ is expected to be fixed for a given impurity in a given host metal. If both λ and μ were independent of temperature, we would have Δ_{SW} similar to that of Kohler, that is,

$\Delta \propto \rho_i$ for $\rho_i << \rho_o$ and $\Delta \propto \rho_o$ for $\rho_i >> \rho_o$. It may be noted in (1.46) that $\Delta_{SW} \equiv 0$, if $\lambda = \mu$, or

$$\frac{\sigma_{o1}}{\sigma_{o2}} = \frac{\sigma_{i1}}{\sigma_{i2}} \quad ,$$

or in other words

$$\frac{\tau_{o1}}{\tau_{o2}} = \frac{\tau_{i1}}{\tau_{i2}} \quad .$$

Thus the ratio of the thermal scattering to the impurity scattering in the first zone must differ from the same ratio in the second zone if deviations from Matthiessen's rule are to occur from this model. Therefore another way of interpreting these deviations is in terms of the anisotropy of τ on the two parts of the Fermi surface.

According to Ziman (1961), the two different parts of the Fermi surface in copper, silver and gold could be identified with the neck and belly regions of the Fermi surface. If the two-band model is to be applied, then most of the scattering processes must have neck electrons in the neck region and the belly electrons in the belly region. The assumption that the two regions are inaccessible to each other is well satisfied for these metals. For such a case, it should be possible to get Δ_{SW} from the variational principle by splitting the integration over the Fermi surface into two parts. Thus

Δ_{SW} can be interpreted as a special case of the general expression (1.45) of Kohler.

It may be pointed out that if the various regions of the Fermi surface in a metal do have an access to each other, the anisotropy of τ will be less serious and therefore the deviations from Matthiessen's rule due to the two-band effect (or the multiband effect) will be very small. Therefore for metals where the Fermi surface is nearly spherical and the anisotropies are small enough, most of the deviations have their origin in the violation of the first assumption.

CHAPTER II

EXPERIMENTAL WORK

2.1 General

Measurement of deviations from Matthiessen's rule over a wide range of temperature involves problems which are not normally encountered in the usual resistivity measurements. Consider for instance the measurement of $\rho(T)$. Assuming that Matthiessen's rule is obeyed,

$$\rho(T) = \rho_o + \rho_i(T) \quad , \tag{2.1}$$

where the residual resistivity ρ_o can be defined as

$$\rho_o = \lim_{T \to 0} \rho(T) \quad ,$$

and the ideal resistivity ρ_i as

$$\rho_i(T) = \lim_{\rho_o \to 0} \rho(T) \quad .$$

The quantity usually measured is the resistance $R(T)=\rho(T)f$, where f is the geometrical shape factor. For a straight uniform wire, $f = \frac{\ell}{a}$, ℓ being the length between potential contacts and a the area of cross-section of the wire. f has the dimensions of L^{-1} and is therefore temperature-dependent. Equation (2.1) can be written as

$$\frac{\rho_i(T)}{\rho_i(273)} = \frac{\rho(T) - \rho_o}{\rho(273) - \rho_o} \quad ,$$

$$= \frac{R(T) - R_o}{R(273) - R_o} \quad ,$$

so that measuring the resistance only of a specimen over a range of temperatures including the ice point is sufficient to determine the normalized ideal resistivity $\rho_i(T)/\rho_i(273)$. If Matthiessen's rule is not obeyed, one has

$$\rho(T) = \rho_i(T) + \rho_o + \Delta(T) \quad , \tag{2.2}$$

where $\Delta(T)$ is the deviation term. The only "a priori" assumption we can make about $\Delta(T)$ is that $\Delta(0)=0$. One can expect $\Delta(T)$ to be small compared to $\rho_i(T)$ or ρ_o in order for Matthiessen's rule to have originated in the first place. The net result is that if $\Delta(T)$ is to be measured, the shape factor f must be determined accurately for the specimen and furthermore $R(T)$ and R_o must be measured accurately if even a modest accuracy is desired for Δ. It is because this small quantity is obtained simply as the difference of relatively large measured quantities. It may be emphasized that there is no way to avoid absolute resistivity measurements without making some further assumptions about Matthiessen's rule or the departures from it (Alley and Serin, 1959).

In the present investigations, resistivity measurements were made simultaneously on a pure specimen and a number of alloys. This ensured firstly that $\rho_i(T)$ could be obtained with an accuracy better than the published values for pure metals; secondly the measurements could be made with all specimens at the same temperature, the temperature itself being required to an accuracy commensurate with the final accuracy of Δ. Specimens were fabricated from alloys made from high purity metals. Considerable care was taken to ensure the homogeneity of the alloys and the uniformity of the cross-section of the wires. In order to appreciate how these requirements were met, the various equipment used and the experimental technique employed will now be discussed.

2.2 The Cryostat and Temperature Control

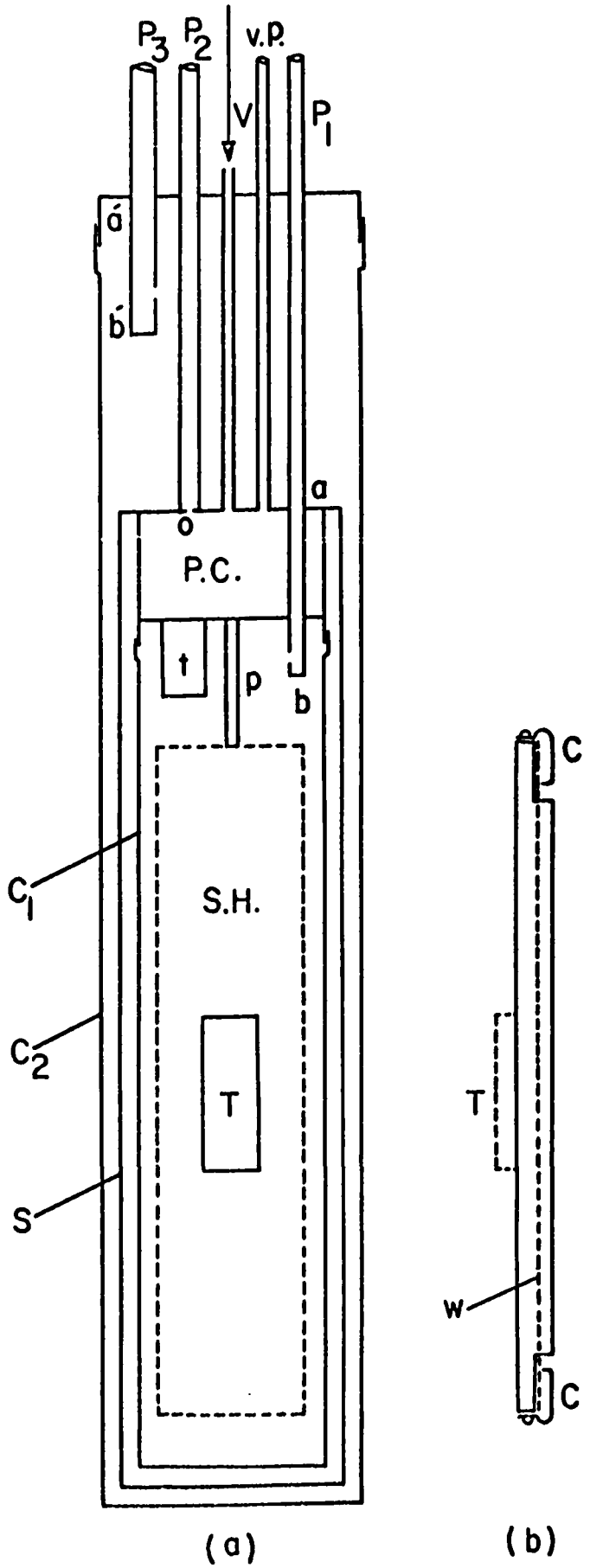
The temperature dependence of the resistivities was measured in a cryostat similar to the one described by White and Woods (1955) and White (1959). In this cryostat, which is shown in Figure 1(a), the specimens and the thermometers were enclosed in a copper vessel C_1, 11 in. long and 2½ in. in diameter. This vessel and the pumping chamber P.C. were entirely surrounded by a shield S kept at the same temperature as the vessel C_1. These were further mounted by stainless steel tubes in a copper vacuum enclosure C_2, 17 in. long and 3½ in. in diameter. This

Figure 1

(a) The Cryostat

(b) The Specimen Holder

P_1, P_2, P_3	Pumping tubes
V	Needle valve
v.p.	Vapor pressure line
a b, a'b'	Copper ends of the tubes
o	Orifice
P.C.	Pumping chamber
t	Post for thermal anchoring of leads
p	Post for mounting specimen holder
C_1, C_2	Inner and outer vessels
S	Shield
S.H.	Specimen holder
T	Thermometers
C	Potential clips
w	Wire specimen


P3
P2
v.p.
V
P1
á
b́
a
o
P.C.
t
p
b
C1
S.H.
C2
T
S
C
T
w
C
(a)
(b)

provided thermal isolation of the specimen chamber C_1 from the refrigerant bath. The specimens and the thermometers were kept at the same temperature through the use of helium exchange gas at a pressure of a few Torr. The electrical leads (40 B. & S. Formel insulated Cu wires) were brought in through the pumping tube P_1 and then thermally anchored to the copper post t. The portion a b of the tube P_1 was made of copper. The end b was closed with a copper cap which absorbed the heat radiation coming through P_1 and conducted it to the rest of the system. The specimen chamber was cooled below the temperature of the bath by pumping through P_2 over the refrigerant which could be let into the pumping chamber P.C. through the needle valve V.

Specimens, up to six at a time, were mounted on an $8\frac{3}{4}$ in. long, 2 in. wide and ½ in. thick 'Tufnol' holder. Tufnol was chosen because compared to other plastics it undergoes lesser contraction between room temperature and liquid helium temperatures. On the other hand compared to the metallic specimens used, it has slightly more contraction in this temperature range. Wire specimens about 0.5 mm or more in diameter were placed in ¼ in. deep channels slightly wider than the specimens and cut parallel to the length of the specimen holder. This prevented the wires from touching each other when there was relative contraction between the

specimens and the holder. The ends of the specimen holder were machined to half the thickness so that wires coming out of the channels could be placed under sharp potential clips. These clips were made from beryllium-copper shimstock and were attached to the holder with small screws [see Figure 1(b)]. Current clips were attached to the back of the specimen holder. The specimen holder could be attached to the post p in the cryostat.

As already mentioned, temperatures below those of the refrigerant bath were obtained by pumping over the liquid in the pumping chamber. The outer vessel C_2 was kept under a vacuum better than 10^{-6} Torr. The pressure in P.C. was controlled and maintained at a steady value by pumping through a manostat. The vapor pressure was measured with mercury and oil manometers connected to the pumping chamber.

Specimens were brought to the temperature of the bath by introducing exchange gas in the vessel C_2. Temperatures above those of the refrigerant bath were obtained by using an electronic temperature controller (Dauphinee and Woods, 1955) to heat the vessel C_1, with outer vessel C_2 again kept under vacuum. A Au + 2%Co:Cu thermocouple between vessels C_1 and C_2 provided a signal which was amplified and used to regulate the power fed to the heater attached to the specimen chamber. The

temperature could be controlled to a constancy of about $0.01^{\circ}K$ during the time required for measurements. This time was typically about 20 minutes, which was sufficient to take a set of readings on six specimens and the thermometer. The heater was a 1000-ohm I.R.C. ½ watt carbon resistor mounted in a copper sleave soldered to the top of the specimen chamber. All electrical leads coming in the vessel C_2 through P_3 were thermally anchored at the end a' b' which was made of copper.

For temperatures above $150^{\circ}K$, the power fed to the 1000-ohm heater was found to be insufficient to maintain the desired temperature. An additional heater, which was an 8 watt 1500-ohm wire-wound resistor was used. This resistor was mounted on a copper rod soldered to the top of the specimen chamber and was fed through a variac by a constant A.C. voltage derived from the mains. At these temperatures, it usually took 3 to 4 hours to reach a steady temperature. Baths of liquid helium, liquid nitrogen or liquid oxygen, dryice in ethyl alcohol, and ice water were used to cover the temperature range from $1.5^{\circ}K$ to $300^{\circ}K$.

2.3 Temperature Measurement

The temperature of the specimen chamber was measured in the range from $1.5^{\circ}K$ to $20^{\circ}K$ by a germanium thermometer. A platinum resistance thermometer was used from $20^{\circ}K$ to

300°K. The germanium thermometer was calibrated up to 5°K against He^4 vapor pressure using the 1958 scale of temperatures. From 5°K to 20°K, it was calibrated against another calibrated germanium resistor (guaranteed to ±0.1°K) obtained from Solitron, Inc. The platinum resistance thermometer supplied by Leeds and Northrup was calibrated from 20°K to 500°K by the National Research Council of Canada. These thermometers were inserted in wells drilled in a small copper block which could be attached to the back of the specimen holder. Silicone grease was used to improve thermal contact between the wells and the thermometers.

The resistance of the thermometers was measured by a D.C. resistance comparator. This instrument utilized an isolating potential comparator (Dauphinee, 1953) in which the potential difference across a pair of voltage terminals is transferred by a capacitor to another pair. If the potential differences across the terminal pairs are unequal, a small detectable charge transfer takes place. Resistance measurements are obtained by passing the same current through a known variable resistor and an unknown resistor (e.g. a thermometer); the two resistors are equal when equal voltages are developed across their potential terminals. The known

resistor in this case was a Guildline 9801T precision four-terminal variable resistor (see Rogers, 1968, for details of this comparator).

This comparator permitted display on a chart recorder of the variation of the thermometer resistance with time. Thus the temperature drifts in the specimen chamber could easily be monitored.

2.4 Resistance Measurement

A four-terminal 0.01 ohm standard resistor was connected in series with the specimens. The temperature of this resistor was monitored throughout the course of the run. A constant current of 20 or 50 milliamperes was maintained through the specimens. Self-heating was not noticeable for these currents. At very low temperatures when current more than 50 milliamperes was required for residual resistance measurements of the pure metal specimens, current through rest of the specimens could be interrupted in order to avoid heating them. Potentials were measured with a Guildline Type 9160 Potentiometer in conjunction with a Type 5214/9460 Photo-cell Galvanometer Amplifier and a Type 9461 A Galvanometer. To minimize thermal emfs, the current and the potential leads emerging from the tube P_1 were connected to copper binding posts attached (through a thin insulating layer) to a thick copper plate. These

were further connected to the binding posts on the potentiometer assembly by stranded copper wires. To eliminate the effect of thermal emfs in the leads, the potential was alternately measured for the standard resistance and the unknown resistance with normal and reversed currents and the mean of the two values of the unknown resistance thus determined was taken. Guildline thermal-free switches were used for potential selection and current reversal.

Since the potentiometer was linear to within 20 parts per million and since the null detection system could detect a change of 0.01 μ-volt, it was posssible to determine relative resistance to within ±0.005% or 1 μ-ohm whichever was greater.

2.5 Specimen Preparation

Silver, aluminum, and cadmium used for preparation of the specimens were obtained from the Consolidated Mining and Smelting Co. of Canada and had 59 grade purity. Magnesium used for alloying was obtained from Johnson, Matthey and Co. and was spectrographically standardized metal with impurities less than 14 parts per million. Magnesium-aluminum alloys and pure magnesium samples were prepared by Dow Chemical Co. from sublimed magnesium which was at least 99.98% pure even after fabrication.

2.5.1 Silver Specimens

A. Pure silver specimen. About 15 gm. of silver obtained in the form of pellets was briefly etched in dilute nitric acid, rinsed several times with distilled water and dried. It was then sealed in a clean, evacuated (~ 10^{-5} Torr) quartz tube of about ¼ in. inner diameter. This capsule was placed vertical in a furnace and its temperature raised to 1000°C in order to melt silver (melting point 961°C). On solidification, a small rod of silver was obtained. After the tube was broken, glass sticking to the surface of this rod at some places was removed by dissolving it in dilute hydrofluoric acid.

The silver rod was first rolled in steel rollers to reduce its cross-section so that it could be drawn through dies. After rolling, it was etched in dilute nitric acid to remove surface contamination. It was occasionally annealed with a hot air gun to remove some of the hardness acquired during cold work. In order to obtain a wire, it was drawn through steel dies till its diameter was about 1.5 mm. Cocoa butter was used as a lubricant and the surface of the wire was wiped with acetone after each draw. After every 3 or 4 draws through steel dies, the specimen was given brief etching in dilute nitric acid and annealed with a hot air gun. The 1.5 mm. diameter wire was further drawn through diamond dies to

get a wire of 0.5 mm. diameter. This wire was finally wiped with acetone and cut in pieces of the required length. The specimens drawn in this manner did not show any surface irregularities when examined carefully under a microscope. It may be pointed out that for drawing wires from other materials, procedure similar to the one outlined above was followed except that different etching reagents were used for different metals.

A tubular wire-wound furnace with a temperature controller was used for annealing the specimens. Straight specimens were placed in a quartz tube of about 1.5 in. diameter. This annealing tube could be evacuated or filled with an inert atmosphere. Pure silver specimens were annealed for 6 hours at 600°C in vacuum better than 10^{-5} Torr. The annealed specimens had a resistance ratio $R(293)/R(4.2) \approx 2000$. Higher temperatures and/or longer durations of annealing did not improve this ratio. Since this ratio is quite adequate for high purity silver, it was considered that the above procedure was suitable for contamination-free specimen preparation.

B. Silver-cadmium alloys. A master alloy containing 10% cadmium was first made. Weighed quantities of cleaned silver pellets and cadmium pellets were sealed in an evacuated quartz tube of about 3/8 in. diameter. Before use, the cadmium pellets were etched in dilute

hydrochloric acid, rinsed with distilled water and dried. The capsule containing the two metals was held at a temperature above the melting point of silver (M.P. of Cd is 321°C). The alloy was kept molten for over 20 minutes and continuously shaken to ensure complete mixing. The ingot thus obtained was cleaned and then sealed in another small evacuated quartz capsule. The alloy was remelted and kept molten for 12 hours and then left at 750-800°C for another 2 days to achieve further homogenization.

Pieces cut from this master alloy ingot were used for making dilute Ag-Cd alloys. Weighed amounts of the master alloy and pure silver were melted and homogenized in the same manner as described for the master alloy. The alloys obtained as rods were then drawn to wires. It was noticed that due to preferential evaporation, cadmium was lost from the specimens if annealing was done in vacuum under continuous pumping. To minimize the loss of cadmium, each Ag-Cd specimen was annealed separately in a sealed, close fitting and evacuated (~ 10^{-6} Torr) Pyrex tube. Annealing was done at 500°C for 12 hours.

C. Silver-magnesium alloys. A master alloy containing 10% magnesium was first prepared by melting together silver and magnesium (M.P. 650°C) in a sealed

quartz tube. The tube was evacuated and then filled with a low pressure (~ 10 Torr) of hydrogen before sealing. This gas would reduce any possible traces of magnesium oxide. Magnesium crystals were etched with very dilute hydrochloric acid before use. Dilute alloys were made from this master alloy.

Silver-magnesium specimens were annealed at 500°C for 12 hours in close-fitting sealed Pyrex tubes containing hydrogen (~ 10 Torr). It may be pointed out that a pure silver specimen annealed in similar manner in a hydrogen atmosphere showed no significant change in its resistance ratio R(293)/R(4.2), indicating that hydrogen at that low pressure did not dissolve in the silver lattice to any appreciable extent.

D. Silver-aluminum alloys. Since aluminum could pick up traces of silicon at high temperatures, these alloys were made in graphite instead of quartz. A small tube (3 in. long, ½ in. O.D. and ¼ in. I.D.) of graphite with graphite stoppers at both ends was machined from high purity material. This tube was outgassed at 1000°C. Weighed quantities of silver and aluminum (M.P. 660°C) were put in this tube and it was further sealed in an evacuated quartz tube. Aluminum pieces were first cleaned with potassium hydroxide solution in water and then with

dilute nitric acid. Dilute alloys were made by mixing a 10% master alloy with pure silver. The silver-aluminum alloys were very hard to draw, so they were annealed at 500°C in vacuum 3 or 4 times during the wire drawing process. The final specimens were annealed in vacuum at 550°C for 12 hours.

2.5.2 Aluminum Specimens

A. Pure aluminum specimen. A 3/16 in. diameter rod of aluminum was used for the preparation of specimens. A piece of this rod was cut, cleaned first with potassium hydroxide solution and then with dilute nitric acid. Wire of diameter 0.5 mm. was drawn from this piece. Pure aluminum wire specimens were annealed at 400°C for 12 hours. Annealing was carried out with specimens in Pyrex tubes placed in a vacuum $\sim 10^{-6}$ Torr. The annealed specimen had the resistance ratio $R(293)/R(4.2) \simeq 4000$. With this resistance ratio, it could be expected that the specimens did not pick up any traces of silicon during annealing at 400°C.

B. Aluminum-magnesium alloys. For these alloys, a 10% master alloy was first made. The two metals were put in a graphite tube 4 in. long and with a 3/8 in. inner diameter similar to the one described above (p.47). This graphite tube was further sealed in a quartz tube

containing hydrogen at a pressure of about 10 Torr. The metals were melted and the alloy kept molten at 700°C for over 24 hours. The molten alloy was shaken several times to ensure thorough mixing and homogenization. The molten alloy was rapidly cooled and the ingot obtained was washed with distilled water and dried. It was weighed and the loss in weight of the metals was attributed to the loss of magnesium which had deposited on the inside of the quartz tube. The magnesium content in the master alloy was then corrected for this loss.

Dilute aluminum-magnesium alloys were made from this master alloy. Wire samples drawn from these alloys were annealed separately in close-fitting sealed Pyrex tubes containing hydrogen at a pressure of about 10 Torr. Annealing was carried out at 400°C for 12 hours.

C. Aluminum-silver alloys. Two very dilute aluminum-silver alloys were prepared from a master alloy containing 1% silver. The alloys were made in a graphite tube sealed in an evacuated quartz tube. The wire samples were annealed at 400°C for 12 hours in vacuum.

2.5.3 Cadmium Specimens

A. Pure cadmium specimen. Cadmium pellets were washed with dilute hydrochloric acid, rinsed with distilled

water and dried. These were then sealed in an evacuated Pyrex tube 4 in. long and ¼ in. in diameter. This tube was placed in a vertical position in a furnace and the cadmium was melted. The molten metal was rapidly cooled and the glass tube was broken away from the cadmium rod. A wire specimen of about 0.8 mm diameter was drawn from this rod. The specimen when annealed in an evacuated tube at 125°C for 12 hours gave the resistance ratio $R(293)/R(4.2) \simeq 1.35 \times 10^{4}$.

B. Cadmium-silver alloys. A master alloy containing 5% silver was first prepared by melting together weighed quantities of metals in a sealed and evacuated quartz capsule of about 3/8 in. diameter. It was noticed that molten cadmium readily dissolved silver. The alloy was kept molten for two days and shaken several times to ensure complete mixing. Dilute alloys were prepared using this master alloy and melting the metals in evacuated sealed Pyrex tubes 3 in. long and 3/8 in. diameter. The alloy ingots were remelted in vacuum and poured into Pyrex tubes of about ¼ in. diameter to obtain rods. Wires of diameter 0.7 mm were drawn from these rods. The specimens were annealed in sealed evacuated close-fitting Pyrex tubes for 12 hours at 125°C.

C. Cadmium-magnesium alloys. Dilute cadmium-magnesium alloys were made from a master alloy containing 10% magnesium. The alloys were prepared in sealed Pyrex tubes containing hydrogen at a pressure of about 10 Torr. The alloy ingots were remelted to obtain rods and wires were drawn. The specimens were annealed for 12 hours at 125°C in evacuated sealed close-fitting Pyrex tubes.

2.5.4 Magnesium Specimens

A pure magnesium specimen and the magnesium-aluminum alloys were prepared by Dow Chemical Company. These specimens were supplied as extruded wires of about 0.035 in. diameter. These wires did not have a very uniform cross-section. Therefore, pieces of wire with nearly uniform cross-section were selected and then carefully drawn through a 0.032 in. diamond die. Uniform smooth wires adequate for our purpose were thus obtained from the extruded samples.

Each specimen was annealed separately at 350°C for 8 hours in a hydrogen atmosphere. Annealing in vacuum and/or at temperatures higher than 400°C resulted in evaporation of magnesium from the surface of specimens with consequent loss in homogeneity. Annealed pure magnesium gave the resistance ratio $R(293)/R(4.2) \simeq 700$.

2.5.5 Specimen Analysis

For the purpose of the investigations reported in this thesis, specimens with impurity concentration from 0.1 atomic percent to 2 atomic percent were prepared. During the specimen preparation, considerable care was taken to ensure that the alloys ended up as homogeneous solid solutions with the desired nominal impurity content. Inspite of the various precautions, it was not possible to avoid preferential evaporation and consequent loss of one of the constituents during melting and annealing of the specimens.

The best indication of the impurity concentration in an alloy is through residual resistivity. In this regard, Ag-Al, Al-Ag, Cd-Mg and Cd-Ag alloys presented no difficulty. The residual resistivity values for each specimen of these alloy systems were found to be proportional to the solute concentration and also agreed with the values published in the literature. For the Mg-Al specimens which were prepared by Dow Chemical Company, spectrographic analyses were provided and the solute concentrations agreed with the residual resistivity measurements.

In case of Ag-Cd, Ag-Mg, and Al-Mg alloys, preferential evaporation of the solute was expected. For

these alloys, chemical analyses were obtained. The results of these analyses were found to be in agreement with residual resistivity values (and the published values)for 1 or 2 at.% solute content. For lower concentrations, the uncertainty in the chemical analyses was expected to be large. For these alloys, their solute content was determined from their residual resistivity values by comparison with values for higher concentrations.

In addition to the above analyses, X-ray micro-analysis with an electron probe was performed* on all the specimens (except Cd-Ag and Cd-Mg alloys). The results obtained from this technique were not adequate for the determination of absolute concentrations of the solute when present in small quantities but they did provide a good idea of the relative concentrations and the homogeneity of the specimens. The analysis was carried out at various positions along the length of each specimen. It was noticed that in case of concentrated alloys (1 or 2% solute) the deviation of the solute concentration from the average was never more than 10% and more typically appeared to be 5%.

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* The author is grateful to Dr. R.H. Packwood of the Department of Energy, Mines and Resources, Ottawa for performing these analyses.

As mentioned in the beginning of this chapter, the geometrical shape factors of the specimens must be known accurately in order to determine absolute resistivities. This factor for each specimen was determined by weighing a measured length of the wire. The mass in conjunction with the length and density of the alloy determined a mean value of its cross-sectional area. By measuring accurately the resistance per unit length along the length of a pure metal wire, it was shown (Seth, 1967) that the deviations from the average were sufficiently small and no appreciable error was introduced in assuming the drawn wires to be uniform in cross-section.

2.6 Experimental Procedure - A Typical Run

Specimens were mounted on the specimen holder and the potential and the current clips were attached. Potential clips were sharp knife edges resting perpendicularly to the length of the wires and were attached carefully so as not to damage the wires. Electrical leads were then connected to the clips and the thermometers. Finally the vessels C_1 and C_2 were soldered and vacuum tested.

Small changes in the resistivity of the specimens on thermal cycling are not uncommon (White, 1959). Since

this effect is not commulative with additional cycling, specimens were thermally cycled twice between room temperature and 77°K before detailed resistance measurements were made.

After thermal cycling, the cryostat was cooled to 4.2°K and below and measurements made in this range. The temperature was then gradually raised using different refrigerants and the measurements continued up to room temperature.

On completion of the run, the specimen holder was taken out of the cryostat and the potential clips carefully removed. The distance ℓ between the marks left on the wire by the potential clips was measured with a cathetometer with a precision of 0.01 mm. The ends of each specimen were cut and the mass per unit length m/ℓ' determined. Weighing was done on a microbalance. The cross-sectional areas were calculated from m/ℓ' and the density of the alloy, accurate alloy densities being obtained from the crystallographic data available in Pearson (1958, 1967).

CHAPTER III

EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Analysis of Results

3.1.1 Data Analysis and Gauge Correction

The deviations from Matthiessen's rule have been defined earlier by the expression

$$\Delta(T) = \rho(T) - \rho_i(T) - \rho_o \ , \qquad (3.1)$$

where $\rho(T)$ is the resistivity of the dilute alloy at temperature T, ρ_o is its residual resistivity measured at very low temperatures and extrapolated to 0^oK. $\rho_i(T)$ is the ideal resistivity measured at temperature T on a pure specimen of the parent metal, the alloy of which is under consideration. If we designate the pure and the alloy samples by subscripts P and A respectively, one can rewrite (3.1) as

$$\Delta(T) = [\rho_A(T) - \rho_A(0)] - [\rho_P(T) - \rho_P(0)] \ , \qquad (3.2)$$

where $\rho(T)$ and ρ_o have been replaced by $\rho_A(T)$ and $\rho_A(0)$ respectively and $\rho_i(T)$ has been replaced by $\rho_P(T) - \rho_P(0)$. We have assumed here that deviations from Matthiessen's rule in very pure metal are extremely small and this is permissible provided $\rho_P(0) \ll \rho_A(0)$.

The resistance-temperature data obtained from the experiments are, in practice, converted to resistivity data using the room-temperature ($293^{o}K$) values for the geometrical shape factor $f = \ell/a$. Thus the measured deviations usually are

$$\Delta(T)\ \text{measured} = [R_A(T) - R_A(0)](\frac{a}{\ell})_A^{293} - [R_P(T) - R_P(0)]\ (\frac{a}{\ell})_P^{293} \quad . \tag{3.3}$$

Since f is temperature-dependent, the measured deviations should be corrected by adding to them the gauge correction $\delta\Delta^{f}_{Th.Ex.}$ which is

$$\delta\Delta^{f}_{Th.Ex.} = ([\rho_A(0) - \rho_P(0)]\alpha(0) - [\rho_A(T) - \rho_P(T)]\alpha(T)) \times 10^{-5} \quad , \tag{3.4}$$

$$\simeq \rho_A(0)[\alpha(0) - \alpha(T)] \times 10^{-5}$$

assuming Matthiessen's rule to be valid. The ρ's in expression (3.4) are the measured values calculated with f(293) and the α's are the expansion coefficients for the pure metals. $\alpha(T)$ is defined by the expression

$$\alpha(T) = \frac{L_{293} - L_T}{L_{293}} \times 10^{5} \quad , \tag{3.5}$$

and its values from $0^{o}K$ to $300^{o}K$ for various solids have

been tabulated by Corruccini and Gniewek (1961). It may be pointed out that since data on alloys are not available, $\alpha(T)$ values for dilute alloys in the expression (3.4) have been assumed to be equal to those for the pure metals.

A typical value for the gauge correction at ice point for Ag + 1.43 at.% Cd alloy is 4.8% of the uncorrected deviation from Matthiessen's rule at that temperature.

3.1.2 Accuracy of Results

The room-temperature values of the absolute resistivity have been measured with an accuracy better than one part in a thousand, the major source of error being the uncertainty in the ℓ/a measurement. At low temperatures, the residual resistance measurements on pure metal specimens were accurate to better than 1%. However, for dilute alloys, the residual resistance could be determined with an accuracy much better than that for the pure metal specimens. According to Alley and Serin (1959), any error in the measurement of the geometrical shape factor f appears as an error in Δ proportional to ρ_i. If the error in f_A is df_A and similarly the error in f_P is

df_p, then the fractional error in Δ is

$$\frac{d\Delta}{\Delta} = \frac{df_A}{f_A} + \frac{\rho_i}{\Delta}\left[\frac{df_A}{f_a} - \frac{df_P}{f_P}\right] \quad . \tag{3.6}$$

Since at high temperatures, $\rho_i >> \Delta$, the error introduced in Δ could indeed be very large. However, since at high temperatures ρ_i is a linear function of temperature and Δ is also expected to vary linearly with temperature, this error should not give a spurious temperature dependence to the deviations.

3.1.3 Corrections due to Change in the Atomic Volume

It has been pointed out by Dugdale and Basinski (1967) (see also Schwerer et al., 1969) that in order to relate deviations from Matthiessen's rule to the scattering processes, the various resistivities $\rho_A(T)$, $\rho_A(0)$, and $\rho_i(T)$ should be compared at the same atomic volume. This means that $\rho_i(T)$ should be corrected for a fixed change in atomic volume at all temperatures, this change in volume being produced by alloying. On the other hand, $\rho_A(0)$ should be corrected for change due to thermal expansion of the atomic volume as the temperature is raised. The resistivity of a dilute alloy at temperature T and having an atomic volume V is

$$\rho(T,V) = \rho_i(T,V) + \rho(0,V) + \Delta(T,V) \quad . \tag{3.7}$$

The ideal resistivity $\rho_i(T,V)$ differs from the resistivity of the pure metal $\rho_i(T,V')$ where V' has changed to V on alloying. Therefore, according to Dugdale and Basinski (1967), $\rho_i(T,V)$ can be written as

$$\rho_i(T,V) = \rho_i(T,V') + \rho_i(T,V') \frac{d\ln \rho_i}{d\ln V} \left(\frac{\delta V}{V}\right)_A , \quad (3.8)$$

where $\left(\frac{\delta V}{V}\right)_A$ is the relative change in the atomic volume on alloying. Similarly

$$\rho(0,V(T)) = \rho(0,V(0)) + \rho(0,V(0)) \frac{d\ln \rho_o}{d\ln V} \left(\frac{\delta V}{V(0)}\right)_{Th.} \quad (3.9)$$

where $\left(\frac{\delta V}{V(0)}\right)_{Th.}$ is the relative change in volume due to thermal expansion. Taking into account these corrections, the measured deviations (after gauge correction) should be further corrected by subtracting from them $\delta\Delta_A$ and $\delta\Delta_{Th.}$ which are given by

$$\delta\Delta_A = \rho_i(T,V') \frac{d\ln \rho_i}{d\ln V} \left(\frac{\delta V}{V}\right)_A , \quad (3.10)$$

and

$$\delta\Delta_{Th.} = \rho(0,V(0)) \frac{d\ln \rho_o}{d\ln V} \left(\frac{\delta V}{V(0)}\right)_{Th.} . \quad (3.11)$$

In order to calculate these corrections, one needs data on $\frac{d\ln \rho_i}{d\ln V}$, $\frac{d\ln \rho_o}{d\ln V}$, $\left(\frac{\delta V}{V}\right)_A$, and $\left(\frac{\delta V}{V(0)}\right)_{Th.}$ Data on $\left(\frac{\delta V}{V}\right)_A$ can be obtained from Pearson (1958, 1967). The

relative change in the lattice parameters on alloying is given in Table 1. $(\frac{\delta V}{V(0)})_{Th.}$ which is equal to $3(\frac{\alpha(0)-\alpha(T)}{10^5-\alpha(0)})$ can be calculated from $\alpha(T)$ values compiled by Corruccini and Gniewek (1961). Data on $\frac{d\ln \rho_i}{d\ln V}$ are available in Bridgman (1964). For Ag, Al, Cd, and Mg these values are 3.9, 3.5, 3.6, and 2.0 respectively. In Calculating $\delta\Delta_A$ it is assumed that $\frac{d\ln \rho_i}{d\ln V}$ is independent of temperature which of course is not strictly true (Dugdale and Gugan, 1957). Unfortunately, no precise data on the measurement of $\frac{d\ln \rho_o}{d\ln V}$ are available in the literature. Linde (1939) has suggested that the pressure coefficient of resistivity increase per atomic percent on alloying, i.e.

$$\frac{1}{\delta\rho}\frac{\partial(\delta\rho)}{\partial p} \quad \text{where} \quad \delta\rho = \rho_A - \rho_P \ ,$$

can be found from room-temperature values of $\frac{\partial \rho}{\partial P}$ versus concentration curves. Using compressibility values for pure metals, one could estimate $\frac{d\ln \rho_o}{d\ln V}$. However, such a procedure is not free from criticism as the measurements are made at room temperature and not at $4.2^{o}K$. Linde (1939) reported measurements of $\frac{1}{\delta\rho}\frac{\partial(\delta\rho)}{\partial p}$ on a number of dilute alloys of Cu, Ag, and Au (see Gerritsen, 1956). Room-temperature data on pressure coefficient of resistance of some dilute alloys are also available in Bridgman (1964)

and these could be used for estimating $\frac{d\ln \rho_o}{d\ln V}$ following Linde's method. Some preliminary results from actual low temperature measurements of $\frac{d\ln \rho_o}{d\ln V}$ on dilute alloys of noble metals have been reported by Dugdale (1965).

Although the necessity for applying corrections resulting from the changes in atomic volume is recognized, these corrections have not been incorporated in the results on deviations from Matthiessen's rule reported here. This has been done because of the following reasons:

According to Dugdale and Basinski (1967), the change in the ideal resistivity due to change in atomic volume on alloying is correlated to the change in the resistivity due to the application of pressure. This results in a large correction to the deviations from Matthiessen's rule. From the theoretical point of view, the observed variation of the electrical resistivity of metals with pressure is not completely understood. One has to know the effect of pressure on different parameters such as pseudopotentials, lattice spectrum, and the Fermi surface before any quantitative or even semi-quantitative interpretation of the resistivity change can be made. With the present limited understanding, one should be cautious in using the expression (3.10) for correlating entirely two different effects which happen to produce a change in the atomic volume. The addition of impurity in

a lattice is a localized effect whereas the application of pressure produces an overall change in the lattice. A correction such as (3.10) is certainly an over-estimation. Therefore, for want of better understanding of this effect, it was decided not to apply this correction to the results. Moreover it is felt that such a correction should come in any theoretical calculation of the deviations from Matthiessen's rule.

The correction to residual resistivity involves a correlation of the change in atomic volume due to thermal expansion to $\frac{d\ln \rho_o}{d\ln V}$, the relative residual resistivity change with volume on application of pressure. For the specimens we studied, information on $\frac{d\ln \rho_o}{d\ln V}$ is available only on three alloys, Ag-Cd, Ag-Mg, and Al-Mg.

For Ag-Cd alloys, Dugdale (1965) has quoted a value for $\frac{d\ln \rho_o}{d\ln V} = 1.0$. Using Linde's method, $\frac{d\ln \rho_o}{d\ln V}$ calculated from room-temperature data of Bridgman (1964, paper 197) on Ag + 1.3 % Cd alloy turns out to be ~2.1. Bridgman's data are not very reliable as $(\rho_A - \rho_P)$ for his Ag-Cd alloy does not agree with the value quoted in the literature. Therefore Dugdale's result could be more acceptable.

For Ag-Mg alloy, $\frac{1}{\delta\rho}\frac{\partial(\delta\rho)}{\partial p} = +1.7 \times 10^{-10}$ m^2/kg according to Linde's measurement on one alloy. Using $-\frac{dV}{V} = 4.73 \times 10^{-3}$ for $p = 5 \times 10^3$ kg/cm^2 from Bridgman

(1964, paper 197), $\frac{d\ln \rho_o}{d\ln V}$ turns out to be ≃ -1.8. Following Linde's procedure, $\frac{d\ln \rho_o}{d\ln V}$ calculated from room-temperature data of Bridgman (1964, paper 197) on Ag + 3.08 % Mg alloy has a value ≃ 0.4 which is in disagreement with the value -1.8 calculated from Linde's data.

For Al-Mg alloys, calculations made from room-temperature data of Bridgman (1964, paper 196) on six alloys (with concentration up to 14.3%) and using Linde's method give $\frac{d\ln \rho_o}{d\ln V} \simeq 1$. No other measurements are available to permit any comparison.

As can be seen, the $\frac{d\ln \rho_o}{d\ln V}$ values given above are conflicting and therefore not very reliable. Moreover, we are interested in making a comparison on complementary alloys and the information on other alloys is lacking. Therefore it was decided to omit this correction to the results for want of better and complete information.

3.1.4 Presentation of Data

On the following pages the data are presented for the electrical resistivity of the alloys and the deviations from Matthiessen's rule. Some additional relevant information on alloys and the ideal resistivities of pure Ag, Al, Cd, and Mg are also tabulated. For the purpose of comparison, residual resistivity per atomic percent of the alloys

is presented in a separate table (Table 6) along with similar measurements reported in the literature. All data on resistivity (except the one taken from the literature) presented in this thesis have been calculated with the room-temperature values of the geometrical shape factor, whereas, the data and graphs on deviations have been corrected for the thermal expansion of the shape factor.

Table 1

Change in Lattice Parameters on 1 at.% alloying and $(M_A - M_B)/M_A$ for Alloys †

Alloy	Relative change * ($\delta a/a$, $\delta c/c$) in Lattice Parameters	$(M_A-M_B)/M_A$
Ag-Cd	3.4×10^{-4}	-4.2×10^{-2}
Ag-Mg	1.3×10^{-4}	7.7×10^{-1}
Ag-Al	-2.9×10^{-4}	7.5×10^{-1}
Al-Mg	9.4×10^{-4}	9.9×10^{-2}
Al-Ag	1.4×10^{-4}	-3.0
Cd-Ag	8.7×10^{-4} in a -5.2×10^{-3} in c	4.0×10^{-2}
Cd-Mg	7.3×10^{-4} in a -1.9×10^{-3} in c	7.8×10^{-1}
Mg-Ag	-1.7×10^{-3} in a -1.9×10^{-3} in c	-3.4
Mg-Al	-1.2×10^{-3} in a -1.1×10^{-3} in c	-1.1×10^{-1}
Mg-Cd	-7.1×10^{-4} in a -6.1×10^{-4} in c	-3.6

† M_A and M_B are respectively the masses of the host and the impurity atoms in an alloy.

* Source of data is Pearson (1958, 1967).

Tables 2a

ρ_A and Δ in $\mu\Omega$-cm as a function of Temperature (^oK) for Ag-Cd Alloys

Ag-Cd 1 (Ag + 0.04 at.% Cd)

$\rho_A(0) = 0.0119\ \mu\Omega$-cm

$\ell/a\ (20^oc) = 10044.4\ cm^{-1}$

Temp.	Ag-Cd 1 ρ_A	Ag-Cd 1 Δ^*	Temp.	Ag-Cd 1 ρ_A	Ag-Cd 1 Δ^*
9.7	0.0121	-	89.84	0.3678	0.0031
15.0	0.0134	0.0005	100.76	0.4380	0.0033
21.30	0.0175	0.0013	114.40	0.5244	0.0037
26.28	0.0247	0.0021	131.54	0.6314	0.0042
30.61	0.0345	0.0025	145.81	0.7194	0.0046
35.42	0.0495	0.0028	161.01	0.8124	0.0050
41.36	0.0737	0.0028	176.10	0.9041	0.0054
45.98	0.0961	0.0028	194.59	1.0156	0.0057
51.81	0.1279	0.0028	195.13	1.0190	0.0059
56.90	0.1577	0.0028	215.27	1.1399	0.0065
63.52	0.1985	0.0027	234.80	1.2570	0.0070
69.91	0.2390	0.0027	254.42	1.3749	0.0077
76.79	0.2833	0.0028	272.90	1.4857	0.0081
82.62	0.3210	0.0029	291.54	1.5980	0.0087

* ρ_i corresponds to Ag 2.

Tables 2a (continued)

Ag-Cd 2(Ag + 0.48 at.% Cd)

$\rho_A(0)$ = 0.1605 μΩ-cm

ℓ/a (20°c) = 9828.3 cm^{-1}

Ag-Cd 3(Ag + 1.43 at.% Cd)

$\rho_A(0)$ = 0.4761 μΩ-cm

ℓ/a (20°c) = 9843.3 cm^{-1}

Temp.	Ag-Cd 2		Ag-Cd 3	
	ρ_A	$\Delta\dagger$	ρ_A	$\Delta\dagger$
10.3	0.1607	-	0.4764	-
12.0	0.1612	0.0003	0.4769	0.0004
14.2	0.1621	0.0007	0.4778	0.0008
16.0	0.1631	0.0012	0.4789	0.0014
18.0	0.1646	0.0018	0.4807	0.0023
20.05	0.1663	0.0025	0.4827	0.0033
22.77	0.1702	0.0038	0.4872	0.0053
26.11	0.1768	0.0058	0.4947	0.0081
29.89	0.1867	0.0078	0.5059	0.0114
35.14	0.2047	0.0101	0.5256	0.0155
39.67	0.2235	0.0113	0.5459	0.0181
47.91	0.2642	0.0118	0.5887	0.0208
57.16	0.3167	0.0111	0.6428	0.0216
67.03	0.3772	0.0100	0.7043	0.0216

† ρ_i corresponds to Ag 1.

Tables 2a (continued)

Temp.	Ag-Cd 2		Ag-Cd 3	
	ρ_A	Δ	ρ_A	Δ
76.87	0.4395	0.0091	0.7671	0/0212
89.81	0.5224	0.0083	0.8505	0.0210
101.62	0.5977	0.0079	0.9264	0.0212
115.62	0.6859	0.0076	1.0154	0.0218
130.54	0.7789	0.0076	1.1092	0.0227
145.90	0.8737	0.0078	1.2051	0.0241
161.07	0.9664	0.0081	1.2989	0.0256
176.12	1.0578	0.0083	1.3915	0.0271
193.96	1.1656	0.0088	1.5007	0.0291
213.91	1.2859	0.0095	1.6226	0.0314
233.26	1.4021	0.0101	1.7405	0.0338
252.47	1.5176	0.0107	1.8576	0.0361
272.66	1.6393	0.0115	1.9809	0.0387
292.35	1.7580	0.0121	2.1013	0.0410

Table 2b

ρ_A and Δ in $\mu\Omega$-cm as a function of Temperature (^oK) for Ag-Mg Alloys

Ag-Mg 1 (Ag + 0.07 at.% Mg)

$\rho_A(0) = 0.0328$ $\mu\Omega$-cm

$\ell/a(20^oc) = 9744.9$ cm^{-1}

Ag-Mg 2 (Ag + 1.09 at.% Mg)

$\rho_A(0) = 0.5399$ $\mu\Omega$-cm

$\ell/a(20^oc) = 9787.9$ cm^{-1}

Ag-Mg 3 (Ag + 1.61 at.% Mg)

$\rho_A(0) = 0.7949$ $\mu\Omega$-cm

$\ell/a(20^oc) = 9952.3$ cm^{-1}

Temp.	Ag-Mg 1		Ag-Mg 2		Ag-Mg 3	
	ρ_A	Δ^*	ρ_A	Δ^*	ρ_A	Δ^*
10.3	0.0333	0.0003	0.5404	0.0002	0.7955	0.0003
12.0	0.0339	0.0007	0.5406	0.0003	0.7962	0.0008
14.2	0.0351	0.0014	0.5418	0.0010	0.7971	0.0013
16.0	0.0365	0.0022	0.5431	0.0017	0.7985	0.0021
18.0	0.0385	0.0034	0.5449	0.0027	0.8005	0.0033
20.05	0.0406	0.0044	0.5470	0.0038	0.8026	0.0043

* ρ_i corresponds to Ag 1.

Table 2b (continued)

Temp.	Ag-Mg 1		Ag-Mg 2		Ag-Mg 3	
	ρ_A	Δ	ρ_A	Δ	ρ_A	Δ
22.77	0.0453	0.0067	0.5517	0.0059	0.8075	0.0067
26.11	0.0531	0.0098	0.5594	0.0090	0.8156	0.0101
29.89	0.0645	0.0133	0.5708	0.0125	0.8275	0.0141
35.14	0.0845	0.0176	0.5909	0.0169	0.8481	0.0191
39.67	0.1050	0.0204	0.6114	0.0197	0.8693	0.0226
47.91	0.1484	0.0236	0.6545	0.0227	0.9131	0.0263
57.16	0.2033	0.0253	0.7087	0.0237	0.9678	0.0278
67.03	0.2657	0.0262	0.7701	0.0235	1.0294	0.0279
76.87	0.3294	0.0266	0.8327	0.0230	1.0923	0.0276
89.81	0.4135	0.0269	0.9157	0.0223	1.1754	0.0272
101.62	0.4894	0.0272	0.9909	0.0219	1.2508	0.0270
115.62	0.5781	0.0274	1.0792	0.0219	1.3391	0.0269
130.54	0.6713	0.0276	1.1722	0.0220	1.4322	0.0272
145.90	0.7662	0.0277	1.2672	0.0224	1.5273	0.0279
161.07	0.8588	0.0280	1.3602	0.0231	1.6204	0.0287
176.12	0.9500	0.0280	1.4518	0.0237	1.7121	0.0294
193.96	1.0575	0.0282	1.5600	0.0246	1.8204	0.0306
213.91	1.1775	0.0283	1.6807	0.0257	1.9413	0.0320
233.26	1.2934	0.0286	1.7972	0.0268	2.0580	0.0334
252.47	1.4084	0.0287	1.9132	0.0280	2.1741	0.0348
272.66	1.5295	0.0289	2.0350	0.0291	2.2963	0.0364
292.35	1.6480	0.0293	2.1542	0.0304	2.4156	0.0378

Table 2c

ρ_A and Δ in $\mu\Omega$-cm as a function of Temperature (^oK) for Ag-Al Alloys

Ag-Al 1 (Ag + 0.10 at.% Al)

$\rho_A(0) = 0.1836$ $\mu\Omega$-cm

$\ell/a(20^oc) = 9740.0$ cm^{-1}

Ag-Al 2 (Ag + 0.88 at.% Al)

$\rho_A(0) = 1.6199$ $\mu\Omega$-cm

$\ell/a(20^oc) = 9817.4$ cm^{-1}

Ag-Al 3 (Ag + 1.93 at.% Al)

$\rho_A(0) = 3.5778$ $\mu\Omega$-cm

$\ell/a(20^oc) = 9820.8$ cm^{-1}

Temp.	Ag-Al 1		Ag-Al 2		Ag-Al 3	
	ρ_A	Δ^*	ρ_A	Δ^*	ρ_A	Δ^*
9.7	0.1840	0.0002	1.6202	0.0001	3.5779	0.0001
15.0	0.1868	0.0021	1.6224	0.0015	3.5806	0.0017
21.30	0.1951	0.0073	1.6306	0.0064	3.5886	0.0065
26.28	0.2087	0.0143	1.6417	0.0110	3.6016	0.0131
30.61	0.2243	0.0206	1.6560	0.0161	3.6173	0.0195
35.42	0.2458	0.0273	1.6764	0.0217	3.6390	0.0265
41.36	0.2766	0.0339	1.7060	0.0272	3.6706	0.0340

* ρ_i corresponds to Ag 2.

Table 2c (continued)

Temp.	Ag-Al 1		Ag-Al 2		Ag-Al 3	
	ρ_A	Δ	ρ_A	Δ	ρ_A	Δ
45.98	0.3028	0.0376	1.7317	0.0305	3.6975	0.0386
51.81	0.3379	0.0410	1.7664	0.0335	3.7339	0.0433
56.90	0.3698	0.0431	1.7985	0.0358	3.7690	0.0488
63.52	0.4123	0.0447	1.8411	0.0376	3.8122	0.0513
69.91	0.4540	0.0458	1.8832	0.0393	3.8566	0.0554
76.79	0.4991	0.0468	1.9299	0.0419	3.9048	0.0597
82.62	0.5372	0.0473	1.9681	0.0426	3.9456	0.0632
89.82	0.5844	0.0479	2.0160	0.0441	3.9959	0.0672
100.76	0.6552	0.0487	2.0888	0.0472	4.0724	0.0743
114.40	0.7420	0.0496	2.1781	0.0509	4.1666	0.0832
131.54	0.8495	0.0505	2.2896	0.0561	4.2832	0.0942
145.81	0.9377	0.0513	2.3814	0.0608	4.3799	0.1041
161.01	1.0309	0.0520	2.4785	0.0657	4.4820	0.1146
176.10	1.1229	0.0527	2.5743	0.0706	4.5826	0.1248
194.59	1.2347	0.0534	2.6912	0.0768	4.7057	0.1379
195.13	1.2381	0.0535	2.6947	0.0770	4.7091	0.1380
215.27	1.3592	0.0544	2.8209	0.0836	4.8419	0.1518
234.80	1.4765	0.0552	2.9436	0.0903	4.9705	0.1652
254.42	1.5944	0.0560	3.0666	0.0967	5.0998	0.1786
272.90	1.7053	0.0565	3.1827	0.1030	5.2215	0.1913
291.54	1.8409	0.0577	3.3235	0.1094	5.3696	0.2041

Table 2d

ρ_i($\mu\Omega$-cm) as a function of Temperature (^oK) for Ag 1†

$\rho_P(0) = 0.0007_8$ $\mu\Omega$-cm

$\ell/a(20^oc) = 9760.7$ cm^{-1}

Temp.	ρ_i	Temp.	ρ_i
10.3	0.0002	67.03	0.2067
12.0	0.0004	76.87	0.2699
14.2	0.0009	89.81	0.3537
16.0	0.0014	101.62	0.4294
18.0	0.0023	115.62	0.5179
20.05	0.0033	130.54	0.6109
22.77	0.0058	145.90	0.7056
26.11	0.0105	161.07	0.7981
29.89	0.0183	176.12	0.8893
35.14	0.0340	193.96	0.9960
39.67	0.0517	213.91	1.1164
		233.26	1.2320
47.91	0.0919	252.47	1.3470
57.16	0.1451	272.66	1.4679
† Cominco, 59 grade.		292.35	1.5861

Table 2e

ρ_i ($\mu\Omega$-cm) as a function of Temperature (^oK) for Ag 2†

$\rho_p(0) = 0.0008$ $\mu\Omega$-cm

ℓ/a (20^oc) = 9896.5 cm^{-1}

Temp.	ρ_i	Temp.	ρ_i
9.7	0.0002	89.84	0.3528
15.0	0.0011	100.76	0.4228
21.30	0.0043	114.40	0.5089
26.28	0.0107	131.54	0.6154
30.61	0.0201	145.81	0.7029
35.42	0.0348	161.01	0.7955
41.36	0.0590	176.10	0.8869
45.98	0.0814	194.59	0.9980
51.81	0.1132	195.13	1.0013
56.90	0.1430	215.27	1.1217
63.52	0.1839	234.80	1.2382
69.91	0.2244	254.42	1.3554
76.79	0.2686	272.90	1.4658
82.62	0.3062	291.54	1.5774

† Cominco, 59 grade.

Table 3a

ρ_A and Δ in $\mu\Omega$-cm as a function of Temperature (^oK) for Al-Mg Alloys

Al-Mg 1 (Al + 0.13 at.% Mg)

$\rho_A(0) = 0.0487\ \mu\Omega$-cm

$\ell/a(25^oc) = 9828.9\ cm^{-1}$

Al-Mg 2 (Al + 0.61 at.% Mg)

$\rho_A(0) = 0.2355\ \mu\Omega$-cm

$\ell/a(25^oc) = 9893.6\ cm^{-1}$

Al-Mg 3 (Al + 1.75 at.% Mg)

$\rho_A(0) = 0.6810\ \mu\Omega$-cm

$\ell/a(25^oc) = 9910.5\ cm^{-1}$

Temp.	Al-Mg 1		Al-Mg 2		Al-Mg 3	
	ρ_A	Δ	ρ_A	Δ	ρ_A	Δ
10.0	0.0489	0.0002	0.2358	0.0003	0.6813	0.0003
21.66	0.0519	0.0022	0.2395	0.0030	0.6847	0.0026
31.25	0.0599	0.0056	0.2497	0.0086	0.6954	0.0088
42.20	0.0810	0.0094	0.2764	0.0180	0.7245	0.0206
51.05	0.1115	0.0113	0.3126	0.0255	0.7637	0.0311
63.30	0.1760	0.0115	0.3842	0.0327	0.8400	0.0431
69.88	0.2215	0.0112	0.4323	0.0351	0.8905	0.0478
76.70	0.2756	0.0107	0.4885	0.0367	0.9490	0.0517

Table 3a (continued)

Temp.	Al-Mg 1		Al-Mg 2		Al-Mg 3	
	ρ_A	Δ	ρ_A	Δ	ρ_A	Δ
89.36	0.3912	0.0097	0.6064	0.0380	1.0707	0.0568
100.92	0.5092	0.0089	0.7255	0.0383	1.1925	0.0600
115.46	0.6678	0.0081	0.8848	0.0382	1.3551	0.0632
129.98	0.8328	0.0076	1.0502	0.0381	1.5235	0.0662
143.10	0.9849	0.0075	1.2024	0.0383	1.6785	0.0692
158.24	1.1617	0.0075	1.3792	0.0383	1.8584	0.0725
176.45	1.3746	0.0075	1.5920	0.0382	2.0750	0.0764
195.17	1.5921	0.0073	1.8098	0.0385	2.2963	0.0802
214.00	1.8098	0.0076	2.0273	0.0387	2.5174	0.0842
230.98	2.0051	0.0074	2.2229	0.0389	2.7162	0.0878
251.87	2.2433	0.0078	2.4611	0.0393	2.9587	0.0927
272.61	2.4790	0.0079	2.6971	0.0398	3.1984	0.0971
296.77	2.7530	0.0078	2.9714	0.0402	3.4771	0.1022

Table 3b

ρ_A and Δ in $\mu\Omega$-cm as a function of Temperature (^oK) for Al-Ag Alloys

Al-Ag 1 (Al + 0.06 at.% Ag)

$\rho_A(0) = 0.0707$ $\mu\Omega$-cm

$\ell/a(25^oc) = 9949.3$ cm^{-1}

Al-Ag 2 (Al + 0.18 at.% Ag)

$\rho_A(0) = 0.1950$ $\mu\Omega$-cm

$\ell/a(25^oc) = 9942.1$ cm^{-1}

Temp.	Al-Ag 1		Al-Ag 2	
	ρ_A	Δ	ρ_A	Δ
10.0	0.0710	0.0002	0.1952	0.0002
21.66	0.0744	0.0026	0.1989	0.0028
31.25	0.0830	0.0067	0.2085	0.0079
42.20	0.1051	0.0115	0.2331	0.0153
51.05	0.1364	0.0141	0.2667	0.0201
63.30	0.2015	0.0149	0.3340	0.0231
69.88	0.2468	0.0145	0.3799	0.0233
76.70	0.3007	0.0137	0.4339	0.0226
89.36	0.4158	0.0121	0.5485	0.0206

Table 3b (continued)

Temp.	Al-Ag 1		Al-Ag 2	
	ρ_A	Δ	ρ_A	Δ
100.92	0.5330	0.0107	0.6649	0.0184
115.46	0.6911	0.0093	0.8218	0.0157
129.98	0.8554	0.0081	0.9850	0.0135
143.10	1.0069	0.0074	1.1357	0.0121
158.24	1.1831	0.0068	1.3109	0.0105
176.45	1.3952	0.0060	1.5220	0.0087
195.17	1.6121	0.0052	1.7381	0.0072
214.00	1.8291	0.0049	1.9542	0.0060
230.98	2.0240	0.0043	2.1483	0.0047
251.87	2.2615	0.0039	2.3847	0.0033
272.61	2.4963	0.0031	2.6190	0.0020
296.77	2.7698	0.0027	2.8916	0.0007

Table 3c

$\rho_i(\mu\Omega\text{-cm})$ as a function of Temperature (^oK) for Aluminum†

$\rho_p(0) = 0.0007\ \mu\Omega\text{-cm}$

$\ell/a(25^oc) = 9921.4\ cm^{-1}$

Temp.	ρ_i	Temp.	ρ_i
10.0	-	129.98	0.7766
21.66	0.0011	143.10	0.9287
31.25	0.0056	158.24	1.1056
42.20	0.0228	176.45	1.3186
51.05	0.0515	195.17	1.5362
63.30	0.1158	214.00	1.7536
69.88	0.1616	230.98	1.9491
76.70	0.2162	251.87	2.1870
89.36	0.3329	272.61	2.4227
100.92	0.4516	296.77	2.6967
115.46	0.6111		

† Cominco, 59 grade.

Table 4a

ρ_A and Δ in $\mu\Omega$-cm as a function of Temperature (^oK) for Cd-Ag Alloys

Cd-Ag 1 (Cd + 0.2 at.% Ag)

$\rho_A(0) = 0.0704$ $\mu\Omega$-cm

$\ell/a(22^oc) = 5028.8$ cm^{-1}

Cd-Ag 2 (Cd + 1.0 at.% Ag)

$\rho_A(0) = 0.3002$ $\mu\Omega$-cm

$\ell/a(22^oc) = 5143.6$ cm^{-1}

Cd-Ag 3 (Cd + 2.0 at.% Ag)

$\rho_A(0) = 0.5468$ $\mu\Omega$-cm

$\ell/a(22^oc) = 5002.3$ cm^{-1}

Temp.	Cd-Ag 1		Cd-Ag 2		Cd-Ag 3	
	ρ_A	Δ^*	ρ_A	Δ^*	ρ_A	Δ^*
10.1	0.0950	0.0117	0.3331	0.0199	0.5771	0.0172
16.5	0.1892	0.0319	0.4485	0.0612	0.6871	0.0532
25.89	0.3764	0.0413	0.6525	0.0872	0.8863	0.0745
32.67	0.5464	0.0428	0.8281	0.0943	1.0595	0.0792
41.94	0.7938	0.0428	1.0785	0.0974	1.3071	0.0796
50.67	1.0330	0.0422	1.3176	0.0968	1.5433	0.0761
64.34	1.4094	0.0401	1.6902	0.0909	1.9106	0.0650

* ρ_i corresponds to Cd 1.

Table 4a (continued)

Temp.	Cd-Ag 1		Cd-Ag 2		Cd-Ag 3	
	ρ_A	Δ	ρ_A	Δ	ρ_A	Δ
76.90	1.7508	0.0373	2.0254	0.0820	2.2400	0.0505
89.84	2.1007	0.0348	2.3659	0.0703	2.5731	0.0315
100.99	2.3994	0.0323	2.6555	0.0588	2.8565	0.0138
115.05	2.7731	0.0282	3.0165	0.0422	3.2084	-0.0117
128.40	3.1262	0.0240	3.3560	0.0247	3.5394	-0.0377
144.62	3.5597	0.0192	3.7701	0.0006	3.9414	-0.0737
159.40	3.9457	0.0135	4.1401	-0.0210	4.3017	-0.1049
174.34	4.3425	0.0079	4.5182	-0.0452	4.6688	-0.1400
194.88	4.8916	0.0008	5.0393	-0.0800	5.1734	-0.1911
214.40	5.4151	-0.0059	5.5362	-0.1132	5.6545	-0.2400
234.46	5.9678	-0.0085	6.0628	-0.1418	6.1649	-0.2847
254.21	6.5063	-0.0163	6.5721	-0.1786	6.6568	-0.3388
273.12	7.0292	-0.0243	7.0671	-0.2145	7.1370	-0.3895
295.13	7.6493	-0.0333	7.6568	-0.2539	7.7096	-0.4459

Tables 4b

ρ_A and Δ in $\mu\Omega$-cm as a function of Temperature (^oK) for Cd-Mg Alloys

Cd-Mg 1 (Cd + 0.75 at.% Mg)

$\rho_A(0) = 0.2217$ $\mu\Omega$-cm

$\ell/a(22^oc) = 5040.2$ cm^{-1}

Cd-Mg 2 (Cd + 1.5 at.% Mg)

$\rho_A(0) = 0.4960$ $\mu\Omega$-cm

$\ell/a(22^oc) = 5083.0$ cm^{-1}

Temp.	Cd-Mg 1		Cd-Mg 2	
	ρ_A	Δ*	ρ_A	Δ*
10.1	0.2432	0.0085	0.5193	0.0103
16.5	0.3312	0.0227	0.6141	0.0312
25.89	0.5090	0.0227	0.7981	0.0374
32.67	0.6723	0.0175	0.9639	0.0347
41.94	0.9122	0.0102	1.2053	0.0289
50.67	1.1462	0.0044	1.4400	0.0240
64.34	1.5169	-0.0034	1.8112	0.0168

* ρ_i corresponds to Cd 1.

Tables 4b (continued)

Temp.	Cd-Mg 1		Cd-Mg 2	
	ρ_A	Δ	ρ_A	Δ
76.90	1.8559	-0.0084	2.1497	0.0112
89.84	2.2037	-0.0130	2.4972	0.0064
100.99	2.5012	-0.0168	2.7942	0.0023
115.05	2.8738	-0.0218	3.1660	-0.0034
128.40	3.2265	-0.0263	3.5175	-0.0090
144.62	3.6567	-0.0344	3.9467	-0.0180
159.40	4.0460	-0.0369	4.3347	-0.0216
174.34	4.4426	-0.0426	4.7298	-0.0288
194.88	4.9902	-0.0511	5.2755	-0.0389
214.40	5.5141	-0.0573	5.7982	-0.0462
234.46	6.0599	-0.0668	6.3459	-0.0536
254.21	6.6014	-0.0715	6.8878	-0.0577
273.12	7.1277	-0.0760	7.4158	-0.0605
295.13	7.7519	-0.0809	8.0462	-0.0589

Tables 4b (continued)

Cd-Mg 3 (Cd + 3.0 at.% Mg)

$\rho_A(0) = 0.9920$ μΩ-cm

$\ell/a(21^oc) = 4562.1$ cm^{-1}

Temp.	Cd-Mg 3		Temp.	Cd-Mg 3	
	ρ_A	$\Delta^\dagger$		ρ_A	$\Delta^\dagger$
10.0	1.0136	0.0098	115.01	3.6201	-0.0197
15.0	1.0828	0.0281	130.06	4.0105	-0.0281
20.02	1.1644	0.0371	145.24	4.4032	-0.0378
26.09	1.2980	0.0407	160.91	4.8106	-0.0469
31.99	1.4410	0.0393	175.66	5.1955	-0.0552
39.20	1.6258	0.0353	194.19	5.6803	-0.0669
46.21	1.8101	0.0304	214.57	6.2218	-0.0751
53.93	2.0157	0.0248	214.58	6.2221	-0.0751
64.98	2.3107	0.0163	234.08	6.7470	-0.0812
76.99	2.6287	0.0084	253.64	7.2851	-0.0831
90.11	2.9735	-0.0009	272.82	7.8204	-0.0828
100.16	3.2359	-0.0080	293.97	8.4221	-0.0795

† ρ_i corresponds to Cd 2.

Table 4c

ρ_i ($\mu\Omega$-cm) as a function of Temperature (^oK) for Cd 1*

$\rho_p(0) = 0.0020\ \mu\Omega$-cm

$\ell/a(22^oc) = 4065.4\ cm^{-1}$

Temp.	ρ_i	Temp.	ρ_i
10.1	0.0129	128.40	3.0318
16.5	0.0867	144.62	3.4702
25.89	0.2645	159.40	3.8620
32.67	0.4330	174.34	4.2645
41.94	0.6803	194.88	4.8206
50.67	0.9201	214.40	5.3510
64.34	1.2987	234.46	5.9063
76.90	1.6430	254.21	6.4526
89.84	1.9954	273.12	6.9836
100.99	2.2967	295.13	7.6127
115.05	2.6745	-	-

* Cominco, 59 grade.

Table 4d

ρ_i($\mu\Omega$-cm) as a function of Temperature (^oK) for Cd 2*

$\rho_p(0) = 0.0022$ $\mu\Omega$-cm

$\ell/a(21^oc) = 4099.5$ cm^{-1}

Temp.	ρ_i	Temp	ρ_i
10.0	0.0118	115.01	2.6499
15.0	0.0625	130.06	3.0492
20.02	0.1351	145.24	3.4521
26.09	0.2650	160.91	3.8690
31.99	0.4095	175.66	4.2626
39.20	0.5985	194.19	4.7597
46.21	0.7878	214.57	5.3100
53.93	0.9992	214.58	5.3103
64.98	1.3030	234.08	5.8418
76.99	1.6293	253.64	6.3824
90.11	1.9838	272.82	6.9178
100.16	2.2535	293.97	7.5169

* Cominco, 59 grade.

Table 5a

ρ_A and Δ in $\mu\Omega$-cm as a function of Temperature (^oK) for Mg-Al Alloys

Mg-Al 1 (Mg + 0.22 at.% Al)

$\rho_A(0) = 0.4692\ \mu\Omega$-cm

$\ell/a(20^oc) = 3885.8\ cm^{-1}$

Mg-Al 2 (Mg + 0.99 at.% Al)

$\rho_A(0) = 2.0548\ \mu\Omega$-cm

$\ell/a(20^oc) = 3854.1\ cm^{-1}$

Mg-Al 3 (Mg + 1.90 at.% Al)

$\rho_A(0) = 3.9497\ \mu\Omega$-cm

$\ell/a(20^oc) = 3873.0\ cm^{-1}$

Tem.	Mg-Al 1		Mg-Al 2		Mg-Al 3	
	ρ_A	Δ	ρ_A	Δ	ρ_A	Δ
10.0	0.4704	0.0003	2.0561	0.0004	3.9513	0.0007
12.1	0.4716	0.0007	2.0573	0.0009	3.9525	0.0011
14.9	0.4739	0.0016	2.0597	0.0018	3.9553	0.0025
18.5	0.4783	0.0034	2.0643	0.0038	3.9596	0.0041
23.81	0.4866	0.0063	2.0734	0.0074	3.9691	0.0083
31.13	0.5096	0.0124	2.0986	0.0158	3.9952	0.0175
39.74	0.5560	0.0199	2.1498	0.0281	4.0473	0.0308
47.77	0.6202	0.0245	2.2196	0.0383	4.1191	0.0431
57.28	0.7225	0.0274	2.3283	0.0477	4.2292	0.0539

Table 5a (continued)

Temp.	Mg-Al 1		Mg-Al 2		Mg-Al 3	
	ρ_A	Δ	ρ_A	Δ	ρ_A	Δ
67.03	0.8535	0.0280	2.4642	0.0532	4.3654	0.0600
76.97	1.0076	0.0270	2.6210	0.0552	4.5215	0.0614
90.05	1.2328	0.0249	2.8470	0.0541	4.7447	0.0579
101.34	1.4388	0.0226	3.0517	0.0508	4.9457	0.0512
115.80	1.7094	0.0194	3.3195	0.0452	5.2076	0.0401
130.07	1.9788	0.0165	3.5849	0.0388	5.4665	0.0276
144.61	2.2530	0.0128	3.8543	0.0306	5.7295	0.0137
160.14	2.5434	0.0095	4.1394	0.0227	6.0073	-0.0009
174.66	2.8113	0.0064	4.4027	0.0155	6.2631	-0.0150
194.11	3.1647	0.0022	4.7490	0.0049	6.6018	-0.0324
213.68	3.5155	-0.0016	5.0924	-0.0055	6.9332	-0.0540
234.34	3.8801	-0.0056	5.4483	-0.0175	7.2794	-0.0747
253.52	4.2156	-0.0089	5.7760	-0.0279	7.5970	-0.0944
272.98	4.5521	-0.0132	6.1051	-0.0388	7.9157	-0.1147
294.43	4.9212	-0.0166	6.4649	-0.0507	8.2642	-0.1369

Table 5b

ρ_i($\mu\Omega$-cm) as a function of Temperature (^oK) for Magnesium*

$\rho_p(0) = 0.0065$ $\mu\Omega$-cm

$\ell/a(20^oc) = 3819.0$ cm^{-1}

Temp.	ρ_i	Temp.	ρ_i
10.0	0.0009	101.34	0.9472
12.1	0.0016	115.80	1.2211
14.9	0.0031	130.07	1.4936
18.5	0.0057	144.61	1.7717
23.81	0.0111	160.14	2.0654
31.13	0.0279	174.66	2.3366
39.74	0.0668	194.11	2.6945
47.77	0.1264	213.68	3.0493
57.28	0.2258	234.34	3.4181
67.03	0.3563	253.52	3.7572
76.97	0.5114	272.98	4.0981
90.05	0.7388	294.43	4.4709

* Dow Chemical, 99.98% pure sublimed Mg.

Table 6

Comparison of Residual Resistivities

ρ_r is residual resistivity in μΩ-cm per at.% and $\delta\rho/c$ is the increase in resistivity in μΩ-cm at room temperature on 1 at.% alloying.

Alloy	ρ_r Present author	ρ_r or $\delta\rho/c$ Values from the Literature	
Ag-Cd	0.33	0.38(a)	0.38(b)
		0.33(c)	
Ag-Mg	0.50	0.50(a)	0.50(b)
Ag-Al	1.84		1.95(b)
Al-Mg	0.39	0.33(d)	0.46(e)
		0.35(f)	
Al-Ag	1.1	1.1 (g)	1.1 (e)
Cd-Ag	0.31		
Cd-Mg	0.33		0.4-0.5(h)
Mg-Al	2.08	1.95(i)	2.0 (j)

(a) Linde (1959)

(b) Linde (1939)

(c) Kemp et al. (1956)

(d) Value quoted from Table 4-2 of Harrison (1966)

(e) Robinson and Dorn (1951)

(f) Value quoted from Figure 1 of Fukai (1968)

(g) Alley and Serin (1959) Chanin, Lynton and Serin (1959)

(h) Norbury (1921)

(i) Hedgcock and Muir (1964)

(j) Salkovitz et al. (1957)

Table 7

Summary of Results

Temperatures (^{o}K) at which $\rho_o \simeq \rho_i$ and $\frac{1}{c}\frac{d\Delta}{dT}$ ($\mu\Omega$-cm/^{o}K at.%) values above T(^{o}K) for the Alloys.

Alloy	Solute conc. (at.%)	Temp.(^{o}K) at which $\rho_o \simeq \rho_i$	$\frac{1}{c}\frac{d\Delta}{dT}$ above T	
			$\frac{10^4}{c}\frac{d\Delta}{dT}$	T(^{o}K)
Ag-Cd 1	0.04	27	7.0	90
Ag-Cd 2	0.48	60	0.7	170
Ag-Cd 3	1.43	110	0.8	170
Ag-Mg 1	0.07	35	~ 1	100
Ag-Mg 2	1.09	120	0.6	180
Ag-Mg 3	1.61	160	0.5	180
Ag-Al 1	0.10	63	~ 4	100
Ag-Al 2	0.88	300	3.8	120
Ag-Al 3	1.93	> 300	3.6	100
Al-Mg 1	0.13	50	-	-
Al-Mg 2	0.61	80	~ 0.3	160
Al-Mg 3	1.75	120	1.2	100
Al-Ag 1	0.06	55	-4.5	190
Al-Ag 2	0.18	75	-3.7	190

Table 7 (continued)

Alloy	Solute conc. (at.%)	Temp.(^{o}K) at which $\rho_o \simeq \rho_i$	$\frac{1}{c}\frac{d\Delta}{dT}$ above T	
			$\frac{10^4}{c}\frac{d\Delta}{dT}$	T(^{o}K)
Cd-Ag 1	0.2	15	-17	100
Cd-Ag 2	1.0	27	-17	150
Cd-Ag 3	2.0	37	-13	150
Mg-Al 1	0.22	75	-9.1	90
Mg-Al 2	0.99	160	-5.6	120
Mg-Al 3	1.90	270	-5.5	140

Table 8

Data obtained from the Literature on
Magnesium-Silver Alloys

Specimen	Solute conc. (at.%)	ρ_o ($\mu\Omega$-cm)	Temp(^oK) at which $\rho_o \simeq \rho_i$	$\frac{1}{c}\frac{d\Delta}{dT}$ above T	
				$\frac{1}{c}\frac{d\Delta}{dT}10^4$ ($\mu\Omega$-cm/^oK at.%)	T(^oK)
Das and Gerritsen (1964)					
Mg-Ag 1	0.56	0.379	70	-4.9 †	150
Mg-Ag 2	1.25	0.717	90	-1.6 †	150
Hedgcock and Muir (1964)					
Mg-Ag 1	0.49	0.339	65	-	-
Mg-Ag 2	1.95	1.422	130	(-2.1±0.4)	100

† Estimated from Temperature vs. Impurity Resistivity ($\rho_A - \rho_P$) graphs given in their paper.

Figure 2

Electrical Resistivity of Magnesium below $10^{o}K$ showing the Resistance Minimum

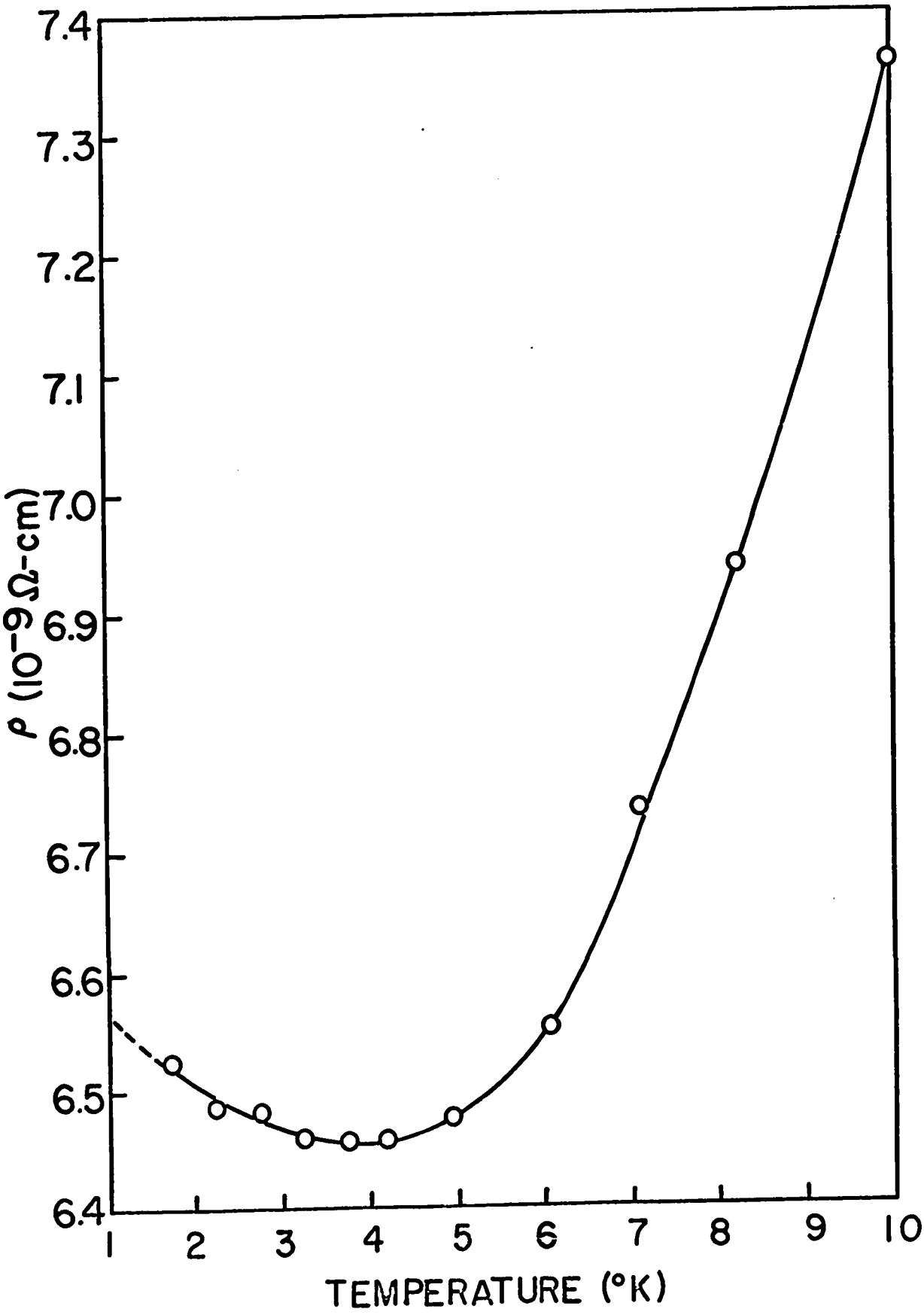

7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
6.4
ρ (10⁻⁹ Ω-cm)
1
2
3
4
5
6
7
8
9
10
TEMPERATURE (°K)

Figure 3

Temperature Dependence of Deviations from Matthiessen's Rule in Silver-Cadmium Alloys

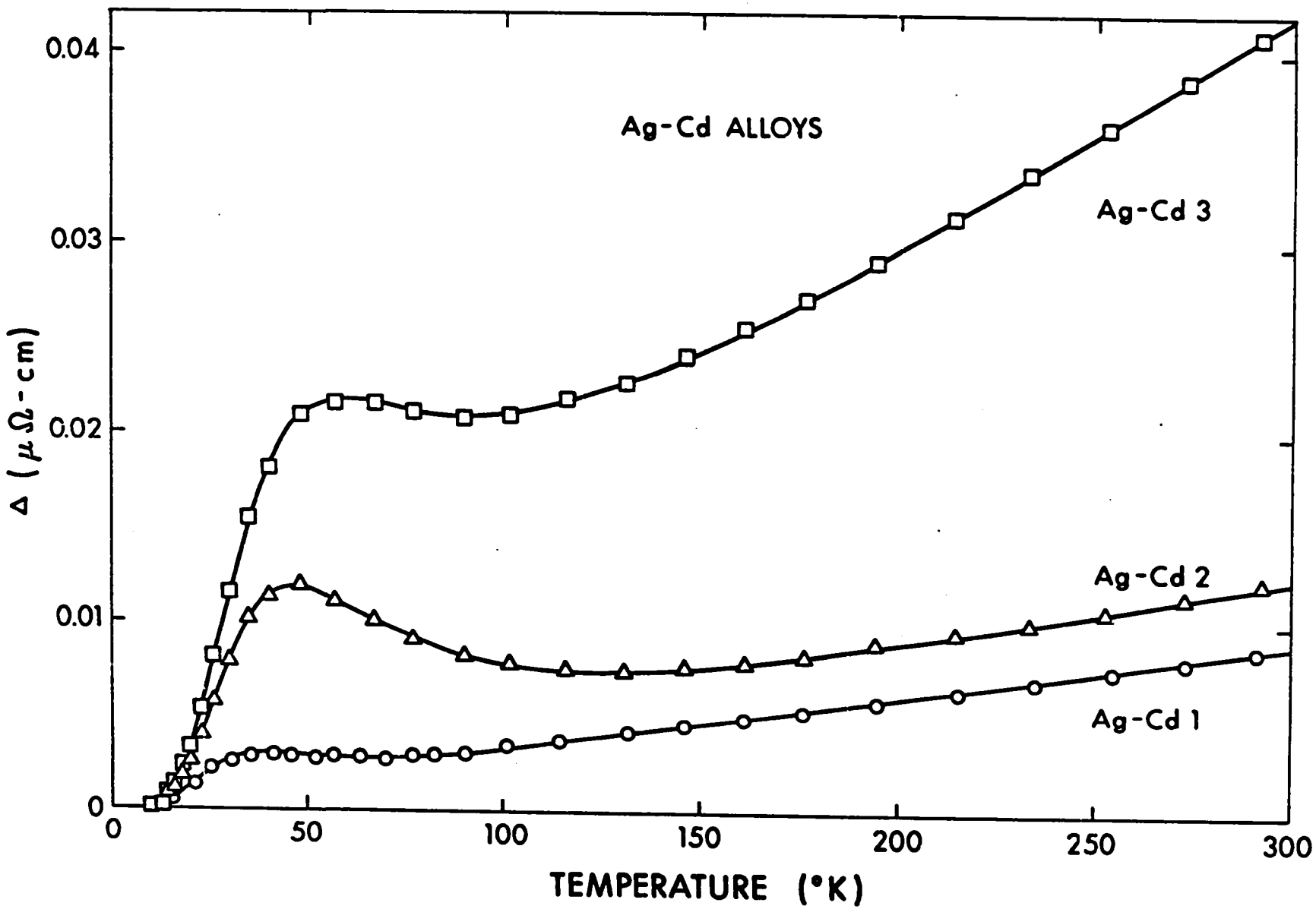

Ag-Cd ALLOYS
Ag-Cd 3
Ag-Cd 2
Ag-Cd 1
Δ (μΩ-cm)
0.04
0.03
0.02
0.01
0
0
50
100
150
200
250
300
TEMPERATURE (°K)

Figure 4

Temperature Dependence of Deviations from Matthiessen's Rule in Silver-Magnesium Alloys

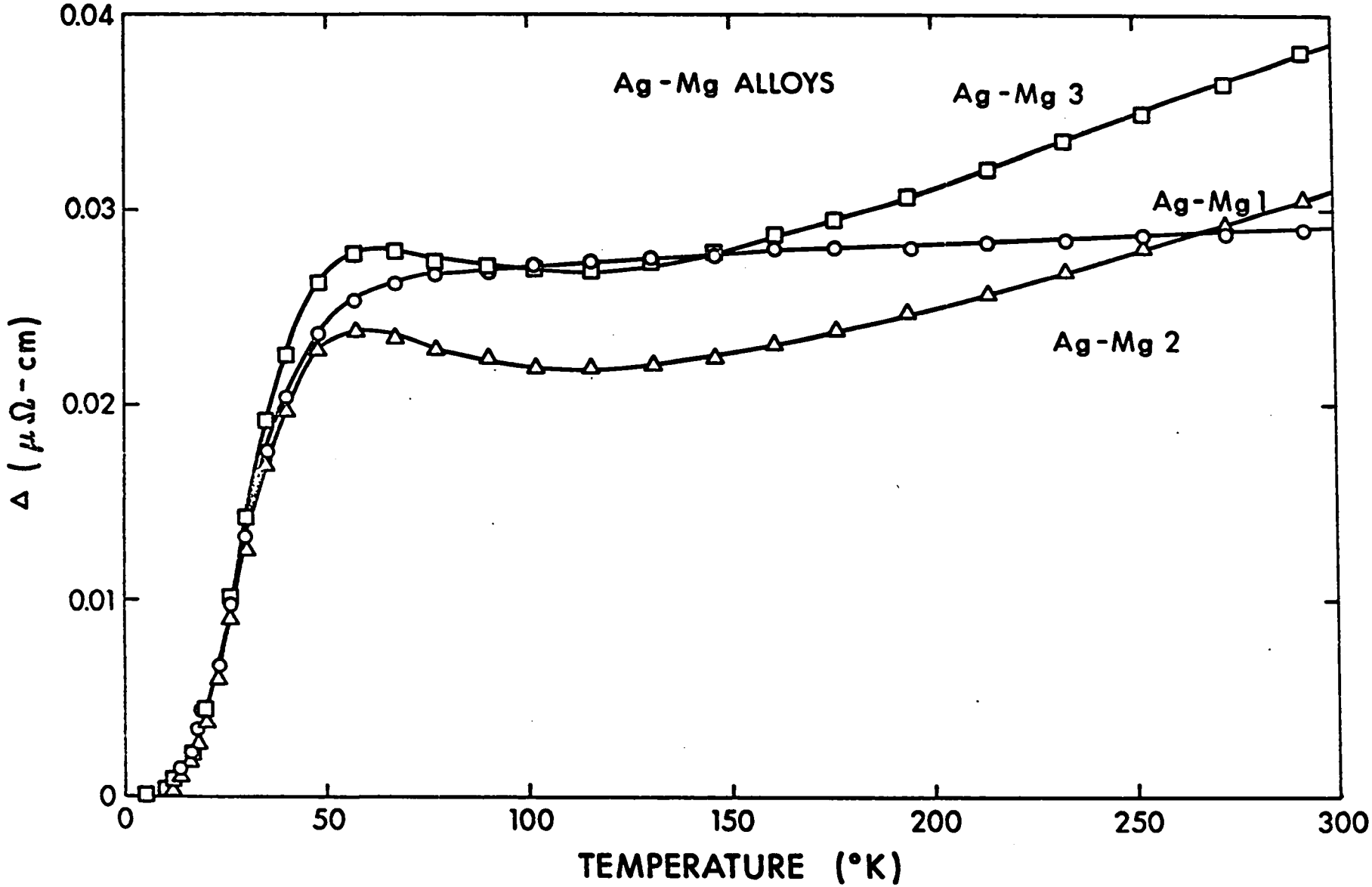

Ag - Mg ALLOYS
Ag - Mg 3
Ag - Mg 1
Ag - Mg 2
Δ (μΩ - cm)
TEMPERATURE (°K)
0.04
0.03
0.02
0.01
0
0
50
100
150
200
250
300

Figure 5

Temperature Dependence of Deviations from Matthiessen's Rule in Silver-Aluminum Alloys

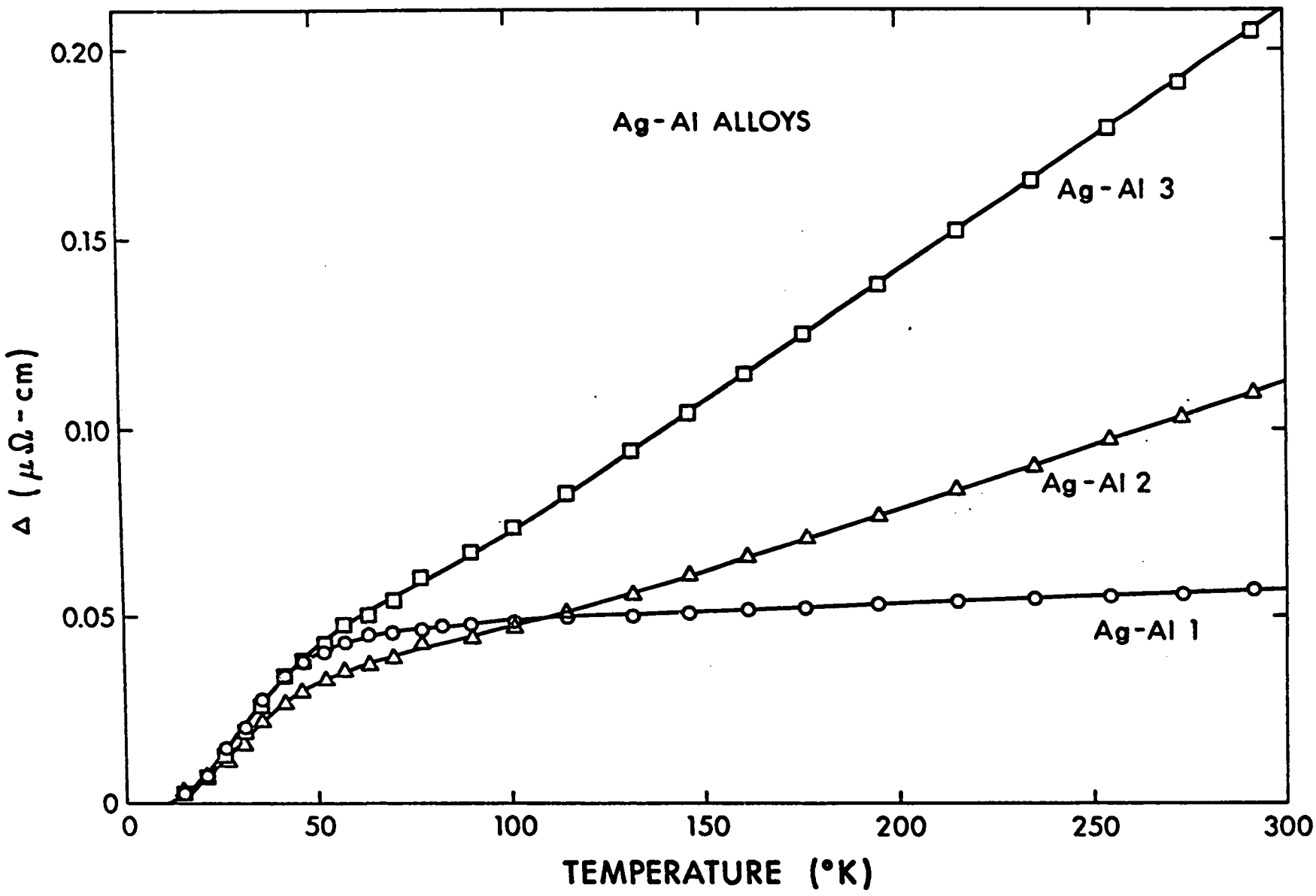

Ag-Al ALLOYS
Ag-Al 3
Ag-Al 2
Ag-Al 1
Δ (μΩ-cm)
0.20
0.15
0.10
0.05
0
0
50
100
150
200
250
300
TEMPERATURE (°K)

Figure 6

Temperature Dependence of Deviations from Matthiessen's Rule in Aluminum-Magnesium Alloys

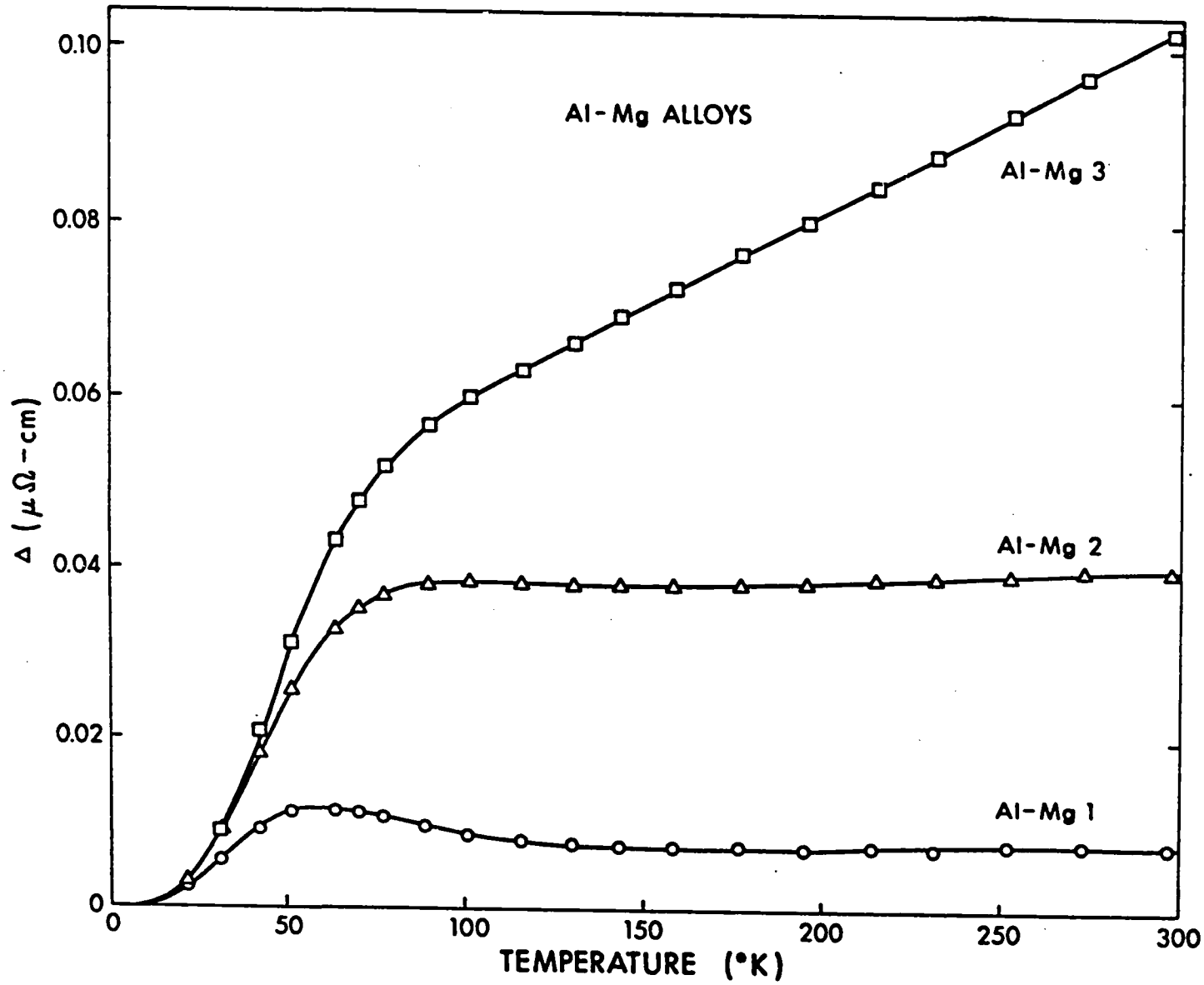

Al-Mg ALLOYS
Al-Mg 3
Al-Mg 2
Al-Mg 1
Δ (μΩ-cm)
0.10
0.08
0.06
0.04
0.02
0
0
50
100
150
200
250
300
TEMPERATURE (°K)

Figure 7

Temperature Dependence of Deviations from Matthiessen's Rule in Aluminum-Silver Alloys

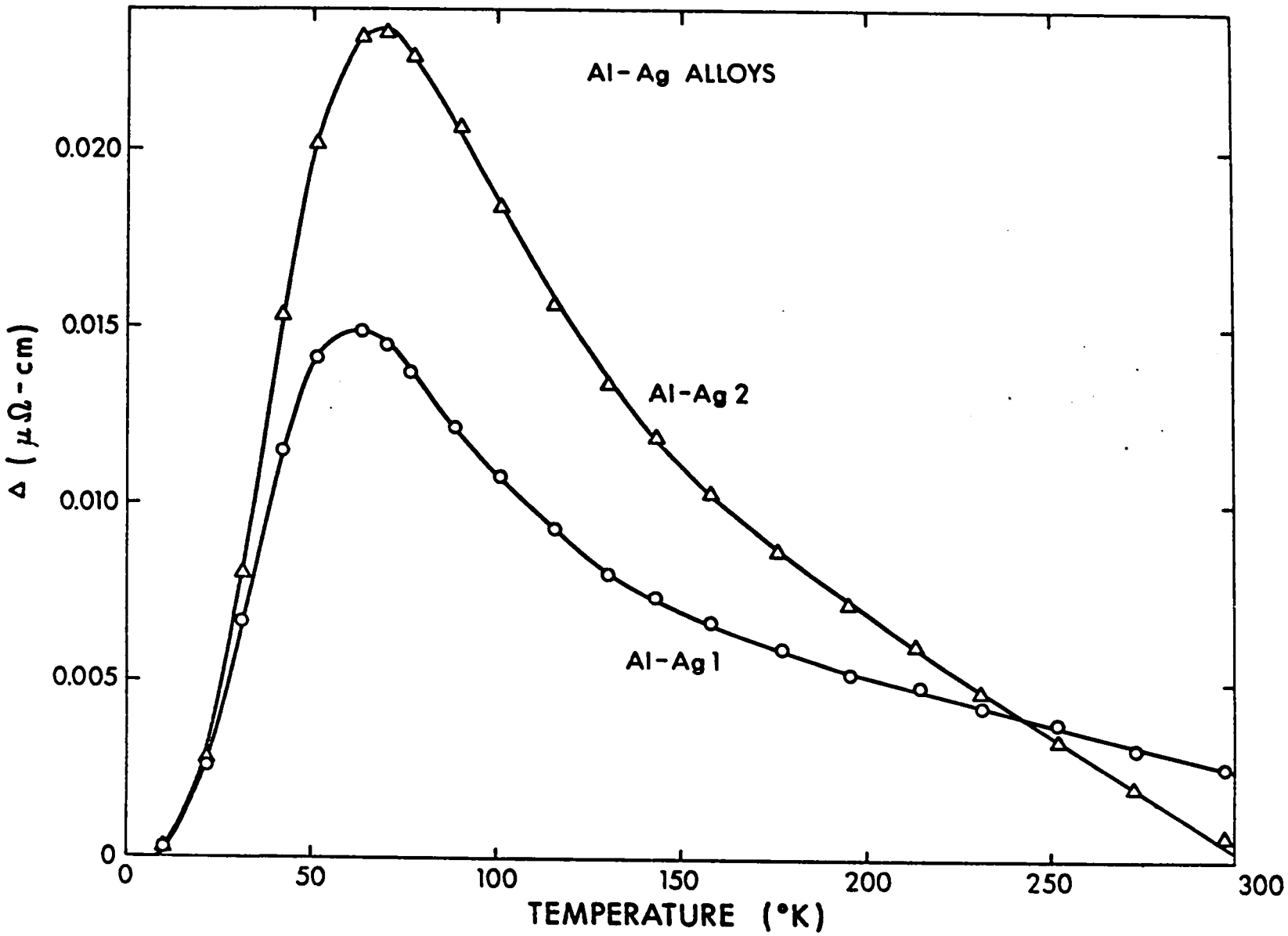

Al-Ag ALLOYS
Al-Ag 2
Al-Ag 1
Δ (μΩ-cm)
0.020
0.015
0.010
0.005
0
0
50
100
150
200
250
300
TEMPERATURE (°K)

Figure 8

Temperature Dependence of Deviations from Matthiessen's Rule in Cadmium-Silver Alloys

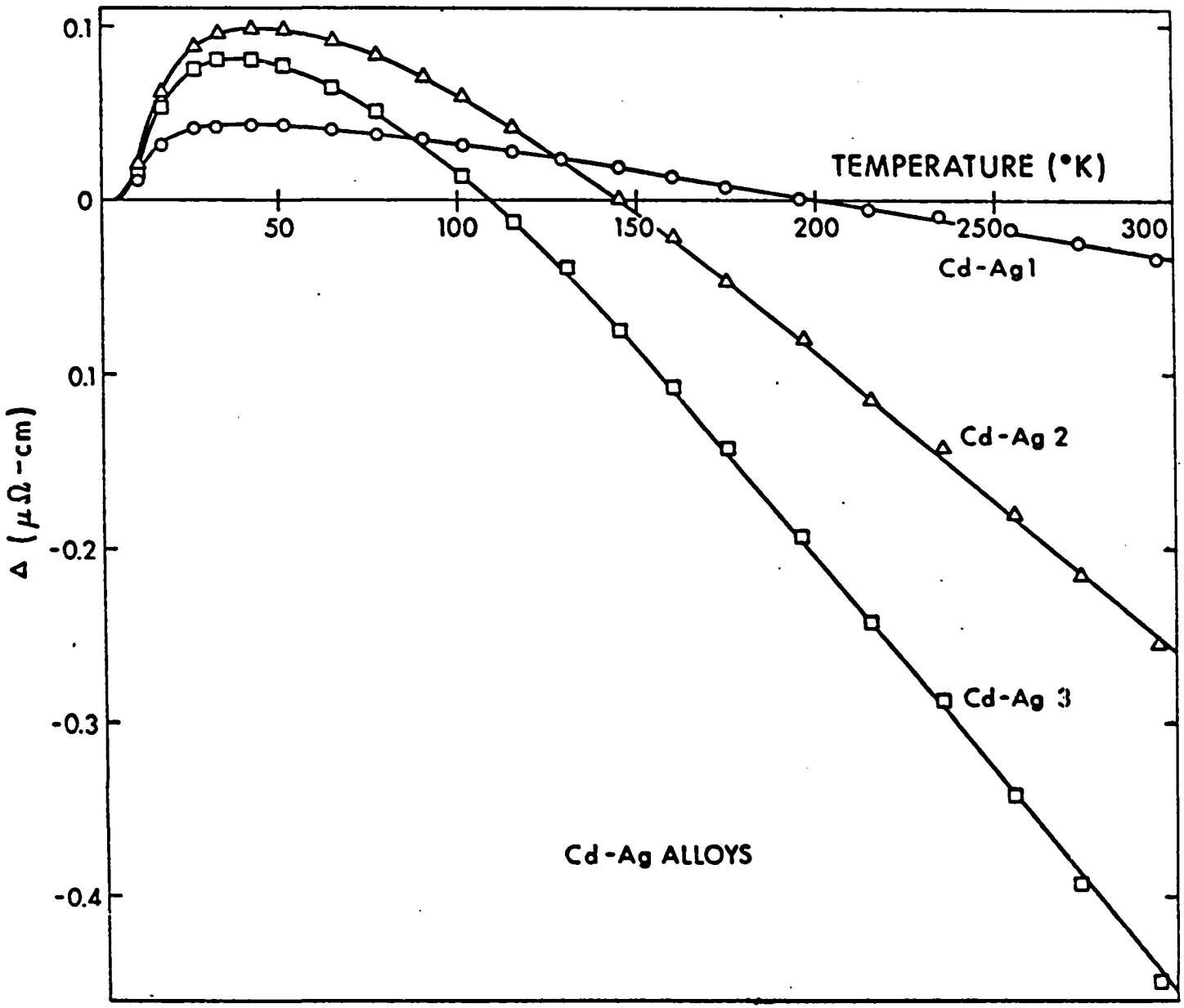

0.1
0
0.1
-0.2
-0.3
-0.4
Δ (μΩ-cm)
50
100
150
200
250
300
TEMPERATURE (°K)
Cd-Ag1
Cd-Ag 2
Cd-Ag 3
Cd-Ag ALLOYS

Figure 9

Temperature Dependence of Deviations from Matthiessen's Rule in Cadmium-Magnesium Alloys

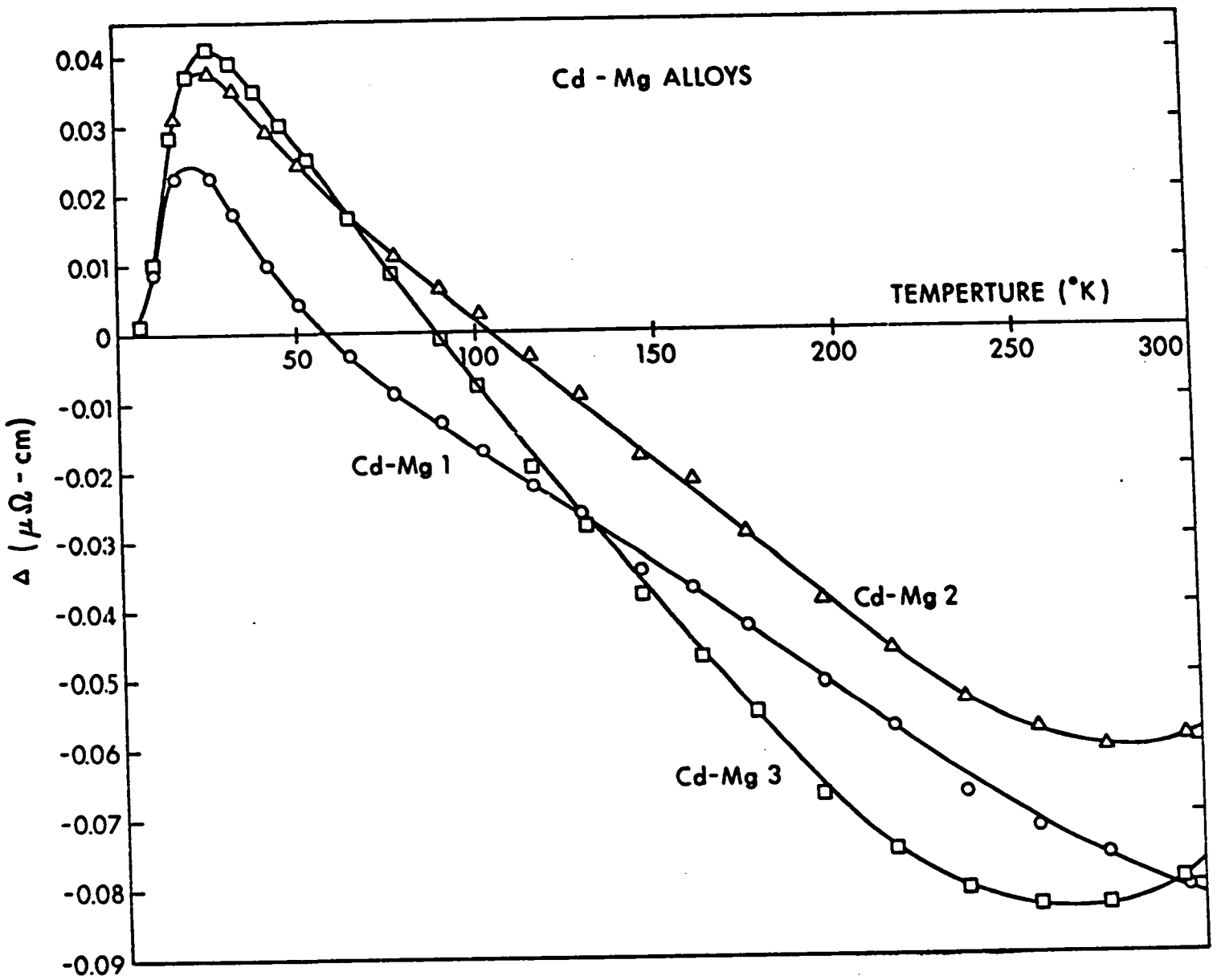
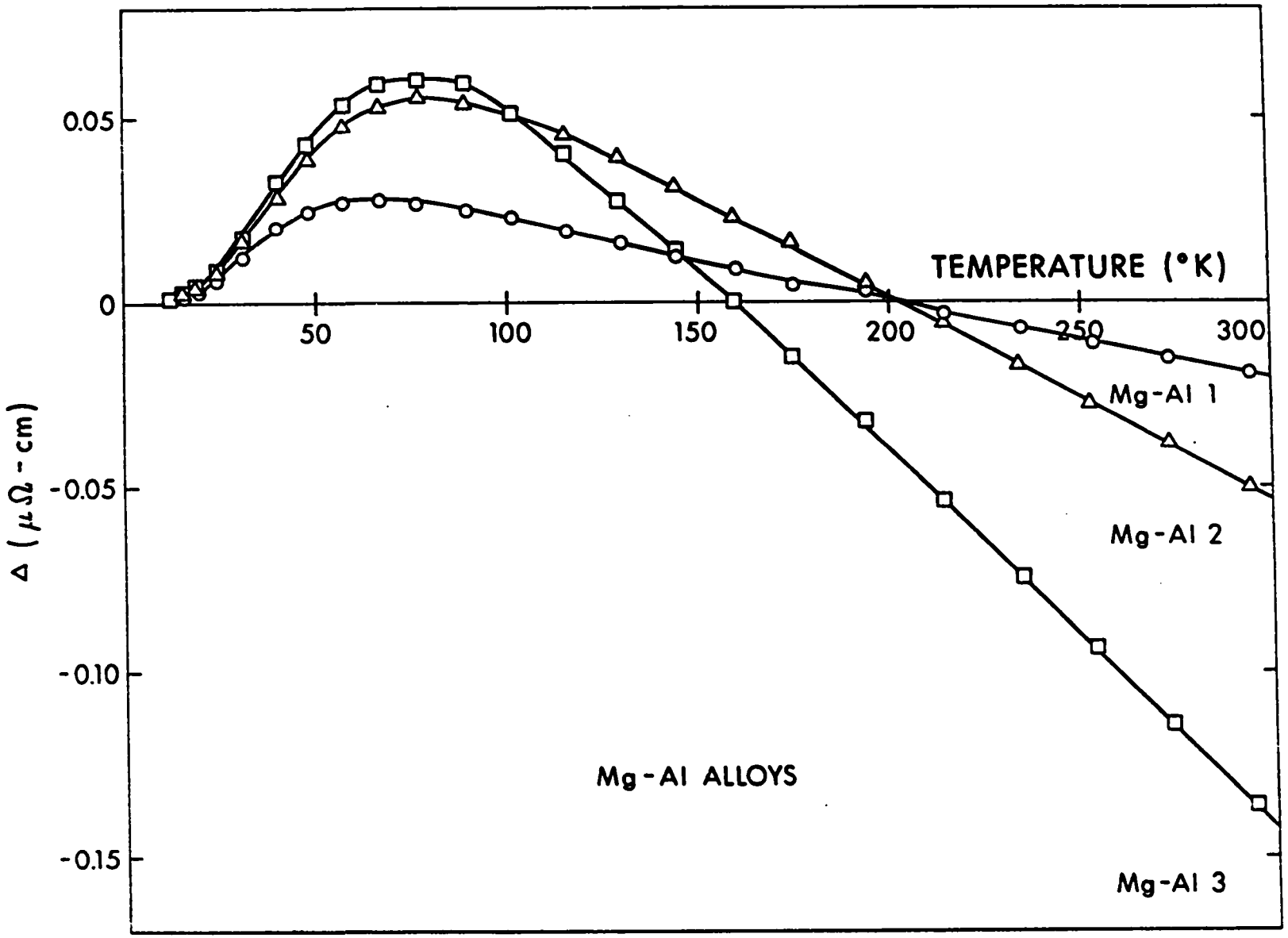

Cd - Mg ALLOYS
TEMPERTURE (°K)
Δ (μΩ - cm)
0.04
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
-0.04
-0.05
-0.06
-0.07
-0.08
-0.09
50
100
150
200
250
300
Cd-Mg 1
Cd-Mg 2
Cd-Mg 3

Figure 10

Temperature Dependence of Deviations from Matthiessen's Rule in Magnesium-Aluminum Alloys


0.05
0
-0.05
-0.10
-0.15
Δ (μΩ-cm)
50
100
150
200
250
300
TEMPERATURE (°K)
Mg-Al 1
Mg-Al 2
Mg-Al 3
Mg-Al ALLOYS

3.2 Discussion of Results

3.2.1 Ideal Resistivity Measurements

Resistivity measurements were made on two specimens of pure silver prepared from different lots of Cominco 59 grade metal. The ideal resistivity values at the ice point (273.15°K) for Ag 1 and Ag 2 were found to be 1.471 μΩ-cm and 1.467 μΩ-cm respectively. These values are in good agreement with the accepted (see Hall, 1968) value 1.47 μΩ-cm. The ideal resistivity of pure aluminum at the ice point was determined to be 2.429 μΩ-cm which again is in agreement with the accepted value 2.44 μΩ-cm.

Cadmium has hexagonal closed-packed structure and its electrical resistivity is anisotropic ($\rho_{\perp}/\rho_{\parallel} = 0.87$ at 273°K). The polycrystalline specimen of such a metal is expected to have preferential orientation acquired during casting, rolling, and drawing and therefore its electrical resistivity will be direction dependent.

For the purpose of investigation of deviations in cadmium alloys, resistivity measurements were made on two specimens of pure cadmium fabricated from two different castings. All specimens of cadmium, including the alloys, were handled in an identical manner. Since highly annealed cadmium wire is very soft and therefore difficult to handle,

specimens were either annealed at room temperature or given a brief annealing at a higher temperature. This was considered quite adequate taking into consideration the high residual resistivity of the cadmium alloys. Cd 1 was annealed at room temperature for one week in vacuum ~ 10^{-3} Torr. Its resistance ratio R(293)/R(4.2) was measured each day and was found to attain a constant value within one week. Cd 2 was annealed in vacuum ~ 10^{-5} Torr at 125°C. The temperature of the furnace was raised to 125°C and then was allowed to cool slowly. The ideal resistivities at the ice point for Cd 1 and Cd 2 were determined to be 6.984 μΩ-cm and 6.927 μΩ-cm respectively. In addition to these two cadmium specimens, two more specimens were made from the Cd 2 casting. Cd 2(a) was annealed at room temperature for four weeks and Cd 2(b) was annealed at room temperature for one week only. Their ideal and residual resistivities (in μΩ-cm) are given below:

Cd 2(a)	$\rho_i(273) = 6.933$	$\rho_o = 2.3\times10^{-3}$
Cd 2(b)	$\rho_i(273) = 6.938$	$\rho_o = 3.1\times10^{-3}$

The difference between the resistivities of the three Cd 2 specimens may be due to the different annealing treatments. On the other hand the difference (1%) between the ρ_i values

for Cd 1 and Cd 2 could be due to the different preferred orientations. It may be worth mentioning that all cadmium specimens were examined under a microscope to determine the grain size. The average grain size was found to be ~ 200 μ(specimen diameter ~ 800 μ). Grains of size as small as 100 μ and as large as 500 μ were also observed.

Unfortunately, accurate data on the resistivity of polycrystalline cadmium is lacking. Jaeger and Diesselhorst (1900) reported the ice-point resistivity of polycrystalline cadmium (with 0.05% impurities of unknown composition) to be 7.07×10^{-6} Ω-cm. Lees (1908) reported the resistivity at the ice point of a specimen turned from a cast stick of pure redistilled cadmium to be 7.12×10^{-6} Ω-cm. These two values are in good agreement with the resistivity of Cd 1. Holborn (1919) has given only ρ/ρ_{273} values from 1.46°K to 194.85°K and no mention is made of the nature of the sample used. Resistivity data on single crystals are available (Goens and Grünesen, 1932) but the method of determining the average resistivity from single crystal values is not well established in the literature. $\rho_{||}$ and $\rho_{\perp}$ reported by these authors at 273°K are 7.73 μΩ-cm and 6.35 μΩ-cm

respectively. Using two different averaging processes, $\bar{\rho}=3\rho_{\perp}\rho_{||}/2\rho_{||} + \rho_{\perp}$ = 6.73 μΩ-cm and $\bar{\rho} = \frac{1}{3}(2\rho_{\perp} + \rho_{||})$ = 6.81 μΩ-cm. The two values differ in themselves by about 1%. In this situation, it was not possible to make a meaningful comparison of the various resistivity values of cadmium. This difficulty was realized only after the present measurements on cadmium alloys were completed.

The ideal resistivity of the pure magnesium used in these experiments was determined to be 4.101 μΩ-cm at the ice point. In terms of the resistance ratio, the purity of this magnesium seems to be high when compared to similar ratios reported in recent papers. The various values of ρ(273) for polycrystalline magnesium are also given here for comparison.

Author	Stock	R(4.2)/R(300) × 10^3	ρ(273) (μΩ-cm)
Present author	Dow Chem.	1.4	4.107
Das and Gerritsen (1964)	"	1.7	4.17±0.02
Hedgcock and Muir (1964)	"	2.3	4.052
Salkovitz et al.(1957)	"	-	4.119

Although the resistivity of magnesium is also anisotropic ($\rho_{\perp}/\rho_{||}$= 1.2), there seems to be good agreement

among the various values quoted above. The accepted value (see Hall, 1968) for $\rho(273)$ is 3.94 μΩ-cm calculated from the single crystal values $\rho_{||}$ = 3.48 μΩ-cm and $\rho_{\perp}$ = 4.18 μΩ-cm and using the averaging relation $\bar{\rho} = 3\rho_{\perp}\rho_{||}/2\rho_{||} + \rho_{\perp}$.

The pure magnesium sample exhibited a minimum in the resistivity around 4°K with a rise of less than 2% at 1°K (Figure 2). The ideal resistivity was computed using the minimum value for the residual resistivity. This resistance minimum could be due to traces of magnetic impurities (0.001% Fe, <0.001% Mn, and <0.001% Ni) in magnesium.

3.2.2 Deviations from Matthiessen's Rule

As pointed out in Chapter 1, a comparison between theory and experiment over the entire temperature range is somewhat difficult. This is because of the large number of contributions to Δ at low temperature. These contributions cannot be estimated quantitatively and also cannot be sorted out. However in the temperature range $T \gtrsim \theta_D$, the situation is somewhat more manageable. The major contributions to Δ come from the interference term and Kohler's calculation (or the two-band effect). Further, in this temperature range, if the phonon scattering dominates over the impurity scattering, i.e. $\rho_i > \rho_o$, the contribution to Δ from Kohler's calculation is expected to

saturate and become constant. This contribution is always positive. On the other hand the contribution from the interference term varies linearly with temperature and can have either sign. Since the structure factor in (1.40) is positive, the sign of $w_A(w_B - w_A)$ for $q \approx 2k_F$ determines the sign of this contribution. Therefore the slope $\frac{d\Delta}{dT}$ in this temperature range is an interesting parameter to study especially in a complementary alloy system where a reversal of sign is expected.

In order to examine the contribution of this interference term and its consequence in case of complementary alloys, we have studied five alloy systems. Measurements have been made on dilute alloys so that changes in the electron spectrum and the Debye temperature on alloying could be neglected. For each alloy system, dependence of Δ on temperature has been studied for different concentrations of the solute and a systematic behaviour has been observed. Errors in the goemetrical shape factor of the expected magnitude (0.1%) could not have produced an effect as large as is apparent from this systematic behaviour of Δ. Consequently the observed behaviour has to be associated with the temperature-dependent part of the impurity resistivity in these alloys.

Let us first of all examine the deviations in the low-temperature limit $T << \theta_D$. According to Kagan and Zhernov (1966), the presence of a heavy impurity in the lattice produces a strong deformation of the phonon spectrum and therefore the deviations are expected to pass through a maximum at a temperature $T \lesssim T^*$. T^* is the temperature that corresponds to ω^*, the quasi-local frequency in the region of which the heavy impurity and environment vibrate (see 1.41). For Al-Ag alloys, $T^* \sim 130^oK$. A maximum in Δ has been observed around 70^oK in these alloys. For Mg-Ag and Mg-Cd alloys, $T^* \sim 100^oK$. Again a maximum has been observed in the impurity resistivity of these alloys around this temperature (Das and Gerritsen, 1964; Hedgcock and Muir, 1964; Panova et al., 1968).

According to Damon et al. (1968) Δ should vary as T^4 at low temperatures. Also, when the residual resistivity ρ_o dominates the ideal resistivity ρ_i, Δ is expected to vary as ρ_i and become independent of concentration. For pure metals, $\rho_i \propto T^n$ where n was found to be 4.1 for Ag, 4.7 for Al, 4.8 for Cd and 3.1 for Mg at low temperatures. For alloys, $\Delta \propto T^n$ and n was found to be ~3.5 for Ag-Cd, ~3.3 for Ag-Mg, ~3.8 for Ag-Al, ~3.1 for Al-Mg, ~3.2 for Al-Ag, ~5 for Cd-Ag and Cd-Mg and ~2.9 for Mg-Al alloys. In view of the large number

of contributions to Δ at low temperature, the above comparison is not very significant. In order to effect a separation of these contributions more alloys of each system would be required (see Damon et al. 1968).

Let us now examine the deviations at temperature $T \gtrsim \theta_D$. In general, the deviations in this temperature range have been found to vary linearly with temperature and this was expected from the theory also. It is noticed that Δ/ρ_o for the alloys with solute concentration less than one percent is greater than the same factor for the more concentrated alloys. This could be explained on the basis that the pseudopotential form factors depend on the nature and the concentration of the impurity. Therefore small changes in concentration might bring about considerable change in $(w_B - w_A)$ and hence Δ/ρ_o. If however we leave from our consideration specimens with very low concentration, then Δ/ρ_o is independent of concentration within a few percent as expected.

To carry out a comparison of the slopes at high temperatures in complementary alloys, the quantity $\frac{1}{c}\frac{d\Delta}{dT}$ is given in Table 7. A reference to Table 1 will be made in order to compare the changes in the atomic volume on alloying. For Ag-Cd and Cd-Ag alloys (Figures 3 and 8), there is an evident reversal of slope but in terms of magnitude the quantity $\frac{1}{c}\frac{d\Delta}{dT}$ is 20 times greater for Cd-Ag

than for Ag-Cd. Also, it may be noticed that the relative decrease in atomic volume on alloying in Cd-Ag is about 3.5 times more than the corresponding increase in Ag-Cd. A suitable correction when applied to Δ for this change in the atomic volume could result in a better agreement between the slopes. Moreover the magnitude of Δ also depends on w_A or w_B and the structure factor of the alloy. Therefore with these unknown parameters, it is only possible to compare the sign of the slopes which depends on the combination $(w_B - w_A)$.

Deviations from Matthiessen's rule in the case of Cd-Ag alloys were calculated using ρ_i values from pure cadmium Cd 1. Since there is uncertainty about the resistivity of cadmium, analyses were carried out with ρ_i values from Cd 2 and ρ_i calculated from single-crystal values published in the literature. Also, the resistivity data on a dilute (0.05 at.%) Cd-Ag alloys were used to calculate deviations in case of 1 and 2 % alloys. In all cases, the Cd-Ag alloys retained a negative slope at high temperatures. Although the magnitude of the deviations is in some doubt, the consistency of the results and the above analyses leave no doubt about the negative slope of the temperature vs. deviation curve for the Cd-Ag system.

Results for the Ag-Mg alloys are compared with the data on Mg-Ag alloys published in the literature (Table 8). Here again there is a reversal of slope although the magnitude of $\frac{1}{c}\frac{d\Delta}{dT}$ for Mg-Ag alloys is about four times greater than for Ag-Mg. On the other hand the relative decrease in atomic volume on alloying in Mg-Ag is 13 times more than the corresponding increase in Ag-Mg. A correction on this account would decrease the slope for Mg-Ag alloys more than that for Ag-Mg alloys.

Solid solubility of Ag in Al is low, therefore only two very dilute alloys of Al-Ag were considered. Comparison with Ag-Al shows (Figures 5 and 7) reversal of slope and a good agreement between the magnitudes. The relative decrease in atomic volume on alloying in Ag-Al is twice the corresponding increase in Al-Ag. A correction to deviations due to this change would increase the magnitude of the slopes in both cases.

Al-Mg and Mg-Al alloys are of particular interest as semi-quantitative estimates of the deviations and the slopes were made by Gupta (1969 b). According to these estimates $\frac{\Delta(273)}{c}$ for Mg-Al alloys is expected to be greater than $\frac{\Delta(273)}{c}$ for Al-Mg alloys. Also, in addition to reversal of slope which is actually observed (Figures 6 and 10), $\frac{1}{c}\frac{d\Delta}{dT}$ for Mg-Al alloys is expected to be twice

that for Al-Mg alloys. Considering the approximations involved in making these estimates, the agreement with the experimentally determined ratio of the slopes (which is ~5) is gratifying. The relative decrease in atomic volume on alloying in Mg-Al is slightly more than the corresponding increase in Al-Mg alloys. The effect of this change in atomic volume, if considered, could improve the agreement.

In the case of Cd-Mg alloys, the deviations from Matthiessen's rule have a temperature dependence different from the expected. The results of Das and Gerritsen (1964) and Hedgcock and Muir (1964) on Mg-Cd alloys show a negative temperature dependence of deviations in the range $T \gtrsim \theta_D$. For Cd-Mg alloys also a negative temperature dependence of deviations in the temperature range 50 to 230°K has been observed (Figure 9). Above 230°K, $\frac{d\Delta}{dT}$ appears to change sign and become positive. Since measurements were made only up to 295°K, nothing definite could be said about this trend. The results on these alloys are not very reliable for two reasons. Firstly, there are the uncertainties in the ideal resistivity of pure cadmium and the resistivity of these alloys due to the orientation dependence. Secondly, these alloys were annealed at 125°C for 12 hours and this could have resulted

in the formation of some ordered structure in the lattice. The order-disorder temperature of $Mg\ Cd_3$ is 80-94°C and the possibility of presence of such a structure in the specimens cannot be ruled out. Further investigations on these alloys are needed to give more meaningful and conclusive results. It may be noticed that both for Cd-Mg and Mg-Cd alloys, there is a relative decrease in atomic volume on alloying.

It should be mentioned that in extracting Δ from measurements, we have assumed that the preferred orientation, if any, of the grains in hexagonal systems is the same in the alloy as in the pure specimen. If this is not the case, then there is a correction term to Δ which can be of either sign and can influence the interpretation of results. X-ray analyses carried out on pure magnesium sample and Mg-Al alloy samples indicate that any such changes in preferred orientation must be very small. It is to be noted that these changes could not explain our experimental results unless one makes the rather unlikely assumption that these changes are roughly proportional to concentration. The same remarks apply to all hexagonal systems studied here although we have not carried out X-ray analyses for these.

3.2.3 Conclusions

The present study provides many accurate data on the electrical resistivity of pure metals and on a number

of dilute binary alloys. The deviations from Matthiessen's rule in these alloys have been determined from measurements in a temperature range from 1.5°K to 300°K. These investigations qualitatively confirm for a number of alloys the predictions of Bhatia and Gupta (1969) regarding the temperature dependence of the deviations. With the inclusion of interference term in the theoretical calculation of resistivity of an alloy, one is able to appreciate the negative deviations from Matthiessen's rule which were not understood before.

As predicted by these authors, reversal of the slope $\frac{d\Delta}{dT}$ at high temperatures has been observed in complementary alloys of silver and cadmium, silver and magnesium, aluminum and silver, and aluminum and magnesium. The theory does not provide as yet any quantitative estimates of the deviations or the slopes. In terms of magnitude of deviations although the results on Cd-Ag alloys are not conclusive due to the possibility of the presence of preferred orientation, a clear evidence of negative slope for $T \gtrsim \theta_D$ for these alloys has been provided. The effect of preferred orientation could cause deviations in all hexagonal alloy systems. However, in case of Mg-Al alloys there is good evidence from X-ray analyses to show that this effect is

small. Results on the cadmium-magnesium system are not conclusive and need further study.

Another possible source of deviations could be inhomogeneous solute distribution in the alloys. The evidence obtained from the electron probe micro-analyses (p. 53) shows that the alloys used here had only very slight inhomogeneities and deviations from this source will therefore be negligible.

As has been pointed out in the beginning of this chapter, corrections to ρ_i and ρ_o arising from the change in atomic volume on alloying and the thermal expansion of the lattice are necessary. It is not clear at this stage how the correction to ρ_i should be calculated. It has been observed in the discussion that this correction would affect the deviations and the slope $\frac{d\Delta}{dT}$ at high temperatures. On the other hand for the correction to ρ_o, data on pressure coefficient of residual resistivity are required. Experimental investigations in this field are sadly lacking. It is not clear as yet how this correction would affect the results. A proper understanding and application of these corrections would certainly make possible a better comparison of the experimental results in this thesis with theory.

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