

DEVIATIONS FROM MATTHIESSEN'S RULE FOR THE ELECTRICAL
RESISTIVITY OF IMPERFECT METALS

by

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ABSTRACT

The deviations from Matthiessen's rule (MR) for the electrical resistivity of metals containing small amounts of chemical solute or physical defects, have been examined from both an experimental and theoretical point of view. The theoretical problems investigated were the internal consistency of the standard two-band model formulation for deviations from MR, the magnitude and solute concentration dependence of the Sondheimer formulation, and the nature of the deviations from MR resulting from a change in the characteristic phonon parameter, Θ_R . The experimental investigations included new determinations of the deviations from MR for slightly impure Pt, for single vacancies in quenched Pt, and for mixed defects in fatigued and hard-drawn Pt. Also, as a demonstration of the importance of deviations from MR, the resistance ratios for ideally pure Pt below 20K have been derived from new measurements on high purity Pt, and compared with resistivity theory. Other topics treated were an improved method of calculating the two-band parameters, a new experimental arrangement for high precision resistance measurements of physical defects in metals, and isochronal annealing studies on quenched, fatigued and hard-drawn platinum.

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CONTENTS

1.	INTRODUCTION	
1-1	Electrical Resistivity	1
1-2	Theoretical Calculation of Resistivity	4
1-3	Matthiessen's Rule (MR)	11
1-4	Determination of Deviations (Δ_T) from MR	16
1-5	Scope of Thesis	21
2.	REVIEW OF EXISTING THEORY AND EXPERIMENT	
2-1	Two-Band Model:	24
	(a) Sondheimer and Wilson Analysis	24
	(b) Early Tests Using Resistance Ratios	27
	(c) Early Tests Using Resistivity Measurements	31
	(d) Two-Band Fermi Surface Model	33
2-2	Kohler's Theory	39
2-3	Sondheimer's Δ_T Calculation	41
2-4	Anisotropic Phonon Spectrum	43
2-5	Change in Θ_R Model	44
2-6	Phonon-Assisted Impurity Scattering	48
2-7	Theory of Masharov	50
2-8	Theory of Kagan and Zhernov	53
2-9	Theory of Bhatia and Gupta	62
2-10	Theory of Rice and Bunce	65
2-11	Electronic Band Structure Changes	66
2-12	Momentum Non-Conservation Theory	68
2-13	Phonon Drag Theory	69

3.	TWO-BAND MODEL TEST ON Pt, W AND Pb	
3-1	Introduction	72
3-2	Calculation of Two-Band Parameters	72
3-3	Results	77
3-4	Discussion	84
4.	DEPENDENCE OF THE SONDHEIMER λ_T FUNCTION ON SOLUTE CONCENTRATION	
4-1	Introduction	86
4-2	Details of the Calculation	87
4-3	Results	90
4-4	Discussion	93
5.	DEVIATIONS FROM MR DUE TO θ_R CHANGES	
5-1	Introduction	96
5-2	Basic Analysis	97
5-3	Comparison of Results	103
5-4	Discussion	107
6.	DEVIATIONS FROM MR FOR VACANCIES IN PLATINUM	
6-1	Introduction	111
6-2	Procedure	113
6-3	Experimental Details	116
6-4	Results	130
6-5	Corrections to the Results	136
6-6	Discussion	141

7.	DEVIATIONS FROM MR FOR PLASTICALLY DEFORMED PLATINUM	
7-1	Introduction	145
7-2	Procedure	148
7-3	Results	151
7-4	Conclusions	159
8.	APPLICATION OF THE DEVIATION FROM MR TO THE DETERMINATION OF THE IDEAL RESISTIVITY OF PLATINUM	
8-1	Introduction	161
8-2	Reduction of Measurements to W_{IT}	162
8-3	Discussion of Earlier Work	163
8-4	Determination of W_{IT} in the Range 4-10K	167
8-5	Comparison With Theory	175
8-6	Accuracy of the New W_{IT} Function	180
8-7	Range of Validity of Equation (8.3)	181
8-8	Two-Band Test on Pt 1 and Pt 2	182
8-9	Discussion	184
9.	CONCLUSIONS	187
	REFERENCES	191

FIGURES

1.1	Typical λ_T functions from published work	15
3.1	The λ_T functions for Pt specimens Ikh3 and B1	81
4.1	Dependence of Sondheimer's λ_T function on temperature and solute concentration	91
4.2	Dependence of Sondheimer's peak λ_T on solute concentration	92
5.1	Deviations from MR given by the θ_R - change model	102
6.1	Specimen holder for defect studies on platinum	118
6.2	Isochronal annealing curves for quenched (SC1) and fatigued (SC3) platinum specimens	129
6.3	The λ_T function for single vacancies in quenched platinum	133
7.1	Isochronal annealing curves for fatigued (SC4) and hard-drawn (SC5) platinum specimens	152
7.2	The λ_T functions for defects in deformed Pt which anneal-out below about 400°C	155
7.3	The λ_T function for defects in deformed Pt which anneal-out above about 400°C	157
7.4	Values of λ_{273} given by defects in deformed Pt for small annealing steps	158
8.1	The λ_T function for Pt specimen 320	173
8.2	$(W_T - W_0)/T^2$ versus T^3 for platinum specimens 320, Pt 1 and Pt 2	177
8.3	Log $(W_{iT} - p_i T^2)$ versus log T for new W_{iT} function	179
8.4	The λ_T function for Pt specimen Pt 1, Pt 2 and 320	183

TABLES

3.1	Two-band parameters for Pt specimens 120 and LN1158062	79
3.2	Two-band parameters for Pt, W and Pb specimens	82
4.1	Dependence of Sondheimer's λ_T function on the order of approximation	89
4.2	Comparison of resistivity ratios given by the Bloch-Gruneisen and the Sondheimer formulation	94
6.1	Estimated measuring uncertainties in T , δR_T and λ_T	123
6.2	Measured resistance changes for quenched Pt specimen SCl	132
6.3	Values of λ_T for various quenched specimens of Pt	135
8.1	Dependence of $\sigma_{\min}$ on N for Van Dijk's resistors	168
8.2	Measured W_T values for specimen 320	171
8.3	Two-band parameters for specimens 320, Pt 1 and Pt 2	171
8.4	W_{iT} values calculated from Eqs. (8.1) and (8.9)	174
8.5	W_{iT} values given by Eq. (8.9) at selected temperatures	176

CHAPTER 1

INTRODUCTION

1-1 Electrical Resistivity

One of the most outstanding and important characteristics of a metal is its ready ability to conduct electricity. Shortly after J.J. Thomson's discovery of the electron in 1897 it was appreciated by Drude¹ (1900) and Lorentz² (1904) that this property of a metal was due to the presence of large numbers of non-localized valence electrons, which were free to move through the metallic lattice under the action of an applied electric field. With the introduction of quantum mechanics and Fermi-Dirac statistics to this problem (Sommerfeld³ (1928) and Bloch⁴ (1930)) it became apparent that an electron -- now visualized as a wave packet -- could in principle travel unimpeded through a metallic crystal lattice as long as the lattice was an ideally perfect periodic structure. In practice of course no lattice is perfect, and the valence or "conduction" electrons are scattered by the various imperfections giving rise to the well known property of electrical resistance.

In macroscopic terms the specific electrical resistivity, ρ , is defined as

$$\rho = \frac{E}{J} = \frac{1}{\sigma} \quad (1.1)$$

where $\vec{E}$ is the electric field and $\vec{J}$ the current density per unit area, and σ is the electrical conductivity. The resistivity of a pure metal is independent of the shape of the specimen, and will be a constant at any particular temperature (Ohm's law), characteristic of the particular metal. The total electrical resistance, R , which is actually measured will of course depend on the shape of the specimen. For a conductor of uniform cross-section A and length l , the resistance R (in ohms) is given by

$$R = \frac{V}{I} = \frac{l}{A} \rho \quad (1.2)$$

where V is the potential difference (in volts) between its ends and I is the resulting current (in amperes). While ρ will be a tensor for certain crystal structures, we shall be dealing only with polycrystalline specimens -- and then mostly cubic crystals -- which both lead to a scalar resistivity⁵.

There are two predominant types of electron-scattering processes creating the electrical resistivity in metals. First there is the scattering by the thermally-stimulated lattice vibrations, often referred to as phonon scattering; and secondly the scattering by static imperfections, such as chemical impurities and physical defects (vacancies, dislocations, etc.). The resistivity component due to phonon scattering, ρ_{IT} -- which of course also represents

the resistivity of an ideally pure metal -- will be zero at a temperature of 0 Kelvin (K) where the lattice vibrations are "frozen-out"; and will increase monotonically with temperature as the amplitude of atomic vibrations increases. The resistivity component due to static imperfections will depend on the type and concentration of the imperfections but is not expected to vary with temperature to a first approximation. It is thus possible to determine the "defect" resistivity fairly accurately by a measurement at (or near) 0(K), which is usually referred to as the residual resistivity, ρ_0 .

The properties of both the ideal and residual resistivities have been investigated experimentally in considerable detail (e.g. see Meaden⁵); and have been qualitatively explained in most cases by various theoretical analyses. However, exact quantitative agreement between theory and experiment has not been achieved in most cases with the over-simplified models used to date. In order to introduce certain concepts and definitions as a basis for later discussions, we shall briefly sketch the theoretical approach to a calculation of the resistivity. Detailed treatments of this type of analysis may be found in books by Ziman^{6,7,8} and Blatt⁹.

1-2 Theoretical Calculation of Resistivity

The basis of modern calculations of ρ (or σ) is the Boltzmann transport equation, which treats the assembly of conduction electrons statistically by means of a distribution function, $f_{\vec{k}}$. The subscript k refers to the wave vector $\vec{k}$ (where $|\vec{k}| = 2\pi / \text{wavelength}$ and the vector sign is deleted in subscripts), and all electrons in state $\vec{k}$ will possess the same velocity $\vec{v}_{\vec{k}}$ and energy $E_{\vec{k}}$. One defines $f_{\vec{k}}$ such that the number of electrons per unit volume with wave vector $\vec{k}$ in the element $d\vec{k}$ is given by $(4\pi^3)^{-1} f_{\vec{k}} d\vec{k}$. Thus $f_{\vec{k}}$ represents the probability that the state $\vec{k}$ will be occupied; and at equilibrium when all external fields are removed, it will be given by the Fermi-Dirac distribution function $f_{\vec{k}}^0$. For steady state conditions, when an electric field (only) is present, the Boltzmann relation simply equates the time rate of change of $f_{\vec{k}}$ due to the field and its opposing rate of change due to scattering processes, which may be written as

$$\left. \frac{\partial f_{\vec{k}}}{\partial t} \right|_{\vec{\mathcal{E}}} = \left. \frac{\partial f_{\vec{k}}}{\partial t} \right|_{\text{scat.}} \quad (1.3)$$

When the appropriate substitutions for these rates are made (keeping each rate on its original side) Eq. (1.3) becomes

$$-\frac{\vec{v}_{\vec{k}} \cdot e \vec{\mathcal{E}}}{\hbar} \frac{\partial f_{\vec{k}}^0}{\partial E_{\vec{k}}} = \frac{1}{K_B T} \int Q(\vec{k}, \vec{k}') f_{\vec{k}}^0 (1 - f_{\vec{k}}^0) (\phi_{\vec{k}} - \phi_{\vec{k}'}) d\vec{k}' \quad (1.4)$$

where e is the electronic charge, K_B the Boltzmann constant, T the Kelvin temperature, $\hbar$ (2π) the Planck constant, $Q(\vec{k}, \vec{k}')$ the intrinsic probability per unit time that an electron in state $\vec{k}$ will be scattered into state $\vec{k}'$ (assuming $\vec{k}$ is full and $\vec{k}'$ empty), and ϕ_k is a new distribution function defined by

$$f_k - f_k^0 = - \phi_k \frac{\partial f_k^0}{\partial E_k} \quad (1.5)$$

The transition probability, $Q(\vec{k}, \vec{k}')$, is usually estimated from time-dependent perturbation theory, using some suitable scattering potential. Similarly, all other quantities appearing in Eqs (1.4) and (1.5) may be estimated, with the exception of the function ϕ_k . Assuming Eq. (1.4) can be solved for ϕ_k , it is then fairly straight forward to find f_k from Eq. (1.5) and the resistivity from the relation

$$\vec{J} = \frac{e}{4\pi^3} \int f_k \vec{v}_k d\vec{k} \quad (1.6)$$

which is derived from a simple summation of the charge transport (and $\vec{J}$ will be linear in $\vec{E}$ by virtue of built-in constraints).

There are two basic methods of solving the Boltzmann equation for ϕ_k (or f_k), namely the relaxation time method and the variational method. In the former, one defines a relaxation time τ such that

$$\left. \frac{\partial f_k}{\partial t} \right|_{\text{scat.}} = - \frac{(f_k - f_k^0)}{\tau} \quad (1.7)$$

where τ has the role of a time constant characterizing the exponential decay of the perturbed distribution f_k to the equilibrium distribution f_k^0 when the field is removed.

When this simplified expression for $(\partial f_k / \partial t)_{\text{scat.}}$ is substituted for the right hand side of Eq.(1.4), f_k is readily determined in terms of τ and the resulting resistivity (for cubic crystals) is given by

$$\frac{1}{\rho} = \sigma = \frac{e^2}{12\pi^3 h} \int \tau v_k dS \quad (1.8)$$

where τ , v_k and the element of area, dS , apply to the Fermi surface. Blatt⁹ has emphasized that the relaxation time will only be a meaningful parameter if the scattering process is quasi-elastic, i.e. where the energy change per collision is $\ll K_B T$, the thermal energy. Such conditions are approximated by impurity scattering and by phonon scattering at high temperatures. Most applications of this method to date involve two further simplifying assumptions, viz. a spherical Fermi surface (applicable to quasi-free electrons) and a scattering probability $Q(\vec{k}, \vec{k}')$ which depends only on the angle θ between $\vec{k}$ and $\vec{k}'$. In this case Eq. (1.8) reduces to

$$\frac{1}{\rho} = \sigma = \frac{ne^2\tau}{m^*} \quad (1.9)$$

where n is the number of electrons per unit volume, m^* their effective mass, and τ is given by

$$\frac{1}{\tau} = \int Q(\theta)(1-\cos\theta)d\vec{k}, \quad (1.10)$$

integrating over the Fermi surface.

The second method of solving the Boltzmann equation, i.e. the variational method, is completely general in that it can be used for both elastic and inelastic scattering. It was first applied to the determination of resistivity by Kohler¹⁰ (1949) and has been discussed in considerable detail by Ziman⁶ and Blatt⁹. The method is based on a mathematical law governing the properties of operators, known as the variational principle; and could be described as a "trial and error" approach to finding ϕ_k and ρ . Briefly the procedure is to express the Boltzmann Eq. (1.4) in the form of an operator equation

$$H_k = P \phi_k \quad (1.11)$$

where H_k is the left hand side of Eq. (1.4) and P is a scattering operator defined so that $P\phi_k$ is the right hand side of Eq. (1.4). From considerations of the entropy, S , of a Fermi "electron gas", the rates of entropy production

are derived (from the rates of change of f_k) separately for the field $\vec{\mathcal{E}}$ and the scattering processes, with the result

$$\left. \frac{\partial S}{\partial t} \right|_{\vec{\mathcal{E}}} = - \frac{1}{T} \langle \phi, H \rangle = - \frac{\rho}{T} J^2 \quad (1.12)$$

and

$$\left. \frac{\partial S}{\partial t} \right|_{\text{scat.}} = \frac{1}{T} \langle \phi, P\phi \rangle \quad (1.13)$$

where the "inner product", $\langle \phi, X \rangle$, is defined by

$$\langle \phi, X \rangle = \int \phi(k) X(k) dk \quad (1.14)$$

Under steady state conditions the two rates of entropy production must balance, and from Eqs. (1.12 and 1.13) one obtains

$$\rho = \frac{\langle \phi, P\phi \rangle}{J^2} = \frac{\langle \phi, P\phi \rangle}{|\langle \phi, H_1 \rangle|^2} \quad (1.15)$$

where H_1 is simply the value of H for unit electric field. The full expressions for $P\phi$ and H , may now be substituted back into Eq. (1.15) to form an integral equation for ρ involving only the unknown ϕ_k . The special significance of this expression, over the original Boltzmann equation, is that according to the variational principle the true solution ϕ_k will make the right hand side of Eq. (1.15)

a minimum value. The problem of finding a suitable trial function for ϕ_k , that will give the above expression a minimum value, is apparently not too difficult; usually linear combinations of easily integrated functions are employed.

Using the above methods of calculation, various theoretical expressions for the phonon resistivity, ρ_{iT} , and the residual defect resistivity, ρ_o , have been derived (e.g. see review by Ziman⁶). The simplest and most widely used expression for ρ_{iT} is the Bloch-Gruneisen relation (Bloch⁴, Gruneisen¹¹) given by

$$\rho_{iT} = c_o \frac{T}{\theta_R} G(\theta_R/T) \quad (1.16)$$

where

$$G(\theta_R/T) = 4 \left(\frac{T}{\theta_R}\right)^4 \int_0^{\theta_R/T} \frac{z^5 dz}{(e^z - 1)(1 - e^{-z})} \quad (1.17)$$

is a tabulated^{11,5} function of (θ_R/T) only, c_o is a constant for any particular metal, and θ_R is a characteristic (phonon) temperature analagous to (but not identical with¹²) the Debye θ_D in specific heat theory. According to this

relation, ρ_{iT} varies as T^5 below about $\theta_R/10$ and as T above about $\theta_R/2$; which is roughly what is observed for a great many metals. Of course some deviations are to be expected since the relation is based on many crude assumptions, such as the "free electron" approximation (Eq.(1.9)), the Debye phonon spectrum, and no Umklapp processes (these are processes in which an electron suffers a Bragg reflection at the Brillouin zone boundary in addition to the normal scattering by a phonon). Since Umklapp processes may cause large angle scattering (79-180 degrees) even at low temperatures, their effect on the resistance can be substantial. Ziman⁶ discusses this point in detail, and outlines more sophisticated expressions for ρ_{iT} which include both normal and Umklapp scattering.

Regarding the various theoretical expressions (e.g. see Ziman^{6,7}) for the defect resistivity, ρ_o , due to chemical solute, the main results of interest here are the predictions that ρ_o shall be independent of temperature, vary directly with the solute concentration and vary as the square of the valence difference between solute and solvent. The latter prediction has been confirmed experimentally for a number of (dilute) alloy series and is usually referred to as Linde's rule. The direct dependence of ρ_o on solute concentration has also been confirmed experimentally for many different alloys in the range of solute concentration

from about 0 to 2 atomic percent. At still higher concentrations, deviations from this proportionality are observed and the situation is much more complex. In this thesis we shall normally be concerned with alloys of sufficiently dilute concentration that the proportional limit is not exceeded.

1-3 Matthiessen's Rule (MR)

The main problem to be studied here is the nature of the total resistivity of a specimen when both phonon and defect scattering processes are active simultaneously. This will be the case for all metals containing either chemical or physical defects when the temperature is not 0 Kelvin. In particular, we wish to know the precise relationship between the total measured resistivity, ρ_T , of an "impure" specimen and the separate resistivities, ρ_{iT} and ρ_0 . We shall not, however, be concerned here with the special case of magnetic impurities.

Over 100 years ago, A. Matthiessen¹³ observed that the increase in resistivity of a metal, produced by the addition of small concentrations of another metal in solid solution, was in general independent of temperature in the range 0°C to 100°C. This may be expressed as

$$\rho_T = \rho_{iT} + \delta\rho \quad (1.18)$$

where $\delta\rho$ is the temperature-independent increase in resistivity. Subsequent work by others, on many different alloys¹⁴⁻¹⁶ and cold worked metals¹⁷, demonstrated the general applicability of this statement as a good first approximation, and it has become widely known as Matthiessen's rule (MR).

Two alternative statements of this rule are in common usage in the literature. The first, which equates the slopes of an impure and pure metal, is exactly equivalent to Eq. (1.18), and may be expressed as

$$\frac{d\rho_T}{dT} = \frac{d\rho_{iT}}{dT} \quad (1.19)$$

The second, which takes the liberty of extending MR down to 0(K), is given by

$$\rho_T = \rho_{iT} + \rho_0 \quad (1.20)$$

which simply sets $\delta\rho = \rho_0$. This last form of MR is the one most often encountered nowadays, and we shall mean Eq. (1.20) when we refer to MR here, unless otherwise noted.

It is possible to qualitatively understand the basis of MR from a consideration of the free electron model and the combined relaxation time, τ , for both scattering processes. If we think of $(1/\tau)$ as crudely representing the average number of collisions per second, then one would intuitively

sum the individual collision rates to obtain the total, and therefore set

$$\frac{1}{\tau} = \frac{1}{(\tau)_{ph}} + \frac{1}{(\tau)_{imp}} \quad (1.21)$$

where $(\tau)_{ph}$ and $(\tau)_{imp}$ correspond to the relaxation times for phonon and impurity scattering respectively, and both are assumed independent of $\vec{k}$ to a first approximation. If now Eq. (1.21) is substituted into the theoretical equation (1.9) for the free electron resistivity, one immediately obtains Eq. (1.20) and MR. In principle then MR is based on Eq. (1.21), which in turn is based on the additivity of the scattering probabilities $Q(\vec{k}, \vec{k}')$ for the two processes (cf. Eq. (1.10)).

In general, small -- but significant -- deviations from MR are observed for most specimens when careful measurements are performed. Such deviations appear to have been first reported by Gruneisen¹¹ in 1933 and have since attracted considerable attention^{18-28, 31-89}. To allow for these deviations it is customary to expand Eq. (1.20) into

$$\rho_T = \rho_{iT} + \rho_o + \Delta_T \quad (1.22)$$

where Δ_T , the deviation from MR, will in general depend on temperature and the solute concentration (or ρ_o). In an analagous manner the relationship between the slopes, Eq.(1.19),

may be adapted to allow for deviations by writing

$$\frac{d\rho_T}{dT} = \frac{d\rho_{1T}}{dT} + \frac{d\Delta_T}{dT} \quad (1.23)$$

During the last decade the temperature dependence of Δ_T over the entire range 2 - 300 K has been determined experimentally for a number of dilute alloys¹⁹⁻²⁵ and plastically deformed^{18,21,26} or quenched²³ metals. Typical examples of the wide variety of deviations obtained are shown in Fig. 1.1, where we have followed the usual practice of plotting the normalized deviation λ_T , i.e.

$$\lambda_T = \Delta_T/\rho_0 \quad (1.24)$$

The λ_T functions for all plastically deformed metals are found to be similar in shape and sign to curve 1; while the λ_T functions for most alloys are found to lie between the extreme curves 2 and 6, and may have either sign above about 50K. The measurements show that for most alloys Δ_T is <30% of ρ_0 over the entire temperature range and that it is not always directly proportional to ρ_0 (see e.g. curves 3 and 4). The wide variety of temperature dependencies exhibited by Δ_T have presented interesting and perplexing theoretical problems, the details of which are left to Chapter 2.

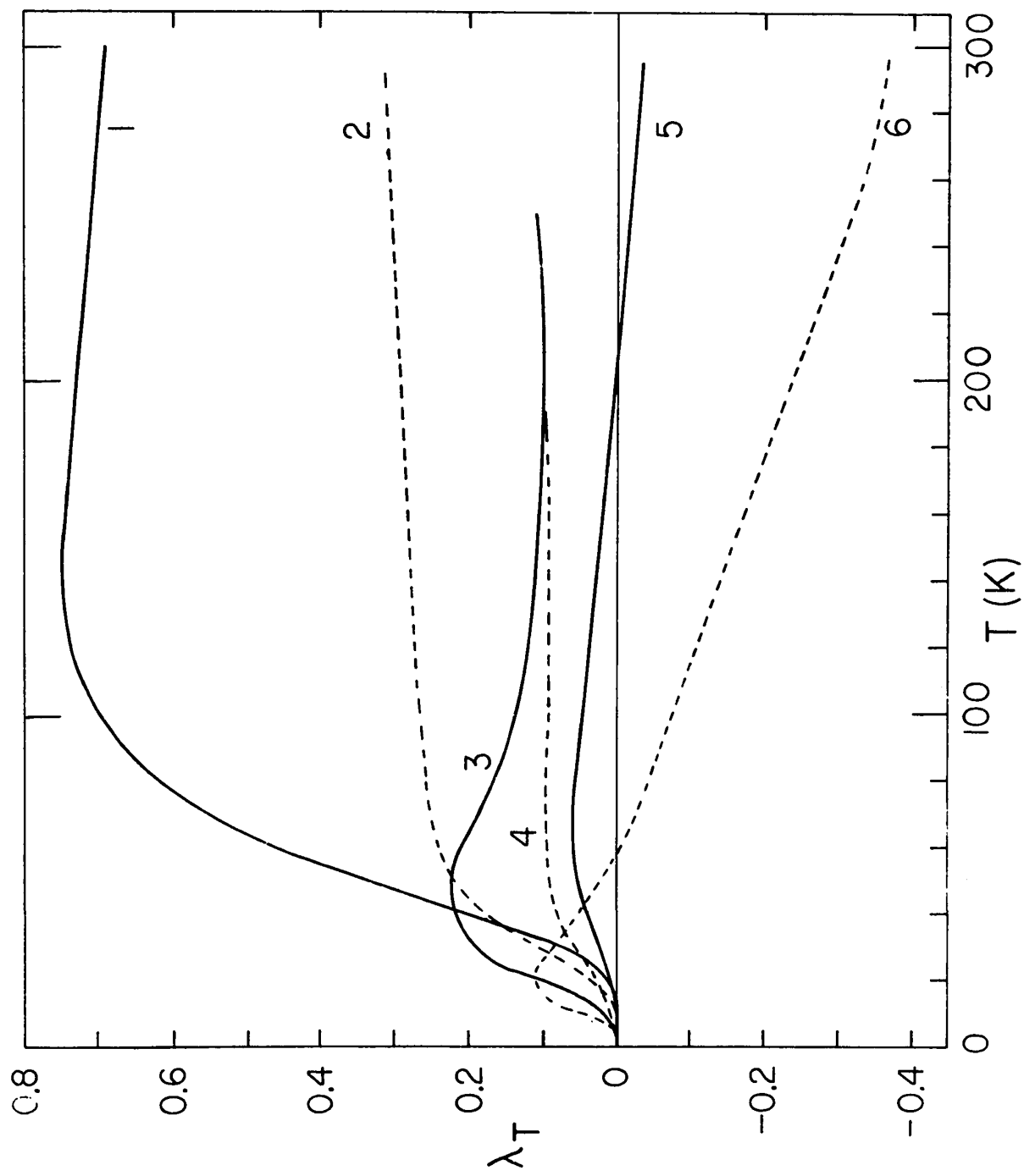


Fig. 1.1 . The λ_T function for six different specimens: (1) cold worked Cu^{21} , (2) Ag 0.1% Al^{24} , (3) Ag 0.1% Au^{21} , (4) Ag 1% Au^{21} , (5) Mg 0.22% Al^{24} , and (6) Cd 0.75% Mg^{24} .

1-4 Determination of Deviations from MR

The determination of Δ_T or λ_T requires highly refined experimental techniques in which all measurements must be made with great care in order to obtain meaningful results. This, of course, results from the fact that Δ_T is a second order effect, normally involving small differences between rather large resistivities.

There are essentially three different methods of determining Δ_T from measurements, and these are outlined briefly below to form a basis for later discussions:

Method 1: The most direct procedure for obtaining Δ_T is to measure the shape factor, $F = \text{area (A)}/\text{length (l)}$, both for the "impure" specimen (F^a) and the relatively pure specimen (F^p) at room temperature; mount the two specimens in a variable temperature cryostat; and measure R_T versus T simultaneously on both specimens at selected temperatures. One then sets $\rho_{1T} = \rho_T^p - \rho_O^p$ for the pure specimen (since MR is adequate in this case as long as $\rho_O^p \ll \rho_O^a$), and calculates Δ_T from Eq. (1.22) in the form

$$\Delta_T = (R_T^a - R_O^a) F^a - (R_T^p - R_O^p) F^p \quad (1.25)$$

where the superscripts "a" and "p" refer to the impure (alloyed) and pure specimens respectively.

The most serious limitation of this method is the

measurement of F ; its uncertainty is frequently reported to be about 1%, but may be as small as 0.1% in the most careful work. The resistance, on the other hand, can usually be measured to much better than 0.01% at high temperatures and should only become a limitation at very low temperatures where R_T approaches R_0 . The error, $d\lambda_T$, in λ_T may be estimated from the error, dF , in the shape factor using the following relation

$$d\lambda_T = \frac{\rho_{1T}}{\rho_0} \left(\frac{dF^a}{F^a} - \frac{dF^p}{F^p} \right) \quad (1.26)$$

which is based on earlier work²⁷. Because of the factor ρ_{1T} , $d\lambda_T$ may become very large at high temperatures and even impart a spurious temperature dependency to the observed λ_T .

A crude estimate for $d\lambda_T$ near room temperature may be obtained for something like the "best possible case" (i.e. $dF/F = 0.1\%$ for both specimens (but assuming opposite signs) and a typical value of $\rho_0/\rho_{1300} \approx 0.1$ per atomic % solute) by using the expression

$$d\lambda_{300} \approx 0.02/c \quad (1.27)$$

where c is the solute concentration in atomic percent. A comparison between this error and the λ_{300} values shown in Fig. 1.1 indicates that both could easily be of the same magnitude when c decreases below 0.3 atomic percent (but note

that the situation improves rapidly as T decreases). In spite of this particular advantage of working with high solute concentrations, most investigators avoid alloys with more than 1 or 2% solute because of other possible side effects, which might significantly alter the phonon resistivity of the host metal and complicate the situation. Thus a compromise between these two factors is necessary in any experiment.

Method 2: Another frequently used procedure for determining Δ_T or λ_T involves the introduction of resistance ratios in an attempt to avoid the use of the shape factor. The basic Eqs. (1.20) and (1.22) are first written in terms of resistivity ratios, ρ_T/ρ_{273} , which are then replaced by the corresponding resistance ratio, $(R_T/R_{273}) = W_T$, using

$$\frac{\rho_T}{\rho_{273}} = \frac{R_T}{R_{273}} \frac{F_T}{F_{273}} \approx \frac{R_T}{R_{273}} \quad (1.28)$$

where 273 refers to the ice point temperature of 273.15K (or 0°C). Although the two ratios are not exactly equal since F_T and F_{273} are slightly different due to thermal expansion, it is found that the quantity (F_T/F_{273}) has a negligible effect on the final equations and so may be deleted²⁸.

When converted to resistance ratios (see e.g. Berry²⁸),

equation (1.20) becomes

$$W_T = W_{iT} + W_O(1 - W_{iT}) \quad (1.29)$$

where $W_{iT} = R_{iT}/R_{i273}$ is the ratio for the ideally pure host metal and $W_O = R_O/R_{273}$ is the ratio for the impure metal at 0(K). This relation is sometimes referred to as the Nernst-Matthiessen rule, and provides a most convenient means of testing the validity of MR. The corresponding conversion for Eq. (1.22) is

$$W_T = GW_{iT} + W_O + \lambda_T W_O \quad (1.30)$$

where

$$G = \frac{R_{i273}}{R_{273}} = 1 - W_O(1 + \lambda_{273}). \quad (1.31)$$

The procedure for determining λ_T with this method is to obtain the basic R_T versus T data as in Method 1; convert it to W_T and W_{iT} ratios; estimate λ_{273} ; and solve equation (1.30) and (1.31) for λ_T . The main drawback is of course the estimation of λ_{273} . In previous work (see section 2-1) this was accomplished by assuming a particular theoretical relation for λ_T in the region of 273K; one then tested the theoretical relation at other temperatures using Eq. (1.30). While this procedure is very useful for disproving a particular theory, it unfortunately cannot be used to

definitively prove the same theory without an independent determination of λ_{273} (Berry²⁸). Stewart and Huebener²³, on the other hand, have recently reported a new method of determining Δ_T using resistance ratios only, which they claim does not require any prior assumptions about Δ_{273} (or λ_{273}). However, this method has not yet been confirmed by direct comparison with Method 1, and is currently being re-examined by others²⁹.

Method 3: The method to be described here is primarily intended for the study of physical defects produced for example by cold working, quenching, or neutron irradiation. The procedure is to introduce the defects into a pure metal; measure R_T at selected, highly reproducible temperatures; remove some (or all) of the defects by annealing, without otherwise disturbing the specimen; and then remeasure R_T at the same temperatures. The value of λ_T for the particular defect (or defects) removed may be calculated from the following relation, which is derived from Eq.(1.22) in a straight-forward manner (see section 6-2),

$$\lambda_T \approx \frac{\delta R_T}{\delta R_0} - 1 \quad (1.32)$$

where δR_T is the decrease in R_T due to the removal of the defects.

The main drawback to this method is the particularly

careful experimentation required, i.e. R_T must be measured at the same temperatures within say 0.001(K) in both runs and the specimen must not be contaminated or otherwise disturbed during annealing. This method does, however, offer the possibility of considerably improved accuracy over other methods for the study of defects.

1-5 Scope of the Thesis

This thesis deals with a number of experimental and theoretical aspects of the deviations from MR, for both chemical solute and physical defects. Most of the new experimental work presented here is concerned with the deviations from MR for platinum either in a slightly impure state (Chapter 3), a quenched state (Chapter 6), a plastically deformed state (Chapter 7), or a relatively pure state (Chapter 8). These studies were undertaken mainly to provide much-needed basic information about the resistivity properties of platinum, for use in problems related to the International Practical Temperature Scale³⁰. This scale is presently based on the R_T versus T relationship of platinum resistance thermometers over the entire range from 10 to 903 K, which may soon be extended up to 1337 K. Aside from these considerations, platinum is an excellent choice for defect studies as it is stable at high temperatures, can be easily quenched or cold-worked, and is readily available

in small diameter wires of extremely high purity.

The theoretical problems treated here mainly arise out of conflicting statements, or interpretations of experimental data, reported in earlier work. An attempt to clarify these situations is made from an experimentalist's point of view, and in so doing a number of interesting and useful conclusions are revealed. The problems investigated here include certain inconsistencies in the two-band Δ_T model³¹ (Chapter 3), the dependence of the Sondheimer Δ_T function³² on solute concentration (Chapter 4), and the Δ_T function for phonon spectrum changes (Chapter 5).

One of the most important applications of the deviations from MR is the derivation of the phonon resistivity, ρ_{iT} , from the measured ρ_T data on relatively pure metals. In order to make a meaningful comparison with theoretical expressions for ρ_{iT} at low temperatures, the deviations from MR must be taken into account even for the highly pure specimens presently available^{21,33}. To demonstrate this application, the ρ_{iT} function for platinum in the range 1-13K is derived in Chapter 8 from new experimental measurements, taking into account the deviations from MR. The results obtained are then compared with existing theoretical expressions for ρ_{iT} in this temperature range.

CHAPTER 2

REVIEW OF EXISTING THEORY AND EXPERIMENT

Specific theoretical explanations for the deviations from MR were first advanced in 1947, with Sondheimer and Wilson's two-band treatment³¹, and have multiplied rapidly in the last decade until now there are something like thirteen different possibilities from which to choose. Unfortunately, very few of these theories have been proven incorrect by either experimental work or more advanced theories, so that at the present time one is forced to consider virtually all existing theories as reasonable possibilities.

In this chapter we shall briefly outline the predictions and basis of the various theories, and where possible critically compare them with existing experimental evidence. As stressed in earlier discussions, the error in experimental work is frequently rather large, so that the comparisons will usually be of a qualitative rather than a quantitative nature. In this regard particular attention will be paid to the temperature dependency and sign of the deviations from MR as a means of identifying their source. Specific theories for magnetic solutes will not be discussed here.

2-1 Two-Band Model

The deviations from MR resulting from the presence of two distinct bands of conduction electrons in a metal was first examined by Sondheimer and Wilson³¹ in 1947. In their analysis the origin of the two bands was considered to be the s and d conduction electrons of transition metals. However, it has since been appreciated that the two distinct types of electrons may in fact be associated with different regions of the Fermi surface of the host metal (Krautz and Schultz³⁴ 1957), and that the same formalism also applies when the "impurities" are distributed non-uniformly between two distinct macroscopic regions of a conductor³⁴. This model has been applied with considerable success in a large number of experimental investigations, and is still considered to be a major source of deviations from MR in many recent publications. Its development and applications are outlined below in considerable detail since it will be used in later chapters.

(a) Sondheimer and Wilson Analysis

In their treatment Sondheimer and Wilson assume for simplicity that the two conduction bands are completely independent, and that MR is valid for each separate band. Under these conditions the total resistivity of each band, ρ_1 for band 1 and ρ_2 for band 2, may be expressed as

$$\rho_1 = \rho_{i1} + \rho_{r1} \quad , \quad \text{and} \quad \rho_2 = \rho_{i2} + \rho_{r2}$$

where ρ_{i1} and ρ_{i2} are the phonon resistivity components, and ρ_{r1} and ρ_{r2} are the defect resistivity components. Since the two bands contribute additively to the total conductivity, their total observed resistivity is given by the usual relation for two parallel resistive networks, i.e.

$$\rho_T = \frac{\rho_1 \rho_2}{\rho_1 + \rho_2}$$

which at $T = 0(K)$ becomes

$$\rho_o = \frac{\rho_{r1} \rho_{r2}}{\rho_{r1} + \rho_{r2}} \quad ,$$

and when the metal is ideally pure becomes

$$\rho_{iT} = \frac{\rho_{i1} \rho_{i2}}{\rho_{i1} + \rho_{i2}}$$

The resulting deviation from MR is obtained by substituting the above relations into the basic Eq. (1.22) defining Δ_T , and may be expressed as

$$\Delta_T = \frac{\rho_{iT} \rho_o}{a\rho_{iT} + b\rho_o} = \lambda_T \rho_o \quad (2.1)$$

where

$$a = \frac{v(1+\mu)^2}{(v-\mu)^2} \quad , \quad b = \frac{\mu(1+v)^2}{(v-\mu)^2} \quad (2.2)$$

and

$$\mu = \rho_{i2}/\rho_{i1} \quad , \quad v = \rho_{r2}/\rho_{r1} \quad (2.3)$$

Of the four parameters a , b , μ , and v appearing in these equations only the last two have any real physical significance, viz. μ represents the ratio of the resistivities for the two bands when the metal is ideally pure, while v represents the ratio when only defect scattering is present, i.e. at $T = 0(K)$. In principle, it is entirely possible that these parameters depend on temperature to some extent; however, for simplicity most investigators prior to about 1967 have assumed that these parameters are temperature independent, and unless otherwise stated this will be assumed here. The special case where $\mu = v$ is trivial since it leads in effect to one band conduction and hence yields $\Delta_T = 0$.

The form of the two-band λ_T function given by Eq. (2.1) is illustrated by curves 1 and 4 of Fig. 1.1, or by the theoretical curve in Fig. 3.1. Its limiting form at high and low temperatures, may be expressed as

$$\lambda_T = 1/a \quad \text{when } \rho_{iT} \gg \rho_0 \quad (\text{high } T) \quad , \quad (2.4)$$

and

$$\lambda_T = \rho_{iT}/b\rho_0 \quad \text{when} \quad \rho_{iT} \ll \rho_0 \quad (\text{low } T) \quad (2.5)$$

Obviously, the larger ρ_0 becomes the higher will be the temperature at which λ_T reaches its temperature-independent saturation value of $1/a$.

(b) Early Tests Using Resistance Ratios

The first experimental tests of this model were performed by Krautz and Schultz on cold-worked W (1954)³⁵, PbIn alloys (1956)³⁶, and AuAg and AgAu alloys (1957)³⁴. They derived values of λ_T from the measured resistance ratios, using essentially the second method described in section 1-4. The value of λ_{273} required in this method was determined from measurements above 190K, where λ_T was assumed to be independent of temperature. In the case of alloys of the multivalent metal Pb, the two bands were attributed to electron and hole conduction, while for the monovalent metals Ag and Au they were attributed to different regions of the Fermi surface. It was found in these tests that the experimental results could be fitted quantitatively with the two-band model in a most impressive manner. This same type of λ_T analysis was subsequently used by Alley and Serin²⁷ for a large number of dilute alloys of Al, Sn and Cu; but unfortunately they measured W_T at only one

temperature between 4 and 198K and thus were unable to test the two-band model adequately.

Numerous attempts have been made to use this model in platinum resistance thermometry in order to establish the W_T -T relationship for various Pt specimens with great accuracy; see for example Schultz (1957)³⁷, Sharevskaya et al (1962)³⁸, Van Dijk (1962)³⁹, Berry and Lovejoy (1962)⁴⁰, Berry (1963)²⁸ and Corruccini (1965)⁴¹. The major problem in this application was the derivation of sufficiently accurate values of W_{1T} to permit a valid calculation of the relatively small correction term $\lambda_T W_0$ in Eq. (1.30). This was accomplished reasonably successfully by Berry²⁸ who extrapolated W_T data on 65 or more thermometers with the aid of a special graphical technique. His subsequent tests revealed that only about 50% of the thermometers tested in the 10 - 90K range could possibly be represented by the two-band model within the limits of accuracy of W_{1T} .

An important fact to emerge from Berry's analysis²⁸ was that none of the earlier two-band studies had actually given strong support to the validity of this model at intermediate and high temperatures -- in spite of the impressive agreements claimed. This resulted from the fact that the critical parameter λ_{273} in Eq. (1.30) could not be determined as reliably as was first thought. For example, Krautz and Schultz³⁵ had argued that the value of the

quantity $Z = [W_T - W_{iT}] / [1 - W_{iT}]$ should be constant for $T > 200\text{K}$ according to the two-band model (and equal to $W_0 (1 + \lambda_{273})$); and since this was found to be the case they were convinced that their λ_{273} estimate must be correct. However, it was demonstrated in Berry's paper that there are an infinite number of plausible λ_T functions which would lead to a constant Z value at high temperatures, even though these functions possessed radically different λ_{273} values and deviated from the two-band model. It was also pointed out that this limitation to the validity of the tests does not apply as strongly in the low temperature region where the calculated λ_T function is only slightly dependent on the selected value of λ_{273} . However, in the above work only the Pt resistance thermometers have been measured in sufficient detail at low temperatures to permit a comparison with theory; and for these we find that the two-band model will fit reasonably well in the 10 - 40K range for only about half of the Pt specimens tested.

In a further effort to fit all Pt resistance thermometer data, including those which appeared to deviate from the two-band model, Lovejoy⁴² introduced a multiband model in which layers of surface contamination on the wire simulated additional 'bands' or conduction paths. He found that a thin surface layer of concentrated impurities, plus a thicker subsurface layer of less concentrated impurities, could account

for the data. However, no evidence to support the existence of such layers was provided, and more recent λ_T values²³ for Pt show that deviations from the two-band model can occur even when the solute or defects are distributed homogeneously.

In 1967 Kos and Lamarche⁴³ attempted to apply the two-band model to thermometric Pt in the restricted range 1 - 11K, not covered by earlier investigations. In their tests the unknown W_{iT} was treated as an adjustable parameter (within limits) but subject to the constraint that it have the form given by Van Dijk⁴⁴, i.e. $W_{iT} = p_i T^2 + q_i T^5$ where p_i , q_i are constants. It was found, however, that no combination of reasonable values for the parameters W_{iT} , a and b would lead to complete agreement between the measured and calculated W_T values, and it was suggested that the 'apparent' failure of the two-band model might be due to the invalidity of the expression used for W_{iT} . This possibility was given further support by Berry's (1967) investigation⁴⁵ in which a slightly different W_{iT} form, i.e. $W_{iT} = p_i T^2 + q_i T^{4.7}$, was found to fit the best available data on Pt in the range 1 - 17K. It was shown that the same form would equally well fit the earlier W_T measurements⁴⁴ of Van Dijk in the region below 4.2K. The latter work is fully described in Chapter 8 of this thesis and indicates that the two-band model is still plausible at low temperatures for some Pt specimens.

In the work reviewed up to this point, the fundamental two-band parameter, $\mu = \rho_{12}/\rho_{11}$, was estimated from the parameters a and b to have a value of 6 ± 1 for six different specimens of Pt by Lovejoy⁴⁶, between 2 and 9 for nine specimens of Pt by Kos and Lamarche⁴³, and about 1 for two specimens of Pb by Krautz and Schultz³⁶. Since μ is by definition characteristic only of the host metal, the variation in μ among different specimens of Pt appeared to violate the two-band model. This particular problem was investigated as a thesis project in 1967 and is described in detail in Chapter 3. The main results, which were published earlier⁴⁷, show that the variation in μ can occur with even less pure specimens of Pt than those mentioned above, and also occurs with two other metals investigated earlier by Krautz and Schultz^{35,36}. It was suggested that this internal inconsistency in the two-band model might be due to the dependence of the parameters on temperature, or to the presence of other sources of deviation from MR. Both of these suggestions are in general supported by more recent work.

(c) Early Tests Using Resistivity Measurements

The first test of the two-band model using Δ_T values determined directly from resistivity measurements (Method 1 of section 1-4) was performed by Das and Gerritsen¹⁹ (1964)

on a number of Mg alloys. They found that the Δ_T function was roughly proportional to ρ_{1T} below 20K in accordance with the two-band model, but above 100K decreased linearly with T in contradiction with this model (assuming the parameter 'a' is temperature independent). To qualitatively account for the observed Δ_T function they superimposed a two-band component and a θ_R - change component which is described later in section 2-5. In contrast to this result Damon and Klemens⁴⁸ found that the two-band model by itself would not fit their more detailed measurements of Δ_T below 20K for a series of gold alloys, even if the parameters a, b were allowed to be temperature dependent. They plotted $[\rho_T - \rho_0]$ (which corresponds to $(\Delta_T + \rho_{1T})$) against ρ_0 at various temperatures and showed that Δ_T was not independent of ρ_0 , at low temperatures -- as would be expected from the two-band model. By the same technique they were able to separate a two-band component in the 10 - 20K region from a second component, which was attributed to 'phonon-assisted impurity scattering' (see section 2-6). The two-band component, which was dominant when the solute concentration was below 1%, was shown to vary roughly as ρ_{1T} in the range 11 - 20K, while ρ_{1T} itself varied as T^5 . Further measurements in the range 80 to 500K by these investigators⁴⁹ showed that Δ_T for all but one of their gold alloys deviated drastically from the two-band model (with constant parameter 'a') by

exhibiting either positive or negative slopes at high temperatures.

In the case of plastically deformed metals, however, Barbee et al⁵⁰ (1966) report that the two-band model is extremely effective. They cite microscopic evidence to show that dislocations are not distributed homogeneously in a specimen, but rather form cells having high dislocation density in the cell walls and low density within the cell. Similar to earlier workers (Schultz³⁴, Van Dijk³⁹) they found that the two parallel regions of different resistivity led to departures from MR analogous to the two-band model. They show that this model gives excellent quantitative agreement with the experimental Δ_T values for deformed Cu, Ag, and Au, reported by Basinski et al¹⁸ (1963), over the complete range 4 - 300K when plausible values are assigned to the cell parameters.

(d) Two-Band Fermi Surface Model

The possibility that the two distinct groups of conduction electrons in the two-band model could arise from two distinct regions of the Fermi surface was recognized as early as 1957 by Krautz and Schultz³⁴. This possibility was confirmed in 1961 by the theoretical calculations of Ziman⁵¹ for noble metal alloys, which showed that the relaxation time (τ) for the electrons from the "neck" (N)

and "belly" (B) regions of the Fermi surface were in general different or anisotropic, and furthermore gave different anisotropies for phonon and impurity scattering. Since the relaxation time is inversely related to the probability of electron scattering (cf. Eq. (1.10)) this meant that the resistivity would in general be different for the neck and belly electrons and thus led to a two-band model for the simplest case where no interband scattering occurs.

Specifically, Ziman made the following predictions concerning the ratio of the relaxation time, τ_N/τ_B , for neck and belly electrons:

(1) that $(\tau_N/\tau_B)_{ph}$ for phonon scattering is temperature dependent (due to preferential freezing-out of Umklapp processes), and possesses a value of about 1.1 near θ_D decreasing monotonically to 0.46 near $\theta_D/5$.

(2) for scattering by an impurity with dissimilar valence, $(\tau_N/\tau_B)_{imp} \approx 0.7$ (and should be independent of temperature for all impurities).

(3) for scattering by a homovalent impurity $(\tau_N/\tau_B)_{imp}$ will be greater than 1 if the atomic volumes of the host and impurity atoms are similar, but may be less than 1 if the relative atomic volumes are dissimilar.

Ziman pointed out that these predictions are all consistent with reported Hall effect measurements on various alloys.

The first detailed application of Ziman's work to deviations from MR was made by Dugdale and Basinski²¹ (1967), who studied a number of Cu and Ag alloys, plus strained Cu and Ag specimens, in the temperature range 4 - 300K. In order to relate the relaxation time ratio, τ_N/τ_B , to the resistivity ratio, ρ_N/ρ_B , for the neck and belly electrons they used the expression

$$\frac{\rho_B}{\rho_N} = \frac{A_N v_N \tau_N}{A_B v_B \tau_B} = C_1 \left(\frac{\tau_N}{\tau_B} \right) \quad (2.6)$$

where (A_N/A_B) and (v_N/v_B) refer to the ratio of the two Fermi surface areas and the two Fermi velocities respectively. This simple relation is presumably based on a relation such as Eq. (1.8) given in section 1-3. Accordingly, the basic two-band parameters μ and ν , given by Eq. (2.3), may be written

$$\mu = \left(\frac{\rho_B}{\rho_N} \right)_{ph} = C_1 \left(\frac{\tau_N}{\tau_B} \right)_{ph} \quad (2.7)$$

and

$$\nu = \left(\frac{\rho_B}{\rho_N} \right)_{imp} = C_1 \left(\frac{\tau_N}{\tau_B} \right)_{imp} \quad (2.8)$$

From their observed λ_T functions Dugdale and Basinski derive values of μ at both low ($\sim 25K$) and high ($\sim 300K$) temperatures for Ag and Cu, and values of ν for the solutes

Au, Ge and Sn. Their results are found to be consistent with this model and Ziman's prediction in that:

(1) the value of μ is the same for each alloy of a particular host metal,

(2) the ratio of μ (and hence $(\tau_N/\tau_B)_{ph}$) at 300K to μ at 25K is about 3 for both Cu and Ag,

(3) the value of μ at 300K yields the expected value of $(\tau_N/\tau_B)_{ph} \approx 1.1$ when a value of $C_1 = 1/7$ -- consistent with known properties of the Fermi surface -- is substituted into Eq. (2.7)

(4) the values of $(\tau_N/\tau_B)_{imp}$, calculated with the above value of C_1 , are in general found to be different from $(\tau_N/\tau_B)_{ph}$ as expected.

The only disagreement with Ziman's predictions is the fact the value of $(\tau_N/\tau_B)_{imp}$ lies in the range 1.6 - 2.7 regardless of the valence or atomic volume of the solute.

Still further support is given to the two-band Fermi surface model in Dugdale and Basinski's work by the fact that it will account for the general features of the temperature dependencies of their λ_T functions for both the alloys and the strained specimens. Specifically they show that the low temperature λ_T peaks (near $\theta_D/5$), which occur in all of their alloys, are consistent with the observed temperature dependency of μ and the fact that $v > \mu$ in these

cases. Even the observed dependence of the peak height and peak temperature on the solute concentration follows directly from this model. It is also demonstrated that the completely different shape of the λ_T curves for the strained metals can be qualitatively understood once the fact that $v < \mu$ in this case is taken into account.

Following this lead, other workers have analysed their observed departures from MR in terms of this particular model. In 1968 Damon, Mathur and Klemens⁵² reported values of μ in the 10 - 40K range for the solvent Au, and values of v (all similar) for the solutes Cu, Pt and In -- all values of μ and v being appreciably smaller than those of Dugdale and Basinski for Cu and Ag alloys. In 1970 Lengeler, Schilling and Wenzl²⁵ demonstrated graphically the variation of μ over the entire range 10 - 500K for the solvent Cu, and report values of v (both similar) for the solutes Au and Ni, all values showing agreement with Dugdale and Basinski's results. Stewart and Huebener²³ also report values of μ and v for several Au and Pt alloys, but unfortunately their values cannot be properly compared with those above since they calculated the parameters from data at 20 and 273K assuming μ was independent of temperature. Surprisingly enough, this model has even been applied to impure and strained potassium in the range 1.2 - 4.2K by Guban⁵³ in spite of the near spherical Fermi surface of

potassium, and hence the unlikely prospect of there being two distinct regions. He found that the deviations from MR could be accounted for by assuming that about 6% of the electrons possess a relaxation time which differs from the rest by about a factor of three.

In summation, then, the two-band Fermi surface model is found to provide a plausible explanation for all, or part, of the observed deviations from MR for a number of dilute alloys and strained specimens of the noble metals. It will also account for certain observed features of other physical parameters for these metals, such as the Hall effect⁵⁴. The fact that this model works as well as it does suggests that the underlying assumption of no interband (neck $\rightleftharpoons$ belly) scattering must be a realistic approximation (but see also the comments of Fert⁵⁵, and Stewart and Huebener²³). The main disagreements between theory and experiment observed thus far with noble metals are the lack of any strong dependence of $(\tau_N/\tau_B)_{\text{imp}}$ on the valence and atomic volume of the solute; the fact that many observed λ_T functions^{49,24} are not independent of temperature in the high temperature range in accordance with Eq. (2.4) and the expectation that μ will be constant there; and the fact that dilute alloys of AgMg and AgAl do not exhibit strong low temperature peaks²⁴. Another experimental result that requires further explanation is the occurrence of low

temperature λ_T peaks in non-noble metal alloys, such as PtAu²³, AlAg²⁴, and MgAl²⁴, that are remarkably similar to those reported for the noble metal alloys, in spite of the differences in the Fermi surfaces.

2-2 Kohler's Theory

Kohler¹⁰ (1949) has used the variational expression for the resistivity, given earlier by Eq. (1.15), to demonstrate quite generally that positive deviations from MR will normally occur when two scattering processes act simultaneously. To do this he writes Eq. (1.15) for the total scattering operator P , and then sets P equal to the sum of the phonon scattering operator, P_i , and the impurity scattering operator, P_o . The total resistivity is then given by

$$\rho_T = \frac{\langle \phi, P \phi \rangle}{J^2} = \frac{\langle \phi, P_i \phi \rangle}{J^2} + \frac{\langle \phi, P_o \phi \rangle}{J^2} \quad (2.9)$$

when ϕ is an exact solution of the Boltzmann equation (1.11) for P . One may also write for the separate resistivities, when only phonon or impurity scattering is present, that

$$\rho_{iT} \geq \frac{\langle \phi, P_i \phi \rangle}{J^2} \quad \text{and} \quad \rho_o \geq \frac{\langle \phi, P_o \phi \rangle}{J^2} \quad (2.10)$$

The equality sign in Eq. (2.10) holds only if the above ϕ is

also an exact solution of the Boltzmann equation for P_1 and P_0 -- which in general will not be the case. Combining Eqs. (2.10) and (2.9) one obtains

$$\rho_T \geq \rho_{1T} + \rho_0 \quad (2.11)$$

which makes Δ_T positive or zero. This prediction agrees with most experimental results, but not all (see e.g. Fig. 1.1 and Chapt. 6). Hence the assumptions on which Eq. (1.15) is based must not hold in all cases.

In the same paper, Kohler also derives an expression for the upper limit to the Δ_T function using the variational method. He writes a trial solution ϕ' for Eq. (2.9) as a linear combination of the true solutions, ϕ_1 , and ϕ_0 , for the Eq. (2.10), i.e.

$$\phi' = n\phi_1 + (1-n)\phi_0 \quad (2.12)$$

After substituting this into Eq. (2.9) and minimizing the expression with respect to n , the result is

$$\Delta_T \leq \beta_1 \beta_2 \frac{\rho_{1T} \rho_0}{\beta_1 \rho_{1T} + \beta_2 \rho_0} \quad (2.13)$$

where all that is known about the parameters β_1 , and β_2 is that they should be much less than unity⁶.

The close similarity between the form of Eq. (2.13) and the two-band expression for Δ_T , Eq. (2.1), has led some

authors to consider Eq. (2.1) as representing deviations from either source. It should be remembered, however, that Eq. (2.13) is an inequality which cannot be properly compared with experiment; and that Kohler's source of deviation should be present for a single conduction band and will therefore represent an additional effect.

It has been suggested by Ziman⁶, based on the variational principle, that Kohler's source of deviation from MR will normally be relatively small. This suggestion is supported by the variational analysis performed by Sondheimer for the special case discussed in the next section.

2-3 Sondheimer's Δ_T Calculation

Sondheimer³², in 1950, calculated the Δ_T function for the special case of quasi-free electrons (spherical Fermi surface) in a monovalent metal lattice, with the aid of Kohler's variational procedure. He obtained a complex expression for the total electrical resistivity of an impure (or pure) metal, which for the first time was valid at all temperatures; and based on this, he calculated ρ_T , ρ_{iT} , and then Δ_T for two selected values of ρ_0 . Since no simple explicit relation for Δ_T could be given, its values were estimated numerically at a number of selected temperatures.

His results show that λ_T approaches 0 at either very high or very low temperatures, and exhibits a positive peak

in the vicinity of the temperature where ρ_{1T} and ρ_0 are of the same order of magnitude. The peak λ_T deviations for the two ρ_0 values tested have magnitudes of roughly 0.01 and occur near a temperature of $0.3 \theta_R$. Peaks in this range were first observed by Krautz and Schultz³⁴ (1957) for Ag and Au alloys. They were able to quantitatively fit their results to Sondheimer's predictions in a rather impressive manner, once they had subtracted another Δ_T component attributed to the two-band model. Such a comparison was possible in this case because their solute concentration of about 1 atomic % corresponded closely to the ρ_0 values used by Sondheimer. More recently however, Dugdale and Basinski²¹ and others^{23,24} have shown that the low temperature peaks may be an order of magnitude greater than Sondheimer's peaks when the solute concentration is an order of magnitude less than that used by Sondheimer.

This of course raised the interesting question of whether Sondheimer's equations would yield a much larger λ_T value for lower solute concentrations. From his original work at two concentrations, one could see that λ_T did indeed increase as ρ_0 decreased. This problem was thoroughly investigated as a thesis project and is described in detail in Chapter 4. It is demonstrated there that the Sondheimer λ_T function saturates at low solute concentrations and therefore will not by itself account for most of the observed

λ_T peaks at low temperatures.

2-4 Anisotropic Phonon Spectrum

Using the variational method for solving the Boltzmann equation, Bross⁵⁶ (1959) has shown that if the lattice vibration spectrum is anisotropic, i.e. the frequency and polarization vector depends on the direction of the propagation vector, then the electron-phonon scattering probability, $Q(\vec{k}, \vec{k}')$, and the relaxation time will also be anisotropic in k - space, and deviations from MR will result. This argument is of course very similar to the two-band Fermi surface model except that the source of anisotropy is not the Fermi surface. The fact that the vibrational spectrum could be anisotropic was demonstrated by Bross's detailed calculation of the spectrum for copper, and is supported by more recent work.

Using results from one of his earlier papers⁵⁷, Bross also derived an explicit expression for the deviation from MR for the case of lattice (point) defects in Cu. This expression is very similar to the two-band Eq. (2.1) except that the parameters 'a' and 'b' are replaced by functions of matrix elements. He demonstrates that this relation will qualitatively fit the experimental results of Magnuson et al⁵⁸ for irradiated copper.

Since Bross's original work, no one else appears to

have discussed or used this particular mechanism for deviations from MR.

2-5 Change in θ_R Model

Many authors have attributed all, or part, of their observed Δ_T functions to changes in the phonon spectrum of a pure metal when defects are introduced. In the simplest case this may be characterized by a change in θ_R in the Bloch-Gruneisen relation (see Eq. (1.16)). The basic argument is that the measured value of ρ_{iT} on 'pure' metals should not be used in Eq. (1.22) for the calculation of Δ_T . Instead one should use a modified ρ_{iT} function corresponding to the modified θ_R value for the alloy, and this of course should then remove any apparent deviation from MR due to this particular source.

The θ_R -change model has been used to account for the total deviation from MR in the following experimental investigations:

Boas and Nicholas⁵⁹ (1953) attribute a decrease in $d\rho_T/dT$ over the range 90-273 K, resulting from cold working on brass and bronze specimens, to an increase in θ_R of about 1%. They appear to be the first to demonstrate analytically that such a change in slope is consistent with the high temperature approximation of the Bloch-Gruneisen equation.

Bowen and Rodeback⁶⁰ (1953) attribute an increase in $d\rho_T/dT$ over the range 4-77 K, resulting from cold working and α particle irradiation of Cu, to a decrease in θ_R of up to 12%.

Magnuson, Palmer and Koehler⁵⁸ (1958) attribute a positive Δ_T function in the range 4-60 K, resulting from deuteron irradiation of Cu, Ag and CuNi alloy, to a decrease in θ_R of up to 7%.

Hedgcock and Muir²⁰ (1964) attribute their Δ_T functions in the range 4-300 K for a number of Mg alloys, to a decrease in θ_R of up to 5% per atomic % solute. A new quantitative test is presented which reportedly demonstrates that MR is valid over the whole range 4-300 K once θ_R is properly adjusted (but see Chapter 5).

Holzhauser⁶¹ (1967) attributes a positive Δ_T function in the range 17-28 K for cold worked Cu and Al to a decrease in θ_R of up to 6%. He finds that Δ_T is proportional to ρ_{iT} in this range.

Conte and Dural⁶² (1968) attribute a positive Δ_T function in the range 4-300 K, for quenched Au, to a decrease in θ_R of about 0.5%.

Crisp and Rungis⁶³ (1970) calculate the change in θ_R for Au and Ag alloys from resistivity measurements at 4.2, 77 and 273 K. They find that θ_R initially decreases by about 12% per atomic % solute in both cases.

In addition, the θ_R -change model has been used to partially account for the observed deviations from MR in the following cases:

Das and Gerritsen¹⁹ (1964) attribute their observed Δ_T functions for Mg alloys in the range 4-300 K to a combination of two Δ_T components of opposite sign. The positive component they associate with a two-band model (see section 2-1) while the negative component (with negative slope) is associated with a decrease in θ_R on alloying of less than 1%.

Grigor'yants, Pervakov and Khotkevich²⁶ (1969) attempt to explain a positive Δ_T function in the range 4-300 K, resulting from cold working of Ag and Au, by a decrease in θ_R of 0.3%. They find that it will not account for the data by itself, but suggest that this plus other possible mechanisms combine to yield the observed Δ_T . This work is of special importance because the specific heat of the samples was also measured and the change in θ_D determined experimentally. The corresponding change in θ_R was assumed to be the same.

Finally, the θ_R -change model was tested and rejected by Barbee, Huggins and Little⁵⁰ in their attempt to explain a positive Δ_T function in the range 4-300 K for cold worked Ag. It was found that the two-band model could account for the results by itself.

To complete the review, it should be noted that a number of investigators tend to discount the phonon spectrum changes as too small or ineffective to contribute significantly to Δ_T . For example, Dugdale and Basinski²¹, and Seth and Woods²⁴, reach this conclusion on the basis that the Δ_T functions of various alloys are not noticeably affected by differences in their solute to solvent mass ratio -- in spite of the fact that these differences should enhance any effects due to phonon spectrum changes. On the other hand, there is a considerable body of evidence from specific heat measurements and lattice dynamical theory (Maradudin⁶⁴ 1966) which show that phonon spectrum changes and θ_D changes do occur.

The situation is made still more confusing by two other factors:

- (1) There are seemingly irreconcilable differences in the direction of θ_R change suggested by the above authors. For example, a decrease in θ_R is used to account for a positive Δ_T by Magnuson et al, for a negative Δ_T by Das and Gerritsen, and both a positive and negative Δ_T by Hedgcock and Muir.
- (2) Hedgcock and Muir²⁰ appear to achieve impressive quantitative agreement with the θ_R -change model.

The present unsatisfactory situation is analysed in more detail in Chapter 5, and some of the difficulties are resolved there.

2-6 Phonon - Assisted Impurity Scattering

Under this heading we shall consider deviations from MR which result from the thermal motion of the impurity or solute ions, and thus involve the simultaneous scattering by both phonons and solute ions. In early work, such as the Bloch theory⁴, the solute ions were treated as rigidly fixed at their lattice sites and all impurity scattering was simply due to the difference in potential (or excess potential) between the solute and solvent ions. The effect of the thermal motion of this excess potential on the electrical resistivity was first treated by Koshino⁶⁵ in 1960. He found that Δ_T should be proportional to the solute concentration, vary as T^2 when $T \ll \theta_D$, and vary as T when $T > \theta_D$. Among other things, this deviation was based on the assumption that the mass difference between solute and solvent ions was very small and that the phonon spectrum of the solvent was not deformed by (or different from) the solute ions. Koshino's theory, however, has been criticized by Taylor⁶⁶, who claims that certain terms were neglected which greatly reduce the magnitude of this effect. This criticism has been confirmed by Kagan and Zhernov⁶⁷ (see section 2-8), and it appears now that Koshino's Δ_T term should only be significant at very low temperatures.

The same phonon-assisted impurity scattering has also

been treated by Klemens⁶⁸ (1963), with the important difference that he considers the perturbation to arise from the change of form of the impurity potential as the displacement of the impurity ion relative to the neighbouring ions oscillates, i.e. due to strain. In this event he shows that the additional Δ_T component is considerably enhanced over Taylor's result, and may be expressed as

$$\Delta_T = A^2 \rho_0 \langle e^2 \rangle \quad (2.14)$$

where $\langle e^2 \rangle$ is the mean square thermal strain and A^2 is a numerical constant of the order of 10. This deviation will depend on temperature through the factor $\langle e^2 \rangle$ which varies as T^4 at low temperatures and as T at high temperatures.

Evidence for such a Δ_T component has been obtained by Damon, Mathur and Klemens⁵² from measurements on a number of gold alloys in the 1.5 to 40 K region. They were able to identify a Δ_T component in the highly restricted range 10-15 K which was proportional to ρ_0 and varied as T^4 . In order to make this identification it was necessary to take account of another strong Δ_T component which varied as ρ_{iT} (or T^5), and was attributed to the two-band Fermi surface model. The separation of the two terms was accomplished by plotting $(\rho_T - \rho_0)$ against ρ_0 at one temperature, and assigning a linear region to Klemens' Δ_T term. The value of the

empirical coefficient, A^2 , obtained in this work was found to be relatively insensitive to the nature of the solute -- a feature which was not readily explained.

Damon and Klemens⁴⁹ also searched for evidence of phonon-assisted impurity scattering in the 80-500 K range, where they anticipated that the temperature dependence of Δ_T would be noticeably altered for solutes of lighter mass than the solvent, since the phonon spectrum has a high frequency peak, or local mode, in this particular case⁶⁴. However, measurements on a number of Au alloys containing solutes of lighter mass, as well as similar mass, exhibited qualitatively the same temperature dependencies, thus giving no evidence of this type of impurity scattering.

No other experimental confirmation of Klemens' strain theory has been reported to date.

2-7 Theory of Masharov

(a) Alloys

Masharov⁶⁹ (1962) has calculated the total resistivity of an impure metal using the Bloch theory⁴, taking into account the influence of impurities on the lattice vibrations -- which were neglected in previous theories. He reports a deviation from MR which may be written as the sum of three separate terms, i.e.

$$\Delta_T = \rho_1' + \rho_2' + \rho_3'$$

where all terms are proportional to solute concentration, and each term has the following origin and temperature dependency:

The term ρ_1' is attributed to changes in the phonon spectrum of the host lattice on alloying and incorporates among other things a change in θ_R . It has the same temperature dependency as ρ_{iT} both when $T \gg \theta_R$ and $T \ll \theta_R$; i.e. it is proportional to T and T^5 respectively in this particular theory.

The term ρ_2' is attributed to scattering by the thermal motion of the solute ions for the case where momentum is conserved in the electron-phonon collision (i.e. $\vec{k} - \vec{k}' = \vec{q}$, the phonon wave vector). It has the same temperature dependency as the term ρ_1' .

The term ρ_3' is attributed to the same source as ρ_2' but applies to the case where momentum is not conserved. It also varies as T (or ρ_{iT}) at high temperatures, but varies as T^2 when $T \ll \theta_R$. The net result of these three terms is that Δ_T should vary as T when $T \gg \theta_R$, and as (a T^2 term + a T^5 term) when $T \ll \theta_R$. This theory was not compared with any specific experimental data in the original paper, and has not been discussed or utilized since that time.

(b) Vacancies

Masharov⁷⁰ (1962) has applied the above results to the special case of quenched-in vacancies in gold. The resulting deviation from MR may be written as

$$\Delta_T = 100 \ c \ \rho_{iT} \quad \text{when } T \gg \theta_R \quad (2.15)$$

and as

$$\Delta_T = c \ \rho_{iT} \left[6 - 5 \left(\frac{\theta_R}{T} \right)^3 \right] \quad \text{when } T \ll \theta_R \quad (2.16)$$

where c is the atomic fraction of vacancies, and the lattice spacing and Fermi energy of gold were used to calculate the numerical constants. It is apparent from these relations that Δ_T will depend on temperature in much the same manner as the preceding case for alloys.

In order to compare the above results with the measurements of Pervakov et al⁷¹ (1961) on vacancies in gold, Masharov has derived an expression for the quantity $(\Delta_{T_1} - \Delta_{T_2})$ where $T_2 \ll \theta_R \ll T_1$. After subtracting Eqs. (2.15 and 2.16), and then substituting the Bloch-Gruneisen approximation in the form (Ref. 5, P. 98)

$$\frac{\rho_{T_2}}{\rho_{T_1}} \approx 497.6 \left(\frac{T_2}{\theta_R} \right)^4 \frac{T_2}{T_1} \quad (2.17)$$

he obtained

$$\Delta_{T_1} - \Delta_{T_2} \approx 100 \text{ c } \rho_{iT} \left(1 - 25 \frac{(T_2)^2}{T_1 \theta_R} \right) \quad (2.18)$$

This quantity, Masharov claims, has a negative value when $T_2 > 0.2\theta_R$ approximately, and therefore is qualitatively consistent with the measurements of Pervakov et al. His arguments may be criticized, however, because Eq. (2.18) is not valid unless $T_2 \ll \theta_R$ and therefore cannot be used even as a crude approximation in the region cited. Based on the properties of the Bloch-Gruneisen ρ_{iT} , it would appear to be a better approximation to assume that Eq. (2.15) applies to the region above 77 K -- which was investigated by Pervakov et al -- and in this event theory and experiment do not agree.

2-8 Theory of Kagan and Zhernov

A detailed theory for the electrical resistivity of a dilute substitutional alloy has been developed by Kagan and Zhernov⁶⁷ (1966), which -- like Masharov's theory -- takes into account the deformation of the phonon spectrum due to solute atoms. After making the customary host of simplifying assumptions, they have derived the electron scattering transition probability ($Q(\vec{k}, \vec{k}')$) from basic theory and substituted this into a generalized solution of the kinetic

equation to obtain the resistivity. This analysis is a much more sophisticated treatment than Masharov used, involving the Green's function formalism and the Van Hove scattering correlation function.

They report a deviation from MR which may be written as the sum of three terms, i.e.

$$\Delta_T = \rho_2 + \rho_3 + \rho_4 \quad (2.19)$$

(using their symbols) where all terms are proportional to solute concentration (c); vanish as T approaches 0; and all except ρ_4 vanish as T increases beyond $\theta_D/2$. Specifically each term has the following origin and temperature dependency:

The term ρ_2 is attributed to scattering by the deformed phonon spectrum of the lattice, which is considered to be superimposed on the normal spectrum of the host matrix. This term varies with temperature in a complicated manner, depending strongly on the solute to solvent atomic mass (M) ratio, ϵ , defined by

$$\epsilon = \frac{M(\text{solute}) - M(\text{solvent})}{M(\text{solvent})} \quad (2.20)$$

At very low temperature ($< \theta_D/50$ probably), much below the characteristic temperature (ω_*) of any resonant phonon mode,

the term ρ_2 is given by

$$\rho_2 = 2 c \epsilon \rho_{iT} \quad (2.21)$$

As the temperature is increased (but still below ω_*) the quantity ρ_2/ρ_{iT} passes through a positive peak whose magnitude and shape depend strongly on the mass ratio ϵ .

At still higher temperatures ρ_2 itself must approach zero.

The term ρ_3 is attributed to that part of the scattering by the thermal motion of the solute ion which is independent of any deformation of the phonon spectrum. It is the same type of scattering considered by Koshino and Taylor (see section 2-6); and as noted earlier varies as T^2 and is significant only at low temperatures.

The term ρ_4 is a 'mixed' term that appears in the analytical equations. It arises mainly from interference between the scattering by the solute ions and by the unperturbed phonon spectrum of the host metal. At low temperatures it is given by

$$\rho_4 \approx 2 c g_2 \rho_{iT} \quad (2.22)$$

(neglecting a much smaller part of this term which varies as T^4) where g_2 may be crudely estimated from the difference in charge (Z) on the ions, i.e.

$$g_2 \approx \frac{Z(\text{solute}) - Z(\text{solvent})}{Z(\text{solvent})} \quad (2.23)$$

At temperatures above $\theta_D/2$, the term ρ_4 is given by

$$\rho_4 \approx 2 c g_3 \rho_{iT} \quad (2.24)$$

Accordingly, it is proportional to T and may have either sign depending on the sign of the constant, g_3 , which is related to the difference (Δa) between the scattering amplitudes of the solute and solvent ions. Normally the sign of g_3 is the same as the sign of the quantity $[Z(\text{solute}) - Z(\text{solvent})]$; however when $Z(\text{solute}) = Z(\text{solvent})$ the sign of Δa is difficult to predict and the theoretical form of Δ_T at both high and intermediate temperatures is somewhat uncertain.

The net result of these terms is that Δ_T has the following temperature dependencies:

(1) At extremely low temperatures, $T \ll \theta_D$ and $T \ll \omega_*$,

$$\Delta_T = c A (T/\theta_D)^2 + 2c \rho_{iT} (\epsilon + g_2) \quad (2.25)$$

where A is a very small constant and ρ_{iT} theoretically varies as T^5 . The second term may have either sign since the constants ϵ and g_2 can be of either sign.

(2) At very high temperatures, $T > \theta_D/2$,

$$\Delta_T \approx 2c g_3 \rho_{iT} \quad (2.26)$$

where the constant g_3 can be of either sign, and ρ_{iT} theoretically varies as T .

(3) At intermediate temperatures Δ_T may depend on temperature in a complex manner since it is influenced by both the magnitude and sign of ϵ , g_2 and Δa .

Some examples of calculated Δ_T functions are presented in the original paper. Qualitatively, they can be divided into three groups characterized crudely by the parameter Δa :

(a) if Δa is negative, then Δ_T will normally exhibit a positive peak below $\theta_D/3$ and be negative in both value and slope at higher temperatures.

(b) if Δa is positive, then Δ_T will be positive at all temperatures, but not necessarily a monotonically increasing function at intermediate temperatures.

(c) if Δa is close to 0 with $Z(\text{solute}) = Z(\text{solvent})$, then Δ_T is probably indeterminate because the sign of Δa (and g_3) will be difficult to predict. In general Δ_T can exhibit either a negative or positive peak at intermediate temperatures depending on the value of ϵ .

It is claimed by Kagan and Zhernov that their theory will qualitatively explain most experimental results prior to 1966, including those given in references 19, 20 and 49. For example, they find that most observed Δ_T functions

are proportional to T at high temperatures and exhibit slopes of the appropriate sign. However, no adequate comparison with theory was possible at low temperatures or in the difficult case where $Z(\text{solute}) = Z(\text{solvent})$; also the data on a MgAl alloy appears to be inconsistent with their predictions. It should be noted that they make no quantitative comparisons with experiment, presumably because of difficulties in estimating numerical values for certain parameters.

A comparison of the three terms given by Masharov's theory with those of the present theory reveals definite differences in their character. For example, the terms ρ_2 and ρ_3 here vanish at high temperatures, whereas all of Masharov's terms are considered significant in this region. In spite of such differences it should be noted that in both cases the net dependence of Δ_T on T at very high and very low temperatures is similar with regards to the power of T involved.

Further tests of Kagan and Zhernov's theory have been conducted on a variety of alloys since 1966. These reveal sources of both disagreement and agreement, which are outlined briefly below.

In two separate investigations in 1968 and 1969, Panova, Zhernov and Kutaitsev²² determined the Δ_T functions for dilute alloys of MgPb, MgAg, AlAu, and AlAg in the range

1-300 K. Theoretical calculations showed that these alloys should exhibit a positive peak at temperatures near $\theta_D/5$ due to the strong deformation of the phonon spectrum by the heavy solutes, and should possess a negative or zero slope at temperatures above $\theta_D/2$. Qualitatively, this behaviour is observed for the experimental results with one important exception, i.e. the slope of the MgPb alloy is strongly positive at high temperatures. Quantitatively, the agreement is poor. For example, the low temperature peaks are as much as five times greater than the theoretical predictions. At very low temperatures, the Δ_T functions of the Al alloys were found to vary as T^2 below 10 K in accordance with the first term of Eq. (2.25); however there was no evidence of the supposedly stronger second term which varies as ρ_{IT} . Unfortunately, similar low temperature comparisons could not be carried out for the Mg alloys, apparently due to paramagnetic contaminants in the samples. The theoretical prediction that Δ_T be proportional to solute concentration was obeyed only when the concentration was less than 0.1-0.3 atomic percent. The results for the MgPb alloys clearly show that Δ_T function radically changes its form as the concentration is increased above 0.1 atomic percent. (A similar effect may be seen in Das and Gerritsen's¹⁹ results for Mg alloys). Accordingly they compared only the measurements on the most dilute alloys with theory, but

these of course are the worst possible cases from the point of view of experimental accuracy (see section 1-4). No other possible sources of deviation from MR are discussed in this work.

Lengeler, Schilling and Wenzl²⁵ (1970) attribute their observed Δ_T functions on a series of CuAu and CuNi alloys in the range 4-350 K primarily to a two-band component. However, at temperatures below 15 K they find another component which varies with concentration (thus violating the two-band model) and is proportional to ρ_{iT} . This component was compared with the second term of Eq. (2.25), but was found to be 20 times greater than its expected value. It is interesting to note that these workers also found this component to be proportional to concentration only above 0.2 atomic % and thus used the alloys with heavy concentration in their calculations. This, of course, is exactly the opposite of the procedure used by Panova et al! Other workers^{53,72,73} have similarly found very poor quantitative agreement between low temperature Δ_T functions -- which are observed to vary as ρ_{iT} -- and the second term in Eq. (2.25).

Krill and Lapierre⁷⁴ (1971) have also compared their observed Δ_T functions for LiAg and LiHg alloys in the range 4-70 K with the theory of Kagan and Zhernov. For their four LiHg alloys they found Δ_T was completely independent of the solute concentration between 0.1 and 0.4 atomic % in

direct contradiction to the theory. For their five LiAg alloys, on the other hand they found Δ_T varied with solute concentration between 0.05 and 0.6 atomic %, but not proportionally in accordance with theory. Without further discussion, the authors attempt to fit the Δ_T function of their most concentrated LiAg alloy to Kagan and Zhernov's Eq. (3.13) -- an equation that was originally intended only for a highly specialized case and temperature range. They found that the agreement was reasonably good below 30 K, but rapidly diverged above this temperature.

Finally, it should be mentioned that Seth and Woods²⁴ examined a wide variety of dilute alloys of Al, Cd, Ag and Mg in the range 1-300 K, and found no systematic dependence of the Δ_T functions on the solute to solvent mass ratio; hence no further attempt was made to compare their results with Kagan and Zhernov's theory. We might also note here that the observed Δ_T functions of Seth and Woods conflict with this theory with regards to their dependence on solute concentration in most cases and with regards to their sign at high temperature in the case of the Mg Al and Al Mg alloys.

In summation, then, the qualitative comparisons of experiment with Kagan and Zhernov's theory show both agreement and disagreement, while the quantitative comparisons are mostly unsatisfactory. Their predicted temperature dependency has been observed at both low and high temperatures,

but this cannot be considered unambiguous evidence since other theories yield the same temperature dependency. In many cases the theoretical proportionality between Δ_T and solute concentration is not observed, even for concentrations below 0.5 atomic percent. Also it has been pointed out by several authors^{49,21,24} that their Δ_T functions do not show any obvious dependence on the solute to solvent mass ratio, as would be expected if the theoretical phonon deformation effects were present. Hence the theory of Kagan and Zhernov will not by itself explain a large number of experimental results.

2-9 Theory of Bhatia and Gupta

(a) Alloys

Using the pseudopotential formalism, Bhatia and Gupta⁷⁵ (1969) have also derived an expression for the deviation from MR starting from basic scattering theory. They have treated the case of a dilute substitutional alloy in which the thermally vibrating solute ions have roughly the same mass and force constants as the host ions, and therefore produce no phonon spectrum deformation. This is essentially the same model treated earlier by Koshino and Taylor, and similar to these authors Bhatia and Gupta find that Δ_T contains a T^2 term at very low temperatures. More importantly, however, they have independently identified (Seth⁷⁶ 1967) an

interference term that is similar to the dominant part of Kagan and Zhernov's ρ_4 term; i.e. it varies as ρ_{iT} at both high and low temperatures, and may have either sign depending upon the sign of the difference between the pseudopotential matrix elements for the solute and solvent atoms.

In addition Bhatia and Gupta have made two important observations, not contained in earlier work. Firstly, they point out that the inclusion of Umklapp processes in the analysis greatly increases the magnitude of the interference term over Kagan and Zhernov's estimate, thus leading to much better quantitative agreement with the observed Δ_T functions at high temperatures. Secondly, they note that a definitive test for the presence of the interference term would be to show that the Δ_T values for a complementary pair of alloys -- i.e. ones where the role of the solute and solvent ions are interchanged -- are equal in magnitude but opposite in sign.

During the period 1965-1969, the above test was performed by Seth and Woods²⁴ on five complementary pairs of alloys involving Ag-Cd, Ag-Mg, Ag-Al, Al-Mg and Mg-Cd. Contrary to theory, they found that the values of Δ_T were not equal and opposite in sign in most cases, and attributed this to the presence of other sources of deviation from MR. In order to avoid this problem they assumed that the other Δ_T sources were temperature independent at high temperatures (similar to the two-band model), and compared only the slopes, $d\Delta/dT$,

normalized to unit solute concentration. In agreement with theory they found that these slopes were opposite in sign for complementary alloy pairs in all except one case; but contrary to theory the magnitudes of the normalized slopes were not equal, and were found to vary with concentration. Indeed, the observed (normalized) slope for the CdAg alloy was found to be about 20 times larger than the corresponding slope for AgCd. They suggest that these discrepancies might be due to changes in the atomic pseudopotentials when the role of the atoms are interchanged, or to the lack of corrections for atomic volume changes (see section 6-5). The one case, mentioned above, where the slopes did not change sign involved the Mg-Cd alloy pair, and this anomaly was tentatively attributed to non-random crystal orientation in the polycrystalline specimens.

They conclude that these experiments confirm qualitatively the presence of the interference term, and emphasize that the negative deviations from MR can only be understood when this term is included. As noted above, however, there are several anomalies which require further investigation.

(b) Dislocations

Bhatia and Gupta⁷⁷ (1970) have also calculated from first principles the defect resistivity (ρ_0) for the case of

a metal containing dislocations and impurities. They find that the dislocation resistivity itself is enhanced by the presence of the impurity scattering, thus causing a non-additivity of the separate defect and impurity resistivities. Furthermore, they argue that the case of combined dislocation plus phonon scattering would be analogous, causing the dislocation resistivity to be ^afunction of ρ_{iT} , and therefore T , up to some saturation point. In this way they are able to qualitatively account for the deviations from MR obtained for cold-worked metals by Basinski et al¹⁸.

2-10 Theory of Rice and Bunce

These authors have claimed⁷⁸ (1970), on the basis of a variational solution of the Boltzmann equation (1.4) using certain simplifying assumptions, that deviations from MR may be present if the relaxation time for the impurity scattering is a function of energy. They derive specific formulae for this effect, and demonstrate that its magnitude is particularly large for the case of magnetic (transition metal) impurities.

Their analysis has, however, been strongly criticized by Smith⁷⁹ (1971), who showed that most -- if not all -- of the above deviations from MR result from a poorly chosen trial function (ϕ_k) for the variational solution, and hence are of no physical significance. In view of this criticism,

and the fact that we are not particularly concerned with magnetic impurities here, no further discussion of this theory will be given.

2-11 Electronic Band Structure Changes

It is well known that the addition of chemical solute to a pure metal will in general alter the number of conduction electrons per unit volume and hence the electron per atom (e/a) ratio; and this in turn may alter the Fermi energy (E_f), the Fermi surface, the effective mass (m^*) of the electron, and the density of states. Such changes in the electronic band structure should of course cause the phonon resistivity of the alloy (ρ_{iT}^a) to be different from that of the pure metal (ρ_{iT}^p), and therefore produce an apparent deviation from MR, analogous to that for the θ_R -change model discussed in section 2-5. Indeed, the elastic constants and θ_R may also be affected by a change in the e/a ratio¹⁹.

Very little work has been reported on this particular source of deviations from MR. Most authors either ignore the effect, or claim that it is negligible for solute concentrations less than 1 or 2 atomic % (see e.g. references 21, 24 and 52). Others^{67,22} have suggested that the effect may be important -- even for solute concentrations below 1 atomic % -- but do not pursue the

matter any further.

Koshino⁶⁵, in a brief discussion of this effect, cites an expression for the fractional change in ρ_{iT} , viz.

$$\frac{\rho_{iT}^a - \rho_{iT}^p}{\rho_{iT}^p} = \frac{1}{2} \left(\frac{\Delta m^*}{m^*} + \frac{\Delta E_f}{E_f} \right) - c\Delta Z \quad (2.27)$$

where c is the atomic fraction of solute atoms and ΔZ is the excess charge ($Z(\text{solute}) - Z(\text{solvent})$). He concludes that the effect may be important but could not make any numerical estimates at that time. Recent de Haas - van Alphen work^{80,81} suggests that Δm^* is probably negligible but that ΔE_f could be significant. Because of the factor ρ_{iT} in Eq. (2.27) it is clear that the apparent deviation from MR, i.e. $\Delta_T = \rho_{iT}^a - \rho_{iT}^p$, will become larger at high temperatures and may have either sign.

Regarding experimental evidence for a correlation between deviations from MR and the electron concentration, none of the recent investigations appear to contain such evidence. Damon et al⁵² report that their observed Δ_T values for Au alloys show no regular dependence on electron concentration, and at low temperatures are much larger than one would expect from this mechanism, assuming Δ_T/ρ_{iT} is comparable to c . Other results also show that Δ_T is not especially small for solutes with $\Delta Z = 0$, as would be

expected in this case. However, in an earlier investigation, Salkovitz et al⁸² reported that the slope, $d\rho_T/dT$, near room temperature for various Mg alloys tends to decrease as the e/a ratio increases, which means that $d\Delta_T/dT$ decreases in this case.

In summation, then, this particular source of deviation from MR does not appear to be a dominant effect for most metals, but its exact magnitude is unknown.

2-12 Momentum Non-Conservation Theory

The deviations from MR, that could result from a breakdown in the usual momentum (or wave vector) conservation requirements for electron-phonon scattering processes, have been examined recently by Campbell et al⁸³, Mills⁸⁴ and Smith⁸⁵, who were all seeking an explanation for the experimental results of Caplin and Rizzuto³³ (1970) on aluminum alloys. These experiments had revealed a comparatively large Δ_T function in the low temperature range, where $\rho_0 \gg \rho_{iT}$, which has the form

$$\Delta_T = B_0 T^3 \quad (2.28)$$

where B_0 is independent of T , roughly proportional to $\ln(\rho_0/\rho_{iT})$, and depends only slightly (if at all) on the nature of the impurity. The temperature region in which this T^3 dependency was observed covered from 8 K up to

20-40 K depending on ρ_0 ; while in the same range the ρ_{iT} function for Al was found to vary as T^5 . The magnitude of this Δ_T function, for even the purest Al specimens examined, was significant compared to ρ_{iT} below 30 K, and actually exceeded ρ_{iT} below 10 K.

To account for the above results Campbell, Caplin and Rizzuto⁸³ presented a heuristic argument based on momentum non-conservation in the phonon scattering process when $\rho_0 \gg \rho_{iT}$, which allowed all phonons to scatter through large angles. This assumption led to a Δ_T function which had the appropriate T^3 dependency but was independent of ρ_0 . Mills⁸⁴ subsequently gave a formal justification of the above assumptions in his treatment of a combined phonon-impurity scattering process in which momentum non-conservation was involved. However, both of these theoretical analyses have been severely criticized by Smith⁸⁵ on the grounds of unrealistic assumptions or incomplete analyses. He concludes that the phonon drag theory of Dworin⁸⁶ (1971) is the only one which gives a satisfactory explanation of the experimental results. This is treated in the next section.

2-13 Phonon Drag Theory

In most theoretical treatments of the phonon resistivity of a pure metal, it is assumed that the phonon distribution is in thermal equilibrium and is unaffected by the passage

of electrons through the crystal. Measurements of the thermoelectric power, however, suggest that in general this is only an approximation (see e.g. reference 87). It is more likely that the electron current will in fact impart some of its momentum to the phonon system causing a phonon current, which will in turn reduce the phonon scattering in the direction of the electron current. This component of the phonon resistivity, which is referred to as the 'phonon-drag' resistivity (ρ_g), has been shown to be less than 2% of the normal phonon resistivity, ρ_{iT} , for Au and Pt (Huebener⁸⁷ 1966).

When 'impurities' are added to the lattice, the phonon drag current will be reduced by defect-phonon scattering, resulting in a decrease in ρ_g of absolute magnitude $\Delta\rho_g$. Thus the total resistivity of the impure metal may be written as

$$\rho_T = \rho_{iT}^* - \rho_g + \Delta\rho_g + \rho_o \quad (2.29)$$

where ρ_{iT}^* is the phonon resistivity when the phonon system is in equilibrium. If we think of $(\rho_{iT}^* - \rho_g)$ as the true phonon resistivity of the pure metal, then $\Delta\rho_g$ represents a positive deviation from MR. Huebener⁸⁷ has calculated the magnitude of this deviation for lattice vacancies in Au and Pt, and finds that it is negligible compared to the usual magnitude of observed Δ_T deviations. A similar conclusion has been reached by Bhandari⁸⁸ (1968) for various alloys of

copper. Dworin⁸⁶ (1971), on the other hand, has derived a different theoretical expression for the phonon drag Δ_T component which he claims accounts for the results of Caplin and Rizzuto³³ discussed in the previous section. In particular, he finds a T^3 dependence on temperature and a $\ln(\rho_0/\rho_{1T})$ dependence on ρ_0 in certain cases. He does not, however, make any numerical estimates of the magnitude of this Δ_T , nor does he mention the work of Huebener or Bhandari cited above. For completeness, we mention the brief discussion of phonon drag resistivity given by Masharov⁸⁹, which adds yet another expression for this Δ_T component.

In summation, then, the various theories for the phonon drag effect lead to contradictory results, and an assessment of its importance is rather difficult at the present time.

CHAPTER 3

TWO-BAND MODEL TEST ON Pt, W AND Pb

3-1 Introduction

In the review of published work on the two-band model, given in section 2-1(b), it was pointed out that this model could plausibly account for the estimated λ_T functions of a number of impure metals, but there was one disturbing factor which cast some doubt on its validity -- namely the two-band parameter, $\mu = \rho_{12}/\rho_{11}$, was found to vary by a factor of four among the different specimens of Pt, in contradiction to its definition as a characteristic property of the particular metal. In the process of investigating this apparent internal breakdown of the two-band model new Pt data has been analysed and a careful reexamination of earlier data on other metals performed. In addition an exact solution of the basic equations (2.2) for the parameters μ and $\nu (= \rho_{r2}/\rho_{r1})$ has been derived, which is much simpler to use than earlier graphical or iterative procedures. The main results of this thesis project were published⁴⁷ in 1967 and are described in detail here.

3-2 Calculation of Two-Band Parameters

The calculation of the parameters 'a' and 'b' appearing

in the basic two-band equation (2.1) is straightforward once this equation, i.e.

$$\lambda_T = \frac{\rho_{iT}}{a\rho_{iT} + b\rho_o} \quad , \quad (3.1)$$

is known at two different temperatures (we assume for now that a, b are independent of T). In the case where only resistance ratios (W_T) are available the following procedure may be used. First Eq. (3.1) is converted to

$$\lambda_T = \frac{W_{iT}}{aW_{iT} + bW_o/G} \quad (3.2)$$

where G was defined earlier (Eq. (1.31)) and may be expressed as

$$G \approx 1 - W_o(1+1/a) \quad (3.3)$$

to a very close approximation in the two-band model. The value of λ_T may then be obtained from the basic relation, Eq. (1.30), which states

$$\lambda_T = \frac{W_T - GW_{iT} - W_o}{W_o} \quad (3.4)$$

Combining Eqs. (3.4) and (3.2) one may write

$$aW_{iT} + bW_o/G = Y_T \quad (3.5)$$

where

$$Y_T = \frac{W_{iT} W_O (1 - W_{iT}) - (b/aG) W_{iT} W_O^2}{W_T - W_{iT} - W_O (1 - W_{iT})} \quad (3.6)$$

Since the term $(b/aG) W_{iT} W_O^2$ contributes $< 1\%$ to Y_T below 90 K, where the equation is usually solved, this term may be determined by an iterative procedure or neglected if the accuracy quoted is sufficient. Hence the values of a and b may be obtained from the essentially linear relationship given by Eq. (3.5) when it is written for two different temperatures, T_1 and T_2 . The explicit solutions are

$$a = \frac{Y_{T_1} - Y_{T_2}}{W_{iT_1} - W_{iT_2}} \quad \text{and} \quad b = \frac{Y_{T_1} - a W_{iT_1}}{W_O/G} \quad (3.7)$$

The calculation of the parameters μ and ν from the values obtained for a and b requires the solution of the equations

$$a = \frac{\nu(1+\mu)^2}{(\nu-\mu)^2} \quad \text{and} \quad b = \frac{\mu(1+\nu)^2}{(\nu-\mu)^2} \quad (3.8)$$

(see section 2-1(a)). This was derived here⁴⁷ for the first time in the following way: First the two separate expressions in Eq. (3.8) were divided, yielding

$$\frac{b(1+\mu)^2}{a\mu} = \frac{(1+\nu)^2}{\nu} \quad ; \quad (3.9)$$

and then the same two expressions were subtracted, yielding

$$b - a = \frac{\mu v - 1}{v - \mu} \quad (3.10)$$

The Eq. (3.10) was then rearranged to read

$$v = \frac{\mu(b-a) - 1}{(b-a) - \mu} \quad (3.11)$$

and substituted back into Eq. (3.9) to obtain

$$\frac{b}{a} = \frac{(b-a-1)^2}{(b-a-\mu)(b-a-1/\mu)}$$

This reduced to the quadratic equation

$$\mu^2 + D\mu + 1 = 0 \quad (3.12)$$

where

$$D = -[1 + 2a + (a-b)^2](1/b) \quad (3.13)$$

The final solution for μ may then be expressed as

$$\mu = -\frac{1}{2}[D \pm (D^2 - 4)^{\frac{1}{2}}] \quad (3.14)$$

The parameter v may in turn be calculated from Eq. (3.11), or can in fact be obtained explicitly by solving Eqs. (3.9) and (3.10) for v instead of μ . In the latter case the resulting solution for v is

$$v = -\frac{1}{2}[D_1 \pm (D_1^2 - 4)^{\frac{1}{2}}] \quad (3.15)$$

where

$$D_1 = -[1 + 2b + (a-b)^2](1/a) \quad (3.16)$$

For completeness we note that when $(b-a) = 1$ the value of v cannot be obtained from Eq. (3.11) which becomes indeterminate, but rather one must use Eq. (3.15).

An examination of the quadratic Eq. (3.12) reveals that its two roots are, in fact, reciprocals of each other. This means that only one value for μ (and hence one value for v) is plausible, viz. the one that attributes greater conduction to the correct band. Precisely which band has greater conduction must be established from other considerations such as density of states, effective mass, relaxation time, or shape of the Fermi surface.

From the above equations it is also possible to determine how the various parameters are interrelated when one is dealing with a number of alloy specimens of the same host metal. In such a group the parameter μ must be the same for all specimens, and since the quantity D is related to μ by

$$D = -(1+\mu^2)/\mu \quad (3.17)$$

it will likewise be the same in all cases. Thus the parameters a and b are dependent on one another through the relation given by Eq. (3.13). Also, from Eq. (3.11), it can be seen that v will not be the same for all specimens of this group unless the quantity $(b-a)$ is likewise the same.

In the event that the two-band parameters should depend

on temperature the above relations will still apply, but only for the particular temperature under consideration. Clearly, the parameters a and b can no longer be determined in this case by the method described above, unless the equations are written for two temperatures in a region where the parameters are expected to be constant. Dugdale and Basinski²¹ have described a method of finding a and b from λ_T measurements at one temperature but this can only be used if a number of specimens of the same alloy, which differ only in solute concentration, have been measured. Since these specimens should all have the same parameters, a plot of $1/\lambda_T$ versus ρ_o/ρ_{iT} at one temperature will result in a line of slope b and intercept a , according to the two-band Eq. (3.1).

3-3 Results

(a) Estimates of μ and ν for Pt

Previous values of μ for Pt are given as 6 ± 1 by Lovejoy⁴⁶ for six different specimens, and as 2 to 9 by Kos and Lamarche⁴³ for nine different specimens. These specimens were all of thermometric grade purity and possessed values of W_o in the range $(3.6-9.4) \times 10^{-4}$. Because of their high purity, their calculated λ_T functions, as well as their two-band parameters, were very sensitive to errors in the estimated values for W_{iT} . This statement may

be put in mathematical form by taking the first derivative of Eq. (3.4), i.e.

$$\frac{d\lambda_T}{dW_{iT}} = - \frac{G}{W_O} \approx - \frac{1}{W_O}$$

In order to obtain some idea of the magnitude of the uncertainties in μ and ν , due to uncertainties in W_{iT} , a detailed analysis has been made for two specimens, one from Lovejoy's group (LN1158062) and one from Kos and Lamarche's group (120). The procedure was to select various plausible pairs of values for W_{iT} , at the same two temperatures as used in the original papers, and calculate all four parameters in each case. The values of W_{iT} were selected from within Berry's²⁸ reported maximum error limits*. The results, along with other pertinent information, are summarized in Table 3.1. The values of the parameters labelled "best fit" refer to the case where a and b have been chosen to give close agreement between the observed and theoretical λ_T functions over the entire 10-90 K range, and not just at two temperatures.

* The worst cases, in which a very low W_{iT} value at one temperature is combined with a very high value at the second temperature, have been excluded, since the actual errors in W_{iT} are most likely to be systematic.

TABLE 3.1

Changes in the four basic parameters, due to small changes in W_{iT} , for two high-purity specimens of Pt. The two values of W_{iT} used to solve Eqs. (3.2) and (3.4) are shown below and were selected from the range given in the footnote.

Specimen 120 ($W_o = 6.89 \times 10^{-4}$)						
$10^6 W_{111}$	$10^6 W_{120}$	a	b	μ	ν	
351	3 660	4.1	6.9	2.0	5	
356	3 660	3.8	8.6	3.4	11	
361	3 660	3.4	10.7	5.6	23	
356	3 668	4.2	8.4	2.9	8	
356	3 652	3.4	8.8	3.9	14	
Best fit		3.4	9.3	4.3	16	

Specimen LN 1158062 ($W_o = 6.52 \times 10^{-4}$)						
$10^6 W_{120}$	$10^6 W_{190}$	a	b	μ	ν	
3 652	242 495	4.1	6.5	1.7	5	
3 660	242 495	4.1	8.6	3.0	9	
3 668	242 495	4.1	11.0	4.9	17	
3 660	242 465	3.3	13.3	8.0	39	
Best fit		4.1	7.9	2.6	7	

Note: Berry's²⁸ W_{iT} values and maximum uncertainties are as follows: $10^6 W_{111} = 356 \pm 5$, $10^6 W_{120} = 3\,660 \pm 8$, $10^6 W_{190} = 242\,495 \pm 30$ (all on N.B.S. 1939 temperature scale).

It can be seen from the results that previous values for μ and ν may be in error by as much as 50% of their "best fit" values, depending on the true value of W_{iT} . In fact, the uncertainties in these parameters for most other specimens in the above two groups will be even greater because of their higher purity. Hence it appears that many or all of the apparent variations in μ between specimens could simply be due to uncertainties in W_{iT} .

In an attempt to obtain more reliable estimates for μ , data on three comparatively low-purity specimens of Pt have been analyzed. The source of data was resistance thermometer calibrations performed by national standardizing laboratories, viz. the National Research Council of Canada for specimens B1 and B2, and the P.R.M.I.⁹⁰ of Russia in the case of specimen Ikh3. In all cases, it was possible to find values of a and b that gave reasonably good agreement between the observed and two-band λ_T functions over the entire 10-180 K range. The closeness of these fits is demonstrated in Fig. 3.1 for two specimens with widely different W_0 values, while in Table 3.2 values of all parameters including W_0 are presented. The maximum uncertainties in μ and ν shown in the table represent the combined effects of uncertainties in choosing $1/a$ (or G) to fit a two-band λ_T function and the small uncertainties due to W_{iT} .

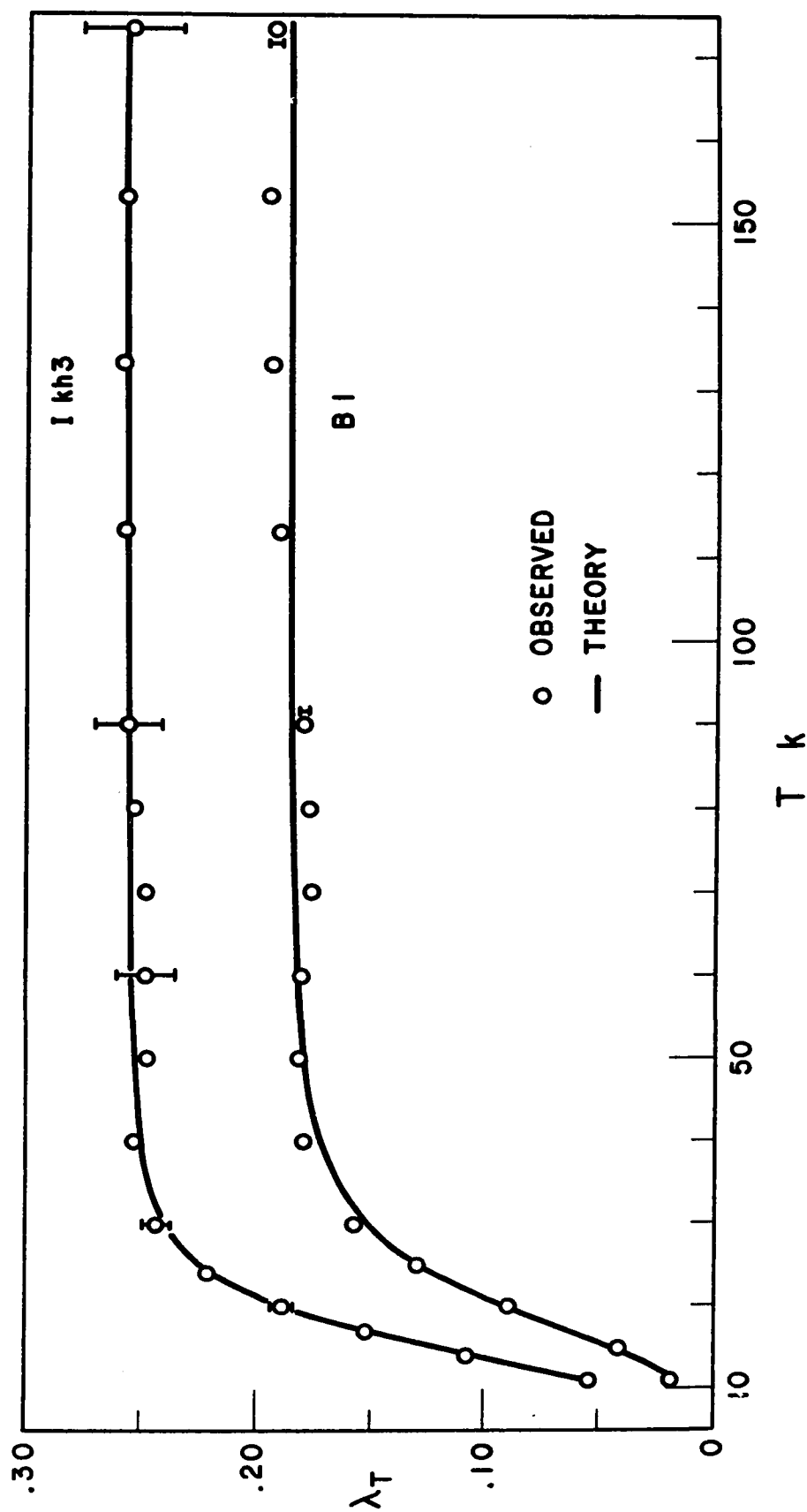


Fig. 3.1 . The λ_T function for Pt specimens Ikh3 and B1 as observed (Eq. (3.4)) and as given by theory (Eq. (3.2)). Berry's W_{iT} function²⁸ was used in the calculations, and the effect of its maximum uncertainty is indicated by the error bands.

TABLE 3.2

Values of the two-band parameters for various
specimens of Pt, W, and Pb

	Spec. No.	W_0	a	b	μ	ν
Pt	Ikh3	0.002 1	3.89	2.43	4.3 ± 1.3	$1.3 \pm .3$
	B1	0.014 5	5.32	1.41	19 ± 4	$3.3 \pm .4$
	B2	0.015 6	5.71	1.36	23 ± 5	$3.7 \pm .5$
W	1	0.283	6.33	1.58	22.8	3.97
	2	0.215	5.71	1.47	20.6	3.56
	3	0.135	5.44	1.54	17.5	3.23
	4	0.096	4.50	1.96	8.3	2.04
	5	0.076	6.83	1.14	41.0	5.01
	6	0.059	6.94	0.88	58.3	5.50
Pb	1	0.037	3.45	5.59	1.61	4.63
	2	0.079	3.25	4.29	1.02	2.95
	3	0.182	3.85	3.15	2.51	0.85
	4	0.270	4.52	4.00	2.11	0.80

The results are quite surprising in that the parameter μ is still found to vary strongly with W_0 , in contradiction to its definition in the two-band theory. In this case, the changes in μ are so large as to be well outside any uncertainties in the calculation. The fact that the parameter ν also depends on W_0 does not necessarily constitute a violation of theory since the type of defect in the different specimens could have changed.

(b) Estimates of μ and ν for W and Pb

To gain more information about the behaviour of μ and ν in specimens of the same metal, we have reexamined the data of Krautz and Schultz on cold-worked W³⁵ and on Pb alloyed with small concentrations of In³⁶. The values of the above parameters have been calculated from the reported "best fit" values of a and b , and are presented in Table 3.2. For each host element all specimens should possess the same value of ν as well as μ , since the same type of defect is present in all cases. The results show, however, that both parameters vary quite strongly with the concentration of 'defects' in the metal, i.e. with W_0 . In the case of Pb, the parameter μ exhibits a trend towards increasing values with increasing W_0 , similar to the results for Pt. In the case of W, however, μ is found to exhibit a strong minimum near $W_0 \approx 0.1$. As with Pt, these variations appear much too

large to be accounted for by errors in the estimated W_{iT} function or in the fitting of the data to the two-band model.

3-4 Discussion

Although the two-band model with constant a , b parameters can often be adjusted to fit the measured data, the preceding results show that such a model leads to internal contradictions, viz, that μ depends on the defect concentration. It may be concluded, therefore, that this model will not account for the experimental results in a self-consistent manner. This conclusion is not affected by the fact that λ_{273} was not measured in this work, since we can always restrict our tests to the region below 50 K where the observed λ_T function is not significantly influenced by λ_{273} , and the a , b parameters used will still fit the data satisfactorily. (Indeed if λ_{273} were appreciably different from the value used here then the two-band model would obviously be invalid at high temperatures as well as at low temperatures).

Whether the two-band model is completely invalid, or just needs slight modifications, is a matter of speculation at this time. It is even possible that this model is still applicable, but that the experimental data are complicated by one or more of the additional sources of deviation from

Matthiessen's rule discussed in Chapter 2. Other possible explanations for a breakdown in the above model are:

- (1) That the parameters a and b are temperature dependent. Such would be the case if either μ or ν were temperature dependent, which is a very plausible hypothesis. For example, a breakdown in the assumption that Matthiessen's rule is valid for each band could make ν dependent on temperature, and as discussed in section 2-1(d) anisotropy of the relaxation time for different regions of the Fermi surface will make μ dependent on temperature.
- (2) That more than two distinct bands or groups of carriers exist, corresponding for example to different regions of the Fermi surface.

The fact that the two-band model with constant parameters has failed to represent the results casts considerable doubt on the values of the basic parameters μ and ν presented both here and elsewhere. It does not, however, have much effect in those cases where the two-band relation (Eq. (3.2)) was employed on a more or less empirical basis; for example, in the interpolation of resistance measurements or in the derivation of W_{iT} from Eq. (3.4) over short temperature intervals.

In conclusion, then, the two-band model in its simplest form does not appear to be adequate for Pt, W, and Pb. Further investigations are required to determine the exact source of difficulty.

CHAPTER 4

DEPENDENCE OF THE SONDHEIMER λ_T FUNCTION ON
SOLUTE CONCENTRATION

4-1 Introduction

The λ_T function calculated by Sondheimer³² (1950) for the case of quasi-free electrons in monovalent metal alloys has been discussed earlier in section 2-3. There, it was pointed out that Sondheimer's prediction of a low temperature λ_T peak was in general confirmed by recent experimental work, but that more detailed comparisons could not be made because of large differences between the experimental and theoretical solute concentrations involved. For example, in Sondheimer's work λ_T was evaluated for only two slightly different solute concentrations corresponding roughly to 1 atomic % solute, while in the experimental work concentrations ranging from 2 down to as low^{as} 0.01 atomic % solute have been used. Such differences in solute concentration make comparisons with theory very difficult because the magnitude and shape of the λ_T peak depends on this concentration. This is demonstrated experimentally by the results of Dugdale and Basinski²¹, which show that the peak height may increase by an order of magnitude as the solute concentration decreases by an order of magnitude.

The calculations of Sondheimer also show a similar trend, but there is insufficient data to make any definite predictions.

In order to facilitate a further comparison between theory and experiment we have undertaken to calculate Sondheimer's λ_T function for a much wider range of solute concentrations.

4-2 Details of the Calculation

The calculations begin with Sondheimer's expression for the total resistivity of an alloy in terms of an infinite series of determinants, viz.

$$\frac{1}{\rho_T} = \frac{1}{B} + \frac{1}{4A} \sum_{n=1}^{\infty} \frac{\left[D_a^{(2n)} \right]^2}{D^{(2n-2)} D^{(2n)}} \quad (4.1)$$

where A is a constant for any particular metal (and ultimately cancels out of the ratio Δ_T/ρ_0), $D_a^{(2n)}$ are specified $2n \times 2n$ determinants (involving quantities like (T/θ) , ρ_0 and the transport integrals $J_n(\theta/T)$), and B is simply the sum of ρ_0 and the ρ_{iT} value given earlier by Eq. (1.16) (note, in this chapter the subscript R on θ_R will be deleted). In the approximation of zeroth order ($n=0$), ρ_T is simply equal to B and Eq. (4.1) reduces to MR and the Bloch-Gruneisen ρ_{iT} . By retaining three more

successive terms of the infinite series we have determined ρ_T (and ρ_{iT}) to the 3rd order of approximation -- i.e. one more term than Sondheimer employed. Once ρ_T and ρ_{iT} have been calculated for a selected (T/θ) and ρ_0 value, then Δ_T and λ_T may be obtained from the basic Eqs. (1.22) and (1.24), and the whole process repeated for other combinations of (T/θ) and ρ_0 values.

All calculations were performed on an IBM 360 computer using 16 digit precision throughout. The necessary transport integrals $J_n(\theta/T)$ were generated to at least 7 figure accuracy and the values of ρ_T , ρ_{iT} and Δ_T were calculated to 7 figure precision. The last three parameters were printed out for all four orders of approximation so that we could examine the convergence of the series in Eq. (4.1). The fact that the series does converge fairly rapidly is demonstrated in Table 4.1 for a value of T/θ and ρ_0 that represents about the worst possible case. However the ultimate accuracy of the above three parameters is still limited by the truncation of the series; a crude estimate of this error is given in Table 4.1, based on graphical analyses. The second order approximations obtained here agree with Sondheimer's original "hand" calculations within the limited precision of his results.

TABLE 4.1

The values of ρ_{iT}/ρ_{i0} , ρ_T/ρ_0 , and Δ_T/ρ_0 given by Sondheimer's equations for the case where $\theta/T = 5$ and $\rho_0/\rho_{i0} \times 23.62 = 0.1$, when successively higher-order approximations are taken into account.

Order of approximation	$100 \rho_{iT}/\rho_{i0}$	ρ_T/ρ_0	Δ_T/ρ_0
0	6.797595	17.08419	0
1	6.296521	15.88993	0.00878
2	6.228175	15.72573	0.01092
3	6.209271	15.68002	0.01183
% error in third order	0.15	0.15	4

4-3 Results

The third order approximation to Sondheimer's λ_T function has been computed at 27 different temperatures (specified in Table 4.2) for each of 17 different solute concentrations (specified in Fig. 4.2). The temperature dependence of the λ_T function is presented in Fig. 4.1 for a number of selected solute concentrations, while the peak λ_T value, λ_T^* , is shown in Fig. 4.2 as a function of solute concentration (ρ_o/ρ_{i0} values). The λ_T values plotted for solute concentrations of (ρ_o/ρ_{i0}) 23.62 equal to 1 and 3 correspond to the concentrations originally used by Sondheimer.

From the results it can be seen that the magnitude of the low temperature λ_T peak tends to zero at high solute concentrations and reaches a saturation height of 0.014 as the concentration tends to zero. Hence we may conclude that Sondheimer's λ_T function will not account for the observed λ_T peaks at low solute concentrations since these may reach heights of 0.1 or more.

Another interesting feature of these results is the fact that the temperature at which the peak occurs does not necessarily correspond to the temperature where ρ_{iT} and ρ_o are of the same order of magnitude, as reported by Sondheimer (and repeated in numerous other publications).

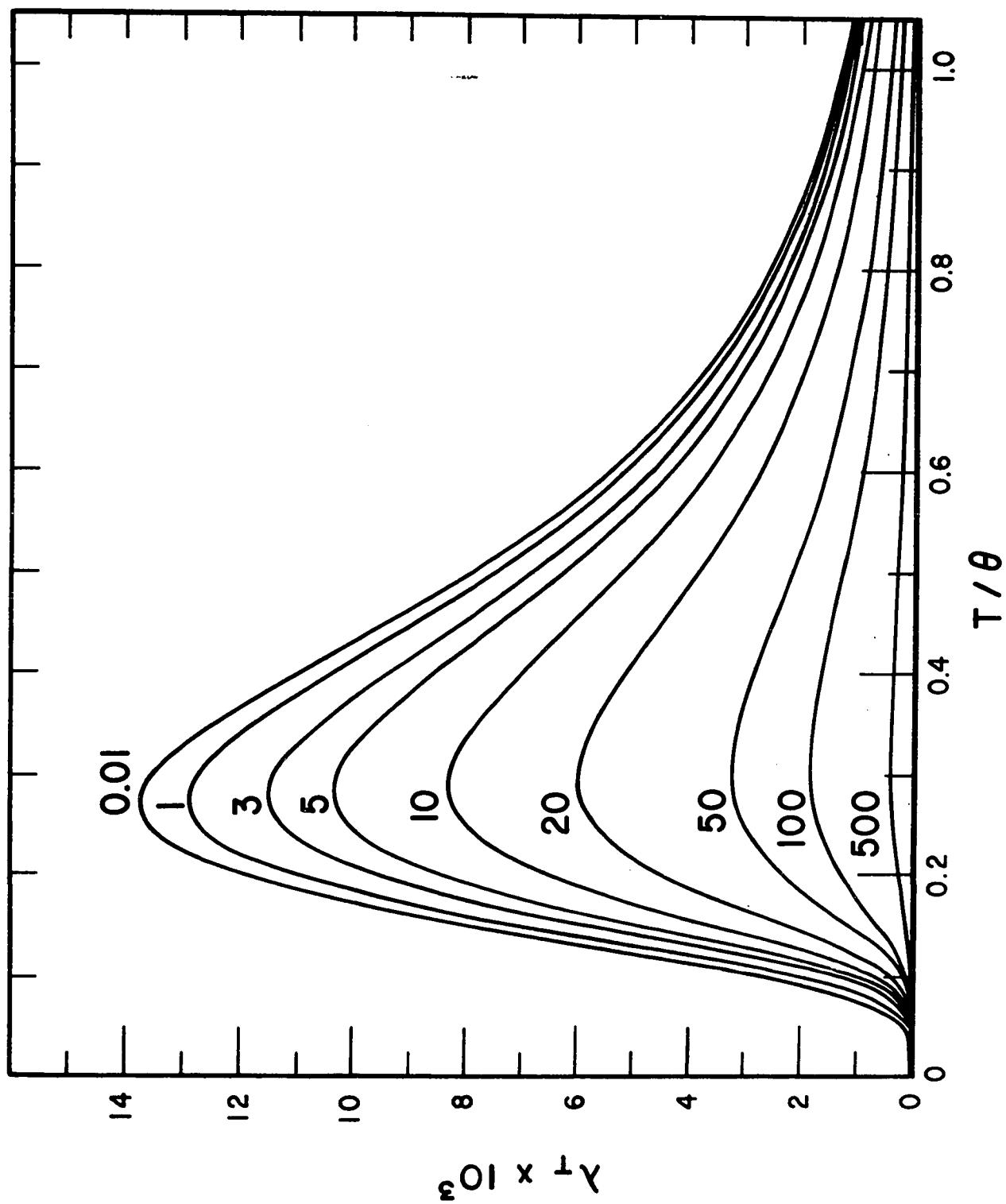


Fig. 4.1 . Dependence of Sondheimer's λ_T function on T and solute concentration. The value of $23.62 \rho_O/\rho_{i0}$ is specified on each curve.

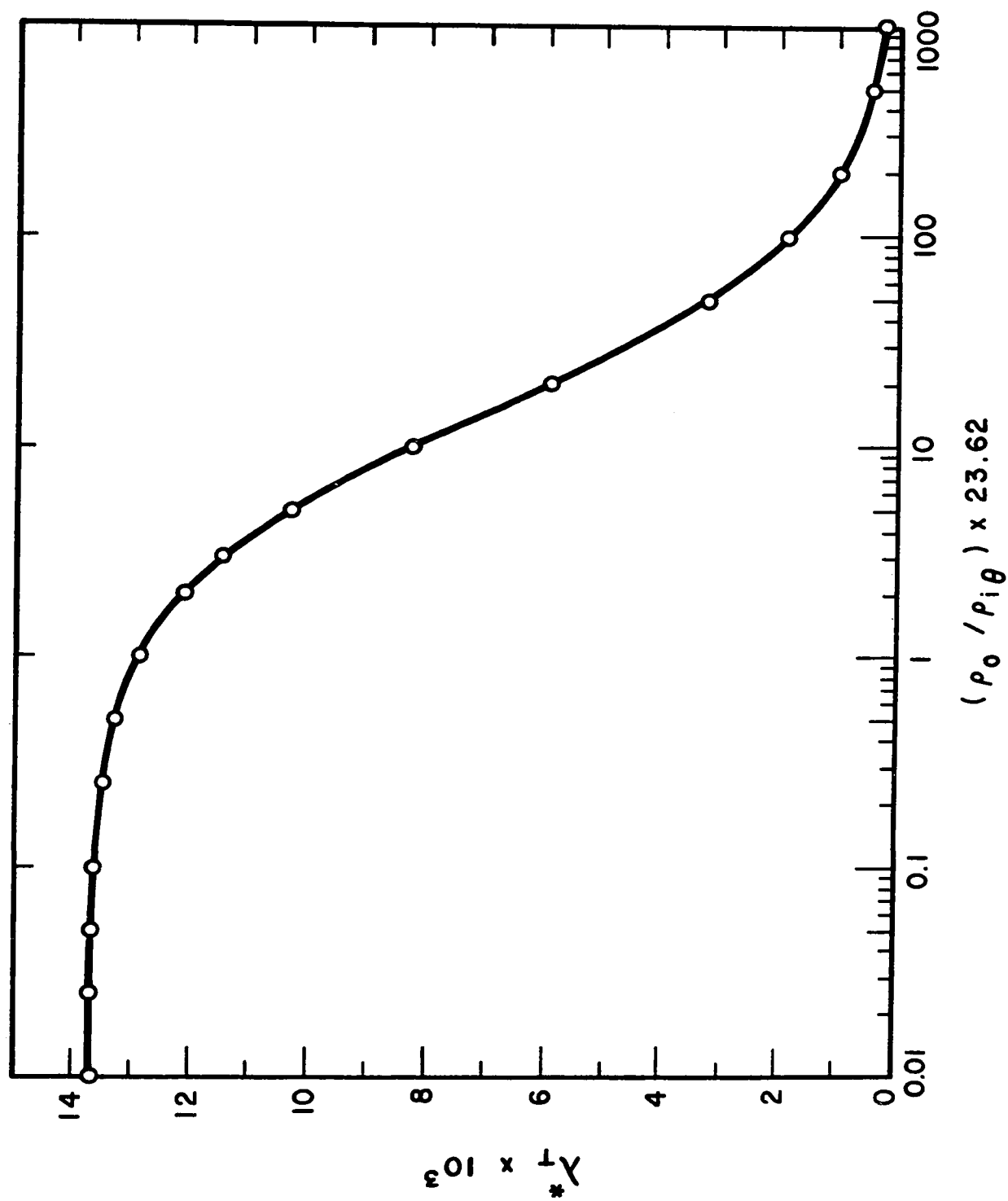


Fig. 4.2 . Dependence of the peak λ_T^* value, λ_T^* , on solute concentration.

Figure 4.1 shows that the "peak" temperature only increases by about 15% when the solute concentration is raised by some five orders of magnitude. One may conclude therefore that the peak temperature is practically independent of solute concentration (or ρ_0) and has an approximate value of 0.28 θ .

In the course of these calculations, values of the much used "reduced" resistivity, ρ_{iT}/ρ_{i0} , have been derived for monovalent metals with greater accuracy than previously reported, both for the case of the elaborate Sondheimer resistivity, Eq. (4.1), and the Bloch-Gruneisen resistivity, Eq. (1.16). These values are presented in Table 4.2 to demonstrate the differences between the two functions and for use by others.

4-4 Discussion

The problem of obtaining definitive experimental evidence for the Sondheimer λ_T function will obviously be a difficult one, because of its small magnitude. The suggestion by Krautz and Schultz³⁴ that the small peaks exhibited by alloys containing about 1 atomic % solute are due to this source is plausible, but then one still requires another source of deviation to account for the larger peaks at low solute concentration. Dugdale and Basinski²¹, on the other hand, have shown that the two-band Fermi surface

TABLE 4.2

Comparison of the ratios $r = \rho_{iT}/\rho_{i0}$, given by the Bloch-Gruneisen function and by the third-order approximation to Sondheimer's function at different reduced temperatures

θ/T	r		% Difference $\left[\frac{r(\text{B.G.}) - r(\text{S})}{r(\text{B.G.})} \right]$
	Bloch-Gruneisen (B.G.)	Sondheimer (S)	
100	5.258789×10^{-8}	5.261298×10^{-8}	-0.05
40	5.135538×10^{-6}	5.106898×10^{-6}	+0.55
25	5.384993×10^{-5}	5.294655×10^{-5}	+1.68
20	1.643258×10^{-4}	1.598805×10^{-4}	+2.71
13	1.401684×10^{-3}	1.314177×10^{-3}	+6.24
10	4.918549×10^{-3}	4.481085×10^{-3}	+8.89
8	1.308812×10^{-2}	1.174350×10^{-2}	+10.27
6	3.851968×10^{-2}	3.469414×10^{-2}	+9.93
5	6.797595×10^{-2}	6.209271×10^{-2}	+8.66
4.5	9.079229×10^{-2}	8.380161×10^{-2}	+7.70
4	0.1217045	0.1137318	+6.55
3.6	0.1543351	0.1458164	+5.52
3.3	0.1848790	0.1761840	+4.70
3	0.2221057	0.2135061	+3.87
2.8	0.2515392	0.2431836	+3.32
2.5	0.3045090	0.2968227	+2.52
2.2	0.3714057	0.3647665	+1.79
2	0.4264942	0.4207523	+1.35
1.8	0.4929550	0.4882460	+0.96
1.7	0.5316215	0.5274692	+0.78
1.5	0.6232603	0.6202773	+0.48
1.3	0.7410233	0.7392439	+0.24
1.2	0.8136698	0.8124906	+0.14
1	1	1	0
0.8	1.274852	1.276008	-0.09
0.6	1.726193	1.728586	-0.14
0.5	2.084053	2.087201	-0.15

model (section 2-1(d)) will account for the low temperature peaks at all solute concentrations. Since their analysis was qualitative in nature, it is still possible however that both sources of deviation are present in the results. If this is the case then one could only hope to identify the Sondheimer λ_T component in metals that exhibit no two-band conduction. The alkali metals, whose Fermi surfaces are closely spherical, should satisfy this requirement reasonably well.

CHAPTER 5

DEVIATIONS FROM MR DUE TO θ_R CHANGES

5-1 Introduction

In a considerable number of experimental investigations the observed deviations from MR have been attributed totally, or in part, to changes in the phonon spectrum of the host metal produced by the addition of chemical or physical defects. The literature available on this subject has already been critically reviewed in section 2-5, where it was noted that in a great many cases the phonon spectrum change has been characterized simply by a change in the θ_R parameter of the Bloch-Gruneisen expression (Eq. (1.16)) for $\rho_i(T)^*$. In papers, such as Hedgcock and Muir's²⁰, this procedure is claimed to account quantitatively for the $\Delta(T)$ functions in a most impressive manner.

A rather confusing situation has arisen, however, from the fact that these published reports contain seemingly irreconcilable predictions about the direction in which θ_R should change. For example a decrease in θ_R is used to

* In this chapter only, we shall put the subscript T in brackets in order to avoid writing subscripts of subscripts.

account for a negative $\Delta(T)$ function by Das and Gerritsen¹⁹, a positive $\Delta(T)$ function by Magnuson et al⁵⁸ and both positive and negative $\Delta(T)$ functions by Hedgcock and Muir²⁰. Because the various analyses used in the literature to obtain changes in θ_R are of a diversified or unstated nature, it is not immediately obvious which reported changes are incorrect.

In the process of resolving the present unsatisfactory situation a comprehensive analysis of the relationship between $\Delta(T)$ and $d\Delta(T)/dT$ and the change in θ_R has been carried out within the framework of the Bloch-Gruneisen relation. Based on this analysis major errors in the papers by Das and Gerritsen¹⁹, and by Hedgcock and Muir²⁰, have been identified, and the strong support given this model by Hedgcock and Muir is shown to be unwarranted. In addition this chapter contains a fresh assessment of the applicability of the θ_R -change model, taking into account the results of the present analysis and other recent investigations.

5-2 Basic Analysis

The basic argument involved in this analysis is that when one substitutes the value of the phonon resistivity, $\rho_1^p(T)$, derived from measurements on the 'pure' metal sample,

into the basic Eq. (1.22) defining $\Delta(T)$, then an apparent $\Delta(T)$ will result given by

$$\Delta(T) = \rho(T) - \rho_i^p(T) - \rho(o) \quad (5.1)$$

If, on the other hand, one substitutes the more appropriate value, $\rho_i^a(T)$, corresponding to the modified phonon spectrum of the strained or alloyed metal, then MR will be satisfied (as far as deviations from this particular source are concerned) and hence

$$\rho(T) = \rho_i^a(T) + \rho(o) \quad (5.2)$$

By comparing Eqs. (5.1) and (5.2) it can be seen that the apparent deviation, $\Delta(T)$, is simply equal to the change in $\rho_i(T)$ produced by the defects, i.e.

$$\Delta(T) = \rho_i^a(T) - \rho_i^p(T) \quad (5.3)$$

In order to relate this apparent $\Delta(T)$ to the change in θ_R , the Bloch-Gruneisen relation (Eqs. (1.16)) for $\rho_i(T)$ is introduced, and in particular we make use of its property that

$$T \rho_i^a(T) = T^* \rho_i^p(T^*) \quad (5.4)$$

when $T/\theta_a = T^*/\theta_p$. If Eq. (5.4) is rewritten as $\rho_i^a(T) = (\theta_p/\theta_a) \rho_i^p(T^*)$, and substituted into Eq. (5.3) one

obtains the desired relation

$$\Delta(T) = \rho_i^p(T) \left[\frac{\theta_p \rho_i^p(T^*)}{\theta_a \rho_i^p(T)} - 1 \right] \quad (5.5)$$

From the above equations it follows that if $\Delta\theta = \theta_a - \theta_p$ is positive then $T > T^*$; $\rho_i^p(T) > \rho_i^p(T^*)$ since $G(\theta_R/T)$ (see Eq. (1.17)) is a monotonically increasing function of T ; and therefore Eq. (5.5) yields a negative $\Delta(T)$ function. Similarly if $\Delta\theta$ is negative it can be shown that $\Delta(T)$ must be positive. This leads to the important conclusion that $\Delta\theta$ and $\Delta(T)$ must have opposite signs at all temperatures.

To facilitate the calculation of $\Delta(T)$ or $\Delta\theta$ we may rewrite Eq. (5.5) in terms of another integral function, $F(\theta_R/T)$, which is associated with the following form of the Bloch-Gruneisen relation,

$$\frac{\rho_i(T)}{\rho_i(\theta_R)} = F(\theta_R/T) = \frac{T G(\theta_R/T)}{\theta_R G(1)} \quad (5.6)$$

where $G(1) = 0.9465$. On substituting the expression for $\rho_i^p(T)$ and $\rho_i^p(T^*)$ from Eq. (5.6) into Eq. (5.5), the final result is

$$\frac{\Delta(T)}{\rho_i^p(\theta_p)} = F(\theta_p/T) \left[\frac{\theta_p F(\theta_p/T^*)}{\theta_a F(\theta_p/T)} - 1 \right] \quad (5.7)$$

At high temperatures, $T > \theta_R/2$, it is well known that the Bloch-Gruneisen function, $F(\theta_R/T)$, varies approximately as (T/θ_R) and therefore Eq. (5.7) reduces to

$$\frac{\Delta(T)}{\rho_i^p(\theta_p)} \approx - 2 \left(\frac{\Delta\theta}{\theta_a} \right) F(\theta_p/T) \quad (5.8)$$

when $\Delta\theta \ll \theta_a$. This equation may also be written explicitly in terms of $\rho_i^p(T)$ as

$$\Delta(T) \approx - 2 \left(\frac{\Delta\theta}{\theta_a} \right) \rho_i^p(T) \quad (5.9)$$

where $\rho_i^p(T)$ varies approximately as T in this range.

Similarly at low temperatures, $T < \theta_R/10$, it is well known that $F(\theta_R/T)$ varies approximately as $(T/\theta_R)^5$ and therefore Eq. (5.7) reduces to

$$\frac{\Delta(T)}{\rho_i^p(\theta_p)} \approx - 6 \left(\frac{\Delta\theta}{\theta_a} \right) F(\theta_p/T) \quad (5.10)$$

when $\Delta\theta \ll \theta_a$. Again, writing this equation explicitly in terms of $\rho_i^p(T)$ we obtain

$$\Delta(T) \approx - 6 \left(\frac{\Delta\theta}{\theta_a} \right) \rho_i^p(T) \quad (5.11)$$

where $\rho_i^p(T)$ varies as T^5 in this range.

From Eqs. (5.7), (5.8) and (5.10) one may readily

calculate $\Delta(T)$ at any temperature for any particular metal once $\Delta\theta$ and $\rho_i^p(\theta_p)$ are known. The required values of $F(\theta_R/T)$ may be derived from the tabulated $G(\theta_R/T)$ function^{5,11} using Eq. (5.6). Alternatively, the value of $\Delta\theta$ may be estimated once the apparent $\Delta(T)$ has been determined at a single temperature. It should also be emphasized here that Eqs. (5.9) and (5.11) lead to the conclusion that $\Delta(T)$ varies directly as $\rho_i^p(T)$ at both high and low temperatures.

In order to demonstrate the general features of the temperature dependency of $\Delta(T)$, the values of $\Delta(T)/\rho_i^p(\theta_p)$ calculated from Eq. (5.7) are plotted as a function of (T/θ_p) in Fig. 5.1 for a number of selected values of $(\Delta\theta/\theta_p)$. It is apparent that these graphs depend only on the properties of $F(\theta_R/T)$ and thus form a set of universal curves applicable to all metals.

Regarding the relationship between the slope, $d\Delta(T)/dT$, and the change in θ_R it can be seen from the graphs in Fig. 5.1 as well as the derivatives of Eqs. (5.9) and (5.11), that this slope will always have the opposite sign to that of $\Delta\theta$ at all temperatures, and that its absolute value will be approximately proportional to the absolute value of $\Delta\theta$. The change in slope between the pure and 'impure' specimen, $d\rho(T)/dT - d\rho_i^p(T)/dT$, which is

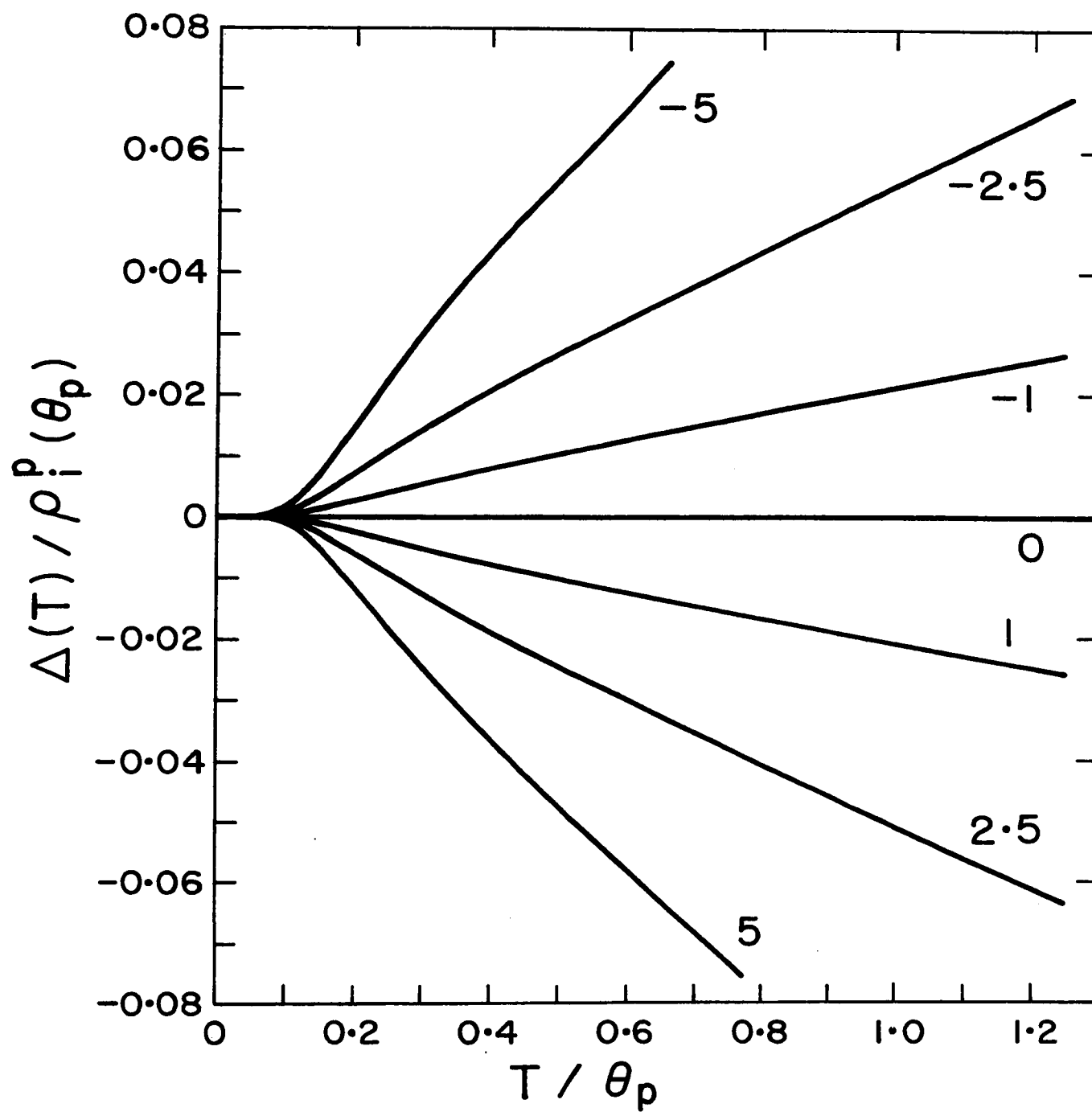


Fig. 5.1 . The normalized deviations from MR given by Eq. (5.7) for seven different values of $\Delta\theta/\theta_p$, indicated on the figure as percentages.

frequently determined in experiments, was shown to be identical to the slope of $\Delta(T)$ in both magnitude and sign in Eq. (1.23), and hence will also depend on $\Delta\theta$ in the above manner.

In summary then the above analysis has shown that θ_a will be $<\theta_p$ when $\Delta(T)$ and $d\Delta(T)/dT$ are positive; whereas θ_a will be $>\theta_p$ when both quantities are negative.

5-3 Comparison of Results

A comparison of the reported changes in θ_R , given in the various publications, with those of the preceding analysis reveals two discrepancies. In Das and Gerritsen's paper¹⁹, the negative $\Delta(T)$ component should have been attributed to an increase in θ_R on alloying, and in Hedgcock and Muir's paper²⁰, the negative $\Delta(T)$ and $d\Delta(T)/dT$ values in certain alloys should have been attributed to an increase in θ_R . The sources of error in these two papers, along with other important considerations, are discussed briefly below in order to clarify certain misleading arguments.

(a) Das and Gerritsen:

The source of error in Das and Gerritsen's paper lies in their assumption that $\rho_1^a(T) = \rho_1^p(T)$ at temperatures below about 100 K. While it is certainly true that the difference between these two quantities (which equals the θ_R component of $\Delta(T)$) is very small at low temperatures, it may be seen

from Eqs. (5.9) and (5.11) that the fractional difference, $\Delta(T)/\rho_i^p(T)$, is much greater at low temperatures than at high temperatures for any particular value of $\Delta\theta$. When this fact is taken into account it can be readily shown that their statement, $[\rho_i^a(T_1)/\rho_i^a(T_2)] > [\rho_i^p(T_1)/\rho_i^p(T_2)]$ when $T_1 < \theta_p < T_2$, is incorrect when $\Delta(T)$ is negative as in their case; and this in turn leads to the incorrect direction of change in θ_R . Their method of determining the change in θ_R can in principle give the correct answers, but is far less direct than using the relations given here.

(b) Hedgcock and Muir

The source of error in Hedgcock and Muir's paper mainly involves a lack of sensitivity in the special test that they devised to show that the observed deviations from MR can be satisfactorily taken into account by a change in θ_R alone.

The basic assumptions and procedures used in their test may be described briefly as follows: First it is assumed that MR is valid for the alloy once the change in θ_R is taken into account, and accordingly the phonon resistivity ratio $\rho_i^a(T)/\rho_i^a(\theta_a)$, is calculated from

$$\frac{\rho_i^a(T)}{\rho_i^a(\theta_a)} = \frac{\rho^a(T) - \rho^a(0)}{\rho^a(\theta_a) - \rho^a(0)} = \frac{W^a(T) - W^a(0)}{W^a(\theta_a) - W^a(0)} \quad (5.12)$$

where $W^a(T) = \rho^a(T)/\rho^a(273)$ is determined experimentally.

Similarly for the pure metal, MR is assumed since any deviations must be comparatively small, and its ratio is calculated from

$$\frac{\rho_1^p(T^*)}{\rho_1^p(\theta_p)} = \frac{W^p(T^*) - W^p(0)}{W^p(\theta_p) - W^p(0)} \quad (5.13)$$

The above two ratios are then closely fitted to the Bloch-Gruneisen function, $F(\theta_R/T)$, by choosing the appropriate values for the parameters θ_p and θ_a ; a procedure which obviously forces the two ratios to be the same as close as possible and makes $T/\theta_a = T^*/\theta_p$. Indeed, if their initial assumption is correct (which implies that no other sources of deviation from MR are present), one would expect the two ratios to be identical at this point. To test this supposition they have derived an expression for the residual resistivity ratio of the alloy, $W^a(0)$, by equating the right-hand sides of Eqs. (5.12) and (5.13). They then calculated $W^a(0)$ from the experimental $W(T)$ data using the chosen values of θ_a and θ_p , and various selected values of the temperature T . The resulting values of $W^a(0)$ given by this equation were indeed found to agree with the measured $W^a(0)$ value to within about 1% for all values of T within the range 4-370 K.

Based on this result, Hedgcock and Muir suggested that

the deviations from MR observed with their alloys could be satisfactorily accounted for by a change in θ_R alone. We find, on the other hand, that if the apparent $\Delta(T)$ functions shown in their Fig. 2(a) are compared with those shown in our Fig. 5.1, there is little or no similarity in the shapes of the graphs. Indeed some of their functions exhibit both positive and negative deviations for the same alloy, in drastic conflict with our θ_R -analysis. We conclude, therefore, that the above suggestion cannot be valid, and that other sources of deviation from MR must be present for their alloys. This in turn means that their resistivity ratios calculated from Eq. (5.12), as well as the corresponding θ_a values, must be seriously in error.

The fact that it was possible to force the resistivity ratios given by Eqs. (5.12) and (5.13) into close agreement for the wide variety of $\Delta(T)$ curves exhibited by their alloys, demonstrates that their particular test is not significantly affected by the shape of the $\Delta(T)$ curves. Indeed, in some cases the close fit was achieved by changing θ_R in the opposite direction to that required by our analysis. A striking example of this is the case of the MgAl alloy whose ratios were made to fit by a 12% decrease in θ_R when actually its observed $\Delta(T)$ function at high temperatures corresponds crudely to a 4% increase in θ_R . Hence the test procedure used by Hedgcock and Muir to confirm the θ_R -change

model was extremely insensitive and led to incorrect conclusions.

5-4 Discussion

It was pointed out in the analysis of Hedgcock and Muir's work that the observed $\Delta(T)$ function could not possibly be accounted for by a change in θ_R alone. A similar conclusion has been reached by others^{19,26,50} with regards to their observed $\Delta(T)$ functions; and we find on examining the remainder of the published $\Delta(T)$ functions^{18,22-25,34-36,49,52,74,91,92} that the same conclusion is still valid.

Indeed, in the above work it is questionable whether there is any convincing evidence to show that a θ_R -component is even partially responsible for the observed $\Delta(T)$ functions. In order to obtain such evidence it would be necessary to positively identify, and take account of, the other sources of deviation from MR. Such an approach has already been attempted by Das and Gerritsen¹⁹ who obtained a qualitative fit to their observed $\Delta(T)$ functions by superimposing a θ_R -component and a two-band $\Delta(T)$ component³¹. However, since their work in 1964 a number of new theoretical sources of deviation^{24,23,67} have been proposed which provide alternative explanations of their results. It should be particularly emphasized that even when $\Delta(T)$ is found to be

proportional to $\rho_i(T)$ at either high or low temperatures, in accordance with the θ_R -change model (Eqs. (5.9) and (5.11)), such a dependency may be attributed to several other theoretical models. Hence at the present time there appear to be too many unknown factors to permit positive identification of a θ_R -component.

The criticism which was directed at Hedgcock and Muir's calculation of θ_a and $\rho_i^a(T)$ for their various alloys, may also be applied to several other publications cited here; for example, references 60, 61, and 63. Because these analyses also neglect all other sources of deviation from MR, without justification, the resulting estimates of θ_a or $(\theta_p - \theta_a)$ must be considered as largely uncertain. Similar to the results of Hedgcock and Muir, their reported changes in θ_R are found to be negative and very large, i.e. ranging from 4 to 12% per atomic percent solute, or heavy deformation. It is possibly significant that these changes are much larger than the corresponding changes in the Debye θ_D discussed below.

Regarding the plausibility of a change in θ_R when 'defects' are introduced, it is of course well established both experimentally and theoretically⁶⁴ that the phonon spectrum of a metal does change under these circumstances. For example, measurements of the lattice specific heat^{64,93} and the elastic constants⁹⁴ both show that the Debye θ_D

(at 0(K)) may change linearly with dilute solute concentration in either direction, and by up to 1% per atomic percent solute. It has also been demonstrated²⁶ that the increase in specific heat in the temperature range between $\theta_D/10$ and θ_D , caused by plastic deformation, can be approximately represented within the Debye theory by a decrease in θ_D of about 0.4% for saturation defect concentration. Based on this type of evidence it is certainly plausible to suggest that the phonon resistivity is altered to some extent by defects and that this change could be crudely represented by a change in θ_R .

Gregor'yants et al²⁶ (1968) appear to be the first to calculate a $\Delta(T)$ correction for the change in θ_R , based on specific heat measurements and to apply this correction to their observed $\Delta(T)$ functions for plastically deformed metals. They assume that the change in θ_R is identical to the change in θ_D given by the specific heat measurements, and calculate the corresponding θ_R -component of $\Delta(T)$ from the Bloch-Gruneisen relation. Unfortunately, the residual $\Delta(T)$ component, obtained by subtracting the θ_R -component, could not be clearly identified with any other theoretical model, and so produced no comprehensive explanation of the measured $\Delta(T)$ function. An obvious limitation to this procedure is the substitution of the value of $\Delta\theta_D$ for $\Delta\theta_R$,

since there is no apparent theoretical reason why the two should be identical¹².

Finally, it should be mentioned that Kagan and Zhernov⁶⁷ have performed a more rigorous theoretical analysis of the deviations from MR resulting from phonon spectrum changes for chemical solute. This is discussed in detail in section 2-8 where it is pointed out that some experimental $\Delta(T)$ functions for alloys are qualitatively consistent with their theory, but a great many others do not show their predicted dependence of $\Delta(T)$ on the atomic mass ratio of the solute to solvent, or on solute concentration.

CHAPTER 6

DEVIATIONS FROM MR FOR VACANCIES IN PLATINUM

6-1 Introduction

For years metallurgists have been studying various properties of lattice site vacancies in metals by monitoring the excess electrical resistance caused by these defects. In most cases the vacancies were "frozen" into the specimen by rapid cooling (quenching) from a temperature near the melting point of the metal to a temperature below say 50°C. The vacancies, which are initially formed at high temperatures by thermal diffusion processes, are unavoidably present in equilibrium concentrations at each temperature, and this concentration increases rapidly as the temperature approaches the melting point. However, once vacancies are frozen into a specimen they remain essentially immobile below a certain characteristic temperature for each metal (about 200°C for Pt¹⁰¹), and in this range their resistivity can be readily measured. To remove these defects, one simply reheats or anneals the specimen (in the region 200-600°C for Pt¹⁰¹) until the vacancies become mobile and disappear at various "sinks", such as the surface of the specimen or the internal grain boundaries. Because the specimen must be exposed to high temperatures during quenching, most studies have been

performed on Pt, Au, and Al since these metals can be heated in air without serious surface or internal oxidation problems.

In spite of the large number of investigations on the excess resistivity due to vacancies, very few tests of MR have been performed for these defects. In most early work the vacancy resistivity was measured near room temperature or at liquid nitrogen temperatures, and was simply assumed to be the same quantity as the defect resistivity at 0(K). It is of course this latter resistivity which is normally required in any comparison with theoretical calculations of the vacancy resistivity. More recently, measurements at liquid helium temperatures have been employed, and inconsistencies¹⁰² between this data and the earlier measurements at higher temperatures have stimulated interest in deviations from MR for vacancies. There has also been considerable interest in this subject by thermometrists, since vacancies are frequently quenched into platinum resistance thermometers in the process of measuring high temperatures.¹⁰³

Recently Zetts, Gripshover and Bass¹⁰⁴ (1969) have reported that the vacancy resistivity at temperature T, i.e. $\delta\rho_T = \rho_0 + \Delta_T$, for quenched Pt and Au is the same at both 4.2 and 303K, and hence is consistent with MR. This result disagreed drastically, however, with earlier measurements by Conte and Dural⁶² on quenched Au, which yield a positive Δ_T (or λ_T) function that increases monotonically with T,

attaining the unusually large value of $\lambda_T \approx 4$ at 273K. In addition this last result also conflicts with the 1961 measurements on quenched Au by Pervakov et al,⁷¹ which show that Δ_{77} is significantly greater than Δ_{273} (but do not allow the actual value of each quantity to be calculated). Thus, the situation prevailing at the time at which our vacancy studies were initiated was highly uncertain.

In this chapter we present more detailed measurements of the resistance due to single vacancies in quenched Pt over the temperature range 4 to 473K. These measurements were performed on several different specimens of Pt, with considerable care being taken to eliminate spurious quenching effects and other possible sources of error. The resulting deviations from MR are shown to be substantial at most temperatures, and are compared with various theoretical predictions.

Parts of this study have already been presented elsewhere -- in particular, a brief report¹⁰⁵ on the deviations from MR obtained with the first specimen was published in 1970, while those phases of the work of interest to thermometrists were presented at the Fifth Symposium on Temperature¹⁰⁶ in 1971. The full details of the investigation are described below.

6-2 Procedure

The general procedure for determining the λ_T function of

the quenched-in vacancies was that given by Method 3 of section 1-4. More specifically, the procedure was to mount the Pt specimen inside a probe or holder, heat the specimen (only) with an electric current up to a predetermined "quenching" temperature, quench by switching off the current, measure R_T at a series of eight reference temperatures, anneal-out all or some of the vacancies at a predetermined annealing temperature, then remeasure R_T at the same reference temperatures. All these operations were conducted with the specimen left undisturbed, once mounted, and hence its dimensions should remain unaltered between the two states at which R_T was measured.

The calculation of the λ_T function, associated with those defects removed by the annealing step, proceeds as follows. For the state of the wire after the defects were removed -- designated state 2 -- one may write from Eqs. (1.22) and (1.24) that

$$^2\rho_T = \rho_{iT} + ^2\rho_O(1 + ^2\lambda_T) \quad (6.1)$$

where $^2\lambda_T$ and $^2\rho_O$ apply to all physical and chemical defects remaining in the specimen. For the state of the wire before the defects were removed -- designated state 1 -- one may similarly write

$$^1\rho_T = \rho_{iT} + ^2\rho_O(1 + ^2\lambda_T) + \delta\rho_O(1 + \lambda_T) \quad (6.2)$$

where λ_T and $\delta\rho_O$ apply only to those defects removed during

the annealing, and at 0(K) the equation reduces to

$$\delta\rho_0 = {}^1\rho_0 - {}^2\rho_0 \quad (6.3)$$

The required expression for λ_T may be obtained by subtracting Eqs. (6.1) and (6.2), yielding the result

$$\lambda_T = \frac{\delta\rho_T}{\delta\rho_0} - 1 \quad (6.4)$$

where $\delta\rho_T = {}^1\rho_T - {}^2\rho_T$. If now the specimen size remains unchanged between the two states, one may also write

$$\lambda_T = \frac{\delta R_T}{\delta R_0} \left(\frac{F_T}{F_0} \right) - 1 \quad (6.5)$$

where $\delta R_T = {}^1R_T - {}^2R_T$, and F_T is the shape factor (A/ℓ) discussed earlier. Since thermal expansion effects on F_T are extremely small, and $\delta R_{4.2}$ is the same as δR_0 to a close approximation, the expression

$$\lambda_T \approx \frac{\delta R_T}{\delta R_{4.2}} - 1 \quad (6.6)$$

may be used with reasonably good accuracy (discussed later). Furthermore, it should be emphasized that Eqs. (6.4-6.6) are valid between any two states of the wire -- and not just between the fully quenched and the fully annealed states -- providing the defects are removed homogeneously over the entire cross-sectional area.

6-3 Experimental Details

(a) Specimens

The measurements were performed on three different polycrystalline specimens of 0.10 mm diameter Pt wire of nominally 99.999% purity. Small diameter wires were used here to make the resistance changes large and to promote a homogeneous distribution of quenched-in vacancies by reducing possible differences¹⁰¹ between the quenching rates at the surface and the interior of the wire. On the other hand, high purity Pt was used in order to minimize spurious resistance changes due to evaporation, oxidation or migration of impurities during the exposure of the Pt to the relatively high quenching and annealing temperatures. The fact that the specimens were polycrystalline is also desirable in order to have a uniform distribution of grain boundaries at which the vacancies can be annihilated during annealing without leaving an inhomogeneous vacancy distribution.

The most detailed measurements were performed on a reference grade specimen (designated SC 1) obtained from S. Cohn Corp.¹⁰⁷ This specimen was extremely pure -- even by present day standards -- as evidenced by its W_T ratios of 3×10^{-4} at 4.2 K and 1.39274 at 100°C for the fully annealed state. Two other specimens, SC 4 and E 2, were also measured in brief auxiliary tests designed to confirm the results on SC 1 under different experimental conditions. Although

specimen SC 4 was taken from the same spool of wire as SC 1, it almost certainly possessed a larger grain size at the time of testing since it had previously been subjected to temperatures of 1200 - 1300°C for about 8 hours. Specimen E 2 was purchased as a reference grade sample from Engelhard Industries,¹⁰⁸ but was found to be much less pure than SC 1 or SC 4, as evidenced by its annealed W_T ratios of about 36×10^{-4} at 4.2 K and 1.39129 at 100°C. Thus the tests presented here include specimens of different purity as well as different grain size.

Before mounting the specimens in their special holder they were first chemically cleaned in organic solvents and distilled water (plus acids in the case of SC 4), using plastic tweezers and plastic gloves during handling operations. Only specimen SC 1, which was supplied in a hard-drawn state, was given any annealing treatment between its initial cleaning and mounting -- it was in fact heated with an electric current at 1100°C for about 1 hour to soften it for easier handling during mounting operations. Specimen E 2 was already supplied in a soft annealed state, while specimen SC 4 was mounted in the hard-drawn state for reasons not related to this test.

(b) Specimen Holder

The specimen holder or probe used here was designed to support the specimen as a four terminal resistor in an undisturbed manner during all quenching, annealing and measuring operations. Its basic construction is shown schematically in Fig. 6.1.

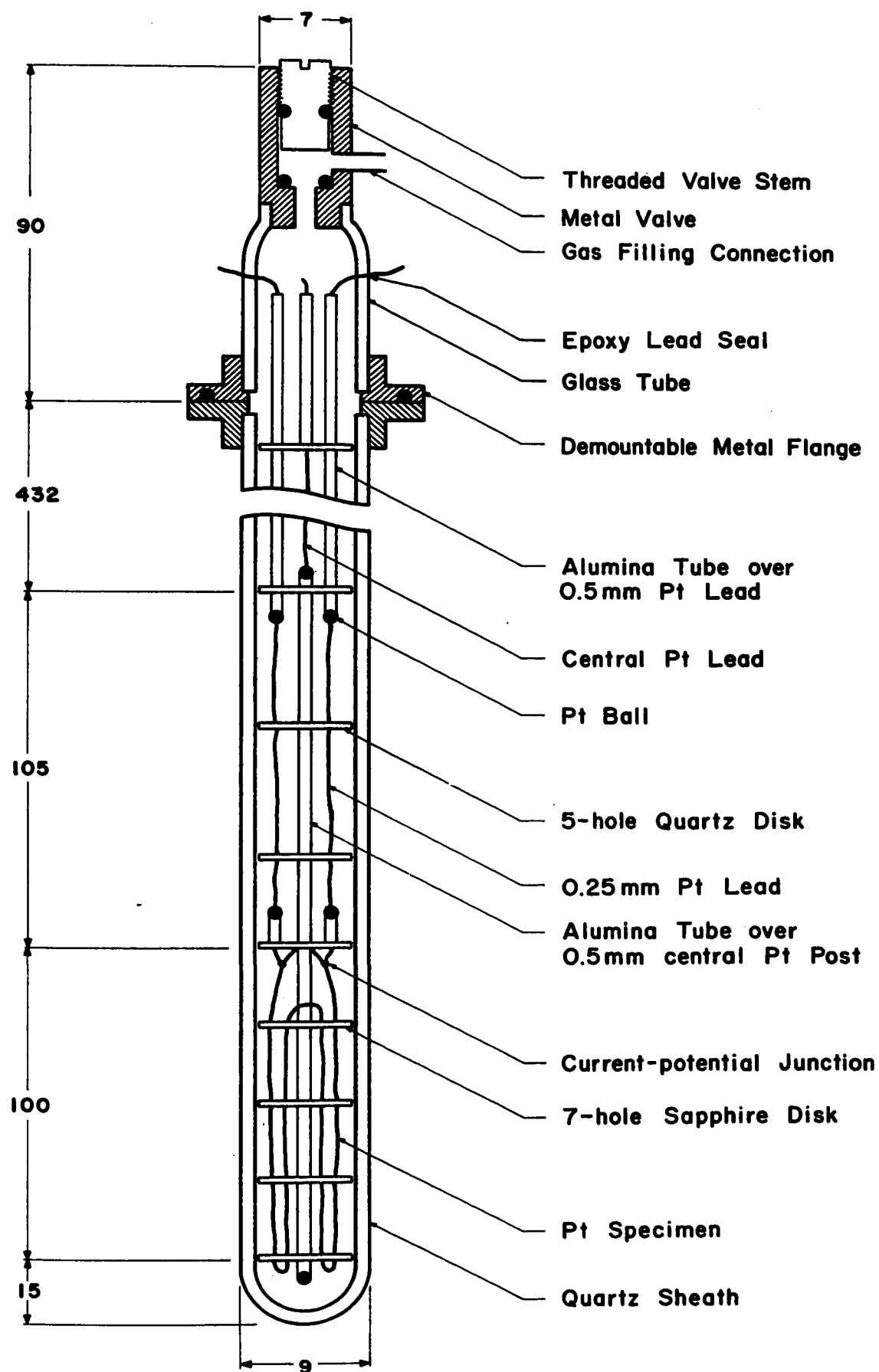


Fig. 6.1 . Specimen holder (dimensions in mm.)

The specimen itself is supported in a ring of holes near the perimeter of four sapphire disks in a "bird-cage" configuration. The six Pt "bars" of the cage allow a total specimen length of 50 cm and are carefully spaced so as to touch only the sapphire support. Sapphire was chosen for this purpose because it is the purest available ceramic that can withstand temperatures of up to 1500°C without itself deteriorating or seriously contaminating the platinum. The holes in the sapphire are drilled oversize (0.5 mm diam.), counter-sunk on each side, and polished so that the specimen can freely expand and contract during thermal cycling. The disks themselves are supported and spaced on a central Pt post by small alumina tubes. Once a specimen is mounted, its two free ends are welded with an oxy-hydrogen torch to the two pairs of (Pt) current-potential leads, which extend the full length of the probes from above. Quartz disks are used to separate these leads, and all disks and spacer tubes are held in place by melted Pt balls on the leads, as shown in the figure. The diameter of the lead wire is made larger than the specimen diameter so that the latter can be heated with an electric current up to at least 1400°C without seriously overheating the leads in the region of the epoxy seals. A section of bare, intermediate-sized Pt wire is installed directly above the specimen in order to reduce thermal conduction losses when the "working" end of the probe is

immersed in the reference temperature baths. The various disks also help to reduce thermal losses by impeding the vertical convection currents in the filling gas. The two current - potential junctions of the specimen are locked in place relative to the sapphire former by Pt balls so that thermal expansion of the leads will not distort the specimen.

The working end of the probe is sheathed in a clear quartz tube of 9 mm outside diameter and 63 cm length; these dimensions are dictated by the requirement for deep immersions in the small access wells of existing temperature baths and annealing furnaces. A demountable flange on the sheath allows the specimen to be readily changed, while a miniature valve at the top of the probe facilitates changes of the filling gas. Epoxy cement and O-ring seals are used at the various joints to make the probe vacuum tight. A fifth central Pt lead is installed in the probe so that the electrical insulation across the disks can be monitored. Four copper leads, enclosed in a flexible 7 foot cable, are soldered to the current-potential leads at the top of the probe to provide convenient connections to the resistance measuring instruments.

Prior to assembly of this probe all disks, alumina tubes and the quartz sheath were chemically cleaned with organic solvents, HCl acid, and distilled water. They were then baked in air at 1100°C for about 1 hour.

(c) Reference Temperature Baths

The eight reference temperatures used in this project were the normal boiling points of liquid He⁴ (4.215K), H₂ (20.28K), N₂ (77.348K), O₂ (90.188K), and water (373.15K, 100°C); the triple point of water (273.16K, 0.01°C), the sublimation point of CO₂ (194.674K), and an oil bath temperature of 200°C.

Eight different experimental baths were used to obtain these reference temperatures. The triple point of water was realized in a commercially-produced cell using standard techniques,¹⁰⁹ while the boiling point of water was reproduced in a high precision calibration bath described earlier.¹¹⁰ The boiling point of He was realized in an open dewar with the specimen immersed 41 cm beneath the surface of the liquid, and small corrections were applied for atmospheric pressure variations and the hydrostatic head of He. The boiling points of O₂, N₂, H₂, and the sublimation point of CO₂ were also realized in open dewars, but using a metal block comparator system described earlier.¹¹¹ With this system one corrects for impurity, atmospheric pressure, and other effects on the fixed point by measuring the actual deviation of the bath temperature from the true fixed point with a calibrated Pt resistance thermometer. Since both the specimen and the thermometer sensor were made of high purity Pt in this case, we simply use the sensitivity, dW_T/dT , of the thermometer to correct the measured specimen resistance to its value at the

true fixed point. Experimentally, the procedure was to insert the specimen holder and the thermometer into two adjacent holes in a metal block immersed in the fixed point medium, and then make alternate measurements on the two resistors to average out any small temperature drifts. By using the same thermometer and the same procedure each time, the specimen resistance could be determined at precisely the same temperature in each run within extremely close limits (see Table 6.1). The oil bath temperature was also realized in a block comparator, but in this case the temperature was controlled by heaters rather than by a fixed point bath.

The reproducibility of the reference temperatures -- and not their absolute accuracy -- is of course the characteristic that affects the determination of λ_T in our particular procedure. Estimates of these reproducibilities, based on our operating experiences, are given in column 2 of Table 6.1, and represent about the worst possible cases. The corresponding uncertainties in R_T caused by these temperature uncertainties are also presented in this Table in column 4; while the sensitivities, dR/dT , used for this conversion are shown in column 3. It might be emphasized that these sensitivities apply fairly closely to all specimens tested here since their size, and therefore their R_T values, are approximately the same (see Table 6.2).

TABLE 6.1

Estimated maximum uncertainty in T , δR_T and λ_T at each reference temperature.

Reference T (K)	Reproduci- bility of T in mK	dR/dT μohms per mK	Equivalent Error in R_T μohms	Bridge Precision μohms	Total Error in δR_T μohms	Typical Error in λ_T
4.215	5	0.08	0.4	0.1	1	0
20.28	0.4	4.6	2	0.1	4	0.003
77.348	0.1	26	3	2	10	0.006
90.188	0.1	26	3	2	10	0.006
194.674	0.1	25	3	2	10	0.006
273.16	0.03	24	1	2	6	0.004
373.15	0.1	24	2	2	8	0.005
473.15	0.2	23	5	2	14	0.008

(d) Resistance Measurements

The specimen resistance was measured with two different resistance bridge systems: a Leeds and Northrup G3 Mueller bridge when R_T was > 1 ohm, and a recently developed direct current comparator bridge¹¹² when R_T was < 1 ohm (i.e. at the He and H₂ points). The measuring precisions of these bridges are given in column 5 of Table 6.1, and their absolute accuracy will not be discussed here since it has no effect on the determination of λ_T . Small corrections have been applied to the bridge readings, where necessary, to compensate for non-linearity of the bridge dials and for the almost negligible self heating of the specimen by the measuring current. The total uncertainty in the determination of δR_T , due to uncertainties in both the temperature reproducibility and the resistance measurement, is given in column 6 of Table 6.1, while the corresponding error in λ_T is given in the last column for a value of $\delta R_{4.2} = 2000$ μ ohms. The error in λ_T for other $\delta R_{4.2}$ values may be obtained by simply multiplying these figures with the factor $(2000/\delta R_{4.2} \text{ (}\mu\text{ohms)})$.

(e) Initial Stabilization

Each specimen, after being mounted in the probe, was annealed and stabilized by suitable heat treatment prior to any quenching studies. Initially the probe was filled with a He -O₂ gas mixture ($\sim 10\%$ O₂) to about atmospheric pressure, and its

specimen end baked in an electric tube furnace at about 800-900°C to anneal-out strains and burn off organic material. The probe was then evacuated and back-filled with 0.4 Torr O₂ plus 1 atmosphere He, and the specimen (alone) was heated with an electric current at about 1200 -1300° C for at least 10 minutes. Measurements of $R_{4.2}$ and R_{273} , taken during the course of these heat treatments as well as during the actual quenching studies, showed that the specimens had attained adequate stability for our purposes. Further annealing studies presented in Chapter 7 show that the above heat treatment would in fact remove most physical defects in the specimen due to wire-drawing and other cold-working operations.

The He - 0.4 Torr O₂ gas filling, which was also used for the final quenching studies, was selected for several reasons. The large He component has relatively good thermal conductivity, even down to 4 K, which promotes rapid cooling of the specimen during quenching and good thermal bonding between the specimen and all reference temperature baths. The small trace of oxygen, on the other hand, helps to stabilize the oxide ceramics and the oxide impurities in the specimen, but is small enough to keep evaporation of the Pt (through the formation of its volatile oxide) at a reasonable level up to temperatures of 1250° C. Excessive evaporation is most undesirable since it can ruin the insulating properties of the ceramic disks. However insulation tests performed

here, using the fifth "dummy" lead, revealed no difficulties when the above gas mixture was used.

(f) Quenching Procedure

The quenching procedure adopted here was to immerse the specimen end of the probe in a large beaker of water, connect each current-potential pair (as one lead) to an adjustable voltage power supply (either AC or DC), increase the current through the specimen until its temperature reached a pre-determined value as read with an optical pyrometer, hold the specimen at this temperature for about 1 minute, then quench by turning off the current with a snap-action toggle switch. A typical cooling time achieved with this system was about 0.1 second from 1250 to 600° C. While this rate of cooling is not nearly fast enough to quench in the equilibrium concentration of vacancies,¹⁰¹ it was capable of producing something like a 5×10^3 μohm increase in resistance when the "quenching" temperature was about 1250° C. Such an increase, coupled with our high measuring precision, permits a determination of the λ_T function to better than ± 0.003 (see Table 6.1). Still higher quenching temperatures and quenching rates were avoided because of the possibility of evaporating or contaminating the specimen, introducing quenching strains due to the surface of the specimen cooling faster than its interior,¹⁰¹ and quenching-in divacancies as well as single vacancies¹¹³ -- all of which would complicate the analysis.

Regarding the concentration of divacancies likely to be quenched-in during our experiments, rough calculations indicate that they should be $< 0.02\%$ of the total defect concentration, and hence will be negligible.

The quenching temperatures quoted here are at most only crude averages of the temperature distribution along the specimen. About 90% of the specimen will be within $\pm 50^\circ\text{C}$ of the temperature cited, but the rest -- mainly in the region of the disks -- may be cooler by up to a few hundred degrees. This temperature distribution will of course result in a somewhat non-uniform vacancy concentration along the wire; but should have little or no effect on the determination of λ_T , since the cross-sectional vacancy concentration will still be highly uniform. To some extent this latter statement is based on the assumption that λ_T is independent of the vacancy concentration; an assumption that is strongly supported by the final results.

(f) Annealing Procedure

In order to establish the temperature range over which the quenched-in resistance is removed from our particular specimens, we have carried out certain preliminary annealing tests using a higher measuring precision than that involved in most earlier studies. In particular we have performed isochronal step-annealing of specimens, quenched from about 1250°C , using steps of 50°C and an annealing time of 30

minutes at each temperature. The annealing, which was done in an electric tube furnace, began with a temperature of 100°C and was increased in successively higher steps up to 850°C . After each annealing step the probe was cooled to room temperature (slowly enough to avoid further quenching effects) and the value of $R_{0^{\circ}\text{C}}$ was determined from a measurement at the triple point of water (0.01°C).

The results of such a test on specimen SC 1 are presented in Fig. 6.2(b), where the fractional change in $R_{0^{\circ}\text{C}}$ caused by each 50°C annealing step is plotted against the temperature reached by that step. This type of graph crudely demonstrates the relative rate of recovery of $R_{0^{\circ}\text{C}}$ as a function of annealing temperature. The primary recovery peak in the $200-600^{\circ}\text{C}$ region, which has been observed many times before,¹⁰¹ is normally attributed to the removal of single vacancies. The secondary recovery "tail" extending up to 850°C has not been observed in such detail before, and could possibly be due to the removal of large vacancy clusters, such as those recently observed¹¹⁴ in microscopic studies of quenched Pt. In any event, the secondary recovery occurs at too high a temperature to be due to divacancies.¹⁰¹ For more details concerning this recovery tail one is referred to the author's preliminary report.¹⁰⁶

Having established that secondary defects were in fact present in our quenched specimens, we restricted the annealing

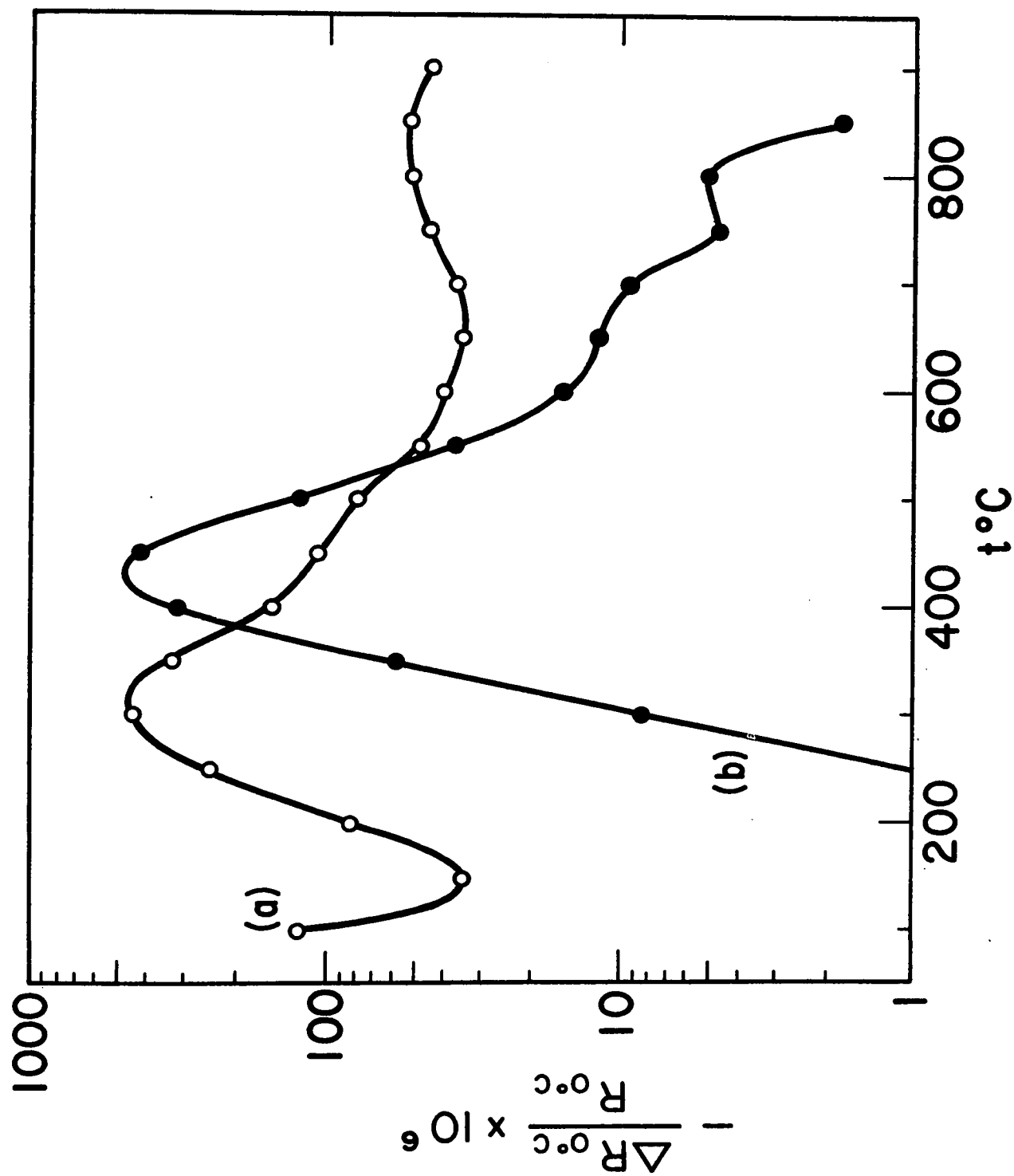


Fig. 6.2 . The fractional change in $R_{0^\circ\text{C}}$ during isochronal annealing of (a) fatigued specimen SC3 and (b) quenched specimen SC1.

to temperature below 450°C in those cases where the λ_T function for single vacancies was to be determined. In other tests, however, the annealing was extended to higher temperatures for the specific purpose of determining the effects of the secondary defects on λ_T .

At no time in this work have we used the fully annealed R_T values prior to quenching for the calculation of λ_T , since these will in general be different from the fully annealed values after quenching, due to permanent changes in the wire size and purity caused by the high quenching temperatures and rapid cooling rates.¹⁰¹ However, it should be emphasized that for the comparatively "favourable" quenching technique used here the changes in the annealed value of $R_{0^{\circ}\text{C}}$ were nearly always less than 20 μohms per quench. This was a useful achievement in that it virtually eliminates the possibility that part of the resistance recovered during annealing was due to spurious impurity effects or quenching strains.

6-4 Results

The most detailed experiment for the determination of λ_T for single vacancies was performed on specimen SC 1. In this test the annealed specimen was quenched from 1250°C , measured at the eight reference temperatures discussed earlier, and then furnace annealed at 375°C in three distinct steps, with measurements being taken at the eight temperatures after each

step. If one defines C_r as the fraction of the total quenched-in resistance, $\delta R_{4.2}$, remaining at any particular time (which is about the same as the fractional defect concentration), then the annealing steps 1, 2 and 3 reduced C_r to 0.75, 0.45 and 0.18 respectively. To investigate the influence of secondary defects on λ_T , a fourth annealing step was performed in which C_r was reduced to < 0.01 by heating the specimen for 4 hours in the $600 - 650^\circ \text{C}$ region, after which measurements were again taken at the various reference temperatures.

The resulting values of δR_T for the four separate annealing steps are presented in Table 6.2, while the λ_T values calculated from Eq. (6.6) are plotted in Fig. 6.3 separately for the first three annealing steps. It can be seen that the three sets of λ_T values agree to within about their experimental uncertainty (c.f. Table 6.1), which suggests that the vacancy distribution remained fairly homogeneous during annealing and that the single-vacancy λ_T function is independent of the vacancy concentration in the narrow range investigated. The solid curve in Fig. 6.3 is a smooth interpolation of the λ_T values corresponding to the total increment produced by the three annealing steps together. The λ_T function for the fourth step, which applies to an indeterminate mixture of single vacancies and secondary defects, is found to be considerably higher in value than the single-vacancy λ_T function, particularly at higher temperatures. For example λ_T is 0.28,

TABLE 6.2

The change in resistance, δR_T , of quenched specimen SC 1 during annealing in the four distinct steps described in the text.

T (K)	R_T (Approx.) in ohms	δR_T in μ ohms			
		Step 1	Step 2	Step 3	Step 4
4.21	0.002	1603	1897	1663	1139
20.28	0.025	1836	2176	1940	1463
77.35	1.15	1763	2068	1817	1434
90.19	1.49	1745	2053	1792	1427
194.67	4.17	1695	1950	1718	1411
273.16	6.10	1636	1899	1669	1394
373.15	8.50	1554	1818	1592	1381
473.15	10.82		1719	1513	1338

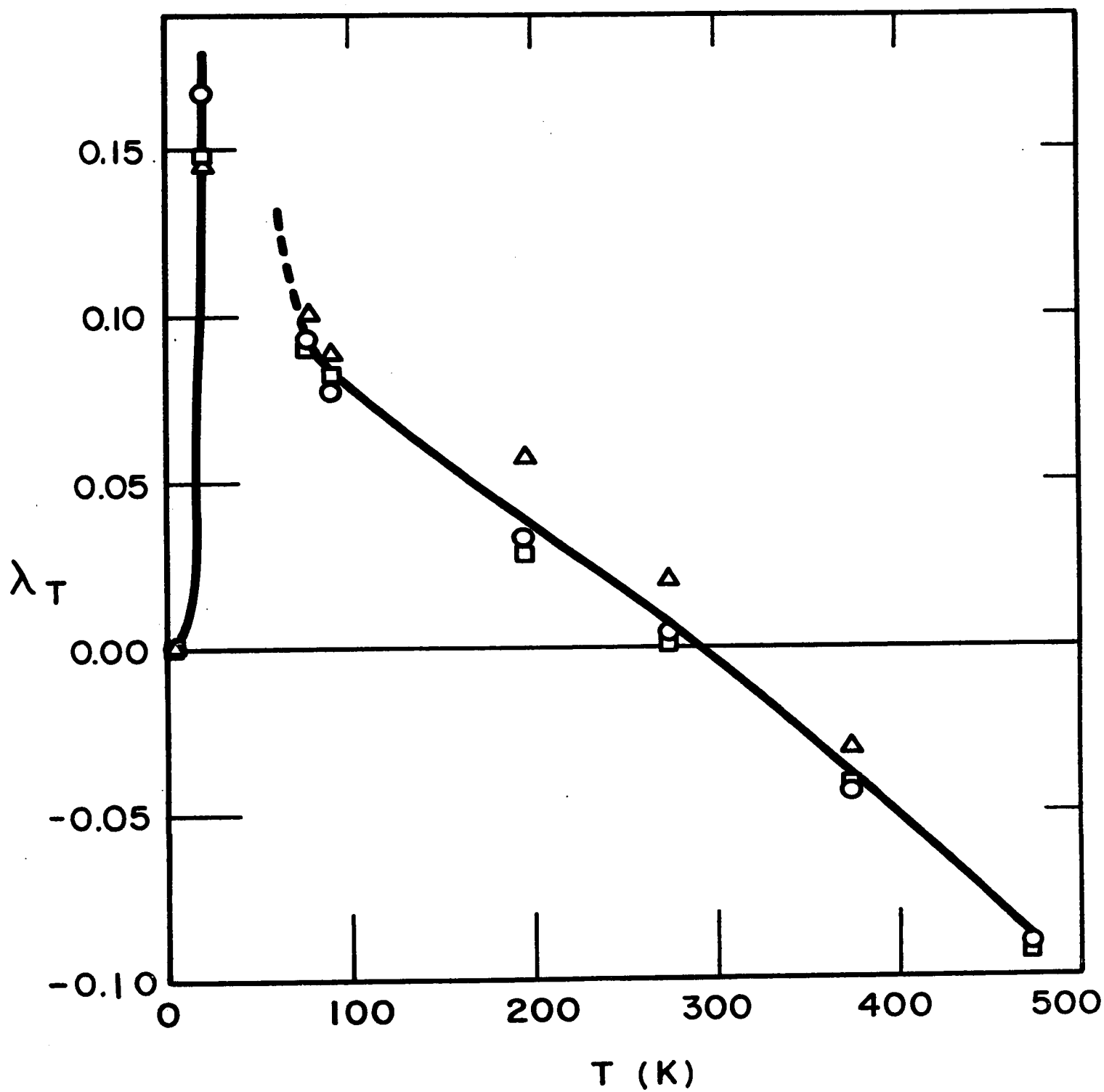


Fig. 6.3 . The λ_T function of single vacancies for three different annealing steps: (Δ) step 1, ($\square$) step 2 and ($\circ$) step 3.

0.25 and 0.17 at temperatures of 20.28 K, 90.19 K and 473.15 K respectively. This suggests that the secondary defects themselves are associated with a higher λ_T function than single vacancies; however one cannot be certain of this statement until the distribution of these defects is shown to be homogeneous. Because of this, and other uncertainties noted above, no attempt is made here to separate out the λ_T function due to secondary quenching defects.

To confirm the above results under different test conditions we have determined the λ_T values at selected reference temperatures for two other quenched specimens (E2 and SC 4) as well as for other quenches of specimen SC 1. The results are presented in Table 6.3 along with all important test parameters, i.e. the quenching temperature, the maximum annealing temperature, the total $\delta R_{4.2}$ increment used to determine λ_T , and the final C_r value after the annealing increment. In all cases the initial R_T values were those of the quenched specimen prior to annealing. The tests, identified as 1a and 1b, apply to the quench-annealing sequence on SC 1 already described above, but in this table the λ_T values corresponding to certain overall annealing increments are presented. The reason that the λ_T values of test 1b, which corresponds to virtually all the quenched-in defects, are only slightly higher than the single vacancy λ_T values of test 1a is that the concentration of secondary defects in test 1b is relatively

TABLE 6.3

The values of λ_T at 90.19 K, 273.16 K and 373.15 K are given for various quenched specimens under 6 different test conditions specified in the table and text.

Test No.	Spec. No.	Quench. Temp. (°C)	Max. Anneal. Temp. (°C)	Final C_r	$\delta R_{4.2}$ Increment (μ ohms)	λ_{90}	λ_{273}	λ_{373}
1a	SC 1	1250	375	0.18	5163	0.083	0.008	-0.039
1b	SC 1	same quench	650	< 0.01	6302	0.113	0.047	0.007
2	SC 1	1120	660	< 0.01	2654	0.074	0.018	-0.026
3	SC 1	1220	800	0	5347	0.091	0.031	-0.004
4	E 2	1250	450	0.08	3555	0.066	0.012	-0.024
5	SC 4	900	800	0	450		-0.03	

small compared to the total defect concentration. The fact that the λ_T values of test 2 are lower than those of test 1b can be plausibly explained by its lower quenching temperature, since this would be expected to produce a smaller fraction of secondary defects. This effect is confirmed by the results of tests 3 and 5, which also involve lower quenching temperatures. Indeed in test 5, where the quench was performed by extracting the probe from a furnace at 900° C, the quenching temperature and quenching rate are low enough that no secondary defects appear to have been produced -- as evidenced by its λ_T value. The results of tests 4 confirm fairly closely the single vacancy λ_T function of test 1a for a specimen of completely different purity. However, there is a slight difference in the slope of λ_T in the two cases, and this could be real since it is outside the estimated error limits. In summation, then, we find that the new tests presented in Table 6.3 support very closely the initial results obtained with specimen SC 1.

6-5 Corrections to the Results

(a) Change in the Shape Factor Correction

In deriving the basic equations (6.5) and (6.6) for λ_T it was assumed that the shape factor, F_T , was not altered by thermal expansion or by the removal of vacancies. If we take these small effects into account, Eq. (6.5) becomes

$$\lambda_T = \frac{{}^1R_T {}^1F_T - {}^2R_T {}^2F_T}{{}^1R_O {}^1F_O - {}^2R_O {}^2F_O} - 1 \quad (6.7)$$

where the superscripts 1 and 2 refer to the states before and after the annealing step, respectively, and the Kelvin temperature is used throughout. It can be readily shown that the contraction of the specimen due to the removal of vacancies leads to the relation

$$\frac{{}^1F_T}{{}^2F_T} \approx 1 + \frac{\Delta l}{l} \approx \frac{{}^1F_O}{{}^2F_O} \quad (6.8)$$

where Δl is the change in length (${}^1l - {}^2l$), and $\Delta l/l$ may be taken as independent of T in this approximation. Furthermore, the contraction $\Delta l/l$ will be roughly 1/3 of the fractional volume contraction due to the removal of atoms from the surface to fill the vacant lattice sites, and hence one can write

$$\frac{{}^1F_T}{{}^2F_T} \approx 1 + \frac{\Delta c}{300} \quad (6.9)$$

where $\Delta c = {}^1c - {}^2c$ is the change in vacancy concentration in atomic %. Substituting this result into Eq. (6.7), one obtains

$$\lambda_T = \frac{F_T}{F_O} \left(\frac{\delta R_T + {}^1R_T (\Delta c / 300)}{\delta R_O + {}^1R_O (\Delta c / 300)} \right) - 1 \quad (6.10)$$

which reduces to

$$\lambda_T = \frac{\delta R_T}{\delta R_O} - 1 + \left(\frac{F_T}{F_O} - 1 \right) \frac{\delta R_T}{\delta R_O} + \frac{F_T}{F_O} \frac{{}^1R_T}{\delta R_O} \frac{\Delta c}{300} \quad (6.11)$$

when ${}^1R_O(\Delta c/300) < 1 \text{ } \mu\text{ohm} \ll \delta R_O$, as in all cases here.

The second term on the right hand side of Eq. (6.11) is the correction that must be added to our reported λ_T values to compensate for thermal expansion effects on the shape factor. Based on the data of Corruccini and Gniewek,¹¹⁵ the value of $(F_T/F_O) - 1$ is given at $T \geq 100 \text{ K}$ by the linear relation

$$(F_T/F_O) - 1 \approx 0.0003 + (T-100)10^{-5} \quad (6.12)$$

Since $\delta R_T/\delta R_O \approx 1$ in our work, this correction is < 0.004 for $T < 500 \text{ K}$, and hence may be considered negligible.

The last term in Eq. (6.11) is the correction which must be added to our reported λ_T values to compensate for the contraction of the specimen as vacancies are removed. To estimate this term the change in concentration, Δc , must first be calculated from δR_O using the relation

$$\Delta c(\text{at.}\%) \approx 2.5 \delta R_O/R_{273} \quad (6.13)$$

which is based on the reported change²³ in ρ_O for Pt of $4 \text{ } \mu\text{ohm-cm}$ per atomic % vacancies, and the known value of $\rho_{273} \approx 10 \text{ } \mu\text{ohm-cm}$. After substituting Eq. (6.13) and the approximation $(F_T/F_O) \approx 1$, the correction term becomes simply $0.008 (R_T/R_{273})$. Since R_T/R_{273} is the same within 1% for all specimens of pure Pt, and the expression is independent of vacancy concentration, this particular correction is the same for all tests presented here. Its magnitude in the range

100 - 500 K may be represented by the linear relation

$$0.008 (R_T/R_{273}) \approx 0.002 + 3.5 \cdot 10^{-5} (T-100) \quad (6.14)$$

and will be 0.008 at 273 K. This correction is about the same magnitude as our estimated errors in Table 6.1, and should be applied to the present results when precise quantitative comparisons with theory become possible.

(b) Correction for the Difference Between $\delta R_{4.2}$ and δR_0

In deriving Eq. (6.6) it was assumed that $\delta R_0 = \delta R_{4.2}$. If we remove this particular approximation Eq. (6.5) becomes

$$\lambda_T \approx \frac{\delta R_T}{\delta R_{4.2}} (1 + \lambda_{4.2}) - 1 \quad (6.15)$$

Hence the correction term, $\lambda_{4.2}(\delta R_T/\delta R_{4.2}) \approx \lambda_{4.2}$, should be added to the reported λ_T values at all temperatures. However, based on the experimental λ_T values reported by Stewart and Huebener²³ for Pt at low temperatures, the magnitude of $\lambda_{4.2}$ will be < 0.003 , and therefore this correction may be considered negligible.

(c) Correction for the Atomic Volume Changes

It has been pointed by Dugdale and Basinski²¹ (1967) that each term in the basic resistivity equation (1.22) should apply to the same atomic volume. Thus, in our case, a correction should be applied to compensate for the fact that ρ_{iT} in Eq. (6.1) is not precisely the same as ρ_{iT} in Eq. (6.2)

because the lattice spacing and hence the atomic volume is slightly increased by the removal of vacancies.¹¹⁶ Also a correction should be applied to the ρ_0 values in these two equations to compensate for the fact that the atomic volume (V_a) at 0(K) is slightly less than the volume at T(K) (where ρ_T and ρ_{iT} were measured), due to thermal dilation of the lattice. Explicit formulae for these corrections have been given by Schwerer et al¹¹⁷ which show that the changes in λ_T will be independent of defect concentration (or Δc in our case) and increase in absolute magnitude linearly with temperature above say 90 K. Unfortunately, these corrections involve the derivative, dp/dV_a (where p corresponds to ρ_{iT} in one case and ρ_0 in the other), and this factor cannot be estimated reliably at the present time (Seth & Woods²⁴). In particular the use of the pressure (p) derivatives, dp/dp and dV_a/dp , to estimate dp/dV_a may be severely criticized, since the measured dp/dp includes the effects of pressure on the phonon spectrum, the Fermi surface, the scattering potentials, etc., and not just its effect on the atomic volume. Because of this and other missing data, we have not attempted to estimate these corrections for atomic volume. In any event, since they vary linearly with T above 90 K, the conclusion that λ_T varies linearly with T in the same range, derived from Fig. 6.3, should still be valid.

6-6 Discussion of Results

(a) Comparison with Other Experiments

The results presented here show that significant departures from MR occur for single vacancy defects in Pt at all temperatures except those in the vicinity of 300 K. Even when all quenching defects (vacancies plus secondary defects) are taken into account, the value of λ_{300} is still very small, i.e. < 0.05 . Thus our results are found to be in good agreement with those reported by Zetts et al,¹⁰⁴ which show a λ_{303} value of $0 \pm \text{about } 0.06$ for the total quenched-in defect concentration in both Pt and Au. Further evidence of the similarity between λ_T for quenched Pt and Au is provided by the close agreement between our value of the difference, $(\lambda_{77} - \lambda_{273})$, for Pt and the value derived from the results of Pervakov et al⁷ for Au. In particular, their difference is 0.07 ± 0.02 for the total defect concentration (with their lowest range of quenching temperatures), while we obtained 0.07 ± 0.01 under somewhat similar circumstances (c.f. Table 6.3). The results of Conte and Dural⁶² for quenched Au, which differ drastically from the results above, could possibly be in error due to dimensional changes of the specimen during quenching since values of the annealed resistance prior to quenching were used in their calculations.

At about the same time as our preliminary results were

published, Stewart and Huebener²³ reported a determination of λ_T for the total quenched-in defect concentration in Pt over the range 1.6 - 300 K. Their results agree with ours reasonably well at low temperatures in that they show a peak with a maximum λ_T of about 0.2 in the 20 - 70 K region, but there is serious disagreement at higher temperatures where, for example, their λ_{273} values fall in the range 0.15 - 0.37 depending on the particular specimen. There are two main differences in the experimental techniques involved here which probably account for this disagreement. Firstly, they have used extremely rapid quenching, which involved plunging the bare, heated specimen directly into ice water; and this would be expected to produce a greater fraction of secondary defects (as well as dimensional changes) in the wire, thus increasing λ_T at high temperatures. Secondly, they have determined λ_T using two different methods, which are both less reliable than the one used here. In particular, they use the resistance ratio procedure discussed earlier in section 1-4 (which is only expected to be reliable at low temperatures), plus another method somewhat similar to our own except that the value of the annealed resistance before quenching is used in the calculation. In view of these comments, the results presented here in Fig. 6.3 are expected to give the more reliable estimate of the true λ_T function for single vacancy defects at high temperatures.

Another very recent paper, by Misek,⁹² on quenched Au reports values of $\delta\rho_T$ in the 4 - 90 K range which yield λ_T values for the total defect population that are ≤ 0.3 approximately. One hesitates to draw any further conclusions from this data because of the large experimental uncertainties in $\delta\rho_T$ and because an indirect method of calculating $\delta\rho_T$ was used, involving assumptions about the form of deviations from MR at high temperatures. In any event these results do not conflict with the most reliable information presently available.

(b) Comparison with Theory

The two main features of the λ_T function for single vacancies, that one would like to explain theoretically, are the positive peak in the 20 - 70 K range and the linear dependence on T (with negative slope) in the 90 - 470 K range. The theory of Masharov (section 2-7(b)), which was intended specifically for vacancies in metals, will not account for either of these two features -- in spite of the author's claims regarding the negative slope at high temperatures (see earlier discussion).. Also the mechanisms for deviations from MR for vacancies suggested by Bross (section 2-4) and Heubener (section 2-13) do not appear to fit our experimental results. The theories of Kagan and Zhernov (section 2-8), and Bhatia and Gupta (section 2-9), might possibly account for both λ_T features, but these theories were derived specifically for substitutional solid solutions, and are not necessarily valid

in this particular case.

It has been suggested in a tentative manner by Pervakov et al⁷¹ (1961), and by Conte and Dural,⁶² that the deviations from MR for vacancies in Au might be due to changes in θ_R (see section 2-5). Calculations performed by Masharov¹¹⁸ (1963) for vacancies show that θ_D should decrease as the vacancy concentration is increased. Thus, according to our analysis in Chapter 5, the λ_T function should be positive and possess a positive slope -- which of course does not agree with the experimental facts.

It has also been suggested in a tentative manner in the author's preliminary report,¹⁰⁵ and by Stewart and Huebener,²³ that the low temperature λ_T peak might be due to the two-band Fermi surface effect (section 2-1(d)), as outlined by Dugdale and Basinski.²¹ The details of this model, as it applies to a complex metal like Pt, remain to be worked out. Also it should be emphasized that this model by itself will not account for the observed temperature dependence of λ_T at high temperatures.

In summation, then, it is apparent that more theoretical work must be done before one can account for the observed λ_T function of single vacancies in a definitive manner.

CHAPTER 7

DEVIATIONS FROM MR FOR PLASTICALLY DEFORMED PLATINUM

7-1 Introduction

Plastic deformation of metals by tension or compression produces a variety of physical defects, consisting of vacancies, interstitials, dislocations (both edge and screw type), and their complexes¹¹³. Providing the deformation takes place at temperatures below about 90K most if not all of the defects will be retained or "frozen" into the metal; however as the sample temperature is increased each type of defect will ultimately become mobile and disappear at various 'sinks'. It is generally believed that the interstitials are removed first, in the warming process, by diffusion to vacancies and dislocations, following which the vacancies are annihilated principally at dislocations and surface or grain boundaries, and finally the dislocations are eliminated by their internal rearrangement and by the simultaneous recrystallization of new strain-free grains^{113,119}. The actual mechanisms by which the defects are removed appear to be fairly complex and not entirely understood at the present time¹¹⁹. Nor are the relative concentrations of each type of defect in strained metals well established -- although resistivity measurements indicate that the component due to point defects (vacancies plus interstitials) is roughly of the same magnitude as that due to dislocations¹⁸.

Isochronal annealing studies¹¹⁹ of plastically deformed

metals show that the various annealing stages frequently occur in fairly well separated temperature regions, and from this point of view it should be possible to study the resistivity changes associated with each particular defect. In the case of platinum most reports^{101,119-122} appear to agree that interstitials are removed in the range - 50 to 100°C, vacancies in the range 100 to 350°C, and dislocations above about 350°C. However, not all reports^{120,121} show a sharp separation between the vacancy and dislocation annealing stages, and not all reports give the same upper temperature limit for the complete removal of dislocations -- in fact estimates run from 450 up to 800°C. Part of the latter uncertainty may be due to different measuring precisions, or to the fact that the recrystallization temperature depends strongly on the degree of deformation¹²⁸.

The deviations from MR associated with the defects in plastically deformed metals have been investigated experimentally for Au^{18,26,71,92}, Ag^{18,21,26,71,126}, Cu^{18,21,60,91,124-126}, Al^{59,61,123,125}, W³⁵, Fe⁵⁹, Ni⁵⁹ and Pt¹²⁷. In the case of the first four metals, the reported deviations apply mainly to dislocations (whether it was intended or not) since the point defects anneal out quite rapidly at room temperature, and all specimens appear to have been exposed to this temperature. In the case of the other metals, however,

the deviations almost certainly apply to some indeterminate mixture of dislocations and vacancies, since no special care was taken to anneal out the vacancy stage above room temperature. This is clearly the case for the work¹²⁷ on Pt where the deviations correspond to those defects removed by an annealing interval of 100 to 450°C. As yet, no one has attempted to measure deviations from MR for interstitials or vacancies in strained metals.

Based primarily on three of the preceding investigations^{18,21,26} we now have a general picture of the Δ_T or λ_T function for dislocations (of unknown distribution) in noble metals over the entire range 4 - 400K. A plot of the λ_T function for Ag was presented earlier in Fig. 1.1 and has been shown to follow the two-band relation, Eq. (3.1), fairly closely⁵⁰. The results for Au and Cu are quite similar, and as near as one can tell the results for the other metals investigated are also consistent with the two-band equation. The claims in some early reports^{59,126} that there are no significant departures from MR in the high temperature region (>90K) for certain metals was simply intended to mean that $(\Delta_T + \rho_0)$ was independent of T in this range, and not that Δ_T was zero.

To date, three plausible theoretical explanations for the shape of the λ_T function for dislocations have been advanced. They are: (1) the two-band Fermi surface model

(section 2-1(d)), (2) the dislocation cell model of Barbee et al⁵⁰ (section 2-1(c)), and (3) the theory of Bhatia and Gupta⁷⁷ (section 2-9(b)). No one of these theories has yet been given more weight or importance, although it should be noted that there is a great deal of direct microscopic evidence to support the existence of dislocation cells in strained metals¹²⁹.

In the present investigation of defects in Pt we have performed isochronal anneals on both fatigued and hard-drawn Pt wires, and have attempted to determine the λ_T function for both the vacancy and dislocation annealing stages separately. The results, which mainly apply to the region 90 - 373K, are compared with previous work and lead to a number of interesting conclusions.

7-2 Procedure

Three separate tests were performed in this investigation; one on each of two specimens that were fatigued by cyclic bending (SC3 and SC4), and one on a specimen in its hard-drawn state as supplied by the refiner¹⁰⁷ (SC5). All three specimens were taken from the same spool of high purity Pt wire as specimen SC1 used in the quenching experiments of Chapter 6. The specimen holder, the measuring equipment, and the general procedure for determining λ_T were also the same as that described in the previous chapter. In this work, however, an isochronal annealing test has been

carried out simultaneously with the actual measurements used for the determination of λ_T , in order to identify the annealing stages for our particular specimens.

The procedure used in each separate test is described below:

(a) Test on SC3

This specimen was initially cleaned in organic solvents and electrically annealed in air at 1100°C for about 10 minutes. After mounting in the special holder its resistance was stabilized by furnace heating at 950°C for 20 hours using a gas filling of 50 Torr O_2 plus 1 atmosphere He, and then by electric heating at 1150°C for 10 minutes using a gas filling of 0.4 Torr O_2 plus 1 atmos. He (for reasons stated earlier). By forcing the platinum into a stable, well annealed, fully oxidized state prior to fatiguing, it was hoped that the resistance changes obtained during subsequent annealing would correspond only to those defects actually introduced by the plastic deformation. The specimen was then fatigued in situ by removing the outer sheath of the holder, clamping the wire in two pairs of plastic tweezers about 3 mm apart, and bending the wire between the tweezers back and forth about three times, with the whole process being repeated about every 2 mm along the 500 mm length of wire. The specimen was then positioned so as to be freely suspended in the supporting disks, washed in solvents, dried in a gas stream, and with the outer sheath replaced was pumped and

backfilled with 0.4 Torr O_2 plus 1 atmos. He. Finally the specimen was isochronally annealed between 100 and 900°C in a tube furnace using 50 degree steps and 30 minute heating periods, with R_{00C} monitored after each step. For the determination of λ_T the value of R_T was measured at certain selected steps during the anneal at the additional reference temperatures of 4.21, 90.19, and 373.15K discussed in Chapter 6.

(b) Test on SC4

This test was essentially a repeat of the test on SC3 except that the initial cleaning was more thorough, including hot nitric acid and cold aqua regia, and the isochronal annealing was extended to higher temperatures to determine the upper limit for complete removal of the defects produced by fatiguing. In this case the initial stabilization after the specimen was mounted included electric annealing at 1300°C for about 5 hours. It was found that this prolonged heating could be carried out fairly uniformly along the wire, and without seriously altering the specimen resistance, by using a low pressure gas filling of 0.05 Torr O_2 plus 0.4 Torr He. The procedure for fatiguing the specimen was identical to that for SC3, while the procedure for isochronal annealing up to 900°C was slightly altered in that 100 degree steps were used. Between 1000 and 1300°C the annealing was performed electrically (to avoid contamination effects) using the low pressure gas filling mentioned

above; but after each annealing step 1 atmos. of He was added to this filling in order to ensure adequate immersion of the specimen in the reference temperature baths. Also with SC4, the value of $R_{4.2K}$ was monitored after each annealing step, instead of $R_{0^\circ C}$, since the latter could be significantly affected by small dimensional changes in the specimen during electric annealing. The value of $R_{4.2K}$, on the other hand, was found to drift less than 25 μ ohms per hour with $1300^\circ C$ heating, after an initial period of stabilization. To determine λ_T the value of R_T was measured at the additional reference temperatures of 273.16 and 373.15K at certain annealing steps. However no data obtained above $900^\circ C$ was used for this purpose because of the spurious resistance changes mentioned above.

(c) Test on SC5

The procedure used in this case was identical to that for SC4, except that the specimen was mounted in its hard-drawn state and there was no initial thermal stabilization prior to the isochronal anneal. Also, this time R_T was measured at 4.2, 273.16 and 373.15K after each annealing step, and at 90.19K after selected annealing steps.

7-3 Results

(a) Isochronal Annealing

The isochronal annealing data for specimens SC3, SC4 and SC5 are presented in Figs. 6.2(a), 7.1(a) and 7.1(b)

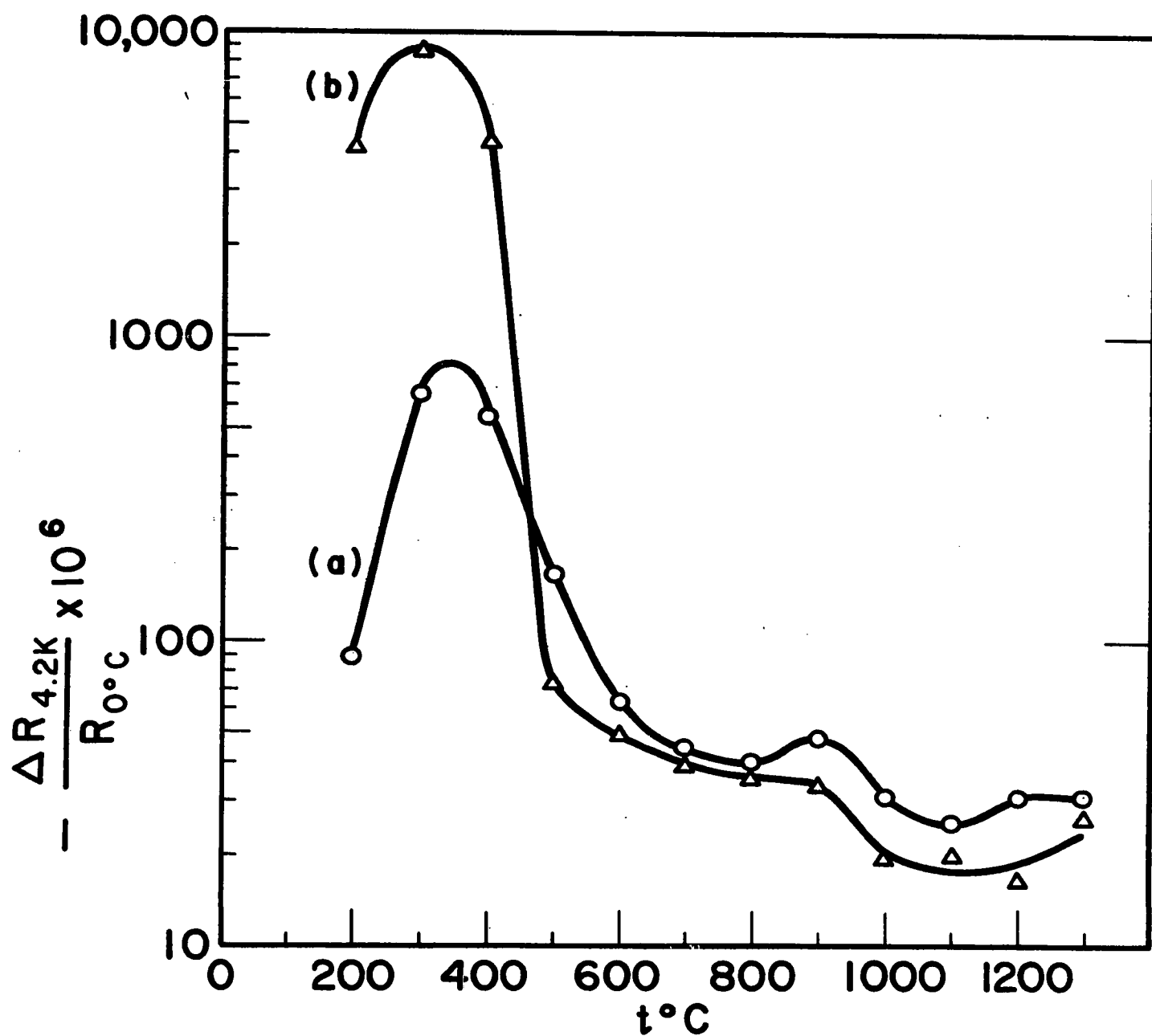


Fig. 7.1 . The fractional change, $\Delta R_{4.2K}/R_{0^\circ C}$, during isochronal annealing of (a) fatigued specimen SC4 and (b) hard drawn specimen SC5.

respectively. Primarily, they show that there is no distinct separation of the vacancy and dislocation annealing stages in the 100 to 600°C range. Thus, we can only hope to obtain a crude estimate of λ_T for these defects by assigning the front edge of the main peak to vacancies and the back edge to dislocations in some arbitrary fashion. The results also show that the defects introduced by fatiguing are not completely removed by short periods of heating until a temperature near 1300°C is approached. In the case of SC4 the value of $W_{4.2K}$ after the final annealing step is in very close agreement with its annealed value just prior to fatiguing, thus indicating that 1300°C is a sufficient temperature limit for this purpose.

Certain other features of the results are consistent with earlier reports. For example, in Fig. 6.2(a) the high reading at 100°C is presumably due to the tail end of the recovery stage for interstitials,¹¹⁹ while the shifting of the vacancy peak to lower temperatures than that for quenched Pt is presumably due to the greatly increased concentration of dislocation sinks¹⁰¹. In addition the striking difference between the two annealing curves of Fig. 7.1 in the 400 - 600°C range may be understood in terms of the established rule that dislocations are removed at a lower temperature when the deformation is increased¹²⁸. The fact that the annealing 'tail' above

600°C is similar for both the fatigued and hard-drawn specimens is rather interesting in view of the large difference between the magnitudes of the primary peaks. This may possibly be due to a similar dislocation cell structure in both cases. Based on this and other observations¹²⁹, it is conceivable that the back edge of the primary peak is due to dislocation rearrangement inside the cells, and the long annealing tail is due to annihilation of the dislocation tangles which form the cell walls. If so, this would mean that the removal of dislocations does not proceed uniformly throughout the specimen, and therefore spurious deviations from MR can be expected.

(b) Deviations from MR

The λ_T functions for the three specimens, derived from Eq. (6.6), are shown as a function of temperature in Fig. 7.2 for those defects annealed out in approximately the front two-thirds of the primary peak (precise annealing ranges are given in the figure caption). While it was our intention to include mainly vacancies in this annealing interval, it seems highly probable from the isochronal anneals that we have unavoidably included a significant fraction of the dislocations, particularly in the case of SC4 and SC5. The results for λ_T confirm this suspicion -- even for SC3 -- since they do not agree with the more reliable vacancy λ_T function of quenched Pt. We may also conclude

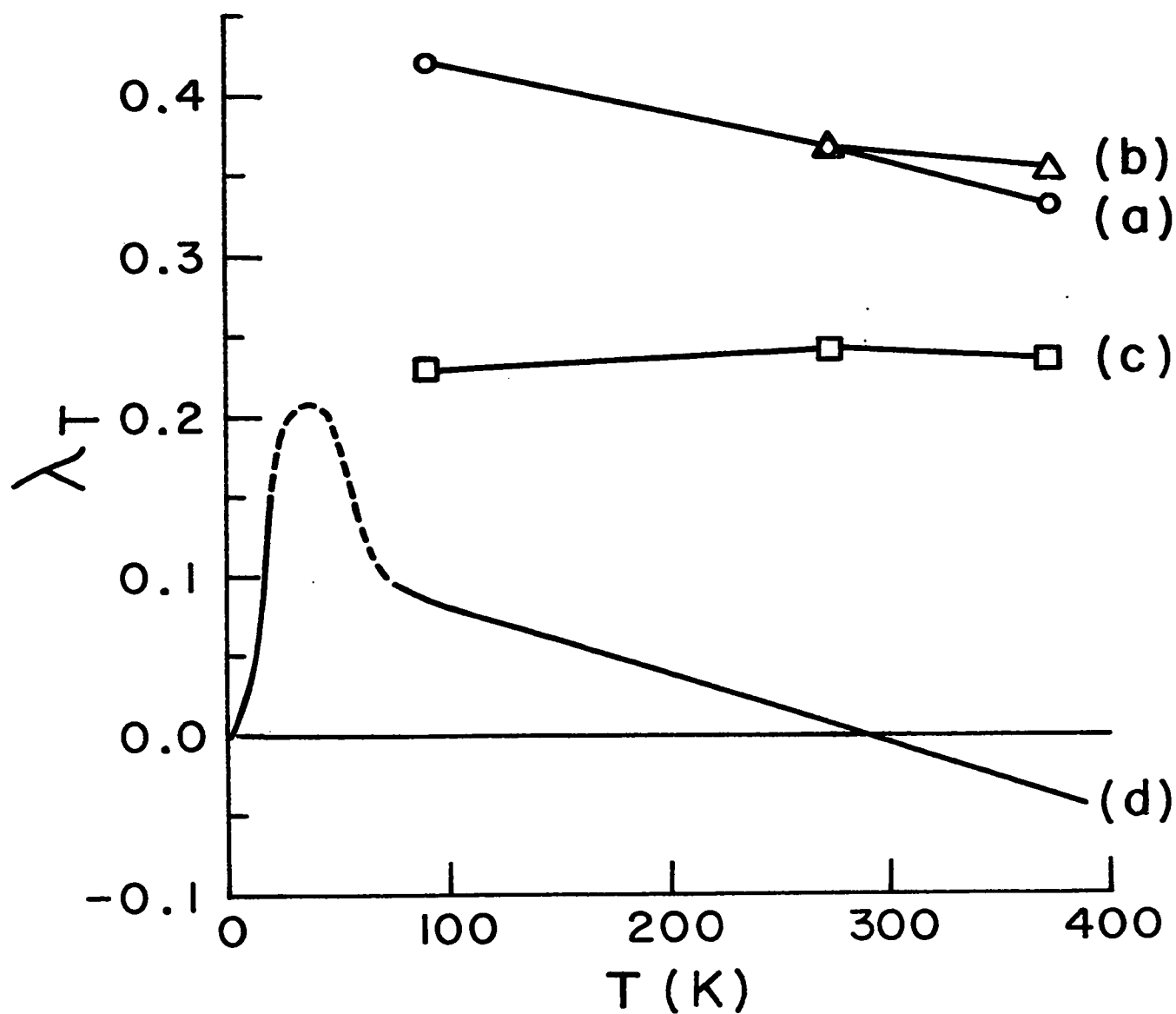


Fig. 7.2 . The λ_T function for the defects annealed out in the range (a) 100 - 350°C for fatigued SC3, (b) 100 - 500°C for fatigued SC4, (c) 100 - 400°C for hard-drawn SC5, and (d) 100 - 375°C for quenched SC1.

from this comparison that the λ_T function for dislocations is almost certainly much greater than that for vacancies. Consistent with this picture, one would then interpret the smaller λ_T function for the hard-drawn wire in Fig. 7.2 as being due to a greater concentration of vacancies; this suggestion is also supported by results presented later in Fig. 7.4.

The λ_T functions corresponding to those defects annealed-out in the back one-third of the primary peak and extending up to about 800°C are shown in Fig. 7.3. These functions should apply mainly to dislocations, but not necessarily to a homogeneous reduction in their density, as one would like. The large scatter in the experimental results could in part be due to such distribution effects, especially since we have used somewhat different annealing intervals in each case (see figure caption). In this connection we note that the use of the wider annealing interval, 350-900°C, for SC3 increases its λ_{273} value to 0.73, which tends to bring the two fatigued specimens into closer agreement.

To demonstrate the dependence of the apparent λ_T value on the annealing interval selected, the "instantaneous" value of λ_{273} is plotted in Fig. 7.4 as a function of each isochronal annealing step for SC5, and each pair of steps in the case of SC4. The results for both specimens indicate that it is not vacancies alone that are annealing-out in the range below 300°C; indeed in only one increment,

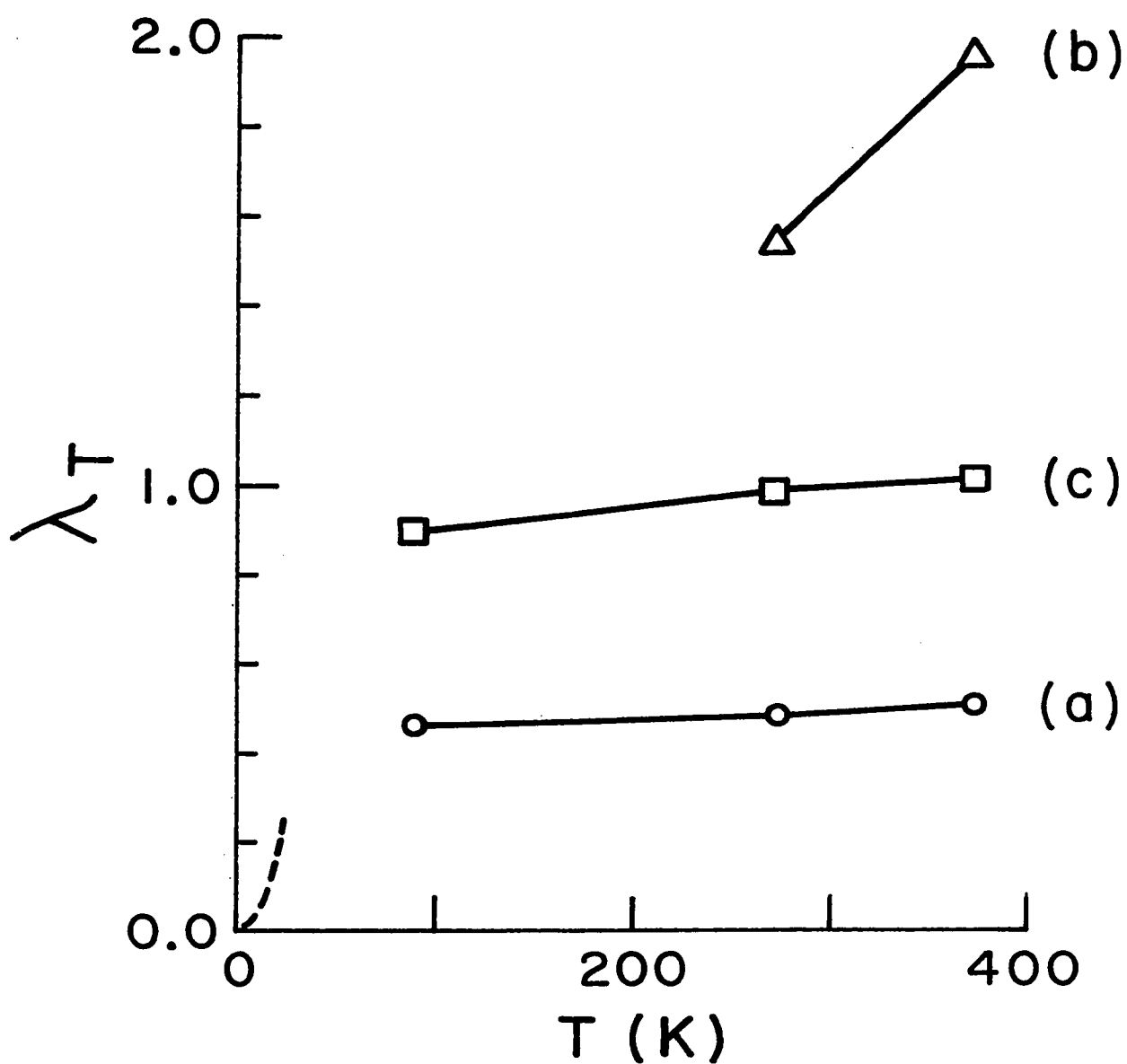


Fig. 7.3 . The λ_T function for the defects annealed out in the range (a) 350 - 750°C for fatigued SC3, (b) 500 - 900°C for fatigued SC4, and (c) 400 - 700°C for hard-drawn SC5.

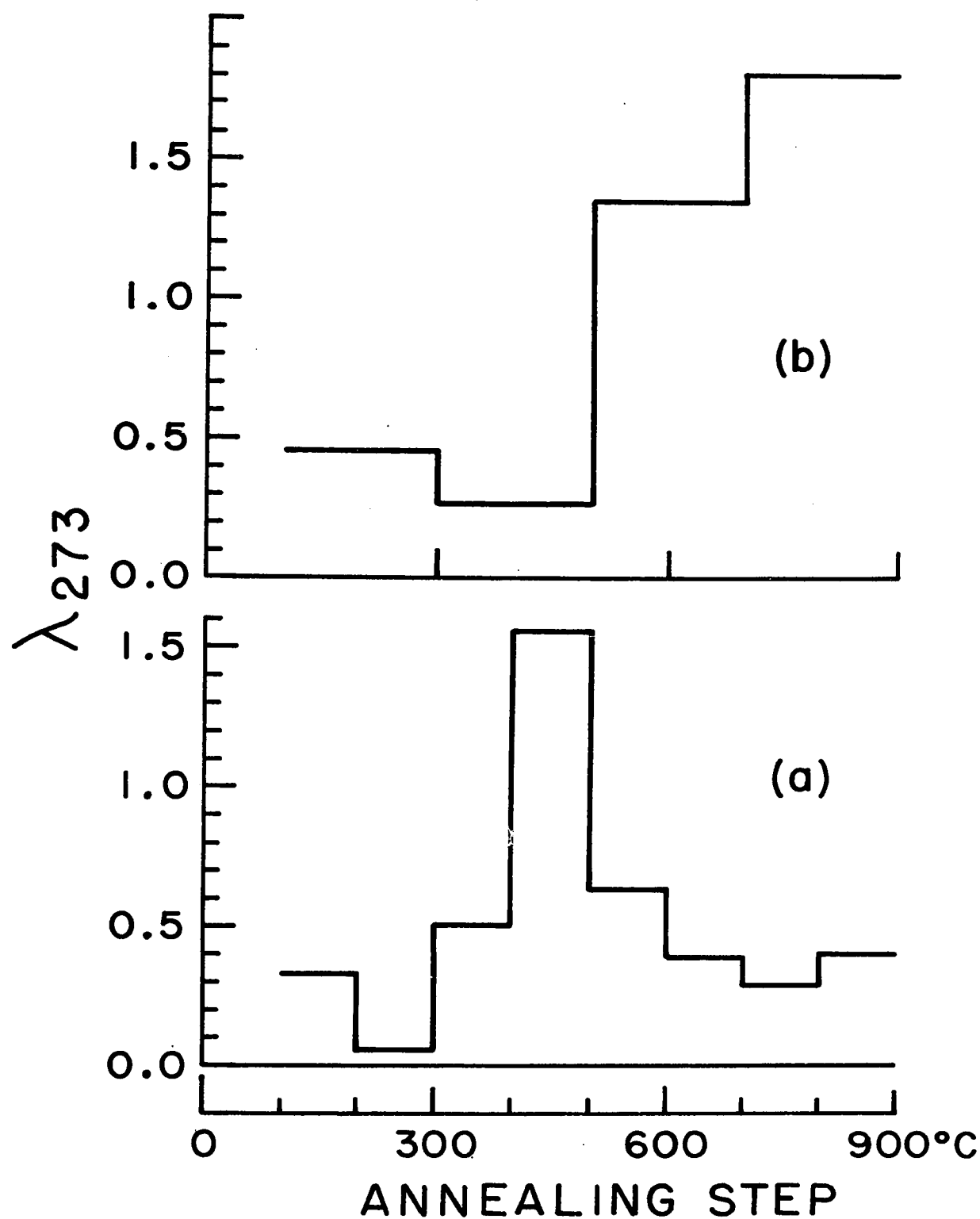


Fig. 7.4 . The value of λ_{273} for the defects removed by (a) each 100°C step of the isochronal anneal of hard-drawn SC5, and (b) each pair of 100°C steps for fatigued SC4.

i.e. the 200 - 300°C step for SC5, does the λ_{273} value approach zero as would be expected for vacancy annihilation. It is also interesting to note that the hard-drawn and fatigued wires show marked differences; e.g. in the annealing range 300 - 500°C the hard-drawn wire has a much larger λ_{273} value, while in the range 500 - 900°C the opposite is true. This latter observation confirms the results shown in Fig. 7.3, even when identical annealing ranges are involved.

7-4 Conclusions

This investigation has shown that there is a considerable overlap in the annealing stages for vacancies and dislocations in Pt; and for this reason (if for no other) it is difficult to determine the λ_T function for either type of defect with much certainty. The results do suggest, however, that the λ_T function for dislocations is much greater than that for vacancies in the 90 - 373K range and is approximately independent of T, similar to that obtained for other metals. The λ_T value of 0.17 obtained by Rosch et al.¹²⁷ for hard-drawn Pt in the range 77 - 194K is confirmed here by the results in Fig. 7.2(c), for the particular annealing interval used in their work. However this value does not have much physical significance since it corresponds to some unknown mixture of vacancies and dislocations.

Based on the results obtained here and elsewhere it

appears certain that the determination of λ_T for vacancies or interstitials in plastically deformed metals will be seriously complicated by the interaction between defects during annealing. Even in the case of dislocations, which anneal-out last, the measurements may be significantly affected by non uniform defect distribution. It would appear then that more controlled experiments are required in order to obtain definitive results, suitable for comparison with theory.

CHAPTER 8

APPLICATION OF THE DEVIATION FROM MR TO THE DETERMINATION OF
THE IDEAL RESISTIVITY OF PLATINUM

8-1 Introduction

In order to test the theoretical expressions for the 'ideal' phonon resistivity of a metal one must first determine experimental values for ρ_{iT} -- or for W_{iT} if only the temperature dependency is to be studied -- from measurements on the real metallic specimens available. This will invariably necessitate that a small correction be applied for the residual impurity and defect resistivity in these specimens. To a first approximation this correction term is given by M R (Eq. (1.20)), or by the Nernst-MR (Eq. (1.29)) in the case of W_{iT} ; and these relationships have been used in nearly all previous investigations. It will be shown here, however, that this procedure may cause serious errors in the determination of ρ_{iT} in the low temperature range, where ρ_{iT} itself becomes relatively small.

In this chapter two methods of determining more accurate values of W_{iT} are discussed* and, by using one of these, improved values of W_{iT} have been derived for Pt in the temperature range 2 - 10K. These values are smoothly fitted to earlier estimates for W_{iT} above 10K, and the temperature

* The analogous procedures for determining ρ_{iT} will be apparent.

dependency of the resulting function is compared with theory over the entire range below $\Theta_R/10$. This work was largely motivated by the results of Kos and Lamarche⁴³, which indicated that the usual theoretical expression for W_{iT} was incorrect for Pt below 10K. The main results of the present investigation were published⁴⁵ in 1967, and are described in detail here.

8-2 Reduction of Measurements to W_{iT}

(a) Graphical Method

The graphical method may be used only if measurements are available on a wide variety of specimens of the same metal. It is then possible, for example, to plot W_T against W_0 at one temperature (T) and extrapolate the data to $W_0 = 0$ to obtain W_{iT} . This technique has already been used with Pt, notably by Berry²⁸, who analysed calibration data on 65 or more Pt resistance thermometers in the range 10 - 700K. While this method is considerably superior to using MR, the extrapolation was limited to some extent by the fact that the specimens did not all lie on a well defined line, due presumably to their somewhat diverse λ_T functions. This difficulty was partly overcome by using for extrapolation a well defined edge on the envelope of plotted points in the belief that it must correspond to some particular λ_T function associated with a particular state of the wire.

(b) Theoretical Method

A method incorporating a theoretical relation for λ_T must be used when measurements of W_T are available on only one metallic specimen. Once this relation is chosen, the W_{1T} values can be derived from the basic equation (3.4) given earlier. The choice of a specific analytical form for λ_T is of course the main difficulty.

In many cases, particularly in the low temperature region, the two-band form (Eq. (3.2)) gives a fairly close fit to experimental data (see section 2-1(b)), and should represent a considerable improvement over simply using MR. When Eq. (3.2) is substituted into Eq. (3.4), the final expression for W_{1T} may be written in the form

$$W_{1T}^2(aG) + W_{1T}[W_O(1+b)-a(W_T-W_O)] - (bW_O/G)(W_T-W_O) = 0 \quad (8.1)$$

This quadratic equation in W_{1T} may then be solved at any particular temperature once the parameters a and b are known, and no ambiguity arises since there is only one positive root. The parameters a and b may be calculated by the method described in section 3-2 once two values of W_{1T} are estimated by method (a), or taken from a temperature region where W_{1T} is already known.

8-3 Discussion of Earlier Work

Based on theoretical considerations, it has been suggested several times^{44,96,97} that the expression for W_{1T} (or ρ_{1T}) at low temperatures be of the form

$$W_{IT} = p_1 T^2 + q_1 T^5 \quad (8.2)$$

where p_1 and q_1 are constants. The T^2 term, which was first discovered by de Haas and de Boer⁹⁵ (1933), has been attributed by Baber⁹⁶ to interband (electron-electron) scattering of the 's' electrons by the more massive 'd' electrons; while the T^5 term has been attributed by Bloch⁴ to normal phonon scattering in the low temperature limit below $\Theta_R/10$ (i.e. below 24K for Pt).

In the experimental investigation of de Haas and de Boer⁹⁵, W_{IT} was calculated from measurements on two Pt specimens in the 1 - 20K region using the Nernst - MR. They clearly identified the T^2 term below about 3K where the T^5 term is practically negligible. White and Woods⁹⁷, on the other hand, calculated $p_1 T$ from measurements on two Pt specimens in the range 6 - 300K using MR. They found in the region 9 - 30K that $p_1 T$ varied as $T^{3.7}$ rather than as T^5 , and suggested that this slower temperature dependency might be due to the influence of interband (s - d) phonon scattering, which according to Wilson⁹⁸ may lead to a T^3 term at low temperatures. In Van Dijk's⁴⁴ detailed investigation in the region 1- 4.2K, the measurements on a large group of Pt resistance thermometers were reduced to W_{IT} using a procedure somewhat analogous to method (a) of the previous section. He found that the W_{IT} function of all specimens could be represented by the equation

$$W_T - W_0 = pT^2 + qT^5 \quad (8.3)$$

and extrapolated graphs of p and q versus W_0 to $W_0 = 0$ (using an average line through the envelope of points) to obtain the values of p_1 and q_1 in Eq. (8.2).

At first glance it is not obvious why Eq. (8.3) should fit the measurements since it appears to neglect the $\lambda_T W_0$ term in the basic Eq. (1.30). It can be shown, however, that Eq. (8.3) is consistent with the two-band relation (Eq. (3.2)) at low temperatures where λ_T varies as W_{1T} ; since then Eq. (1.30) becomes

$$W_T - W_0 = W_{1T}(G - G/b) \quad (8.4)$$

and $(W_T - W_0)$ should have the same temperature dependency as W_{1T} . From Eqs. (8.3) and (8.4) it follows that

$$p = p_1(G + G/b), \text{ and } q = q_1(G + G/b) \quad (8.5)$$

Hence Van Dijk's confirmation of Eq. (8.3) tends to support the two-band model as well as Eq. (8.2) for W_{1T} . It should also be noted that the use of Eq. (8.3) at temperatures above 4.2K could yield spurious results since the low temperature approximation, $bW_0/G \gg aW_{1T}$, may no longer hold in this region.

The only experimental evidence for a T^5 term in the above work is that given by Van Dijk⁴⁴, and this is severely limited by the fact that he investigates a temperature range where this particular term is very small. For example, typical values of the qT^5 term in Eq. (8.3) are

2×10^{-6} , 0.4×10^{-6} , and 0.05×10^{-6} at 4.2, 3, and 2K respectively; while in comparison the pT^2 term has values of about 24×10^{-6} , 11×10^{-6} , and 5×10^{-6} at these same temperatures. Even with the high experimental accuracy for W_T ($\pm 0.1 \times 10^{-6}$) achieved by Van Dijk it is apparent that the qT^5 term cannot be evaluated reliably below about 3K.

In order to check whether Van Dijk's experimental data could be equally well represented by an equation of the form

$$W_T - W_0 = pT^2 + qT^N \quad (8.6)$$

with $N \neq 5$, we have programmed an electronic computer to perform a least-squares fit of his data to Eq. (8.6).

The procedure was to convert Eq. (8.6) into the linear relation

$$Z_0 = p_0 + q_0 X_0 \quad (8.7)$$

where $Z_0 = (W_T - W_0)/T^2$ and $X_0 = T^{N-2}$. Then for a given value of N and W_0 , the computer was programmed to find Z_0 and X_0 for each data point and make a least-squares fit of their values to Eq. (8.7). This yielded, for one particular N , W_0 pair, the best fit values of p_0 , q_0 , and the standard deviation (σ_0) of the W_T data points. Holding N constant and varying W_0 , the procedure was repeated until a value of W_0 was found that yielded the minimum σ_0 value ($\sigma_{\min}$). In this way the best fit values of W_0 , p_0 , and q_0 were determined for a selected value of N . The actual W_T data fitted to Eq. (8.6) was calculated from information given in Table 1A and Fig. 3 of Van Dijk's paper⁴⁴. For

each resistor, seven data points in the 1-4.2K region were used.

The values of this minimum standard deviation, $\sigma_{\min}$, corresponding to certain selected values of N , are presented in Table 8.1 for six of Van Dijk's resistors. For any particular resistor, $\sigma_{\min}$ is found to vary rather slowly with N , exhibiting a broad minimum round its lowest value, which we shall designate as $\sigma'_{\min}$. The value of N (designated N'), which corresponds to $\sigma'_{\min}$, is the best estimate that one can make for the true value of N using this data.

From the results presented in Table 8.1 it can be seen that values of N other than 5.0 often give better fits to the experimental data. Furthermore, additional tests have shown that the reported uncertainty of about $\pm 1 \times 10^{-7}$ in the measured W_T values may lead to changes in N' of up to ± 1 . Our results indicate, therefore, that the true value of N could lie anywhere in the range 3 to 7, and that the theoretical value of 5 has not yet been confirmed for Pt. In any further attempt to identify the value of N in the relation

$$W_{iT} = p_i T^2 + q_i T^N, \quad (8.8)$$

it appears necessary to include data from the 4 - 10K region, where the last term is fairly significant.

8.4 Determination of W_{iT} in the Range 4 - 10K

TABLE 8.1

Variation of $\sigma_{\min}$ with N for Van Dijk's resistors (The values of q, when N = 5.0, are presented to indicate the relative magnitude of the qT^N terms for different specimens).

Specimen No.	$\sigma_{\min} \times 10^7$ for N equal to								N'	q $\times 10^9$
	3.0	4.0	4.5	5.0	5.5	6.0	7.0			
127	0.56	0.46	0.43	0.41	0.39	0.39	0.39	6.5	.77	
146	0.19	0.18	0.19	0.19	0.19	0.20	0.20	4.2	.07	
157	0.54	0.23	0.10	0.03	0.12	0.20	0.35	4.9	1.83	
148	0.50	0.29	0.23	0.23	0.27	0.32	0.44	4.8	1.75	
149	0.73	0.49	0.41	0.35	0.33	0.34	0.41	5.7	1.86	
LN7601	0.90	0.74	0.67	0.60	0.55	0.50	0.41	> 8	1.15	

The only high precision experimental data available on Pt in the 4 - 10K region is that reported by de Haas and de Boer⁹⁵ for their specimens Pt 1 and Pt 2. While this data is suitable for a W_{IT} analysis from the point of view of specimen purity (i.e. a low W_0), it does possess certain undesirable features; viz., (1) it does not appear to follow the two-band relation very closely in the 10 - 20K range (see section 8-8), (2) the absence of measurements above 20K prevents a more complete two-band test, (3) the measurements exhibit significant random scatter, and (4) the measurements are based on older temperature scales, the accuracy of which was not stated.

(a) Source of New Data

In order to provide more suitable data for a determination of W_{IT} , new measurements on a high purity Pt specimen were undertaken in cooperation with Dr. D.L. Martin at the National Research Council of Canada (N.R.C.C.) The specimen comprised the sensing element of a standard platinum resistance thermometer (Serial No. 320), possessing a 25.5 ohm ice-point resistance. Its resistance values were measured in the 3 - 90K range on the following temperature scales: (a) in the 11-90K range, on the U.S. National Bureau of Standards (N.B.S.) 1939 gas thermometer scale; (b) in the 2-4.2K range, on the 1958 ^4He vapor pressure scale; and (c) in the 4.3-10K range, on a gas thermometer scale maintained by Martin⁹⁹ at N.R.C.C..

The last scale is reported to have an overall accuracy of 5 mK in the 4-20K region (relative to a value of 20.378K for the boiling point of normal hydrogen) and to be in close agreement with the N.B.S. scale in the 10-20K region.

The resistance itself was measured potentiometrically, using a galvanometer amplifier detector for the more difficult 3-10K region. The sensitivity of this system, with a 10 mA measuring current, was sufficient to permit a determination of W_T to within 1×10^{-7} .

The measured values of W_T are reported in Table 8.2 for the region 2.7-20K. The value of W_0 was calculated to be 434.37×10^{-6} by solving Eq. (8.6) with $N = 5$ for the three lowest values of W_T . It should be noted that W_0 would still be the same to within $\pm 0.2 \times 10^{-6}$ for any value of N in the range 4.5 to 5.5.

(b) Two-Band Test and Determination of Parameters

Before deriving W_{iT} from the data on resistor 320, using method (b) of section 8-2, we first examined its observed λ_T function (Eq.(3.4)) for qualitative two-band behavior (Eq. (3.2)). To make this comparison, an earlier W_{iT} function, estimated by Berry²⁸ for the 10-90K region and based on the N.B.S. 1939 scale, was used. The parameters a and b required in Eq. (3.2) were obtained by substituting the values of W_{i13} and W_{i20} into Eq. (3.7), in accordance with the procedure described in section 3-2, and the resulting values are reported in Table 8.3.

TABLE 8.2

Measured W_T values for resistor 320

T (K*)	$W_T \times 10^6$	T (K)	$W_T \times 10^6$
2.785	444.51	12.5	1028.9
3.933	455.55	13	1123.6
5.019	471.45	13.5	1230.4
6.014	492.46	14	1350.4
7.125	526.75	14.5	1484.5
8.101	569.36	15	1633.8
9.051	625.83	16	1981.4
10.003	701.55	17	2400.6
10.5	750.6	18	2898.9
11	807.2	19	3483.1
11.5	871.8	20	4160.2
12	945.3	373.15	1392647.

* On N.B.S. 1939 temperature scale in the 10.1-20 K range.

TABLE 8.3

Two-band parameters for specimens 320, Pt 1, and Pt 2

Parameters	320	Pt I	Pt 2
$W_0 \times 10^6$	434.37	362.3	484.5
a	4.18	1.69	0.80
b	18.77	5.71	5.43
G	0.9994617	0.999424	0.998991

It should be noted that this procedure only forces the observed and theoretical λ_T functions to agree at 13 and 20K. The final λ_T functions which are presented in Fig. 8.1, indicate extremely close agreement in the 11-21K range, while elsewhere the agreement is well within the reported uncertainty in Berry's W_{iT} function (cf. error bands in Fig. 8.1). We may conclude, therefore, that resistor 320 follows the two-band relation fairly closely below about 40K. A further desirable feature of this resistor is its relatively small λ_T and W_0 values, since this tends to reduce the importance of any uncertainties in the $\lambda_T W_0$ correction term.

For the new determination of W_{iT} we have used the above values for the parameters a and b , which means that the new W_{iT} function will be a smooth extension of Berry's 10-90K function down to lower temperatures. In the absence of two exact values for W_{iT} in the 10-20K region, this appeared to be the best procedure to follow. No attempt has been made here to reestimate the W_{iT} function in the 20-90K range, since it is difficult to improve on previous work until more is known about departures from the two-band model in this particular range.

(c) Results

The resulting W_{iT} values, calculated from Eq. (8.1) at the measuring temperatures cited in Table 8.2 are presented in column (2) of Table 8.4 for the 2 - 15K range.

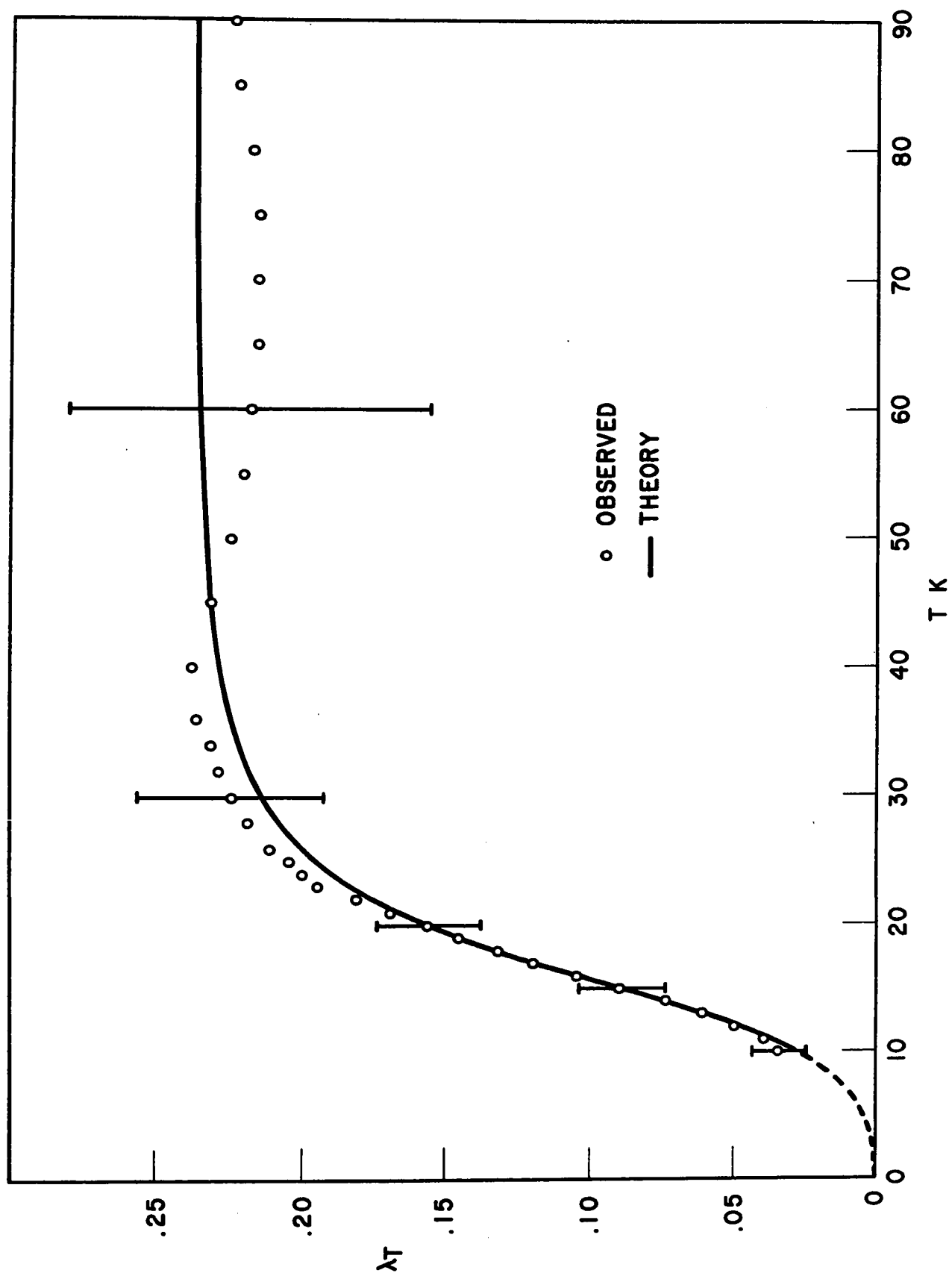


Fig. 8.1 . The λ_T function for specimen 320 as observed (Eq. (3.4)) and as given by theory (Eq. (3.2)).

TABLE 8.4

W_{iT} values calculated from Eqs. (8.1) and (8.9).

T (K)	$W_{iT} \times 10^6$ Eq. (8.1)	$W_{iT} \times 10^6$ Eq. (8.9)	Sensitivity ($\Delta W_{iT} / 0.01 \text{ K}$) 10^6
2.785	9.64	9.64	.07
3.933	20.13	20.13	.11
5.019	35.26	35.23	.17
6.014	55.26	55.34	.24
7.125	87.94	87.88	.35
8.101	128.63	128.58	.49
9.051	182.66	182.72	.66
10.003	255.30	255.48	.88
10.5	302.4	302.4	1.01
11	357.0	356.8	1.16
11.5	419.2	419.1	1.33
12	490.4	490.4	1.52
12.5	571.3	571.5	1.73
13	663.3	663.4	1.95
13.5	767.1	767.2	2.20
14	884.1	884.0	2.47
14.5	1015.1	1015.0	2.77
15	1161.3	1161.4	3.09

These values are found to depart only slightly from Berry's 1963 estimates in the 10-12K range. Thus, in order to obtain a smooth function over the entire 3-90K region, it is recommended that one use the new values below 13K and the 1963 tables²⁸ above this temperature. Values of the new function at any temperature in the 2-13K range may be obtained from the empirical relation

$$W_{iT} = \sum_{n=0}^5 C_n T^n \quad (8.9)$$

using the values of the coefficients, C_n , given in Table 8.5. For convenience, certain selected values of W_{iT} in the region below 13K are reproduced in Tables 8.4 and 8.5.

A comparison of the W_{iT} values in columns (2) and (3) of Table 8.4 shows that the above 5th degree polynomial fits the data to within the equivalent of 0.003 degrees, i.e. to within the uncertainty in the original W_T measurements.

8-5 Comparison With Theory

The validity of the theoretically based relation, Eq. (8.2), may be qualitatively tested with the new W_{iT} function by plotting W_{iT}/T^2 against T^3 . Where the equation is valid, the graph must be linear. From the results presented in Fig. 8.2 it is apparent that Eq. (8.2) is not obeyed over the entire 0-11K range, but it may possibly be obeyed over the restricted range 0-6K when $p_1 = 1.21 \times 10^{-6}$ and $q_1 = 1.48 \times 10^{-9}$. The reason for caution in the latter state-

TABLE 8.5

W_{iT} values given by Eq. (8.9) at convenient temperatures using the coefficients:*

$$C_0 = 1.290613 \times 10^{-6},$$

$$C_2 = 1.898575 \times 10^{-6},$$

$$C_4 = 2.184403 \times 10^{-8},$$

$$C_1 = -1.473118 \times 10^{-6}$$

$$C_3 = -1.681871 \times 10^{-7}$$

$$C_5 = 2.854901 \times 10^{-10}$$

T (K)	$W_{iT} \times 10^6$	T (K)	$W_{iT} \times 10^6$
3	11.26	6.5	68.05
3.5	15.61	7	83.57
4	20.90	7.5	101.97
4.215	23.49	8	123.73
4.5	27.27	8.5	149.35
5	34.91	9	179.38
5.5	44.06	9.5	214.45
6	55.00	10	255.22

* These coefficients were obtained by a least-squares fit of the column (2) data in Table 8.4 to Eq. (8.9).

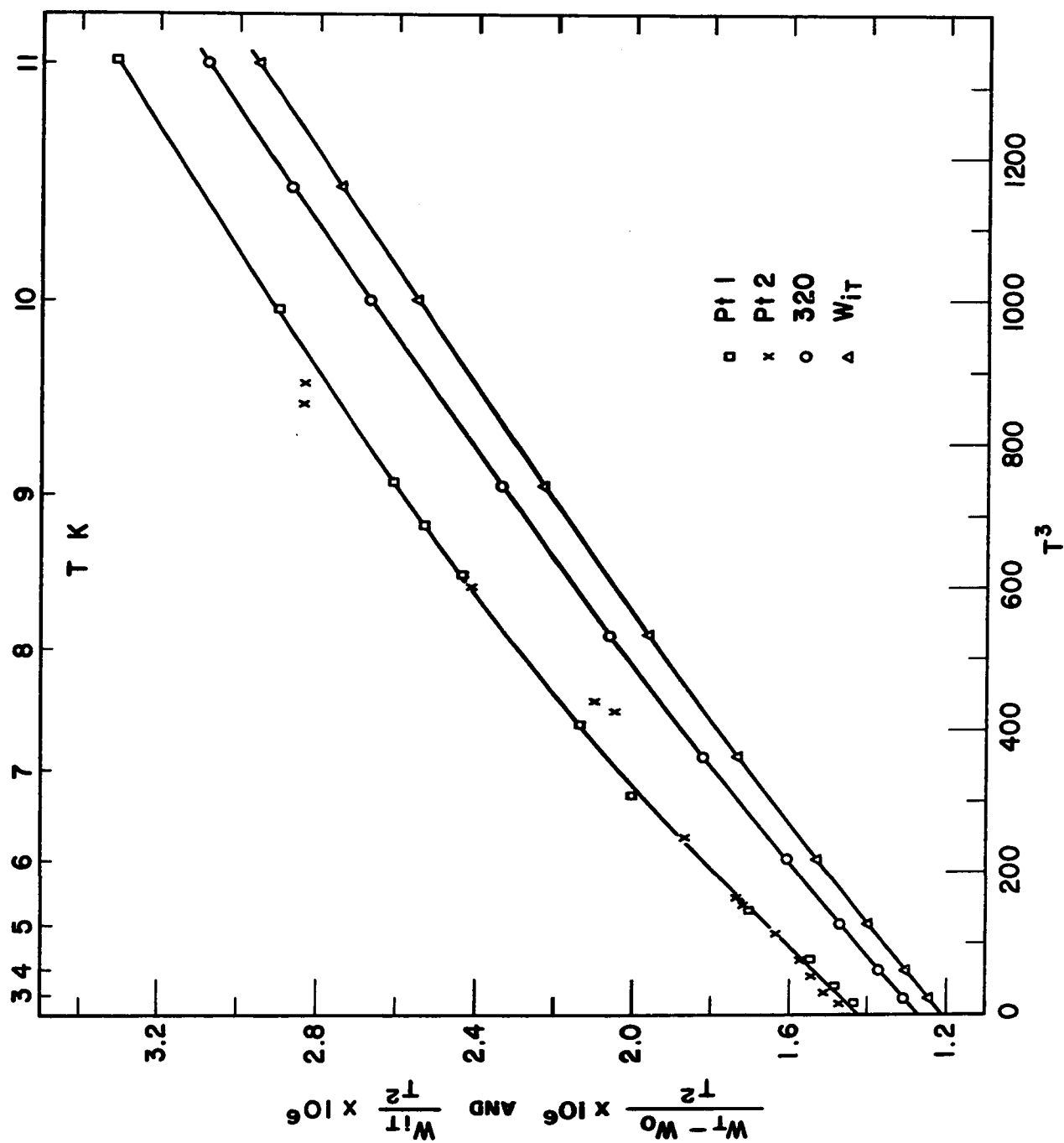


Fig. 8.2 . A plot of $(W_T - W_0)/T^2$ versus T^3 for specimens 320, Pt1 and Pt2, and a plot of W_{IT}/T^2 for the W_{IT} function given in col. (2) of Table 8.4 .

ment will become apparent.

To determine whether the W_{iT} function could be better represented by Eq. (8.8) with $N \neq 5$, we have plotted $\log (W_{iT} - p_i T^2)$ against $\log T$ for various arbitrarily chosen values of p_i . Since the slope of this graph at any point is equal to the value of N , one can readily determine how N depends on the temperature and on the assumed value for p_i . Three of these graphs (curves 1 to 3) are presented in Fig. 8.3, covering the most plausible range of values for p_i , i.e. from $(1.16 \text{ to } 1.22) \times 10^{-6}$. These curves exhibit an average slope of $N = 4.62 \pm 0.02$ over the 10-17K region, 4.75 ± 0.12 over the 6-10K region, and 4.7 ± 0.5 over the 4-6K region. Curve (2) demonstrates that Eq. (8.8), with a constant N value, can be made to represent W_{iT} up to as high as 14K when $p_i = 1.19 \times 10^{-6}$, $N = 4.67$, and $q_i = 2.90 \times 10^{-9}$. The graph for the total W_{iT} function is shown by curve (4) in Fig. 8.3, and yields values of N that start out at 2.2 near 4K, and rise to a maximum of 4.0 near 18K.

The above results show that Eq. (8.8), with N approximately equal to 4.7, is considerably superior to Eq. (8.2) for the region 7-17K. Below 7K it is impossible to say which equation gives the better representation because of uncertainties in the value of p_i , and hence N . It seems highly probably, however, that the low temperature

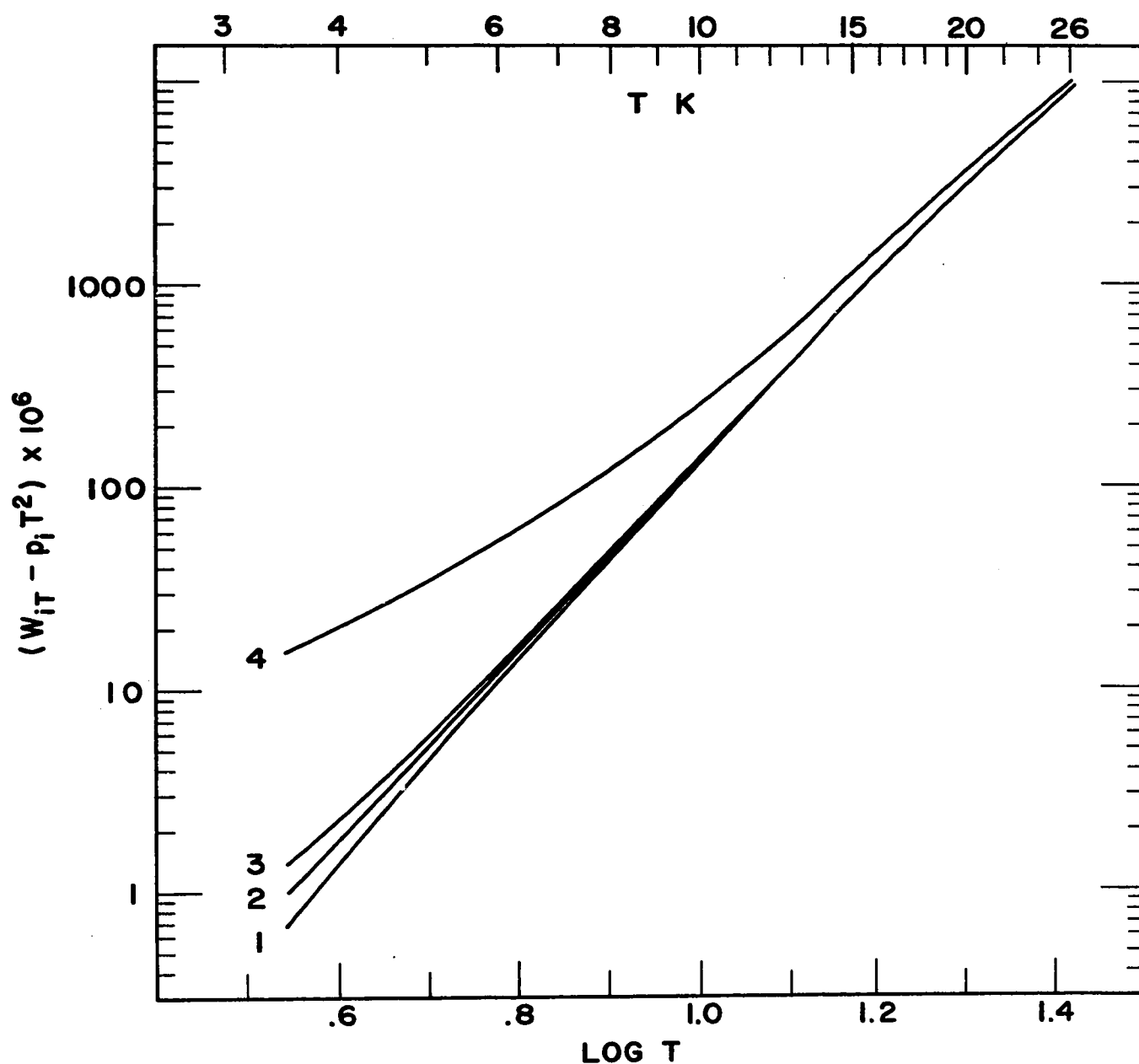


Fig. 8.3 . The dependence of $\log (W_{iT} - p_i T^2)$ on $\log T$ for the following values of $p_i \times 10^6$: 1.22 for curve (1), 1.19 for curve (2), 1.16 for curve (3), and 0 for curve (4).

value of N will lie in the range 4.7 ± 0.5 , since N remains within the narrow limits of 4.7 ± 0.2 over the entire 7-17K range. If we adopt this reasonable estimate for N below 7K, then the curves (1) and (3) in Fig. 8.3 represent the limiting cases for plausible curves.

It may also be concluded from the above results that if a T^5 region does exist it cannot extend much above $\Theta_R/40$, i.e. 6K. This in turn means that the Bloch-Gruneisen relation will definitely not represent the resistivity of Pt between about $\Theta_R/40$ and $\Theta_R/10$, since here the relation leads to a T^5 dependency. Assuming for the moment that this relation is valid below 6K, the coefficient $q_1 = 1.48 \times 10^{-9}$ for the T^5 term leads to a value for the Θ_R parameter in this relation of about 187K (as determined from Eq. (4.5) of reference 5).

8-6 Accuracy of the New W_{iT} Function

There are three possible sources of uncertainty in the estimate of W_{iT} presented here: (1) the uncertainty in the measured W_T values for resistor 320, (2) the uncertainty in the assumed values of W_{i13} and W_{i20} , and (3) a breakdown in the two-band model with constant a , b parameters. The effect of type (1) uncertainties is virtually negligible above 4K; e.g. it is approximately $\pm 1 \times 10^{-7}$ at 4K and $\pm 5 \times 10^{-7}$ at 10K. The effect of type (2) uncertainties may be readily evaluated by recalculating W_{iT} with various plausible pairs of W_{i13} and W_{i20} chosen from

the ranges $W_{113} = (663.3 \pm 6) \times 10^{-6}$ and $W_{120} = (3660.1 \pm 8) \times 10^{-6}$, which represent about the maximum possible spread in these two quantities (cf. Berry²⁸). The worst possible cases are of course those where the highest W_{113} value is combined with the lowest W_{120} and vice versa; these cases are highly improbable however since the reported W_{1T} values are mainly subject to systematic errors. If we make the reasonable assumption that the worst plausible cases are those where the highest or lowest W_{113} value is coupled with the average W_{120} value, then the maximum error in W_{1T} due to type (2) uncertainties is $\pm 0.5 \times 10^{-6}$ at 4K, $\pm 1.7 \times 10^{-6}$ at 7K, and $\pm 5 \times 10^{-6}$ at 11K. Further analysis has shown that systematic errors of this magnitude would not appreciably alter any of our previous conclusions.

The effect of type (3) uncertainties on the absolute values of W_{1T} cannot be properly assessed until accurate measurements are available on a wide variety of Pt specimens in the 3-11K region.

8-7 Range of Validity of Equation (8.3)

The range of validity of Eq. (8.3) has been examined qualitatively by plotting $(W_T - W_0)/T^2$ versus T^3 for resistors 320, Pt 1, and Pt 2. Where the equation is valid, the graphs must be linear. The values of W_0 for resistors Pt 1 and Pt 2, which are given in Table 8.3, were derived from a least-squares fit of the W_T data to Eq. (8.6) below 5K. While a value of $N = 5$ was used in Eq. (8.6), further

tests have shown that values of N between 4.5 and 5.5 yield the same W_0 to within $\pm 1 \times 10^{-7}$.

The graphs for all three resistors, which are shown in Fig. 8.2, are found to exhibit similar shapes and are at best linear below about 6K. The breakdown of Eq. (8.3) above 6K is presumably due in part to a breakdown of Eq. (8.2) on which it is based, and to a breakdown in the low-temperature (two-band) approximation, $\lambda_T \approx GW_{iT}/bW_0$. As in earlier tests, it is found that Eq. (8.6) works just as well for many values of N other than 5. The graphs also demonstrate the considerable random scatter in the W_T measurements for Pt 1 and Pt 2; this is found to be as large as the equivalent of 0.1K for Pt 2 and 0.02K for Pt 1.

8-8 Two-band Test on Pt 1 and Pt 2

Using the new W_{iT} function, we have compared the observed λ_T function (Eq. (3.4)) for specimens Pt 1 and Pt 2 with the theoretical two-band relation (Eq. (3.2)). The parameters a , b required in Eq. (3.2) were calculated by substituting W_{i10} and W_{i20} into Eq. (3.7), and are presented in Table 8.3. The λ_T function of each resistor is shown in Fig. 8.4 for the 0-20K range. In the case of Pt 1 it is found that the two-band model gives a rather poor fit to the observed function, while for Pt 2 the fit appears reasonably good within the severe limitation of the missing data in the 10-15K range. It is possible

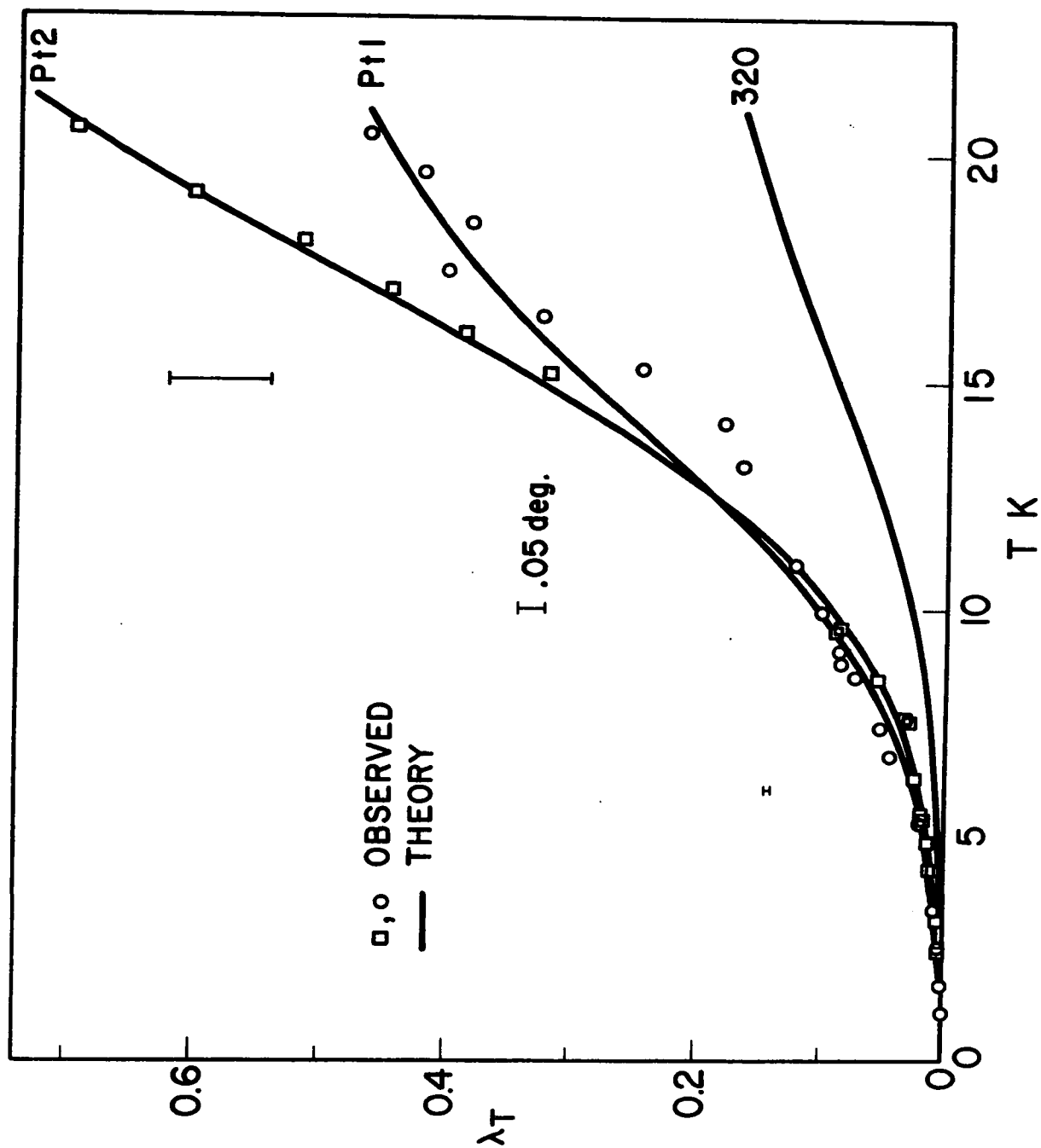


Fig. 8.4 . The λ_T function for specimens Pt1, Pt2 and 320 as observed (Eq. (3.4)) and as given by theory (Eq. (3.2)). The error bands show the change in λ_T corresponding to a change in w_T (or w_{iT}) equivalent to 0.05 K.

that part of the observed departures from theory are due to differences between the temperature scales on which W_T and W_{iT} are based. Indications of such difficulties are the linearity of the λ_T function for Pt 1 in the 4-14K region, and the abrupt change in its slope at 14K where the experimenters⁹⁵ changed scales.

The λ_T function for resistor 320 is included in Fig. 8.4 to demonstrate that resistors Pt 1 and Pt 2 have relatively large λ_T values -- in fact, their values compare with the highest of any reported previously^{28,41}. As noted elsewhere²⁸, it is normally found that resistors with large λ_T functions deviate quite drastically from the two-band model in the 10-90K region. For this, and other reasons given in section 8-4, we have not attempted to derive W_{iT} values from a two-band analysis of Pt 1 and Pt 2.

8-9 Discussion

In the present investigation new values of the W_{iT} function for Pt have been derived taking into account the deviations from MR. It has been found that in the range 0-17K, W_{iT} may be represented by a T^2 (electron-electron) scattering term plus a $T^{4.7}$ (electron-phonon) scattering term. It should be emphasized that, in the region below 6K, a phonon scattering term proportional to T^5 gives an equally good fit to the experimental data.

Further analysis has shown that if we had simply used MR for our derivation of W_{iT} , then we would have

obtained values that were too high by about 5% below 10K, decreasing to 3% at 16K. Such errors would have decreased the exponent N of the phonon scattering term from 4.7 to about 4.4. An even larger decrease in N would be expected for less pure specimens, since the absolute error in using MR is approximately $\lambda_T W_0$, and is therefore proportional to the residual resistivity or impurity content. Following our preliminary report⁴⁵, other investigators^{21,33} have also noted that the use of MR may cause serious errors in the determination of $\rho_i T$ -- apparently as large as $\rho_i T$ itself in some cases.

From the results presented here it is apparent that the value of $N = 3.7$ reported by White and Woods⁹⁷ is low mainly because the T^2 term was not eliminated from their graphs of $\log W_{iT}$ versus $\log T$ -- under similar circumstances our data would have yielded $N = 4.0$ in the vicinity of 18K. In addition their exponent N must also be low because of their application of MR to specimens that possessed 3 to 12 times the W_0 value of specimen 320.

The results presented here indicate that the temperature dependency of the phonon scattering term is close, but not identical, to the T^5 term predicted by the Bloch-Gruneisen relation for the entire range below $\theta_R/10$. There are of course many plausible reasons for a breakdown of the T^5 law since this theoretical dependency is based on many simplifying assumptions (see section 1-2), which should at

best apply to an idealized monovalent metal at low temperatures. Thus, it is somewhat surprising that the behavior of a complex metal like Pt can be represented as well as it is by such a simple model. We may also conclude that there is little evidence for the T^3 dependency which Wilson⁹⁸ has predicted for phonon interband scattering.

CHAPTER 9

CONCLUSIONS

In the course of this investigation, approximately thirteen different theoretical treatments or sources of deviation from MR have been reviewed and critically compared with existing experimental results. The main conclusion reached here is that no single theory will account for all observed results, but that there is substantial evidence supporting the two-band Fermi surface model at low temperatures ($<100\text{K}$), and the interference term of Bhatia and Gupta (and Kagan and Zhernov) at high temperatures. Certainly, all theories -- including the two mentioned above -- warrant further investigation and experimental confirmation.

Three of the possible sources of deviation from MR have been examined here in greater detail, resulting in the following conclusions:

- (1) The two-band model with constant parameters, which appeared to work so well in earlier applications, has been shown to lead to serious internal inconsistencies in those cases tested. The more recently proposed two-band Fermi surface model, which does provide for temperature-dependent parameters (in a limited range), removes some of the difficulties, but not those at high temperatures.
- (2) The Sondheimer λ_T component has been shown to never exceed

the value of 0.014, regardless of solute concentration or temperature. Thus, we may now safely conclude that it is much too small to account for most experimental results. Furthermore, since this component is based on Kohler's variational method, our results also indicate that Kohler's source of deviation from MR will likewise be relatively small.

(3) The Θ_R -change model, which attempts to allow for phonon spectrum changes, has been shown to lead to a form of λ_T function that will not account for most experimental results; hence the strong support given this model by others was unwarranted. It is still possible, however, that such a component forms part of the total observed deviations from MR.

The experimental work performed here has also led to a number of interesting conclusions. For example the new, high precision determination of λ_T for single vacancies in quenched Pt, has revealed the existence of a positive peak in the 20-70K region and a linear dependence on temperature above 90K with negative slope. While various possible theoretical explanations have been explored, it was found that none would provide a completely satisfactory explanation of these features. It was also shown that secondary defects in quenched Pt tend to make the apparent vacancy λ_T function somewhat larger than normal, and that great care must be taken to prevent dimensional changes of the specimen from disturbing the results.

The determination of separate λ_T functions for dislocations and vacancies in plastically deformed Pt has proved to be very difficult, partly because the annealing stages for the two defects can not be readily separated, and partly because of other complications. The evidence gathered here and elsewhere suggests that defect interaction produces a spuriously large λ_T function for vacancies and that inhomogeneous defect distribution complicates the λ_T function for dislocations. In any case, the results obtained here for the combination of dislocations plus vacancies, as they actually occur in deformed Pt, are useful and do indicate that the dislocation λ_T function is much greater than that for vacancies.

The importance of taking account of the deviations from MR in the determination of the resistivity of an ideally pure metal is demonstrated for the case of Pt. It is found that the errors in the W_{iT} ratio given by MR may exceed 5% at low temperatures, even when the measurements are made on high purity specimens. Also, it is shown that the new W_{iT} function for Pt, may be represented by a T^2 electron-electron scattering term plus a $T^{4.7}$ electron-phonon term, where the latter term is not too different from Bloch-Gruneisen theory.

Based on the wide range of experiment and theory examined here, it appears likely that the observed deviations from MR for any particular specimen will originate from several

different sources. If so, then significant progress in this area will probably depend on the calculation of theoretical estimates for the relative magnitudes of all possible λ_T components. Also, further experimental investigations of the influence of different host metals and imperfections on the λ_T function, as well as improved estimates of the atomic volume corrections, appear desirable at this time.

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