TRANSPORT THEORY

TRANSPORT THEORY IN METALS

By

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SCOPE AND CONTENTS:

The theoretical formulation of the electronic
transport properties (in the absence of a magnetic field)
of pure single crystals of simple metals is extended to
incorporate the effect of a non-spherical Fermi surface,
using a multiple orthogonalized plane wave description
of the conduction electrons. Two approaches are
considered, one using a variational principle, and the
other employing a scattering time approximation.

Formal results for the electrical resistivity and
the electronic contribution to the thermal resistivity
are expressed in terms of effective phonon frequency
distributions. These distributions are particularly
convenient for numerical computations and are
generalizations of those previously used for the case of
a spherical Fermi surface.

The generalization of the scattering time method to dilute nonmagnetic substitutional alloys is applied to hexagonal close-packed metals. It is shown that the addition of small amounts of impurities to pure Zn leads to measurable changes in the temperature dependence of the electrical resistivity ratio $\rho_{||}/\rho_{\perp}$. The corresponding deviations from Matthiessen's rule for polycrystalline samples are also calculated.

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TABLE OF CONTENTS

CHAPTER I

INTRODUCTION

1.1 Scope of Thesis

There are two alternative theoretical descriptions
of the electronic transport properties of pure single
crystals of simple (non-transition) metals in the absence
of a magnetic field. The variational method, which is
usually employed, uses trial solutions of the Boltzmann
transport equations to calculate transport coefficients
such as the electrical resistivity and the electronic
contribution to the thermal resistivity; this approach is
reviewed in the book by Ziman [11]. The electrical
resistivity has also been discussed by Robinson and Dow [26]
in terms of a scattering time solution of the Boltzmann
transport equation. In both formalisms the approximation
of a spherical Fermi surface was made in order to simplify
calculations. These methods will be extended in Chapters
II, III, IV and V to consider a non-spherical Fermi surface,
with a multiple orthogonalized plane wave description of the
conduction electrons; a scattering time formalism for the
electronic contribution to the thermal resistivity will also
be introduced. The resulting expressions will be presented
in terms of effective phonon frequency distributions which

1

are generalizations of the ones previously used [4, 21, 22, 23, 29, 30, 31] for the case of a spherical Fermi surface; these distributions are particularly convenient for computation and it is hoped that our formulae will lead to quantitative results.

For simple metals the electronic and lattice problems may be separated, with their coupling described by the electron-phonon interaction. In Section 2.1 the theory of lattice dynamics in the harmonic approximation is reviewed briefly, and in Section 2.2 an expression is obtained for the coupling between the conduction electrons and the lattice vibrations, utilizing a pseudopotential formalism based upon multiple orthogonalized plane waves for the conduction electrons.

For ordinary transport phenomena, the application of constant outside constraints, such as temperature gradients and electric fields, prevents the establishment of a strict equilibrium state, and a steady state is established with the scattering (due to the electron-phonon interaction in pure single crystals) balancing the effect of the external constraints. In Section 3.1 the linearized Boltzmann transport equations for the electrons and phonons in the absence of a magnetic field are reviewed; these are the steady state equations for the electron and phonon distribution functions. The explicit forms of the scattering terms in these equations are obtained in Section 3.2, using

the expression for the electron-phonon interaction from Section 2.2.

The variational method approach to the calculation of transport coefficients is discussed in Chapter IV, using the results of Chapters II and III. In Section 4.1 we present the details of a general formulation using a variational principle to express the solutions of the coupled electron and phonon Boltzmann equations in terms of given trial functions. In Sections 4.2 and 4.3 we generalize previous lowest order trial function results for the electrical resistivity and the electronic contribution to the thermal resistivity to the case of a non-spherical Fermi surface. Phonon drag effects are ignored (i.e., the phonons are assumed to be in equilibrium) and our results are formulated in terms of effective phonon frequency distributions.

The scattering time approach to the calculation of transport coefficients is discussed in Chapter V, using the results of Chapters II and III. In Section 5.1 the theory of Robinson and Dow [26] for the electrical resistivity of pure single crystals is presented for the case of a non-spherical Fermi surface, and in Section 5.2 a scattering time theory for the electronic contribution to the thermal resistivity of pure single crystals is introduced. The resulting expressions are formulated in terms of effective phonon frequency distributions.

The scattering time method of Robinson and Dow [26]
has been generalized [30, 31] to consider dilute
nonmagnetic substitutional alloys of simple metals. In
Chapter VI we show that the change in scattering time
anisotropy resulting from the addition of small amounts of
impurities to pure Zn leads to measurable changes in the
temperature dependence of the resistivity ratio $\rho_{||}/\rho_{\perp}$;
$\rho_{||}$ ($\rho_{\perp}$) is the electrical resistivity with the electric
field parallel (perpendicular) to the c-axis. We also
calculate the corresponding deviations from Matthiessen's
rule for polycrystalline samples.

The Appendices contain the detailed derivation of
several expressions used in Chapters IV, V and VI.

LATTICE DYNAMICS AND THE ELECTRON-PHONON INTERACTION

2.1 Lattice Dynamics

In this section we review the theory of lattice
dynamics in the harmonic approximation, following
Maradudin et al. [1]. For simple (non-transition) metals,
we make the usual distinction between conduction electrons,
which are nearly free, and core electrons, which are
tightly bound to the ions, and separate the electronic and
lattice problems, describing their coupling by the electron-
phonon interaction (Section 2.2). Using the adiabatic
approximation [1, 2, 3], we may consider the motion of the
core electrons to contribute to the effective interionic
forces, and not include them in the lattice dynamical
problem. Then the crystal potential energy, Φ, is a function
of the instantaneous ion positions, where the ions are
assumed to execute small excursions from their equilibrium
positions due to thermal fluctuations.

Consider a crystal with N unit cells and r ions per
unit cell, and write

$$\underline{R}(\ell,\kappa;t) = \underline{R}^0(\ell,\kappa) + \underline{u}(\ell,\kappa;t)$$

for the position vector of the κth ion in the ℓth unit cell at time t, where $\underline{R}^0(\ell,\kappa)$ is the equilibrium position and $\underline{u}$ is the excursion from equilibrium. We may write

$$\underline{R}^0(\ell,\kappa) = \underline{R}^0_\ell + \underline{\rho}(\kappa)$$

where $\underline{R}^0_\ell$ locates the origin of the ℓth unit cell and $\underline{\rho}(\kappa)$ specifies the equilibrium position of the κth ion with respect to the origin of a unit cell, with $\kappa = 1, 2, \ldots, r$.

In the harmonic approximation, valid for small displacements, the crystal potential energy Φ is expanded in a Taylor's series to second order in the displacements, and the classical lattice Hamiltonian is

$$H = \Phi_0 + \frac{1}{2} \sum_{\ell\kappa\alpha} M_\kappa \dot{u}^2_\alpha(\ell,\kappa;t)$$

$$+ \frac{1}{2} \sum_{\substack{\ell\kappa\alpha \\ \ell'\kappa'\beta}} \Phi_{\alpha\beta}(\ell\kappa;\ell'\kappa') u_\alpha(\ell,\kappa;t) u_\beta(\ell',\kappa';t) \qquad (2.1)$$

where Φ_0 is the static equilibrium potential energy, M_κ is the mass of the κth type of ion, $\alpha = 1, 2, 3$ are the Cartesian components, and

$$\Phi_{\alpha\beta}(\ell\kappa;\ell'\kappa') = \left. \frac{\partial^2\Phi}{\partial u_\alpha(\ell,\kappa)\,\partial u_\beta(\ell',\kappa')} \right|_0$$

are the atomic force constants, where the subscript zero means the derivatives are evaluated in the equilibrium

configuration. From Hamilton's equations and (2.1), we
obtain the classical equation of motion:

$$M_\kappa \ddot{u}_\alpha(\ell,\kappa;t) = - \sum_{\ell'\kappa'\beta} \Phi_{\alpha\beta}(\ell\kappa;\ell'\kappa')u_\beta(\ell',\kappa';t) \ . \quad (2.2)$$

If we assume a solution to (2.2) of the form

$$u_\alpha(\ell,\kappa;t) = \frac{u_\alpha(\kappa,\underline{q})}{\sqrt{M_\kappa}} e^{-i\omega t + i\underline{q}\cdot\underline{R}_\ell^0} \quad (2.3)$$

the equation of motion (2.2) becomes

$$\omega^2 u_\alpha(\kappa,\underline{q}) = \sum_{\kappa'\beta} D_{\alpha\beta}(\kappa\kappa'|\underline{q})u_\beta(\kappa',\underline{q}) \quad (2.4)$$

where the dynamical matrix $D_{\alpha\beta}$ is

$$D_{\alpha\beta}(\kappa\kappa'|\underline{q}) = \frac{1}{\sqrt{M_\kappa M_{\kappa'}}} \sum_{\ell'} \Phi_{\alpha\beta}(\ell\kappa;\ell'\kappa')e^{i\underline{q}\cdot(\underline{R}_\ell^0,-\underline{R}_\ell^0)} \quad (2.5)$$

which is Hermitian and independent of ℓ since $\Phi_{\alpha\beta}(\ell\kappa;\ell'\kappa')$ is
a function of $(\ell'-\ell)$ only and not ℓ' and ℓ separately. The
original problem of solving 3rN coupled differential equations
(2.2) has been reduced to the diagonalization of a 3r by 3r
matrix $D_{\alpha\beta}(\kappa\kappa'|\underline{q})$ for each value of $\underline{q}$.

We assume cyclic boundary conditions [1]; that is, we
consider an infinite periodic crystal composed of macrocrystals
with N unit cells, and any one of the macrocrystals may be
regarded as the physical crystal we are studying. Consideration

of the boundary conditions and the expression (2.3) shows
that all distinct solutions are obtained for the N allowed
values of the wavevector $\underline{q}$ uniformly distributed throughout
the first Brillouin zone (F.B.Z.). The eigenvalues $\omega_j^2(\underline{q})$,
j = 1, 2, ..., 3r of the dynamical matrix are the squares
of the phonon (normal mode) frequencies, and the eigenvectors,
denoted by $\underline{\varepsilon}(\kappa|\underline{q}j)$, are the phonon polarization vectors,
corresponding to the phonon of wavevector $\underline{q}$.

We now write the equation of motion (2.4) in its
usual form:

$$\omega_j^2(\underline{q})\varepsilon_\alpha(\kappa|\underline{q}j) = \sum_{\kappa'\beta} D_{\alpha\beta}(\kappa\kappa'|\underline{q})\varepsilon_\beta(\kappa'|\underline{q}j) \quad . \qquad (2.6)$$

We assume orthonormality and closure for the eigenvectors,

$$\sum_{\kappa\alpha} \varepsilon_\alpha^*(\kappa|\underline{q}j)\varepsilon_\alpha(\kappa|\underline{q}j') = \delta_{jj'}$$

$$\sum_j \varepsilon_\beta^*(\kappa'|\underline{q}j)\varepsilon_\alpha(\kappa|\underline{q}j) = \delta_{\alpha\beta}\delta_{\kappa\kappa'} \quad , \qquad (2.7)$$

where δ is the Kronecker delta and * denotes the complex
conjugate. We have $\omega_j^2(-\underline{q}) = \omega_j^2(\underline{q})$ and we adopt the
convention of Born and Huang [2]:

$$\underline{\varepsilon}^*(\kappa|-\underline{q}j) = \underline{\varepsilon}(\kappa|\underline{q}j) \quad . \qquad (2.8)$$

The frequencies and polarization vectors are periodic in the

reciprocal lattice since the dynamical matrix is.

The excursions from equilibrium may be written in general as a superposition of normal modes ($\underline{q}j$) where the normal coordinates $Q(\underline{q}j)$ diagonalize the Hamiltonian (2.1):

$$\underline{u}(\ell,\kappa) = \frac{1}{\sqrt{NM_\kappa}} \sum_{\substack{\underline{q}j \\ (F.B.Z.)}} \underline{\varepsilon}(\kappa|\underline{q}j)Q(\underline{q}j)e^{i\underline{q}\cdot\underline{R}_\ell^0} \tag{2.9}$$

where the sum over $\underline{q}$ is restricted to the F.B.Z. and we have suppressed the explicit time dependence of $\underline{u}$ and Q. Since $\underline{u}$ is real, we have

$$Q(-\underline{q}j) = Q^*(\underline{q}j) \quad . \tag{2.10}$$

The normal coordinates may be expressed in terms of the phonon creation ($a^\dagger$) and annihilation (a) operators as [1]

$$Q(\underline{q}j) = \sqrt{\frac{\hbar}{2\omega_j(\underline{q})}} \; (a^\dagger_{-\underline{q}j} + a_{\underline{q}j}) \tag{2.11}$$

where $\hbar$ is Planck's constant divided by 2π, and the phonon operators satisfy the usual commutation relations for Bose operators.

Finally, we note that for more than one ion per unit cell (r > 1), there is an alternative definition of the dynamical matrix [1, 4] as

$$C_{\alpha\beta}(\kappa\kappa'|\underline{q}) = e^{-i\underline{q}\cdot\underline{\rho}(\kappa)} D_{\alpha\beta}(\kappa\kappa'|\underline{q})e^{i\underline{q}\cdot\underline{\rho}(\kappa')} \tag{2.12}$$

which is not periodic in the reciprocal lattice. The
polarization vectors are then

$$\underline{w}(\kappa|\underline{q}j) = e^{-i\underline{q}\cdot\underline{\rho}(\kappa)}\underline{\epsilon}(\kappa|\underline{q}j) \tag{2.13}$$

such that

$$\omega_j^2(\underline{q})w_\alpha(\kappa|\underline{q}j) = \sum_{\kappa'\beta} C_{\alpha\beta}(\kappa\kappa'|\underline{q})w_\beta(\kappa'|\underline{q}j) \tag{2.14}$$

is the equation of motion.

2.2   The Electron-Phonon Interaction

In this section we obtain an expression for the
coupling between the conduction electrons and the lattice
vibrations (phonons), using a pseudopotential formalism [5]
based upon orthogonalized plane waves. For simple (non-
transition) metals we may separate the electron states into
localized core states and nonlocal conduction band states,
which must be orthogonal. In the pseudopotential method,
the orthogonalization manifests itself as a repulsive
contribution added to the attractive potential between the
conduction electrons and the ions, and the resulting
effective potential, the pseudopotential, W, is then weak.
The pseudopotential equation for the pseudo wave function
is formally the same as the Schrödinger equation for a
free electron gas with perturbing potential, W, and the
true wave function can be obtained from the pseudo wave
function by orthogonalization to the core states. Since W
is weak, we may expand the pseudo wave function in plane
waves, and if m plane waves are used, this is the m
orthogonalized plane wave (OPW) approximation.

In the diffraction model [5] we deal with pseudo
wave functions and pseudopotentials, and the potential
energy (pseudopotential) W of a conduction electron at
position $\underline{r}$ may be separated into a sum of individual
electron-ion pseudopotentials centred upon the individual

ions:

$$W(\underline{r}) = \sum_{\ell \kappa} w(\underline{r} - \underline{R}(\ell, \kappa)) \qquad (2.15)$$

where we have assumed all ions to be identical (this implies $M_\kappa = M$, $\kappa = 1, 2, \ldots, r$ in Section 2.2) and we suppress explicit time dependence. In the m OPW approximation the pseudo wave function may be written as

$$\phi_{\underline{k}}(\underline{r}) = \frac{1}{\sqrt{\Omega}} e^{i\underline{k} \cdot \underline{r}} u_{\underline{k}}(\underline{r}) \quad , \qquad (2.16)$$

where Ω is the crystal volume, $\underline{k}$ is the wavevector suitably restricted by the cyclic boundary conditions, and $u_{\underline{k}}(\underline{r})$ has the Bloch form

$$u_{\underline{k}}(\underline{r}) = \sum_{\underline{\kappa}_n}^{(m)} a_{\underline{\kappa}_n}(\underline{k}) e^{i\underline{\kappa}_n \cdot \underline{r}} \qquad (2.17)$$

where $\underline{\kappa}_n$ are m reciprocal lattice vectors including the origin, and the $a_{\underline{\kappa}_n}$ are coefficients in the expansion (with $a_0 \equiv 1$).

If we sum the interaction (2.15) over all conduction electrons, situated at positions $\underline{r}_i$, we have

$$\sum_i W(\underline{r}_i)$$

which is a sum of one-body operators. In the notation of second quantization this becomes

$$\int d^3r \ \psi^\dagger(\underline{r})W(\underline{r})\psi(\underline{r}) \tag{2.18}$$

where $\psi(\psi^\dagger)$ is the annihilation (creation) field operator for an electron at $\underline{r}$. We may make the expansion

$$\psi(\underline{r}) = \sum_{\underline{k}\sigma} \phi_{\underline{k}}(\underline{r})|\sigma\rangle C_{\underline{k}\sigma}$$

and its adjoint, where $C_{\underline{k}\sigma}$ annihilates an electron of spin σ in the state $\phi_{\underline{k}}$. Then the interaction Hamiltonian (2.18) becomes

$$\sum_{\underline{k}'\underline{k}\sigma} \langle\phi_{\underline{k}'}|W|\phi_{\underline{k}}\rangle C_{\underline{k}'\sigma}^\dagger C_{\underline{k}\sigma} \tag{2.19}$$

where $\langle\phi_{\underline{k}'}|W|\phi_{\underline{k}}\rangle = \int d^3r \ \phi_{\underline{k}'}^*(\underline{r})W(\underline{r})\phi_{\underline{k}}(\underline{r})$.

Using (2.15), (2.16) and (2.17), we have

$$\langle\phi_{\underline{k}'}|W|\phi_{\underline{k}}\rangle = \frac{1}{\Omega} \sum_{\underline{\kappa}_n}^{(m)} \sum_{\underline{\kappa}_n}^{(m)} a_{\underline{\kappa}_n}^*(\underline{k}')a_{\underline{\kappa}_n}(\underline{k})$$

$$\times \sum_{\ell\kappa} \int d^3r \ e^{-i(\underline{k}'+\underline{\kappa}_n')\cdot\underline{r}} w(\underline{r}-\underline{R}(\ell,\kappa))$$

$$\times e^{i(\underline{k}+\underline{\kappa}_n)\cdot\underline{r}} . \tag{2.20}$$

If we make the substitution $\underline{y} = \underline{r} - \underline{R}(\ell,\kappa)$ for each

term in the sum over ℓ and κ, the integral in (2.20) becomes

$$
e^{-i(\underline{k}'+\underline{\kappa}_n'-\underline{k}-\underline{\kappa}_n)\cdot(\underline{R}_\ell^0+\underline{\rho}(\kappa))}[1 - i(\underline{k}'+\underline{\kappa}_n'-\underline{k}-\underline{\kappa}_n)\cdot\underline{u}(\ell,\kappa)]
$$

$$
\times \int d^3y\ e^{-i(\underline{k}'+\underline{\kappa}_n')\cdot\underline{y}}\ w(\underline{y})e^{i(\underline{k}+\underline{\kappa}_n)\cdot\underline{y}} \tag{2.21}
$$

where we have used $\underline{R}(\ell,\kappa) = \underline{R}_\ell^0 + \underline{\rho}(\kappa) + \underline{u}(\ell,\kappa)$ and expanded $e^{-i(\underline{k}'+\underline{\kappa}_n'-\underline{k}-\underline{\kappa}_n)\cdot\underline{u}(\ell,\kappa)}$ to first order in $\underline{u}$, since the displacements are assumed to be small. The first term in (2.21) when inserted in (2.20) does not depend on the displacements from equilibrium and simply describes Bragg scattering from the static lattice. The second term gives the electron-phonon interaction, and we denote its contribution to $<\phi_{\underline{k}'}|W|\phi_{\underline{k}}>$ by $<\phi_{\underline{k}'}|\overline{W}|\phi_{\underline{k}}>$, and write for the electron-phonon interaction

$$
H_{e-p} = \sum_{\underline{k}'\underline{k}\sigma} <\phi_{\underline{k}'}|\overline{W}|\phi_{\underline{k}}>C_{\underline{k}'\sigma}^\dagger C_{\underline{k}\sigma} \tag{2.22}
$$

using (2.19).

Using (2.9) and (2.11) to write $\underline{u}(\ell,\kappa)$ in terms of phonon operators, the sum over ℓ in (2.22) restricts $\underline{q}$ by

$$
\underline{k}' - \underline{k} = \underline{q} + \underline{\kappa}_n'' \tag{2.23}
$$

where $\underline{\kappa}_n''$ is a reciprocal lattice vector, and contributes a

factor of N. Defining the volume per ion as

$$\Omega_0 = \frac{\Omega}{rN} \qquad (2.24)$$

and

$$\langle \underline{k}' + \underline{\kappa}_n' | w | \underline{k} + \underline{\kappa}_n \rangle = \frac{1}{\Omega_0} \int d^3 y \; e^{-i(\underline{k}' + \underline{\kappa}_n') \cdot \underline{y}}$$

$$\times \; w(\underline{y}) e^{i(\underline{k} + \underline{\kappa}_n) \cdot \underline{y}} \qquad , \qquad (2.25)$$

(2.22) becomes, using the periodicity in the reciprocal lattice of $\omega_j(\underline{q})$, $\underline{\varepsilon}(\kappa | \underline{q}j)$, and the phonon operators:

$$H_{e-p} = \sum_{\substack{\underline{k}'\underline{k} \\ \sigma j}} g_{\underline{k}', \underline{k}; j} \; C^\dagger_{\underline{k}'\sigma} C_{\underline{k}\sigma} (a^\dagger_{-(\underline{k}'-\underline{k})j} + a_{(\underline{k}'-\underline{k})j}) \qquad (2.26)$$

where the electron-phonon coupling constant is

$$g_{\underline{k}', \underline{k}; j} = - i \sqrt{\frac{\hbar}{2MN\omega_j(\underline{k}'-\underline{k})}} \; \frac{1}{r} \sum_\kappa \underline{\varepsilon}(\kappa | (\underline{k}'-\underline{k})j)$$

$$\circ \left\{ \sum_{\underline{\kappa}_n}^{(m)} \sum_{\underline{\kappa}_n'}^{(m)} a^*_{\underline{\kappa}_n'}(\underline{k}') a_{\underline{\kappa}_n}(\underline{k}) \right.$$

$$\times \; e^{-i(\underline{k}' + \underline{\kappa}_n' - \underline{k} - \underline{\kappa}_n) \cdot \underline{\rho}(\kappa)} \; (\underline{k}' + \underline{\kappa}_n' - \underline{k} - \underline{\kappa}_n)$$

$$\times \; \langle \underline{k}' + \underline{\kappa}_n' | w | \underline{k} + \underline{\kappa}_n \rangle \bigg\} \qquad . \qquad (2.27)$$

We note that in the one OPW approximation this becomes

$$g_{\underline{k}',\underline{k};j} = -i \sqrt{\frac{\hbar}{2MN\omega_j(\underline{k}'-\underline{k})}} \frac{1}{r} \sum_{\kappa} \underline{\varepsilon}(\kappa|(\underline{k}'-\underline{k})j)$$

$$\cdot \{e^{-i(\underline{k}'-\underline{k})\cdot\underline{\rho}(\kappa)} (\underline{k}'-\underline{k})<\underline{k}'|w|\underline{k}>\} \quad . \qquad (2.28)$$

In terms of the alternative definitions discussed in Section 2.1, this becomes, using (2.13) and (2.23):

$$g_{\underline{k}',\underline{k};j} = -i \sqrt{\frac{\hbar}{2MN\omega_j(\underline{q})}} \frac{1}{r} \sum_{\kappa} e^{-i\underline{\kappa}_n''\cdot\underline{\rho}(\kappa)}$$

$$\times \underline{w}(\kappa|\underline{q}j)\cdot(\underline{k}'-\underline{k})<\underline{k}'|w|\underline{k}> \qquad (2.29)$$

with

$$\underline{k}' - \underline{k} = \underline{q} + \underline{\kappa}_n'' \qquad (2.23)$$

where $\underline{q}$ is in the F.B.Z.. This agrees with the result of Truant [4].

Furthermore, in the one OPW approximation for a Bravais lattice ($r = 1$) we have

$$g_{\underline{k}',\underline{k};j} = -i \sqrt{\frac{\hbar}{2MN\omega_j(\underline{k}'-\underline{k})}} (\underline{k}'-\underline{k})\cdot\underline{\varepsilon}((\underline{k}'-\underline{k})j)<\underline{k}'|w|\underline{k}>$$
$$(2.30)$$

which is the usual result [6].

We note for future reference that it is easily shown from (2.27) that

$$g^*_{\underline{k},\underline{k}';j} = g_{\underline{k}',\underline{k};j} \qquad (2.31)$$

using the facts that w is real, $\omega_j(-\underline{q}) = \omega_j(\underline{q})$, and also (2.8). Thus we have

$$|g_{\underline{k}',\underline{k};j}|^2 = |g_{\underline{k},\underline{k}';j}|^2 \quad . \qquad (2.32)$$

CHAPTER III

THE BOLTZMANN TRANSPORT EQUATIONS FOR

THE ELECTRONS AND THE PHONONS

3.1 The Linearized Boltzmann Equations

In this section we consider the linearized Boltzmann transport equations for the electrons and the phonons [3, 7, 8, 9]. As mentioned previously, we consider independent systems of conduction electrons and phonons for a pure single crystal of a simple metal, and the effect of the electron-phonon interaction is to produce transitions between the unperturbed states of these systems. The electron distribution function, $f_{\underline{k}}$, and the phonon distribution function, $n_{\underline{q}j}$, are the probable occupation numbers for the electron state of wavevector $\underline{k}$ and the phonon mode $(\underline{q}j)$, respectively. The explicit time dependence is suppressed, and the distribution functions depend on position $\underline{r}$ only through their dependence on external parameters such as the temperature T. We shall consider ordinary transport phenomena, in which the application of constant outside constraints (temperature gradients and electromagnetic fields) prevents the establishment of a strict equilibrium state, and a steady state is established, with the scattering due to the

electron-phonon interaction balancing the effect of the external constraints.

In the absence of interactions and external constraints, the equilibrium electron distribution function is

$$f_{\underline{k}}^0 = \frac{1}{e^{\beta(\epsilon_{\underline{k}} - \mu)} + 1} \quad , \tag{3.1}$$

where

$$\beta = \frac{1}{k_B T} \quad ,$$

with k_B the Boltzmann constant and T the absolute temperature, μ is the chemical potential, and $\epsilon_{\underline{k}}$ is the energy of the electron state of wavevector $\underline{k}$. We assume that the equilibrium phonon distribution function is

$$n_{\underline{q}j}^0 = \frac{1}{e^{\beta(\hbar\omega_j(\underline{q}))} - 1} \quad . \tag{3.2}$$

Considering first the electron distribution function, in the steady state we have [7, 8]

$$\frac{\partial f_{\underline{k}}}{\partial t} = \frac{\partial f_{\underline{k}}}{\partial t}\bigg]_{diff} + \frac{\partial f_{\underline{k}}}{\partial t}\bigg]_{field} + \frac{\partial f_{\underline{k}}}{\partial t}\bigg]_{scatt} = 0 \quad , \tag{3.3}$$

where the first equality is the statement of a generalized equation of continuity. The diffusion term gives the rate

of change of f_k due to thermal gradients, the field term
gives the change due to external electromagnetic fields,
and the scattering term gives the change due to the electron-
phonon interaction. This assumed Boltzmann equation may be
linearized [3, 7, 8, 9] under the assumption that the
external constraints causing the deviation from equilibrium
are small, in which case we may use f_k^0 in the diffusion and
field terms for small deviations of f_k from f_k^0, and neglect
gradients of the correction term. In the absence of a
magnetic field, the linearized Boltzmann equation for the
conduction electrons is then

$$\frac{\partial f_k^0}{\partial \varepsilon_k} \underline{V}_{\underline{k}} \cdot \{e\underline{E} - \frac{(\varepsilon_k - \mu)}{T} \nabla T\} = \frac{\partial f_k}{\partial t}]_{scatt} \quad , \qquad (3.4)$$

where $\underline{V}_{\underline{k}} \equiv \frac{1}{\hbar} \frac{\partial \varepsilon_k}{\partial \underline{k}}$ is the velocity of an electron of wavevector
$\underline{k}$, e is the electronic charge, $\underline{E}$ is the observed [10] electric
field, and we have used (3.1) to write $\partial f_k^0/\partial T$ in terms of
$\partial f_k^0/\partial \varepsilon_k$. We have also used the fact that f_k^0 depends on $\underline{k}$ only
through ε_k, so that

$$\frac{\partial f_k^0}{\partial \underline{k}} = \frac{\partial f_k^0}{\partial \varepsilon_k} \frac{\partial \varepsilon_k}{\partial \underline{k}} \quad \circ$$

By similar reasoning, we obtain the linearized
Boltzmann equation for the phonons:

$$\frac{\partial n^0_{qj}}{\partial T} \, \underline{V}_{qj} \cdot \nabla T = \frac{\partial n_{qj}}{\partial t}]_{scatt} \tag{3.5}$$

where $\underline{V}_{qj} \equiv \dfrac{\partial \omega_j(\underline{q})}{\partial \underline{q}}$ is the group velocity of the phonon of wavevector $\underline{q}$ and polarization branch j, and the scattering term is due only to the electron-phonon interaction since we have assumed that we have a pure single crystal.

3.2   The Electron-Phonon Scattering Terms

In this section we obtain the explicit form of the scattering terms in the linearized Boltzmann equations (3.4) and (3.5) for pure single crystals, using the expression for the electron-phonon interaction from Section 2.2. The Golden Rule transition probability per unit time for a conduction electron of spin σ scattering from $\underline{k}$ to $\underline{k}'$ with the absorption of a phonon of wavevector

$$\underline{Q} = \underline{k}' - \underline{k} \quad ,$$

with

$$\underline{q} = \underline{Q}_R = (\underline{k}' - \underline{k})_R \tag{3.6}$$

where $\underline{q}$ is the reduction (denoted by R) of $\underline{Q}$ to the F.B.Z., is

$$\sum_j \frac{2\pi}{\hbar} \left| \langle \phi_{\underline{k}'}, \sigma; \ldots, (n_{\underline{q}j} - 1), \ldots | H_{e-p} | \phi_{\underline{k}}, \sigma; \ldots, n_{\underline{q}j} \ldots \rangle \right|^2$$

$$\times \delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}} - \hbar\omega_j(\underline{q})) \tag{3.7}$$

where the delta function expresses energy conservation. Using (3.6) and the periodicity of the phonon operators, we may write the electron-phonon interaction (2.26) in the form

$$H_{e-p} = \sum_{\substack{\underline{k}'\underline{k} \\ \bar{\sigma}j}} g_{\underline{k}',\underline{k};j} \, c_{\underline{k}'\sigma}^{\dagger} c_{\underline{k}\sigma} (a_{-\underline{q}j}^{\dagger} + a_{\underline{q}j}) \quad .$$

The matrix element in (3.7) is then

$$g_{\underline{k}',\underline{k};j} \, \sqrt{n_{\underline{q}j}}$$

since the $\phi_{\underline{k}}$ are basis states for the electron operators and the phonon operators satisfy [1]

$$a|n\rangle = \sqrt{n} \, |n-1\rangle$$

$$\hspace{10cm} (3.8)$$

$$a^{\dagger}|n\rangle = \sqrt{n+1} \, |n+1\rangle \quad .$$

The transition probability (3.7) becomes

$$\frac{2\pi}{\hbar} \sum_{j} |g_{\underline{k}',\underline{k};j}|^2 \, n_{\underline{q}j} \, \delta_{(\underline{k}'-\underline{k})_R, \underline{q}} \, \delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}} - \hbar\omega_j(\underline{q}))$$

$$\hspace{10cm} (3.9)$$

where the first delta is the Kronecker delta stating that $\underline{q}$ is $(\underline{k}'-\underline{k})$ reduced to the F.B.Z.. In the same way, using (3.8) again, we find that the transition probability for scattering from $\underline{k}$ to $\underline{k}'$ with the creation of a phonon is

$$\frac{2\pi}{\hbar} \sum_{j} |g_{\underline{k}',\underline{k};j}|^2 \, (n_{\underline{q}j}+1) \, \delta_{(\underline{k}-\underline{k}')_R, \underline{q}} \, \delta(\varepsilon_{\underline{k}'} + \hbar\omega_j(\underline{q}) - \varepsilon_{\underline{k}}) \quad .$$

$$\hspace{10cm} (3.10)$$

The rate of change of the electron distribution function is the difference between the probabilities

for scattering into and out of the state of wavevector $\underline{k}$ caused by emission and absorption of phonons. These probabilities are given by (3.9) and (3.10) and their analogues for $\underline{k}'$ scattering into $\underline{k}$, multiplied by the appropriate Fermi factors expressing the occupation probabilities of the electronic states concerned. Using (2.32) and the fact that the delta function is even, we may write this as

$$
\frac{\partial f_{\underline{k}}}{\partial t}\Big]_{scatt} = \frac{2\pi}{\hbar} \sum_{\underline{k}'j} |g_{\underline{k}',\underline{k};j}|^2 \{[f_{\underline{k}'}(1-f_{\underline{k}})n_{\underline{q}j}
$$

$$
- f_{\underline{k}}(1-f_{\underline{k}'})(n_{\underline{q}j}+1)]\delta(\underline{k}-\underline{k}')_{R,\underline{q}}
$$

$$
\times \delta(\varepsilon_{\underline{k}'}+\hbar\omega_j(\underline{q})-\varepsilon_{\underline{k}}) + [f_{\underline{k}'}(1-f_{\underline{k}})(n_{\underline{q}j}+1)
$$

$$
- f_{\underline{k}}(1-f_{\underline{k}'})n_{\underline{q}j}]\delta(\underline{k}'-\underline{k})_{R,\underline{q}}
$$

$$
\times \delta(\varepsilon_{\underline{k}'}-\varepsilon_{\underline{k}}-\hbar\omega_j(\underline{q}))\} \quad . \tag{3.11}
$$

In the equilibrium situation this must vanish and thus we have the conditions

$$
f^0_{\underline{k}'}(1-f^0_{\underline{k}})n^0_{\underline{q}j} = f^0_{\underline{k}}(1-f^0_{\underline{k}'})(n^0_{\underline{q}j}+1)
$$

$$
\tag{3.12}
$$

$$
f^0_{\underline{k}'}(1-f^0_{\underline{k}})(n^0_{\underline{q}j}+1) = f^0_{\underline{k}}(1-f^0_{\underline{k}'})n^0_{\underline{q}j} \quad .
$$

It is conventional [8] to express the deviation from equilibrium of the electron and phonon distribution functions in terms of deviation functions $\Phi_{\underline{k}}$ and $\Psi_{\underline{q}j}$ defined by

$$f_{\underline{k}} = f_{\underline{k}}^0 - \Phi_{\underline{k}} \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \tag{3.13}$$

$$n_{\underline{q}j} = n_{\underline{q}j}^0 - \Psi_{\underline{q}j} \frac{\partial n_{\underline{q}j}^0}{\partial (\hbar \omega_j(\underline{q}))} \quad . \tag{3.14}$$

Using (3.1) and (3.2) we see that these equations can be written as

$$f_{\underline{k}} = f_{\underline{k}}^0 + \beta \Phi_{\underline{k}} f_{\underline{k}}^0 (1 - f_{\underline{k}}^0) \tag{3.15}$$

$$n_{\underline{q}j} = n_{\underline{q}j}^0 + \beta \Psi_{\underline{q}j} n_{\underline{q}j}^0 (n_{\underline{q}j}^0 + 1) \tag{3.16}$$

where $\beta = \frac{1}{k_B T}$ as before.

We now expand the factors in (3.11) using (3.15) and (3.16), and the conditions (3.12); the result to first order in the deviation functions $\Phi_{\underline{k}}$ and $\Psi_{\underline{q}j}$ is

$$\frac{\partial f_{\underline{k}}}{\partial t}]_{scatt} = \frac{-2\pi\beta}{\hbar} \sum_{\underline{k}'j} |g_{\underline{k}',\underline{k};j}|^2 \{ f_{\underline{k}}^0 (1 - f_{\underline{k}'}^0)(n_{\underline{q}j}^0 + 1)$$

$$\times (\Phi_{\underline{k}} - \Psi_{\underline{q}j} - \Phi_{\underline{k}'}) \delta(\underline{k} - \underline{k}')_{R'} \underline{q} \, \delta(\varepsilon_{\underline{k}'} + \hbar\omega_j(\underline{q}) - \varepsilon_{\underline{k}})$$

$$+ f_{\underline{k}}^0 (1 - f_{\underline{k}'}^0) n_{\underline{q}j}^0 (\Phi_{\underline{k}} + \Psi_{\underline{q}j} - \Phi_{\underline{k}'}) \delta(\underline{k}' - \underline{k})_{R'} \underline{q}$$

$$\times \delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}} - \hbar\omega_j(\underline{q})) \} \quad . \tag{3.17}$$

Define

$$P^{\underline{k}'}_{\underline{k};\underline{q}j} = \frac{2\pi}{\hbar} \, |g_{\underline{k}',\underline{k};j}|^2 \, f^0_{\underline{k}}(1-f^0_{\underline{k}'})\, n^0_{\underline{q}j} \; \delta(\varepsilon_{\underline{k}'}-\varepsilon_{\underline{k}}-\hbar\omega_j(\underline{q}))$$

(3.18)

$$P_{\underline{k}}^{\underline{k}';\underline{q}j} = \frac{2\pi}{\hbar} \, |g_{\underline{k}',\underline{k};j}|^2 \, f^0_{\underline{k}}(1-f^0_{\underline{k}'})\, (n^0_{\underline{q}j}+1)\, \delta(\varepsilon_{\underline{k}'}-\varepsilon_{\underline{k}}+\hbar\omega_j(\underline{q}))$$

(3.19)

Then (3.17) becomes

$$\frac{\partial f_{\underline{k}}}{\partial t}\Big]_{scatt} = - \beta \sum_{\underline{k}'j} \{ (\Phi_{\underline{k}}+\Psi_{\underline{q}j}-\Phi_{\underline{k}'})\, \delta(\underline{k}'-\underline{k})_{R,\underline{q}} \; P^{\underline{k}'}_{\underline{k};\underline{q}j}$$

$$+ (\Phi_{\underline{k}}-\Psi_{\underline{q}j}-\Phi_{\underline{k}'})\, \delta(\underline{k}-\underline{k}')_{R,\underline{q}} \; P_{\underline{k}}^{\underline{k}';\underline{q}j} \} \quad . \quad (3.20)$$

We note that the spin σ of the conduction electron of wavevector $\underline{k}$ does not occur explicitly in the above equations since it is not changed by the scattering.

We now obtain the expression for the rate of change of the phonon distribution function $n_{\underline{q}j}$, where q is in the F.B.Z., due to electron-phonon scattering only. This distribution function is decreased by processes in which a conduction electron scatters from $\underline{k}$ to $\underline{k}'$ with the absorption of a phonon of reduced wavevector $\underline{q}$, such that

$$\underline{k}' - \underline{k} = \underline{q} + \underline{\kappa}_n$$

(3.21)

for any reciprocal lattice vector $\underline{\kappa}_n$, whereas it is increased by processes in which a conduction electron

scatters from $\underline{k}'$ to $\underline{k}$ with the creation of a phonon of reduced wavevector $\underline{q}$ such that (3.21) again holds. (The roles of $\underline{k}$ and $\underline{k}'$ are interchanged in the second process for simplification in the following results.) Using the transition probabilities (3.9) and (3.10) (with $\underline{k}$ and $\underline{k}'$ interchanged in the latter) multiplied by the appropriate Fermi factors, we obtain, summing over $\underline{k}$, $\underline{\kappa}_n$, and spin σ ($\underline{k}'$ is then fixed by (3.21) since we know $\underline{q}$) and omitting the sum over j since we are considering a particular polarization branch:

$$\frac{\partial n_{\underline{q}j}}{\partial t}]_{scatt} = \sum_{\underline{k}\sigma\underline{\kappa}_n} \frac{2\pi}{\hbar} |g_{\underline{k}',\underline{k};j}|^2 [f_{\underline{k}'}(1-f_{\underline{k}})(n_{\underline{q}j}+1)$$

$$- f_{\underline{k}}(1-f_{\underline{k}'})n_{\underline{q}j}]\delta_{\underline{k}'-\underline{k},\underline{q}+\underline{\kappa}_n}\delta(\epsilon_{\underline{k}'}-\epsilon_{\underline{k}}-\hbar\omega_j(\underline{q}))$$

(3.22)

where we have also used (2.32) and the fact that the delta function is even. In the equilibrium situation the rate of change (3.22) must be zero and we have the condition

$$f_{\underline{k}'}^0(1-f_{\underline{k}}^0)(n_{\underline{q}j}^0+1) = f_{\underline{k}}^0(1-f_{\underline{k}'}^0)n_{\underline{q}j}^0 \quad . \tag{3.23}$$

Using the expressions (3.15) and (3.16) (for the distribution functions in terms of the deviation functions) and the condition (3.23) to expand the factors in (3.22) to first order in the deviation functions, we have

$$\frac{\partial n_{\underline{q}j}}{\partial t}]_{scatt} = \frac{-2\pi\beta}{\hbar} \sum_{\substack{\underline{k}\sigma\underline{\kappa}_n}} |g_{\underline{k}',\underline{k};j}|^2 \, f_{\underline{k}}^0(1-f_{\underline{k}'}^0) n_{\underline{q}j}^0 (\Phi_{\underline{k}}+\Psi_{\underline{q}j}-\Phi_{\underline{k}'})$$

$$\times \; \delta_{\underline{k}'-\underline{k},\underline{q}+\underline{\kappa}_n} \; \delta(\varepsilon_{\underline{k}'}-\varepsilon_{\underline{k}}-\hbar\omega_j(\underline{q})) \quad . \tag{3.24}$$

By the definition (3.18), we obtain

$$\frac{\partial n_{\underline{q}j}}{\partial t}]_{scatt} = -\beta \sum_{\substack{\underline{k}\sigma\underline{\kappa}_n}} (\Phi_{\underline{k}}+\Psi_{\underline{q}j}-\Phi_{\underline{k}'})\delta_{\underline{k}'-\underline{k},\underline{q}+\underline{\kappa}_n} \; P_{\underline{k};\underline{q}j}^{\underline{k}'} \quad . \tag{3.25}$$

We may summarize the results of Sections 3.1 and 3.2 in a convenient form by combining Eqs. (3.4) and (3.20) and Eqs. (3.5) and (3.25). The coupled linearized Boltzmann transport equations for the electrons and phonons in the absence of a magnetic field are, to first order in the deviation functions,

$$\frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \underline{V}_{\underline{k}} \cdot \{e\underline{E} - \frac{(\varepsilon_{\underline{k}}-\mu)}{T} \nabla T\} = -\beta \sum_{\underline{k}'j} \{(\Phi_{\underline{k}}+\Psi_{\underline{q}j}-\Phi_{\underline{k}'})\delta_{(\underline{k}'-\underline{k})_R,\underline{q}} \; P_{\underline{k};\underline{q}j}^{\underline{k}'}$$

$$+ (\Phi_{\underline{k}}-\Psi_{\underline{q}j}-\Phi_{\underline{k}'})\delta_{(\underline{k}-\underline{k}')_R,\underline{q}} \; P_{\underline{k}}^{\underline{k}';\underline{q}j}\}$$

$$\tag{3.26}$$

and

$$\frac{\partial n_{\underline{q}j}^0}{\partial T} \underline{V}_{\underline{q}j} \cdot \nabla T = -\beta \sum_{\substack{\underline{k}\sigma\underline{\kappa}_n}} (\Phi_{\underline{k}}+\Psi_{\underline{q}j}-\Phi_{\underline{k}'})\delta_{\underline{k}'-\underline{k},\underline{q}+\underline{\kappa}_n} \; P_{\underline{k};\underline{q}j}^{\underline{k}'} \quad . \tag{3.27}$$

We note that the situation in which the phonons are in equilibrium, expressed mathematically by

$$n_{\underline{q}j} = n^0_{\underline{q}j}$$

and

$$\Psi_{\underline{q}j} = 0 \quad,$$

is often considered, in which case the linearized Boltzmann transport equation for the conduction electrons in the absence of a magnetic field is (from (3.26))

$$\frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \, \underline{V}_{\underline{k}} \cdot \{e\underline{E} - \frac{(\varepsilon_{\underline{k}}-\mu)}{T} \, \nabla T\} = \beta \sum_{\underline{k}'} \, (\Phi_{\underline{k}'} - \Phi_{\underline{k}}) f^0_{\underline{k}} (1-f^0_{\underline{k}'}) W^{\underline{k}'}_{\underline{k}} \tag{3.28}$$

where

$$W^{\underline{k}'}_{\underline{k}} = \frac{2\pi}{\hbar} \sum_j \, |g_{\underline{k}',\underline{k};j}|^2 \, n^0_{\underline{q}j} \, \delta_{(\underline{k}'-\underline{k})_R,\underline{q}} \{\delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}} - \hbar\omega_j(\underline{q}))$$

$$+ \, e^{\beta\hbar\omega_j(\underline{q})} \, \delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}} + \hbar\omega_j(\underline{q}))\} \quad. \tag{3.29}$$

We have used $n^0_{\underline{q}j} = n^0_{-\underline{q}j}$, which follows from $\omega_j(\underline{q}) = \omega_j(-\underline{q})$, the definitions (3.18) and (3.19), and Eq. (3.2) (to express $(n^0_{\underline{q}j}+1)$ in terms of $n^0_{\underline{q}j}$).

CHAPTER IV

FORMAL TRANSPORT THEORY: VARIATIONAL METHOD

4.1 General Formulation

The use of a variational principle to solve the coupled Boltzmann equations (3.26) and (3.27) is discussed by Ziman [11], and we follow his formulation with slight changes in notation. We note that Ziman discusses in detail only the case where the phonon system is assumed to be in equilibrium ($\Psi_{\underline{q}j} \equiv 0$); therefore, we present some of the details of the more general formulation including phonon drag effects ($n_{\underline{q}j} \neq n_{\underline{q}j}^0$), for which Ziman gives only the results. It is important to note further that Ziman's expressions ignore dependence on the phonon branch index j.

In calculations which include phonon drag, it is usually assumed that [11, 12, 13, 14]

$$\Psi_{\underline{q}j} \equiv \Psi_{\underline{q}} \tag{4.1}$$

for $j = 1, 2, \ldots, 3r$. This is the case if we assign only wavevector ($\underline{q}$) dependence to the phonon deviation function, and assume it is independent of energy ($\hbar\omega_j(\underline{q})$) and polarization vector ($\underline{\varepsilon}(\kappa|\underline{q}j)$). The use of a branch-dependent

phonon deviation function leads to a complexity in the formalism (for example, it would be necessary to introduce 3r trial functions instead of the single trial function given by (4.19)) which seems unwarranted in the present context; hence we adopt the convention (4.1). In this case, the Boltzmann equation (3.26) for the conduction electrons may be written as

$$
-\frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \, \underline{V}_{\underline{k}} \cdot \{e\underline{E} - \frac{(\varepsilon_{\underline{k}}-\mu)}{T} \nabla T\} = \beta \sum_{\underline{k}'} \{ (\Phi_{\underline{k}}+\Psi_{\underline{q}}-\Phi_{\underline{k}'}) \delta_{(\underline{k}'-\underline{k})_R, \underline{q}} \; P_{\underline{k};\underline{q}}^{\underline{k}'}
$$

$$
+ (\Phi_{\underline{k}}-\Psi_{\underline{q}}-\Phi_{\underline{k}'}) \delta_{(\underline{k}-\underline{k}')_R, \underline{q}} \; P_{\underline{k}}^{\underline{k}';\underline{q}} \}
\tag{4.2}
$$

where, by summing (3.18) and (3.19) over j, we have

$$
P_{\underline{k};\underline{q}}^{\underline{k}'} = \frac{2\pi}{\hbar} \sum_{j} |g_{\underline{k}',\underline{k};j}|^2 \, f_{\underline{k}}^0 (1-f_{\underline{k}'}^0) n_{\underline{q}j}^0 \, \delta(\varepsilon_{\underline{k}'}-\varepsilon_{\underline{k}}-\hbar\omega_j(\underline{q}))
\tag{4.3}
$$

and

$$
P_{\underline{k}}^{\underline{k}';\underline{q}} = \frac{2\pi}{\hbar} \sum_{j} |g_{\underline{k}',\underline{k};j}|^2 \, f_{\underline{k}}^0 (1-f_{\underline{k}'}^0) (n_{\underline{q}j}^0+1) \, \delta(\varepsilon_{\underline{k}'}-\varepsilon_{\underline{k}}+\hbar\omega_j(\underline{q})) \quad .
\tag{4.4}
$$

The Boltzmann equation for the phonons (3.27), summed over j, becomes

$$
-\sum_{j} \frac{\partial n_{\underline{q}j}^0}{\partial T} \, \underline{V}_{\underline{q}j} \cdot \nabla T = \beta \sum_{\underline{k}\sigma\underline{\kappa}_n} (\Phi_{\underline{k}}+\Psi_{\underline{q}}-\Phi_{\underline{k}'}) \delta_{\underline{k}'-\underline{k},\underline{q}+\underline{\kappa}_n} \; P_{\underline{k};\underline{q}}^{\underline{k}'} \quad .
\tag{4.5}
$$

Using (2.32), (3.12), and the even property of the delta function, it is easily shown that

$$P\frac{\underline{k};\underline{q}}{\underline{k}'} = P\frac{\underline{k}'}{\underline{k};\underline{q}} \tag{4.6}$$

as expected.

We next consider some definitions necessary for the formulation of the variational principle. A vector function of $\underline{k}$ and $\underline{q}$ may be formed from the deviation functions:

$$\underline{\phi}(\underline{k};\underline{q}) \equiv (\Phi_{\underline{k}}, \Psi_{\underline{q}}) \quad . \tag{4.7}$$

Using the R.H.S. of the Boltzmann equations (4.2) and (4.5), we define an operator $\underline{P}$ which acts on $\underline{\phi}$ by

$$\underline{P}(\underline{\phi}) = (P_1(\underline{\phi}), P_2(\underline{\phi})) \tag{4.8}$$

where

$$P_1(\underline{\phi}) = \beta \sum_{\underline{k}'} \{ (\Phi_{\underline{k}} + \Psi_{\underline{q}} - \Phi_{\underline{k}'}) \delta(\underline{k}'-\underline{k})_{R}, \underline{q} \, P\frac{\underline{k}'}{\underline{k};\underline{q}}$$

$$+ (\Phi_{\underline{k}} - \Psi_{\underline{q}} - \Phi_{\underline{k}'}) \delta(\underline{k}-\underline{k}')_{R}, \underline{q} \, P\frac{\underline{k}';\underline{q}}{\underline{k}}\} \tag{4.9}$$

is a function of $\underline{k}$ and

$$P_2(\underline{\phi}) = \beta \sum_{\underline{k}\sigma\underline{\kappa}_n} (\Phi_{\underline{k}}+\Psi_{\underline{q}}-\Phi_{\underline{k}'})\,\delta_{\underline{k}'-\underline{k},\underline{q}+\underline{\kappa}_n}\ P_{\underline{k};\underline{q}}^{\underline{k}'} \tag{4.10}$$

is a function of $\underline{q}$. Finally, for two vector functions of $\underline{k}$ and $\underline{q}$,

$$\underline{\phi}_1(\underline{k};\underline{q}) \equiv (f_1(\underline{k}),g_1(\underline{q}))$$

and

$$\underline{\phi}_2(\underline{k};\underline{q}) \equiv (f_2(\underline{k}),g_2(\underline{q})) \quad ,$$

we define an inner product by

$$<\underline{\phi}_1,\underline{\phi}_2> = \sum_{\underline{k}\sigma} f_1(\underline{k})f_2(\underline{k}) + \sum_{\substack{\underline{q}\\(F.B.Z.)}} g_1(\underline{q})g_2(\underline{q}) \quad . \tag{4.11}$$

Writing the L.H.S. of the Boltzmann equations (4.2) and (4.5) as

$$\underline{X}(\underline{k};\underline{q}) = (X_1(\underline{k}),X_2(\underline{q})) \tag{4.12}$$

with

$$X_1(\underline{k}) = -\frac{\partial f_{\underline{k}}^0}{\partial \epsilon_{\underline{k}}}\,\underline{V}_{\underline{k}}\cdot\{e\underline{E} - \frac{(\epsilon_{\underline{k}}-\mu)}{T}\,\nabla T\} \tag{4.13}$$

and

$$X_2(\underline{q}) = - \sum_j \frac{\partial n^0_{qj}}{\partial T} \underline{V}_{\underline{q}j} \cdot \nabla T \quad , \tag{4.14}$$

we may summarize the electron and phonon Boltzmann equations in the form

$$\underline{X} = \underline{P}(\underline{\phi})$$

where explicit dependence on $\underline{k}$ and $\underline{q}$ has been suppressed.

If

$$\underline{\phi}(\underline{k};\underline{q}) = (\Phi_{\underline{k}}, \Psi_{\underline{q}}) \quad \text{and} \quad \underline{\phi}'(\underline{k};\underline{q}) = (\Phi'_{\underline{k}}, \Psi'_{\underline{q}}) \quad ,$$

by (4.11) and (4.8),

$$<\underline{\phi}', \underline{P}(\underline{\phi})> = \sum_{\underline{k}\sigma} \Phi'_{\underline{k}} P_1(\underline{\phi}) + \sum_{\substack{\underline{q} \\ (F.\overline{B}.Z.)}} \Psi'_{\underline{q}} P_2(\underline{\phi}) \quad .$$

We use the expressions (4.9) and (4.10), interchange $\underline{k}$ and $\underline{k}'$ in the second term of the first summation and use (4.6); in the second summation, the sum over $\underline{k}$, $\underline{q}$ and $\underline{\kappa}_n$ is equivalent to a sum over $\underline{k}$ and $\underline{k}'$ with $\underline{q} = (\underline{k}'-\underline{k})_R$. The result is

$$<\underline{\phi}', \underline{P}(\underline{\phi})> = \beta \sum_{\underline{k}\sigma\underline{k}'} (\Phi'_{\underline{k}}+\Psi'_{\underline{q}}-\Phi'_{\underline{k}'})(\Phi_{\underline{k}}+\Psi_{\underline{q}}-\Phi_{\underline{k}'}) \delta_{(\underline{k}'-\underline{k})_R,\underline{q}} P^{\underline{k}'}_{\underline{k};\underline{q}} \quad . \tag{4.15}$$

In particular,

$$\langle \underline{\phi}, \underline{P}(\underline{\phi}) \rangle = \beta \sum_{\underline{k}\sigma\underline{k}'} (\Phi_{\underline{k}} + \Psi_{\underline{q}} - \Phi_{\underline{k}'})^2 \, \delta(\underline{k}'-\underline{k})_{R}, \underline{q} \; P^{\underline{k}'}_{\underline{k};\underline{q}} \qquad (4.16)$$

The operator $\underline{P}$ is obviously linear from its definition (4.8);
moreover, from (4.15) we have $\langle \underline{\phi}', \underline{P}(\underline{\phi}) \rangle = \langle \underline{\phi}, \underline{P}(\underline{\phi}') \rangle$, and
from (4.16) we have $\langle \underline{\phi}, \underline{P}(\underline{\phi}) \rangle \geq 0$. From these properties one
can prove [11] the variational principle: Of all functions
$\underline{\phi}$ which satisfy $\langle \underline{\phi}, \underline{P}(\underline{\phi}) \rangle = \langle \underline{\phi}, \underline{X} \rangle$, the solution
$\underline{\phi}(\underline{k};\underline{q}) = (\Phi_{\underline{k}}, \Psi_{\underline{q}})$ of the coupled Boltzmann equations (4.2)
and (4.5) gives to

$$\frac{\langle \underline{\phi}, \underline{P}(\underline{\phi}) \rangle}{\{\langle \underline{\phi}, \underline{X} \rangle\}^2} \qquad (4.17)$$

its minimum value.

In order to apply the variational principle to the
calculation of transport coefficients, we expand the
deviation functions in terms of known trial functions
$\phi_i(\underline{k})$, $i = 1, \ldots, M$, and $\phi_L(\underline{q})$:

$$\Phi_{\underline{k}} = \sum_{i=1}^{M} \eta_i \phi_i(\underline{k}) \qquad (4.18)$$

$$\Psi_{\underline{q}} = \eta_L \phi_L(\underline{q}) \qquad (4.19)$$

where η_i ($i = 1, \ldots, M$) and η_L are arbitrary coefficients
to be determined by the minimization of (4.17). Contact
with transport properties is made by noting that the
electric current density

$$\underline{J} = \frac{1}{\Omega} \sum_{\underline{k}\sigma} e\underline{V}_{\underline{k}} f_{\underline{k}}$$

may be written, using (3.13), (4.18), and the fact that $\underline{J}$ is zero in the equilibrium situation, as

$$\underline{J} = \frac{1}{\Omega} \sum_{i=1}^{M} \eta_i \underline{J}_i \qquad (4.20)$$

where

$$\underline{J}_i = - \sum_{\underline{k}\sigma} e\underline{V}_{\underline{k}} \phi_i(\underline{k}) \frac{\partial f_{\underline{k}}^{0}}{\partial \varepsilon_{\underline{k}}} \qquad (4.21)$$

for $i = 1, \ldots, M$.

If we introduce

$$\underline{J}_L = 0 \qquad (4.22)$$

we may write (4.20) in the convenient form

$$\underline{J} = \frac{1}{\Omega} \sum_{i=1,\ldots,M;L} \eta_i \underline{J}_i \quad . \qquad (4.23)$$

Furthermore, the heat current density, given by [11, 15]

$$\underline{U} = \frac{1}{\Omega} \sum_{\underline{k}\sigma} \underline{V}_{\underline{k}} (\varepsilon_{\underline{k}} - \mu) f_{\underline{k}} + \frac{1}{\Omega} \sum_{\substack{\underline{q}j \\ (F.B.Z.)}} \underline{V}_{\underline{q}j} \hbar\omega_j(\underline{q}) n_{\underline{q}j} \quad ,$$

may be written, using (3.13), (3.14), (4.18), (4.19), and the fact that $\underline{U}$ is zero in the equilibrium situation, as

$$\underline{U} = \frac{1}{\Omega} \underset{i=1,\ldots,M;L}{\Sigma} \eta_i \underline{U}_i \tag{4.24}$$

where

$$\underline{U}_i = - \underset{\underline{k}\sigma}{\Sigma} \underline{V}_{\underline{k}} (\varepsilon_{\underline{k}} - \mu) \phi_i(\underline{k}) \frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \tag{4.25}$$

for $i = 1, \ldots, M$, and

$$\underline{U}_L = - \underset{\substack{\underline{q}j \\ (F.\overline{B}.Z.)}}{\Sigma} \underline{V}_{\underline{q}j} \hbar\omega_j(\underline{q}) \phi_L(\underline{q}) \frac{\partial n^0_{\underline{q}j}}{\partial(\hbar\omega_j(\underline{q}))} \quad . \tag{4.26}$$

Using (4.18) and (4.19) in (4.16), we have

$$\langle \underline{\phi}, \underline{P}(\underline{\phi}) \rangle = \underset{\substack{i=1,\ldots,M;L \\ j=1,\ldots,M;L}}{\Sigma} \eta_i \eta_j P_{ij} \tag{4.27}$$

where

$$P_{ij} = \beta \underset{\underline{k}\sigma\underline{k}'}{\Sigma} [\phi_i(\underline{k}) - \phi_i(\underline{k}')][\phi_j(\underline{k}) - \phi_j(\underline{k}')]\delta_{(\underline{k}'-\underline{k})_R,\underline{q}} P^{\underline{k}'}_{\underline{k};\underline{q}} \tag{4.28}$$

for $i = 1, \ldots, M$ and $j = 1, \ldots, M$,

$$P_{iL} = \beta \underset{\underline{k}\sigma\underline{k}'}{\Sigma} [\phi_i(\underline{k}) - \phi_i(\underline{k}')]\phi_L(\underline{q})\delta_{(\underline{k}'-\underline{k})_R,\underline{q}} P^{\underline{k}'}_{\underline{k};\underline{q}} \tag{4.29}$$

for $i = 1, \ldots, M$, and

$$P_{LL} = \beta \underset{\underline{k}\sigma\underline{k}'}{\Sigma} [\phi_L(\underline{q})]^2 \delta_{(\underline{k}'-\underline{k})_R,\underline{q}} P^{\underline{k}'}_{\underline{k};\underline{q}} \quad . \tag{4.30}$$

From (4.11), (4.12), (4.18), (4.19), (4.21), (4.22), (4.25), and (4.26), and also

$$\frac{\partial n_{\underline{q}j}^{0}}{\partial T} = \frac{-\hbar\omega_{j}(\underline{q})}{T} \frac{\partial n_{\underline{q}j}^{0}}{\partial(\hbar\omega_{j}(\underline{q}))} \quad,$$

we have

$$<\underline{\phi},\underline{X}> = \sum_{i=1,\ldots,M;L} \eta_{i}[\underline{J}_{i}\cdot\underline{E} - \frac{1}{T}\underline{U}_{i}\cdot\nabla T] \quad. \tag{4.31}$$

Using (4.27) and (4.31) we minimize (4.17) with respect to η_{i} (i = 1, ..., M) and η_{L}; moreover, these parameters are determined by this procedure and we then use them in (4.23) and (4.24). The result is [11]

$$\underline{J} = \frac{1}{\Omega} \sum_{ij} \underline{J}_{i}(P^{-1})_{ij}\underline{J}_{j}\cdot\underline{E} - \frac{1}{\Omega T} \sum_{ij} \underline{J}_{i}(P^{-1})_{ij}\underline{U}_{j}\cdot\nabla T \tag{4.32}$$

$$\underline{U} = \frac{1}{\Omega} \sum_{ij} \underline{U}_{i}(P^{-1})_{ij}\underline{J}_{j}\cdot\underline{E} - \frac{1}{\Omega T} \sum_{ij} \underline{U}_{i}(P^{-1})_{ij}\underline{U}_{j}\cdot\nabla T \tag{4.33}$$

where the sum is over i = 1, ..., M;L and j = 1, ..., M:L, and P^{-1} is the inverse of the matrix P_{ij}. The transport coefficients such as electrical resistivity, thermal conductivity, and the thermopower can be obtained directly from (4.32) and (4.33).

4.2   Phonon-Limited Electrical Resistivity

In this section we derive a formula for the ideal, phonon-limited electrical resistivity in terms of effective phonon frequency distributions, and demonstrate that this reduces to the forms previously obtained [20, 21, 22, 23] for a spherical Fermi surface (F.S.). The electrical conductivity tensor, $\underline{\sigma}$, is defined by

$$\underline{J} = \underline{\sigma} \cdot \underline{E} \quad .$$

Using (4.32) in the absence of a temperature gradient, we have

$$\underline{\underline{\sigma}} = \frac{1}{\Omega} \sum_{ij} \underline{J}_i (P^{-1})_{ij} \underline{J}_j \tag{4.34}$$

where $i,j = 1, \ldots, M;L$. If we neglect phonon drag effects by assuming

$$\Psi_{\underline{q}} \equiv 0 \quad ,$$

which, according to Bass [16], is likely to be a good approximation for most metals above 5-10°K, and use only a single trial function $\phi_1(\underline{k})$, (4.34) becomes

$$\underline{\underline{\sigma}} = \frac{1}{\Omega P_{11}} \underline{J}_1 \underline{J}_1 \quad . \tag{4.35}$$

We note that calculations involving more than one trial function could be done by using (4.34); Greene and Kohn [25] and Ekin and co-workers [17, 18] have done this for the case of a spherical F.S..

For the trial function we use the usual [11, 12] lowest order approximation

$$\phi_1(\underline{k}) = e\tau\underline{V}_{\underline{k}} \cdot \underline{E} \qquad (4.36)$$

where τ is some characteristic relaxation time (which is unimportant since it will cancel out in (4.35)). One way of motivating this choice is to consider the Boltzmann equation for the conduction electrons, (3.4), in the absence of a temperature gradient,

$$\frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \underline{V}_{\underline{k}} \cdot e\underline{E} = \frac{\partial f_{\underline{k}}}{\partial t}]_{scatt} \quad,$$

and make the phenomenological assumption [7]

$$\frac{\partial f_{\underline{k}}}{\partial t}]_{scatt} = - \frac{(f_{\underline{k}} - f_{\underline{k}}^0)}{\tau} \quad. \qquad (4.37)$$

The use of definition (3.13) then leads to the solution (4.36). We stress that we are not making the approximation (4.37) in the following; we simply use (4.36) as a given trial function.

It is shown in Appendix A that the use of the trial function (4.36) in the expression (4.35) for the conductivity tensor leads to the form

$$\underline{\underline{\sigma}}^V = \frac{e^2 \hbar}{\Omega \beta \pi} \left\{ \left[\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, \underline{V}_{\underline{k}} \underline{V}_{\underline{k}} \cdot \underline{u} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \, \underline{V}_{\underline{k}'} \underline{V}_{\underline{k}'} \cdot \underline{u} \right] \Big/ \left[\int_0^\infty d\omega R(\omega) \right. \right.$$

$$\left. \left. \times \left\{ \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} [\underline{V}_{\underline{k}} \cdot \underline{u} - \underline{V}_{\underline{k}'} \cdot \underline{u}]^2 \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega - \omega_j(\underline{k}'-\underline{k})) \right\} \right] \right\}$$

(4.38)

where the surface integrals in $\underline{k}$-space are over the Fermi surface, $\underline{u}$ is a unit vector in the direction of $\underline{E}$, and V denotes the variational method. The approximations used in deriving (4.38) are discussed in Appendix A, and the function $R(\omega)$ is defined by

$$R(\omega) = \frac{\hbar\omega}{(e^{\beta\hbar\omega}-1)(1-e^{-\beta\hbar\omega})} \quad . \tag{4.39}$$

We note that $R(\omega)$ also depends on the temperature.

The electrical resistivity tensor, $\underline{\underline{\rho}}$, is the inverse of the conductivity tensor $\underline{\underline{\sigma}}$,

$$\underline{\underline{\rho}}^{-1} = \underline{\underline{\sigma}} \quad , \tag{4.40}$$

and therefore (4.38) gives us an expression for the resistivity $\underline{\underline{\rho}}^V$ in the variational method.

So far we have not utilized any of the symmetry properties of the crystal lattice involved; however, we now specialize our results and consider a lattice with cubic

symmetry. In this case, the conductivity tensor is

$$\underline{\underline{\sigma}} = \begin{pmatrix} \sigma & 0 & 0 \\ 0 & \sigma & 0 \\ 0 & 0 & \sigma \end{pmatrix} . \tag{4.41}$$

For a lattice with cubic symmetry, the F.S. must also have this symmetry; therefore, suppressing $\underline{k}$ dependence,

$$\int_{F.S.} \frac{dS}{|\underline{V}|} V_x^2 = \ldots = \frac{1}{3} \int_{F.S.} \frac{dS}{|\underline{V}|} |\underline{V}|^2 , \tag{4.42}$$

whereas cross terms such as

$$\int_{F.S.} \frac{dS}{|\underline{V}|} V_x V_y = 0 . \tag{4.43}$$

This is easily seen from the definition $\underline{V}_{\underline{k}} \equiv \frac{1}{\hbar} \frac{\partial \varepsilon_{\underline{k}}}{\partial \underline{k}}$. Consider the x-component of

$$\int_{F.S.} \frac{dS}{|\underline{V}|} \underline{V} \ \underline{V} \cdot \underline{u}$$

which is, by (4.42) and (4.43),

$$\frac{1}{3} u_x \int_{F.S.} \frac{dS}{|\underline{V}|} |\underline{V}|^2 .$$

Thus we have

$$\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \cdot \underline{V}_{\underline{k}} \, \underline{V}_{\underline{k}} \cdot \underline{u} = \frac{1}{3} \, \underline{u} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2 \quad .$$

The tensor character of (4.38) is now given by the dyadic $\underline{u}\underline{u}$; moreover, this may be replaced by unity in the scalar conductivity σ defined by (4.41), since $\underline{u}$ is a unit vector. Since the x, y, and z directions are equivalent in cubic symmetry, we may average over directions of $\underline{u}$ and replace $[(\underline{V}_{\underline{k}} - \underline{V}_{\underline{k}'}) \cdot \underline{u}]^2$ by $\frac{1}{3} |\underline{V}_{\underline{k}} - \underline{V}_{\underline{k}'}|^2$ in the denominator of (4.38). The resultant resistivity from (4.38), (4.40), and (4.41) is

$$\rho^V(T) = \frac{3\Omega\pi}{e^2 \hbar k_B T} \left[\int_0^\infty d\omega R(\omega) \left\{ \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} |\underline{V}_{\underline{k}} - \underline{V}_{\underline{k}'}|^2 \right. \right.$$

$$\left. \left. \times \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega - \omega_j(\underline{k}' - \underline{k})) \right\} \right] \Big/ \left([\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} |\underline{V}_{\underline{k}}|^2]^2 \right) \qquad (4.44)$$

where the temperature (T) dependence is now explicit and we again note that $R(\omega)$ also depends on T.

We now proceed to the definition of effective phonon frequency distributions analogous to those previously used [20, 21, 22, 23] for a spherical F.S.. For convenience, we incorporate a volume factor in the electron-phonon coupling constant:

$$|\tilde{g}_{\underline{k}',\underline{k};j}|^2 = \Omega |g_{\underline{k}',\underline{k};j}|^2 \quad . \qquad (4.45)$$

In practical terms, this means that the factor of $\frac{1}{N}$ in the square root of Eq. (2.27) is replaced by $(r\Omega_0)$, where r is the number of ions per unit cell and Ω_0 is the volume per ion. We define the isotropic (transport) effective phonon frequency distribution by

$$\beta_{tr}^2 F(\omega) = \frac{1}{32\pi^4 \hbar^2} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2 \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left(1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}\right)$$

$$\times \sum_j |\tilde{g}_{\underline{k}',\underline{k};j}|^2 \frac{1}{\hbar} \delta(\omega - \omega_j(\underline{k}' - \underline{k})) \qquad (4.46)$$

where the subscript tr denotes transport. It is convenient at this point to also define an anisotropic (transport) effective phonon frequency distribution by

$$\beta_{tr}^2 F(\omega, \underline{k}) = \frac{1}{8\pi^3 \hbar} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left(1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}\right)$$

$$\times \sum_j |\tilde{g}_{\underline{k}',\underline{k};j}|^2 \frac{1}{\hbar} \delta(\omega - \omega_j(\underline{k}' - \underline{k})) \quad . \qquad (4.47)$$

From (4.46) and (4.47), we then have

$$\beta_{tr}^2 F(\omega) = \frac{1}{4\pi\hbar} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2 \, \beta_{tr}^2 F(\omega, \underline{k}) \quad . \qquad (4.48)$$

The reason for the choice of numerical coefficients in (4.46) and (4.47) will become evident in the following.

For the case of a free-electron spherical F.S., the anisotropic and isotropic transport effective phonon frequency distributions previously used [20, 21, 22, 23] are

$$\alpha^2_{tr} F(\omega, \underline{k}) = N(0)_{F.E.} \int_{F.S.} \frac{d\Omega_{\underline{k}'}}{4\pi} (1 - \cos(\underline{k}, \underline{k}'))$$

$$\times \sum_j |g_{\underline{k}', \underline{k}; j}|^2 \frac{1}{\hbar} \delta(\omega - \omega_j(\underline{k}' - \underline{k})) \qquad (4.49)$$

and

$$\alpha^2_{tr} F(\omega) = \int_{F.S.} \frac{d\Omega_{\underline{k}}}{4\pi} \alpha^2_{tr} F(\omega, \underline{k}) \quad , \qquad (4.50)$$

where the integrals are over a solid angle at the F.S., $\cos(\underline{k}, \underline{k}')$ is the cosine of the angle between $\underline{k}$ and $\underline{k}'$ (which are on the F.S.), and

$$N(0)_{F.E.} = \frac{\Omega m k_F}{2\pi^2 \hbar^2} \qquad (4.51)$$

is the free-electron single spin density of states in energy at the Fermi energy ε_F, with m the electron mass and k_F the Fermi wavevector defined by $\varepsilon_F = \hbar^2 k_F^2 / 2m$.

For a free-electron spherical F.S., $V_{\underline{k}} = \frac{\hbar}{m} \underline{k}$, and

$$\int_{F.S.} dS_{\underline{k}} = k_F^2 \int_{F.S.} d\Omega_{\underline{k}} \quad ;$$

therefore, the distributions (4.46) and (4.47) take the forms

$$[\beta_{tr}^2 F(\omega)]_{\substack{spherical \\ F.S.}} = \frac{k_F^3}{m} \alpha_{tr}^2 F(\omega) \tag{4.52}$$

and

$$[\beta_{tr}^2 F(\omega,\underline{k})]_{\substack{spherical \\ F.S.}} = \alpha_{tr}^2 F(\omega,\underline{k}) \quad . \tag{4.53}$$

Since $\alpha_{tr}^2 F(\omega)$ and $\alpha_{tr}^2 F(\omega,\underline{k})$ are dimensionless, we see from (4.52) and (4.53) that $\beta_{tr}^2 F(\omega,\underline{k})$ is dimensionless whereas $\beta_{tr}^2 F(\omega)$ has dimensions $[(length)^3 (mass)]^{-1}$.

Consider now the expression (4.44) for $\rho^V(T)$. The factor $|\underline{V}_{\underline{k}} - \underline{V}_{\underline{k}'}|^2$ is, on expanding,

$$\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}} + \underline{V}_{\underline{k}'} \cdot \underline{V}_{\underline{k}'} - 2\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'} \quad ;$$

hence, if we interchange $\underline{k}$ and $\underline{k}'$ in the integration of the middle term above (noting that $|g_{\underline{k}',\underline{k};j}|^2$ and $\omega_j(\underline{k}'-\underline{k})$ are invariant under this interchange), we may replace this expression by

$$2|\underline{V}_{\underline{k}}|^2 (1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}) \quad .$$

Then (4.44) and (4.46) lead to the expression

$$\rho^V(T) = \frac{192\pi^5\hbar^2}{e^2 k_B T} \frac{\int_0^\infty d\omega R(\omega) \beta_{tr}^2 F(\omega)}{[\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} |\underline{V}_{\underline{k}}|^2]^2} \qquad . \tag{4.54}$$

The notable feature of this expression is that, aside from the 1/T factor, all temperature dependence is contained in the function $R(\omega)$. The effect of the phonons is contained in $\beta_{tr}^2 F(\omega)$ and this need only be calculated once, and not for each temperature.

For the case of a free-electron spherical F.S., we have from (4.54) and (4.52),

$$[\rho^V(T)]_{\substack{\text{spherical} \\ \text{F.S.}}} = \frac{m}{ne^2} \frac{4\pi}{k_B T} \int_0^\infty d\omega R(\omega) \alpha_{tr}^2 F(\omega) \tag{4.55}$$

where

$$n = \frac{k_F^3}{3\pi^2}$$

is the number of conduction electrons per unit volume. Equation (4.55) is the usual result [21, 23] for a spherical F.S..

4.3   Thermal Resistivity (Electronic Contribution)

In this section we derive a formula for the ideal, phonon-limited electronic contribution to the thermal resistivity in terms of effective phonon frequency distributions in which we do not assume the F.S. to be spherical.   The thermal conductivity tensor, $\underline{\underline{\kappa}}$, is defined by

$$\underline{U} = - \underline{\underline{\kappa}} \cdot \nabla T$$

where $\underline{U}$ is the heat current density (Section 4.1). According to Ziman [11], the usual experimental situation for measuring thermal conductivity is that the electric current density $\underline{J}$ is zero.   Considering Eq. (4.32), we would have an equation for $\underline{E}$ in terms of ∇T (related by the thermopower) which could be used in Eq. (4.33) for $\underline{U}$. It is conventional [11] to ignore this (thermopower) contribution to the thermal conductivity, in which case we obtain from Eq. (4.33)

$$\underline{\underline{\kappa}} = \frac{1}{\Omega T} \sum_{ij} \underline{U}_i (P^{-1})_{ij} \underline{U}_j \tag{4.56}$$

where $i,j = 1, \ldots, M;L$. We shall neglect phonon drag effects and use only a single trial function $\phi_2(\underline{k})$, and we then have

49

$$\underline{\underline{\kappa}} = \frac{1}{\Omega T F_{22}} \underline{U}_2 \underline{U}_2 \quad .$$

(4.57)

Calculations involving more than one trial function could be done by using (4.56) and Ekin [24] has done this for the case of a spherical F.S..

For the trial function we use the usual [11, 24] lowest order approximation

$$\phi_2(\underline{k}) = - \tau \frac{(\epsilon_{\underline{k}} - \mu)}{T} \underline{V}_{\underline{k}} \cdot \nabla T$$

(4.58)

where τ is some characteristic relaxation time (which is unimportant since it cancels in Eq. (4.57)). This choice can be motivated by considering the Boltzmann equation (3.4) for the conduction electrons in the absence of an electric field,

$$- \frac{\partial f_{\underline{k}}^0}{\partial \epsilon_{\underline{k}}} \underline{V}_{\underline{k}} \cdot \nabla T \frac{(\epsilon_{\underline{k}} - \mu)}{T} = \frac{\partial f_{\underline{k}}}{\partial t} \bigg]_{scatt} \quad ,$$

and again making the phenomenological assumption (4.37). By definition (3.13) this leads to (4.58), but we stress again, as in Section 4.2, that we do not make the approximation (4.37) and we simply use (4.58) as a given trial function.

It is shown in Appendix C that the use of the trial function (4.58) in the expression (4.57) for the thermal conductivity tensor leads to the form

$$\underline{\underline{\kappa}}^V = \frac{\pi k_B^3 T^2 \hbar}{6\Omega} \left\{ \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \underline{V}_{\underline{k}} \underline{V}_{\underline{k}} \cdot \underline{u} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \underline{V}_{\underline{k}'} \underline{V}_{\underline{k}'} \cdot \underline{u} \right\} / \left\{ \int_0^\infty d\omega R(\omega) \right.$$

$$\times \left\{ \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left[(\underline{V}_{\underline{k}} \cdot \underline{u})^2 (1 + (\frac{\hbar\omega}{\pi k_B T})^2) \right. \right.$$

$$\left. \left. - (\underline{V}_{\underline{k}} \cdot \underline{u})(\underline{V}_{\underline{k}'} \cdot \underline{u})(1 - \frac{1}{2}(\frac{\hbar\omega}{\pi k_B T})^2) \right] \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega - \omega_j(\underline{k}' - \underline{k})) \right\} \right\}$$

$$(4.59)$$

where the surface integrals in $\underline{k}$-space are over the Fermi
surface (F.S.), $\underline{u}$ is a unit vector in the direction of ∇T,
V denotes the variational method, and $R(\omega)$ is defined by
(4.39) and depends on the temperature (T). The
approximations used in deriving (4.59) are discussed in
Appendix C.

The thermal resistivity tensor, $\underline{\underline{W}}$, is the inverse
of the thermal conductivity tensor,

$$\underline{\underline{W}} = \underline{\underline{\kappa}}^{-1} \quad , \tag{4.60}$$

and thus (4.59) gives us an expression for the electronic
contribution to the thermal resistivity, $\underline{\underline{W}}^V$, in the
variational method.

The result (4.59) is general in that we have not
used any of the symmetry properties of the crystal lattice
involved. We now specialize our results to consider a

lattice with cubic symmetry, in which case

$$
\underline{\underline{\kappa}} = \begin{pmatrix} \kappa & 0 & 0 \\ 0 & \kappa & 0 \\ 0 & 0 & \kappa \end{pmatrix} . \tag{4.61}
$$

For cubic symmetry we may write

$$
\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \underline{V}_{\underline{k}} \underline{V}_{\underline{k}} \cdot \underline{u} = \frac{1}{3} \underline{u} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} |\underline{V}_{\underline{k}}|^2
$$

as in Section 4.2, and by (4.61) the dyadic $\underline{u}\underline{u}$ in (4.59) may be replaced by unity in the expression for the scalar thermal conductivity κ^V. The equivalence of the x, y, and z directions in cubic symmetry implies that $(\underline{V}_{\underline{k}} \cdot \underline{u})^2$ may be replaced by $\frac{1}{3} |\underline{V}_{\underline{k}}|^2$ and $(\underline{V}_{\underline{k}} \cdot \underline{u})(\underline{V}_{\underline{k}'} \cdot \underline{u})$ by $\frac{1}{3} \underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}$ in (4.59) by averaging over directions of $\underline{u}$. The resultant electronic contribution to the thermal resistivity is

$$
W^V(T) = \frac{18\Omega}{\pi k_B^3 T^2 \hbar} \left(\int_0^\infty d\omega R(\omega) \left\{ \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left[(|\underline{V}_{\underline{k}}|^2 - \underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}) \right. \right. \right.
$$

$$
\left. \times \left(1 - \frac{1}{2}\left(\frac{\hbar\omega}{\pi k_B T}\right)^2\right) + \frac{3}{2}\left(\frac{\hbar\omega}{\pi k_B T}\right)^2 |\underline{V}_{\underline{k}}|^2 \right] \sum_j |g_{\underline{k}',\underline{k};j}|^2
$$

$$
\left. \times \delta(\omega - \omega_j(\underline{k}' - \underline{k})) \right\} \left. \middle/ \left(\left[\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} |\underline{V}_{\underline{k}}|^2 \right]^2 \right) \right. \tag{4.62}
$$

where the temperature dependence is now explicit and we recall that $R(\omega)$ also depends on the temperature.

In addition to the transport effective phonon frequency distributions already defined in Section 4.2, we shall introduce another two which are generalizations of the anisotropic and isotropic distributions for a spherical F.S. [4, 6, 23], which are given by

$$\alpha^2 F(\omega,\underline{k}) = N(0)_{F.E.} \int_{F.S.} \frac{d\Omega_{\underline{k}'}}{4\pi} \sum_j |g_{\underline{k}',\underline{k};j}|^2$$

$$\times \frac{1}{\hbar} \delta(\omega - \omega_j(\underline{k}'-\underline{k})) \tag{4.63}$$

and

$$\alpha^2 F(\omega) = \int_{F.S.} \frac{d\Omega_{\underline{k}}}{4\pi} \alpha^2 F(\omega,\underline{k}) \quad . \tag{4.64}$$

As in (4.49) and (4.50), the integrals are over a solid angle at the F.S., and $N(0)_{F.E.}$ is given by (4.51). We define the isotropic effective phonon frequency distribution by

$$\beta^2 F(\omega) = \frac{1}{32\pi^4 \hbar^2} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} |\underline{V}_{\underline{k}}|^2 \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|}$$

$$\times \sum_j |\tilde{g}_{\underline{k}',\underline{k};j}|^2 \frac{1}{\hbar} \delta(\omega - \omega_j(\underline{k}'-\underline{k})) \tag{4.65}$$

and the anisotropic distribution by

$$\beta^2 F(\omega,\underline{k}) = \frac{1}{8\pi^3 \hbar} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \sum_j |\tilde{g}_{\underline{k}',\underline{k};j}|^2 \frac{1}{\hbar} \delta(\omega - \omega_j(\underline{k}' - \underline{k})) \quad .$$

(4.66)

From (4.65) and (4.66) we see that

$$\beta^2 F(\omega) = \frac{1}{4\pi \hbar} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} |\underline{V}_{\underline{k}}|^2 \beta^2 F(\omega,\underline{k}) \quad .$$

(4.67)

We recall that

$$|\tilde{g}_{\underline{k}',\underline{k};j}|^2 = \Omega |g_{\underline{k}',\underline{k};j}|^2 \quad .$$

(4.45)

As in Section (4.2), for a free-electron spherical F.S., we have the relations

$$[\beta^2 F(\omega)]_{\substack{\text{spherical} \\ \text{F.S.}}} = \frac{k_F^3}{m} \alpha^2 F(\omega)$$

(4.68)

and

$$[\beta^2 F(\omega,\underline{k})]_{\substack{\text{spherical} \\ \text{F.S.}}} = \alpha^2 F(\omega,\underline{k}) \quad ,$$

(4.69)

which imply that $\beta^2 F(\omega,\underline{k})$ is dimensionless whereas $\beta^2 F(\omega)$ has dimensions $[(\text{length})^3 (\text{mass})]^{-1}$.

We now consider the expression (4.62) for the thermal resistivity. Using the definitions (4.46) and (4.65) and the Lorentz number [11]

$$L_0 = \frac{\pi^2 k_B^2}{3e^2} \quad , \tag{4.70}$$

we have

$$W^V(T) = \frac{1}{L_0 T} \frac{4\pi}{k_B T} \frac{48\pi^4 \hbar^2}{e^2} \left\{ \int_0^\infty d\omega R(\omega) [(1 - \frac{1}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2) \beta_{tr}^2 F(\omega) \right.$$

$$\left. + \frac{3}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2 \beta^2 F(\omega)] \right\} / \left\{ [\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} |\underline{V}_{\underline{k}}|^2]^2 \right\} \quad . \tag{4.71}$$

This expression has the advantage that the effect of the phonons is contained in the distributions $\beta_{tr}^2 F(\omega)$ and $\beta^2 F(\omega)$ which are independent of temperature and need only be calculated once.

For the case of a free-electron spherical F.S. we have, from (4.71), (4.52), and (4.68),

$$[W^V(T)]_{\substack{spherical \\ F.S.}} = \frac{1}{L_0 T} \frac{m}{ne^2} \frac{4\pi}{k_B T} \int_0^\infty d\omega R(\omega)$$

$$\times [(1 - \frac{1}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2) \alpha_{tr}^2 F(\omega)$$

$$+ \frac{3}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2 \alpha^2 F(\omega)] \tag{4.72}$$

where n, the number of conduction electrons per unit volume, is given by

$$n = \frac{k_F^3}{3\pi^2} \quad .$$

CHAPTER V

FORMAL TRANSPORT THEORY: SCATTERING TIME APPROXIMATION

5.1   Phonon-Limited Electrical Resistivity

In this section we obtain a formula, written in terms of the anisotropic transport effective phonon frequency distribution defined in Section 4.2, for the ideal, phonon-limited electrical resistivity in the scattering time (S.T.) approximation introduced by Robinson and Dow [26].   Our formulation will not assume a spherical Fermi surface, and cubic symmetry will be introduced as a special case.

Neglecting phonon drag effects (see Section 4.2), the linearized Boltzmann transport equation for the conduction electrons (3.28) is, in the absence of a temperature gradient,

$$\frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \, \underline{V}_{\underline{k}} \cdot e\underline{E} = \beta \sum_{\underline{k}'} (\Phi_{\underline{k}'} - \Phi_{\underline{k}}) f^0_{\underline{k}} (1 - f^0_{\underline{k}'}) W^{\underline{k}'}_{\underline{k}} \qquad (5.1)$$

where $W^{\underline{k}'}_{\underline{k}}$ is given by (3.29).   In the scattering time method, the electron deviation function $\Phi_{\underline{k}}$ is written as [9, 26, 27]

$$\Phi_{\underline{k}} = e\underline{\Lambda}_{\underline{k}} \cdot \underline{E} \qquad (5.2)$$

in terms of an unknown vector mean free path for the electrons, $\underline{\Lambda}_{\underline{k}}$, which is independent of $\underline{E}$. Since $\underline{\Lambda}_{\underline{k}}$ is approximately parallel to the electron velocity $\underline{V}_{\underline{k}}$, a temperature dependent anisotropic scattering time, $\tau(\underline{k},T)$, may be defined by the approximation [27]

$$\underline{\Lambda}_{\underline{k}} = \tau(\underline{k},T)\underline{V}_{\underline{k}} \quad . \tag{5.3}$$

At this point we note the similarity of (5.2) and (5.3) to the elementary solution (4.36) of Section 4.2. Robinson and Dow [26] showed that it was possible to obtain an approximation to the scattering time $\tau(\underline{k},T)$ from the Boltzmann equation (5.1) (We note that Robinson and Dow considered cubic systems and assumed a spherical F.S. in their calculations.).

It is shown in Appendix D that inserting the deviation function (5.2) in (5.1) and integrating over $\varepsilon_{\underline{k}}$ leads to

$$\underline{V}_{\underline{k}} = \frac{\beta\Omega}{2\pi^2\hbar^2} \int_0^\infty d\omega R(\omega) \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} [\underline{\Lambda}_{\underline{k}} - \underline{\Lambda}_{\underline{k}'}]$$

$$\times \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega - \omega_j(\underline{k}'-\underline{k})) \tag{5.4}$$

where $\underline{k}$ is on the F.S., $R(\omega)$ is given by Eq. (4.39) and depends on the temperature, (3.29) has been used, and the surface integral in $\underline{k}'$-space is over the Fermi surface.

Using (5.3) we may write

$$\underline{\Lambda}_{\underline{k}} - \underline{\Lambda}_{\underline{k}'} = \tau(\underline{k})[\underline{V}_{\underline{k}} - \underline{V}_{\underline{k}'}] + [\tau(\underline{k}) - \tau(\underline{k}')]\underline{V}_{\underline{k}'} \qquad (5.5)$$

where the temperature dependence has been suppressed. We use (5.5) in (5.4) and take the dot product of $\underline{V}_{\underline{k}}$ ($\underline{k}$ on the F.S.) with Eq. (5.4) to obtain

$$1 = \frac{\beta\Omega}{2\pi^2\hbar^2} \int_0^\infty d\omega R(\omega) \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left\{ \tau(\underline{k}) \left[1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}\right] \right.$$

$$\left. + [\tau(\underline{k}) - \tau(\underline{k}')] \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2} \right\} \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega - \omega_j(\underline{k}' - \underline{k})) \qquad (5.6)$$

where $\underline{k}$ is on the F.S..

The first term in brackets in (5.6) may be written as

$$\tau(\underline{k})\left[1 - \frac{|\underline{V}_{\underline{k}'}|}{|\underline{V}_{\underline{k}}|} \cos(\underline{V}_{\underline{k}}, \underline{V}_{\underline{k}'})\right] \qquad (5.7)$$

where $\cos(\underline{V}_{\underline{k}}, \underline{V}_{\underline{k}'})$ is the cosine of the angle between $\underline{V}_{\underline{k}}$ and $\underline{V}_{\underline{k}'}$; hence, it is expected to be mainly positive and, in fact, for a spherical F.S. it would be strictly greater than or equal to zero. The second term in brackets in (5.6) may be written as

$$[\tau(\underline{k}) - \tau(\underline{k}')] \frac{|\underline{V}_{\underline{k}'}|}{|\underline{V}_{\underline{k}}|} \cos(\underline{V}_{\underline{k}}, \underline{V}_{\underline{k}'}) \tag{5.8}$$

and is both positive and negative, and has a number of zeroes not shared by (5.7). It vanishes for scattering by 90° when the cosine vanishes; moreover, whenever $\underline{k}'$ belongs to the star [28] of $\underline{k}$, $\tau(\underline{k}')$ will be equal to $\tau(\underline{k})$ by symmetry and (5.8) will again vanish (for a general point $\underline{k}$ this will happen 48 times in cubic symmetry, 24 times in hexagonal symmetry, and so on). The positive and negative contributions to (5.8) will lead to cancellations, and we make the reasonable approximation of retaining only the term (5.7). Writing (5.6) in the form

$$\frac{1}{\tau(\underline{k})} = \frac{\beta\Omega}{2\pi^2\hbar^2} \int_0^\infty d\omega R(\omega) \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left\{ [1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}] \right.$$

$$\left. + [1 - \frac{\tau(\underline{k}')}{\tau(\underline{k})}] \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2} \right\} \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega - \omega_j(\underline{k}'-\underline{k})) , \tag{5.9}$$

our approximation can also be viewed as the first iteration of (5.9). Further iterations could be carried out, but the considerable increase in computational labour seems unwarranted at present.

Using the definition (4.47) of the anisotropic transport effective phonon frequency distribution $\beta_{tr}^2 F(\omega, \underline{k})$, we have, as a first approximation,

$$\frac{1}{\tau(\underline{k},T)} = \frac{4\pi}{k_B T} \int_0^\infty d\omega R(\omega) \beta_{tr}^2 F(\omega,\underline{k}) \quad .$$ (5.10)

We recall that $R(\omega)$ depends on the temperature whereas $\beta_{tr}^2 F(\omega,\underline{k})$ does not, and need only be calculated once and not for each temperature.

For a spherical F.S. we have, by (4.53),

$$\left[\frac{1}{\tau(\underline{k},T)}\right]_{\substack{\text{spherical} \\ \text{F.S.}}} = \frac{4\pi}{k_B T} \int_0^\infty d\omega R(\omega) \alpha_{tr}^2 F(\omega,\underline{k})$$ (5.11)

which is the usual [21, 29] result.

We now obtain an expression for the phonon-limited electrical resistivity in terms of the scattering time defined by (5.10). The electric current density is

$$\underline{J} = \frac{1}{\Omega} \sum_{\underline{k}\sigma} e\underline{V}_{\underline{k}} f_{\underline{k}}$$

as in Section 4.1. Using the fact that $\underline{J}$ is zero in the equilibrium situation we may subtract a contribution with $f_{\underline{k}}$ replaced by $f_{\underline{k}}^0$, and use (3.13) to write

$$\underline{J} = \frac{-2e}{\Omega} \sum_{\underline{k}} \underline{V}_{\underline{k}} \Phi_{\underline{k}} \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}}$$

in terms of the electron deviation function $\Phi_{\underline{k}}$, where the factor 2 comes from the sum over spin. From (5.2) we then have

$$\underline{J} = \frac{-2e^2}{\Omega} \sum_{\underline{k}} \underline{V}_{\underline{k}} \underline{\Lambda}_{\underline{k}} \frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \cdot \underline{E}$$

and therefore the electrical conductivity tensor is

$$\underline{\underline{\sigma}} = \frac{-2e^2}{\Omega} \sum_{\underline{k}} \underline{V}_{\underline{k}} \underline{\Lambda}_{\underline{k}} \frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \cdot \tag{5.12}$$

With the approximation (5.3) the conductivity is

$$\underline{\underline{\sigma}}^{ST} = \frac{-2e^2}{\Omega} \sum_{\underline{k}} \tau(\underline{k},T) \frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \underline{V}_{\underline{k}} \underline{V}_{\underline{k}} \tag{5.13}$$

where ST denotes the scattering time approximation. Using (A.4), (A.5), and (A.7) of Appendix A, (5.13) becomes

$$\underline{\underline{\sigma}}^{ST}(T) = \frac{e^2}{4\pi^3 \hbar} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \tau(\underline{k},T) \underline{V}_{\underline{k}} \underline{V}_{\underline{k}} \tag{5.14}$$

where we have neglected derivatives with respect to energy (evaluated at the F.S.) of electron velocities, the scattering time, and the surface element. The resistivity tensor is then given by

$$\underline{\underline{\rho}}^{ST}(T) = [\underline{\underline{\sigma}}^{ST}(T)]^{-1} \tag{5.15}$$

in the scattering time approximation.

We now specialize our results to a lattice with cubic symmetry, in which case the conductivity is

$$\sigma = \frac{1}{3} \, \text{Tr} \underline{\underline{\sigma}}$$

where Tr denotes the trace. Thus we have

$$\rho^{ST}(T) = \frac{12\pi^3 \hbar}{e^2} \, [\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2 \, \tau(\underline{k},T)]^{-1} \quad . \tag{5.16}$$

For purposes of comparison, we note that the variational method formula (4.54) can be written in terms of the scattering time defined by (5.10) as

$$\rho^{V}(T) = \frac{12\pi^3 \hbar}{e^2} \, \frac{\displaystyle\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2 \, \frac{1}{\tau(\underline{k},T)}}{[\displaystyle\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2]^2} \tag{5.17}$$

where we have used Eq. (4.48).

For the case of a free-electron spherical F.S., we have the usual result [21]

$$[\rho^{ST}(T)]_{\substack{\text{spherical} \\ \text{F.S.}}} = \frac{m}{ne^2} \, \frac{1}{\langle \tau(\underline{k},T) \rangle} \tag{5.18}$$

where n is the number of conduction electrons per unit volume and

$$\langle \tau(\underline{k},T) \rangle = \int_{F.S.} \frac{d\Omega_{\underline{k}}}{4\pi} \, [\tau(\underline{k},T)]_{\substack{\text{spherical} \\ \text{F.S.}}} \quad . \tag{5.19}$$

In (5.19) $\tau(\underline{k},T)$ is given by Eq. (5.11). By (4.50), (4.55),

and (5.11) the variational method result is

$$[\rho^V(T)]_{\substack{\text{spherical} \\ \text{F.S.}}} = \frac{m}{ne^2} \left\langle \frac{1}{\tau(\underline{k},T)} \right\rangle \qquad (5.20)$$

where again $\tau(\underline{k},T)$ is given by (5.11). Robinson and Dow [26] have pointed out that the variational formula (5.20) is equivalent to summing partial resistivities whereas the formula (5.18) is equivalent to summing partial conductivities which is more physical.

5.2 Thermal Resistivity (Electronic Contribution)

In this section we derive an approximate formula for the ideal, phonon-limited electronic contribution to the thermal resistivity, written in terms of the effective phonon frequency distributions defined in Sections 4.2 and 4.3. We use a scattering time (S.T.) approximation analogous to the one introduced by Robinson and Dow [26] for the electrical resistivity. As in Section 4.3, we take $\underline{E}$ to be zero, thus ignoring thermopower contributions to the thermal resistivity. Neglecting phonon drag effects, the linearized Boltzmann transport equation for the conduction electrons (3.28) is

$$- \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \frac{(\varepsilon_{\underline{k}} - \mu)}{T} \underline{V}_{\underline{k}} \cdot \nabla T = \beta \sum_{\underline{k}'} (\Phi_{\underline{k}'} - \Phi_{\underline{k}}) f_{\underline{k}}^0 (1 - f_{\underline{k}'}^0) W_{\underline{k}}^{\underline{k}'} \qquad (5.21)$$

where $W_{\underline{k}}^{\underline{k}'}$ is given by Eq. (3.29).

Having noted in Section 5.1 the similarity between the deviation function (5.2) in the scattering time approximation (5.3) and the elementary solution (4.36) for the case of electrical resistivity, we are guided by the elementary solution (4.58) for the thermal resistivity case to write the deviation function $\Phi_{\underline{k}}$ as

$$\Phi_{\underline{k}} = - \frac{(\varepsilon_{\underline{k}} - \mu)}{T} \underline{\Lambda}_{\underline{k}}^W \cdot \nabla T \qquad (5.22)$$

where $\underline{\Lambda}_{\underline{k}}^{W}$ is an unknown vector mean free path for the electrons. The superscript W (denoting the thermal resistivity) is used to distinguish this mean free path from the one in Section 5.1. We then make the S.T. approximation

$$\underline{\Lambda}_{\underline{k}}^{W} = \tau_{W}(\underline{k},T)\underline{V}_{\underline{k}} \qquad (5.23)$$

where $\tau_{W}(\underline{k},T)$ is a temperature dependent anisotropic scattering time for thermal resistivity W. From the Boltzmann equation (5.21) it is possible to obtain an approximation to the scattering time $\tau_{W}(\underline{k},T)$ as we now demonstrate.

In Appendix E it is shown that inserting the deviation function (5.22) in the Boltzmann equation (5.21), multiplying both sides by $(\varepsilon_{\underline{k}}-\mu)$, and integrating both sides over $\varepsilon_{\underline{k}}$ leads to

$$\underline{V}_{\underline{k}} = -\frac{\beta\Omega}{2\pi^{2}\hbar^{2}} \int_{0}^{\infty} d\omega R(\omega) \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left\{ (1 + \frac{1}{\pi^{2}} (\frac{\hbar\omega}{k_{B}T})^{2}) \right.$$

$$\times (\underline{\Lambda}_{\underline{k}}^{W}-\underline{\Lambda}_{\underline{k}'}^{W}) + \frac{3}{2\pi^{2}} (\frac{\hbar\omega}{k_{B}T})^{2}\underline{\Lambda}_{\underline{k}'}^{W} \left\} \sum_{j} |g_{\underline{k}',\underline{k};j}|^{2}\delta(\omega-\omega_{j}(\underline{k}'-\underline{k})) \right.$$

$$(5.24)$$

where $\underline{k}$ is on the F.S., $R(\omega)$ is given by Eq. (4.39) and depends on temperature, (3.29) has been used, and the surface integral in $\underline{k}'$-space is over the F.S..

We now take the dot product of $\underline{V}_{\underline{k}}$ (with $\underline{k}$ on the F.S.) with Eq. (5.24). The dot product of $\underline{V}_{-\underline{k}}$ with the quantity in brackets in (5.24) is, using the approximation (5.23),

$$(1 + \frac{1}{\pi^2} (\frac{\hbar\omega}{k_BT})^2) [\tau_W(\underline{k}) |\underline{V}_{\underline{k}}|^2 - \tau_W(\underline{k}') \underline{V}_{-\underline{k}} \cdot \underline{V}_{-\underline{k}'}]$$

$$+ \frac{3}{2\pi^2} (\frac{\hbar\omega}{k_BT})^2 \tau_W(\underline{k}') \underline{V}_{-\underline{k}} \cdot \underline{V}_{-\underline{k}'}$$

where explicit temperature dependence has been suppressed. This may be written in the form

$$(1 + \frac{1}{\pi^2} (\frac{\hbar\omega}{k_BT})^2) \tau_W(\underline{k}) [|\underline{V}_{\underline{k}}|^2 - \underline{V}_{-\underline{k}} \cdot \underline{V}_{-\underline{k}'}]$$

$$+ \frac{3}{2\pi^2} (\frac{\hbar\omega}{k_BT})^2 \tau_W(\underline{k}) \underline{V}_{-\underline{k}} \cdot \underline{V}_{-\underline{k}'}$$

$$+ (1 - \frac{1}{2\pi^2} (\frac{\hbar\omega}{k_BT})^2) [\tau_W(\underline{k}) - \tau_W(\underline{k}')] \underline{V}_{-\underline{k}} \cdot \underline{V}_{-\underline{k}'} \quad .$$

Thus we have

$$1 = \frac{\beta\Omega}{2\pi^2\hbar^2} \int_0^\infty d\omega R(\omega) \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left\{ \left(1 + \frac{1}{\pi^2}(\frac{\hbar\omega}{k_B T})^2\right) \tau_W(\underline{k}) \left[1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}\right] \right.$$

$$+ \frac{3}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2 \tau_W(\underline{k}) \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}$$

$$+ \left(1 - \frac{1}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2\right) \left[\tau_W(\underline{k}) - \tau_W(\underline{k}')\right] \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2} \right\}$$

$$\times \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega - \omega_j(\underline{k}'-\underline{k})) \quad . \tag{5.25}$$

The reduction of (5.25) to a form from which we can obtain a reasonable first approximation to the scattering time is not as straightforward as in the electrical resistivity case of Section 5.1 because of the presence of thermal factors and the middle term in brackets. However, the first term in brackets is mainly positive (and in fact would be strictly non-negative for a spherical F.S.) whereas the third term is both positive and negative and therefore cancellations will occur. The third term has the zeroes mentioned in Section 5.1 due to the $\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}$ factor and the symmetry of the scattering times. In addition we note that the delta function restricts ω to be less than the maximum phonon frequency and the thermal factor $R(\omega)$ is a rapidly decreasing function of $\frac{\hbar\omega}{k_B T}$ and thus gives higher ω values lower weights. Thus we drop the third term, but we shall retain the second as well as the first, even though it also alternates in sign and may have a small coefficient if

$(\frac{\hbar\omega}{k_B T})$ is small. This can be partially justified by noting that the third term still has additional zeroes (those required by the symmetry of the scattering times) not shared by the second term. Alternatively, we can look at our resultant approximation (5.26) as the first iteration of (5.25). Further iterations could of course be done, but the resultant increase in computational labour is not warranted at present. We also note that our approximation leads us to a scattering time which will be seen to be present in the variational formula for the thermal resistivity (see Eq. (5.32)).

In this approximation we then have (for $\underline{k}$ on the F.S.)

$$
\frac{1}{\tau_W(\underline{k},T)} = \frac{\beta\Omega}{2\pi^2\hbar^2} \int_0^\infty d\omega R(\omega) \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|}
$$
$$
\times \left\{ (1 + \frac{1}{\pi^2} (\frac{\hbar\omega}{k_B T})^2) [1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}] \right.
$$
$$
\left. + \frac{3}{2\pi^2} (\frac{\hbar\omega}{k_B T})^2 \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2} \right\}
$$
$$
\times \sum_j |g_{\underline{k}',\underline{k};j}|^2 \, \delta(\omega - \omega_j(\underline{k}'-\underline{k})) \qquad (5.26)
$$

with the temperature dependence of the scattering time now explicit. Using the definitions (4.47) and (4.66) of the anisotropic effective phonon frequency distributions, this may be written as ($\underline{k}$ on the F.S.)

$$\frac{1}{\tau_W(\underline{k},T)} = \frac{4\pi}{k_B T} \int_0^\infty d\omega R(\omega) \left[(1 - \frac{1}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2) \beta_{tr}^2 F(\omega,\underline{k}) \right.$$

$$\left. + \frac{3}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2 \beta^2 F(\omega,\underline{k}) \right] \quad . \tag{5.27}$$

The function $R(\omega)$ depends on the temperature; however, the effect of the phonons is contained in $\beta_{tr}^2 F(\omega,\underline{k})$ and $\beta^2 F(\omega,\underline{k})$ which need only be calculated once. For a spherical F.S. we have, by (4.53) and (4.69),

$$[\frac{1}{\tau_W(\underline{k},T)}]_{\substack{\text{spherical} \\ \text{F.S.}}} = \frac{4\pi}{k_B T} \int_0^\infty d\omega R(\omega) \left[(1 - \frac{1}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2 \alpha_{tr}^2 F(\omega,\underline{k}) \right.$$

$$\left. + \frac{3}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2 \alpha^2 F(\omega,\underline{k}) \right]$$

$$\tag{5.28}$$

where $\underline{k}$ is on the F.S.

We now obtain an expression for the phonon-limited electronic contribution to the thermal resistivity in terms of the scattering time defined by (5.27). The heat current density $\underline{U}$ is given by [11, 15]

$$\underline{U} = \frac{1}{\Omega} \sum_{\underline{k}\sigma} \underline{V}_{\underline{k}} (\varepsilon_{\underline{k}} - \mu) f_{\underline{k}}$$

as in Section 4.1, where the phonon contribution vanishes since the phonons are in equilibrium (by our assumption of no phonon drag effects). $\underline{U}$ must be zero in the equilibrium situation; therefore, subtracting a (zero) contribution with $f_{\underline{k}}$ replaced by $f_{\underline{k}}^0$, and using (3.13), we have

$$\underline{U} = -\frac{1}{\Omega} \sum_{\underline{k}\sigma} \underline{V}_{-\underline{k}} (\varepsilon_{\underline{k}} - \mu) \Phi_{\underline{k}} \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \quad ,$$

where $\Phi_{\underline{k}}$ is the electron deviation function. The sum over spin gives a factor of 2, and the use of (5.22) and the definition of the thermal conductivity tensor $\underline{\underline{\kappa}}$,

$$\underline{U} = -\underline{\underline{\kappa}} \cdot \nabla T \quad ,$$

leads to

$$\underline{\underline{\kappa}} = -\frac{2}{\Omega T} \sum_{\underline{k}} (\varepsilon_{\underline{k}} - \mu)^2 \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \underline{V}_{-\underline{k}} \underline{\Lambda}_{-\underline{k}}^W \quad .$$

With the S.T. approximation (5.23), and using (A.4), (A.5), and (A.7) of Appendix A, this becomes

$$\underline{\underline{\kappa}}^{ST}(T) = L_0 T \frac{e^2}{4\pi^3 \hbar} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \tau_W(\underline{k}, T) \underline{V}_{\underline{k}} \underline{V}_{\underline{k}} \quad , \tag{5.29}$$

where the Lorentz number is

$$L_0 = \frac{\pi^2 k_B^2}{3e^2}$$

and we have neglected derivatives with respect to energy (evaluated at the Fermi energy) of the surface element, electron velocities, and the scattering time. The superscript ST denotes the scattering time approximation. The thermal resistivity tensor is given by

$$\underline{\underline{W}}^{ST}(T) = [\underline{\underline{\kappa}}^{ST}(T)]^{-1} \quad .$$ (5.30)

We now specialize our results to a lattice with cubic symmetry in which case the thermal conductivity is

$$\kappa = \frac{1}{3} \, \text{Tr} \underline{\underline{\kappa}}$$

where Tr denotes the trace. By (5.29) and (5.30) we have

$$W^{ST}(T) = \frac{1}{L_0 T} \frac{12\pi^3 \hbar}{e^2} \left[\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2 \, \tau_W(\underline{k},T) \right]^{-1}$$ (5.31)

for the thermal resistivity. We compare this with the formula (4.71) in the variational method, which may be written in terms of the scattering time defined by Eq. (5.27), by use of (4.48) and (4.67), as

$$W^V(T) = \frac{1}{L_0 T} \frac{12\pi^3 \hbar}{e^2} \frac{\displaystyle\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2 \, \frac{1}{\tau_W(\underline{k},T)}}{\left[\displaystyle\int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \, |\underline{V}_{\underline{k}}|^2 \right]^2}$$ (5.32)

Comparing the relationship between (5.32) and (5.31) to that between (5.17) and (5.16), we see that we might have predicted the form of $\tau_W(\underline{k},T)$ (Eq. (5.27)) from the variational method formula (4.71); however, as we have seen, the approximations made in deriving (5.27) are not as obvious or as justifiable as those leading to the scattering

time for electrical resistivity.

For the case of a free-electron spherical F.S., we have

$$[W^{ST}(T)]_{\substack{spherical \\ F.S.}} = \frac{1}{L_0 T} \frac{m}{ne^2} \frac{1}{<\tau_W(\underline{k},T)>} \qquad (5.33)$$

where

$$<\tau_W(\underline{k},T)> = \int\limits_{F.S.} \frac{d\Omega_{\underline{k}}}{4\pi} [\tau_W(\underline{k},T)]_{\substack{spherical \\ F.S.}} \quad ,$$

n is the number of conduction electrons per unit volume, and the scattering time is now given by Eq. (5.28). The variational formula is

$$[W^V(T)]_{\substack{spherical \\ F.S.}} = \frac{1}{L_0 T} \frac{m}{ne^2} <\frac{1}{\tau_W(\underline{k},T)}> \quad , \qquad (5.34)$$

with the scattering time again given by (5.28).

CHAPTER VI

ELECTRICAL RESISTIVITY OF DILUTE Zn ALLOYS

6.1 Introduction

In Section 5.1, the electrical resistivity of pure single crystals of simple metals was expressed in terms of an anisotropic, temperature-dependent transport scattering time for the conduction electrons; this scattering time concept can be generalized [30, 31] to dilute nonmagnetic substitutional alloys of simple metals. In this chapter we show that the change in scattering time anisotropy resulting from the addition of small amounts of impurities to pure Zn leads to measurable changes in the temperature dependence of the resistivity ratio $\rho_{||}/\rho_{\perp}$; $\rho_{||}(\rho_{\perp})$ is the electrical resistivity with the electric field parallel (perpendicular) to the c-axis. We also calculate the corresponding deviations from Matthiessen's rule for polycrystalline samples.

The arrangement of ions in hexagonal close-packed (h.c.p.) metals such as Zn consists of two interpenetrating simple hexagonal sublattices, and this crystal structure may be analyzed in terms of a unit cell containing two ions [4, 23] (this implies that r = 2 in the results of

Chapter II). We note that it is conventional to refer to the z-axis as the c-axis in discussions of the h.c.p. metals. Furthermore, the electrical conductivity tensor in h.c.p. metals is given by

$$
\underline{\underline{\sigma}} = \begin{pmatrix} \sigma_\perp & 0 & 0 \\ 0 & \sigma_\perp & 0 \\ 0 & 0 & \sigma_{||} \end{pmatrix} ,
$$

and therefore the electrical resistivity tensor, $\underline{\underline{\rho}} = \underline{\underline{\sigma}}^{-1}$, is

$$
\underline{\underline{\rho}} = \begin{pmatrix} \rho_\perp & 0 & 0 \\ 0 & \rho_\perp & 0 \\ 0 & 0 & \rho_{||} \end{pmatrix} \tag{6.1}
$$

where $\rho_{||}$ ($\rho_\perp$) is the electrical resistivity of the specimen with the electric field parallel (perpendicular) to the c-axis.

Theoretical results for the temperature (T) variation of the resistivity ratio $\rho_{||}(T)/\rho_\perp(T)$ of pure single crystal Zn have been obtained by Truant and Carbotte [29], using the concept of an anisotropic scattering time solution of the Boltzmann transport equation. They found that the scattering times due to the electron-phonon interaction are very anisotropic as a function of position on the Fermi surface (F.S.). The amount of

anisotropy decreases with increasing temperature, but it is still significant at higher temperatures. The change in anisotropy with temperature implies that $\rho_{||}/\rho_{\perp}$ in pure Zn depends on temperature, and the temperature variation calculated by Truant and Carbotte [29] is in qualitative agreement with experiment.

More recently, Kus and Carbotte [30, 31] have developed a theory of deviations from Matthiessen's rule for the resistivity of dilute metallic alloys, and this has been quite successful in applications to K, Li, and Al. The theory is based on the simple idea that the ideal (pure metal) scattering times are very anisotropic and that the addition of impurities will tend to change this anisotropy in the scattering times for the dilute alloy. Matthiessen's rule, which states that the alloy resistivity at any temperature is simply the sum of the pure metal resistivity at that temperature plus the residual resistivity of the alloy, is valid only when the scattering times are isotropic; hence deviations from the rule result, and these are of the right order of magnitude and have the qualitatively correct temperature variation. The changes in the anisotropy of the scattering times on alloying will also lead to modifications in the temperature variation of the ratio $\rho_{||}/\rho_{\perp}$ in dilute h.c.p. alloys, and we have calculated the magnitude of this effect for the case of Zn. We find that small amounts of impurities can change this ratio significantly

from the predicted and observed structure in the T variation of $\rho_{||}/\rho_{\perp}$ for pure Zn.

In Section 6.2 we present the basic theory of the effect and discuss the scattering times for Zn. Section 6.3 contains our results for the ratio $\rho_{||}/\rho_{\perp}$ as a function of temperature and impurity content, and also our calculations of the deviation from Matthiessen's rule for polycrystalline samples.

6.2 Theory

We begin by generalizing the scattering time concept
of Section 5.1 to dilute nonmagnetic substitutional alloys
of simple metals; we note that the scattering time approach
is much more convenient than the variational method approach
for a simple treatment of dilute alloys. First of all, it
is clear that the arguments leading to the expression (5.14)
for the electrical conductivity tensor do not depend on the
preceding explicit form (5.10) of the scattering time for
pure single crystals, but only on the assumption that the
electron deviation function can be written approximately as

$$\Phi_{\underline{k}} = e\tau(\underline{k},T)\underline{V}_{\underline{k}}\cdot\underline{E} \quad , \tag{6.2}$$

in terms of an anisotropic, temperature-dependent scattering
time $\tau(\underline{k},T)$ for the conduction electrons. Hence we now take
$\tau(\underline{k},T)$ to be the scattering time for the dilute alloy; we
will obtain an expression for this alloy scattering time
which relates it to the ideal scattering time given by
(5.10). Thus, in the anisotropic scattering time approximation
for the solution of the linearized Boltzmann transport equation,
the electrical conductivity tensor $\underline{\underline{\sigma}}$ is given by (Eq. (5.14))

$$\underline{\underline{\sigma}} = \frac{e^2}{4\pi^3\hbar} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \underline{V}_{\underline{k}}\tau(\underline{k},T)\underline{V}_{\underline{k}} \tag{6.3}$$

where the surface integral is over the F.S..

In a pure single crystal the scattering times $\tau(\underline{k},T)$ are entirely due to the electron-phonon interaction and we will write them as $\tau_0(\underline{k},T)$. Truant [23] has calculated $\tau_0(\underline{k},T)$ for Zn in a one O.P.W. (orthogonalized plane wave) approximation with a spherical Fermi surface In this approximation we have, from Section 5.1,

$$\frac{1}{\tau_0(\underline{k},T)} = \frac{4\pi}{k_B T} \int_0^\infty d\omega R(\omega) \alpha_{tr}^2 F(\omega,\underline{k})$$

where (Eq. (4.49))

$$\alpha_{tr}^2 F(\omega,\underline{k}) = N(0)_{F.E.} \int_{F.S.} \frac{d\Omega_{\underline{k}'}}{4\pi} (1 - \cos(\underline{k},\underline{k}')$$

$$\times \sum_j |g_{\underline{k}',\underline{k};j}|^2 \frac{1}{\hbar} \delta(\omega - \omega_j(\underline{k}'-\underline{k}))$$

and $g_{\underline{k}',\underline{k};j}$ is given by (2.28) or (2.29) with r = 2. The method of calculation of transport scattering times in h.c.p. metals has been discussed by Truant and Carbotte [4] and it would be repetitive to give further details here. Thus we simply show in Fig. 1 the results for $\tau_0(\underline{k},T)$ in pure Zn at two temperatures, as obtained by Truant [23] and reported briefly by Truant and Carbotte [29]. For a given temperature we have denoted $\tau_0(\underline{k},T)$ by $\tau_0(\theta,\phi)$, where (θ,ϕ) are ordinary spherical coordinates giving the position on the irreducible $\frac{1}{24}$'th of the F.S., and the ratio $\tau_0(\theta,\phi)/\tau_0(0,0)$ is plotted

Figure 1: Comparison at two temperatures of the Zn ideal
transport scattering times as a function of
position (θ, ϕ) on the Fermi surface, with
$\tau_0 (0,0) = 2.89 \times 10^{-13}$ sec. at 20°K and
$\tau_0 (0,0) = 6.36 \times 10^{-15}$ sec. at 300°K.

Figure 1
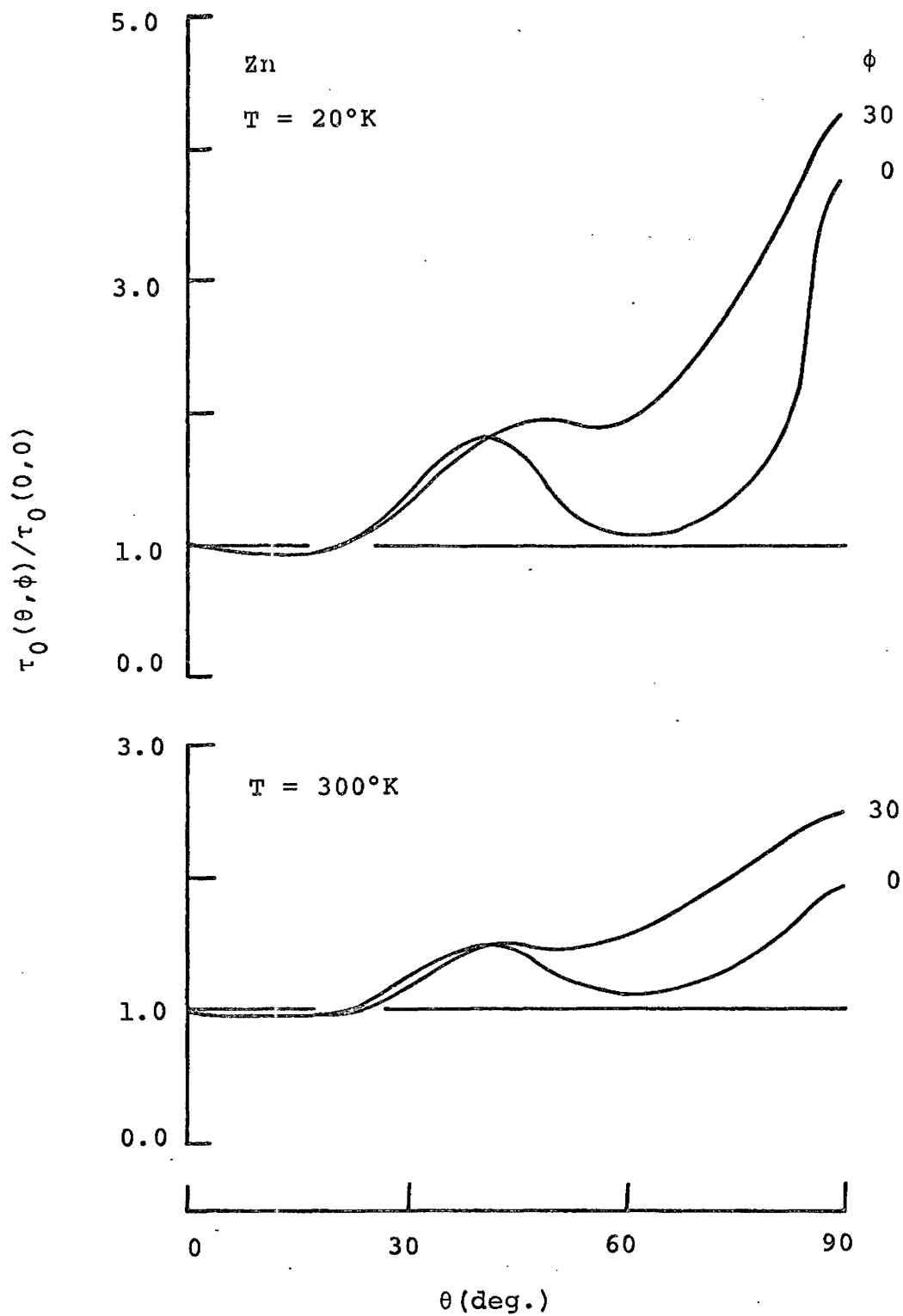
as a function of θ for two constant ϕ arcs. It is evident from the figure that $\tau_0(\underline{k},T)$ is very anisotropic and also that the anisotropy is quite temperature dependent.

The resistivity ratio for h.c.p. metals is, from (6.3) and (6.1),

$$\frac{\rho_{||}(T)}{\rho_{\perp}(T)} = \frac{\int\limits_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V_k}|} \frac{1}{2} [\,|\underline{V_k}|^2 - V_{z\underline{k}}^2]\,\tau(\underline{k},T)}{\int\limits_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V_k}|} V_{z\underline{k}}^2 \,\tau(\underline{k},T)} \tag{6.4}$$

where $V_{z\underline{k}}$ is the z-component of $\underline{V_k}$. We first note that if the scattering times $\tau(\underline{k},T)$ were isotropic they would cancel in (6.4), and this would lead to a temperature independent value for $\rho_{||}/\rho_{\perp}$, even though the resistivity itself is, of course, a very strong function of temperature. The constant value of the resistivity ratio would then depend only on the band structure, through the Fermi velocities $\underline{V_k}$ and the integrals over the F.S. in (6.4). In the model of a spherical F.S. this constant value would in fact be unity, and hence deviations from one would reflect band structure effects. However, the ideal scattering times in Zn are far from being isotropic, as illustrated in Fig. 1, and thus (6.4) will depend on temperature. We will concentrate on this temperature variation of the resistivity ratio $\rho_{||}/\rho_{\perp}$, and discuss, in particular, the effect of the addition of small amounts of impurities.

We now wish to find an expression for the alloy scattering times $\tau(\underline{k},T)$. The addition of small amounts of impurities to a pure metal opens an extra channel for scattering of the conduction electrons and, in the presence of both the electron-phonon interaction and impurity scattering, the alloy scattering times may be written approximately as [30, 31]

$$\frac{1}{\tau(\underline{k},T)} = \frac{1}{\tau_0(\underline{k},T)} + \frac{1}{\tau_R} \quad . \tag{6.5}$$

In (6.5), τ_R accounts for the additional scattering due to the impurities, and it is related to the residual resistivity ρ_R by

$$\rho_R = \frac{m}{ne^2\tau_R} \quad , \tag{6.6}$$

where n is the number of conduction electrons per unit volume and m is the electron mass. The approximation (6.5) is discussed in Appendix F. Although we characterize the impurity scattering by the residual resistivity and do not concern ourselves with the specific type of impurity, there is some experimental evidence to support this viewpoint, as stated by Salvadori et al. [36] for their results on the deviation from Matthiessen's rule (DMR):

"The agreement of our results (representing ZnAl and ZnAg alloys) with the previous data (including mainly ZnCd alloys and various grades of pure zinc) seems to indicate the DMR in zinc alloys (as well as in aluminum alloys) merely depend on the residual resistivity and not on the particular type of impurity."

We have assumed in (6.5) that the residual scattering time τ_R is a constant. Although it is a good approximation to take τ_R to be independent of temperature, τ_R certainly must vary over the F.S.. For simplicity, we will ignore this complication here, as it does not affect our main arguments in any important way.

It is clear from Eq. (6.5) that, in the temperature region where impurity scattering dominates $(\frac{1}{\tau_R} >> \frac{1}{\tau_0(\underline{k},T)})$, the effective scattering times $\tau(\underline{k},T)$ become equal to τ_R, and the anisotropy in the ideal scattering times $\tau_0(\underline{k},T)$ is no longer relevant. In our approximation τ_R is isotropic and we can say that the impurities completely wash out the anisotropy in the scattering times in this temperature region; however, in a more realistic model, τ_R would depend on $\underline{k}$ and we could only say that the anisotropy is changed to that in τ_R. The important result is that the anisotropy in the effective scattering times $\tau(\underline{k},T)$ for the alloy can be quite different from the anisotropy in the ideal scattering times $\tau_0(\underline{k},T)$; therefore the temperature dependence of the ratio $\rho_{||}/\rho_{\perp}$ can be affected in an important way. This effect is discussed in detail in the next section.

The anisotropy of the scattering times also leads
to deviations from Matthiessen's rule in the case of a
polycrystalline sample. There are two ways [37] to derive
from single crystal data mean resistivity values which would
be appropriate for polycrystalline h.c.p. specimens of the
same material. One formula is for the case of a specified
direction of the current density and corresponds to averaging
the resistivities:

$$\rho^{poly} = \frac{1}{3} \, (2\rho_{\perp} + \rho_{||}) \quad . \tag{6.7}$$

The other formula is for a specified direction of the
electric field and corresponds to averaging the
conductivities:

$$\rho^{poly} = \frac{3\rho_{\perp}\rho_{||}}{2\rho_{||} + \rho_{\perp}} \quad . \tag{6.8}$$

We pointed out in Section 5.1 that the formula for the
resistivity in the scattering time method is equivalent
to summing partial conductivities; thus we will use (6.8)
to be consistent. However, we will note the changes in
our results if (6.7) is used instead of (6.8). For a
spherical F.S. we then have, from (6.1), (6.3), and (6.8),

$$\rho^{poly}(T) = \frac{m}{ne^2} \cdot \frac{1}{\langle \tau(\underline{k},T) \rangle} \tag{6.9}$$

which is easily seen by writing (6.8) in the form

$\dfrac{3}{2\sigma_\perp + \sigma_{||}}$. The brackets $<\ \ >$ in (6.9) denote an average

over the (spherical) F.S.; that is,

$$<\tau(\underline{k},T)> \ = \ \int\limits_{F.S.} \frac{d\Omega_{\underline{k}}}{4\pi}\ \tau(\underline{k},T)$$

where $d\Omega_{\underline{k}}$ is an element of solid angle on the F.S.. For an

alloy we have, from Eqs. (6.5) and (6.9),

$$\rho_{alloy}^{poly}(T) = \frac{m}{ne^2}\ \frac{1}{<\frac{\tau_0(\underline{k},T)\tau_R}{\tau_0(\underline{k},T)+\tau_R}>} \qquad \text{(6.10)}$$

which does not separate to give the sum of the ideal

resistivity ρ_{ideal}^{poly}, given by

$$\rho_{ideal}^{poly}(T) = \frac{m}{ne^2}\ \frac{1}{<\tau_0(\underline{k},T)>}\ , \qquad \text{(6.11)}$$

plus the residual resistivity ρ_R. Thus we define a

deviation from Matthiessen's rule, $\Delta(c,T)$, for a given

impurity concentration c and temperature T, by

$$\Delta(c,T) = \rho_{alloy}^{poly}(T) - \rho_{ideal}^{poly}(T) - \rho_R\ .$$

This may be written as

$$\Delta(c,T) = \frac{m}{ne^2} \left\{ \frac{1}{\left\langle \frac{\tau_0(\underline{k},T)\tau_R}{\tau_0(\underline{k},T)+\tau_R} \right\rangle} - \frac{1}{\langle \tau_0(\underline{k},T) \rangle} - \frac{1}{\tau_R} \right\} \qquad (6.12)$$

and we note that τ_R depends on c. In the next section we calculate the resistivity ratio $\rho_{||}/\rho_{\perp}$ and the deviation from Matthiessen's rule $\Delta(c,T)$.

6.3 Results

In the approximation of a spherical Fermi surface, the expression (6.4) for the resistivity ratio takes the simple form

$$\frac{\rho_{||}(T)}{\rho_{\perp}(T)} = \frac{\displaystyle\int_{F.S.} d\Omega_{\underline{k}} \frac{1}{2} \sin^2\theta\, \tau(\theta,\phi)}{\displaystyle\int_{F.S.} d\Omega_{\underline{k}} \cos^2\theta\, \tau(\theta,\phi)} \qquad (6.13)$$

where $\tau(\theta,\phi)$ is the total scattering time associated with the electron at position (θ,ϕ) on the F.S.. Truant and Carbotte [29] evaluated (6.13) for pure single crystal Zn, using the ideal scattering times $\tau_0(\theta,\phi)$ illustrated in Fig. 1, and obtained good qualitative agreement with the experimental data. In the case of dilute alloys, the scattering times in Eq. (6.13) are given by formula (6.5), and in Fig. 2(a) we present results for pure Zn and for several dilute Zn alloys characterized by differing values of the residual resistivity ρ_R. We first note that at very low temperatures the ideal scattering times are large compared to the residual scattering times τ_R, since the ideal resistivities become small in this temperature region. The alloy scattering times are then essentially equal to τ_R by formula (6.5), and our assumption of an isotropic τ_R implies that the resistivity ratio will approach a constant value (unity for our model of a spherical F.S.) at very low temperatures, as shown in Fig. 2(a) for temperatures of 5°K

Figure 2(a): The theoretical temperature variation in Zn of the resistivity ratio $\rho_{||}/\rho_{\perp}$. The solid curve is for pure Zn and the other curves (from top to bottom) are for alloys with residual resistivities ρ_R of 0.005, 0.05, 0.1, 0.3, and 0.5 $\mu\Omega$-cm.

(b): The theoretical temperature variation in Zn alloys of the ratio $(\rho_{||}-\rho_R)/(\rho_{\perp}-\rho_R)$ for $\rho_R = 0.005$ $\mu\Omega$-cm. (solid curve) and 0.5 $\mu\Omega$-cm. (dotted curve).

Figure 2
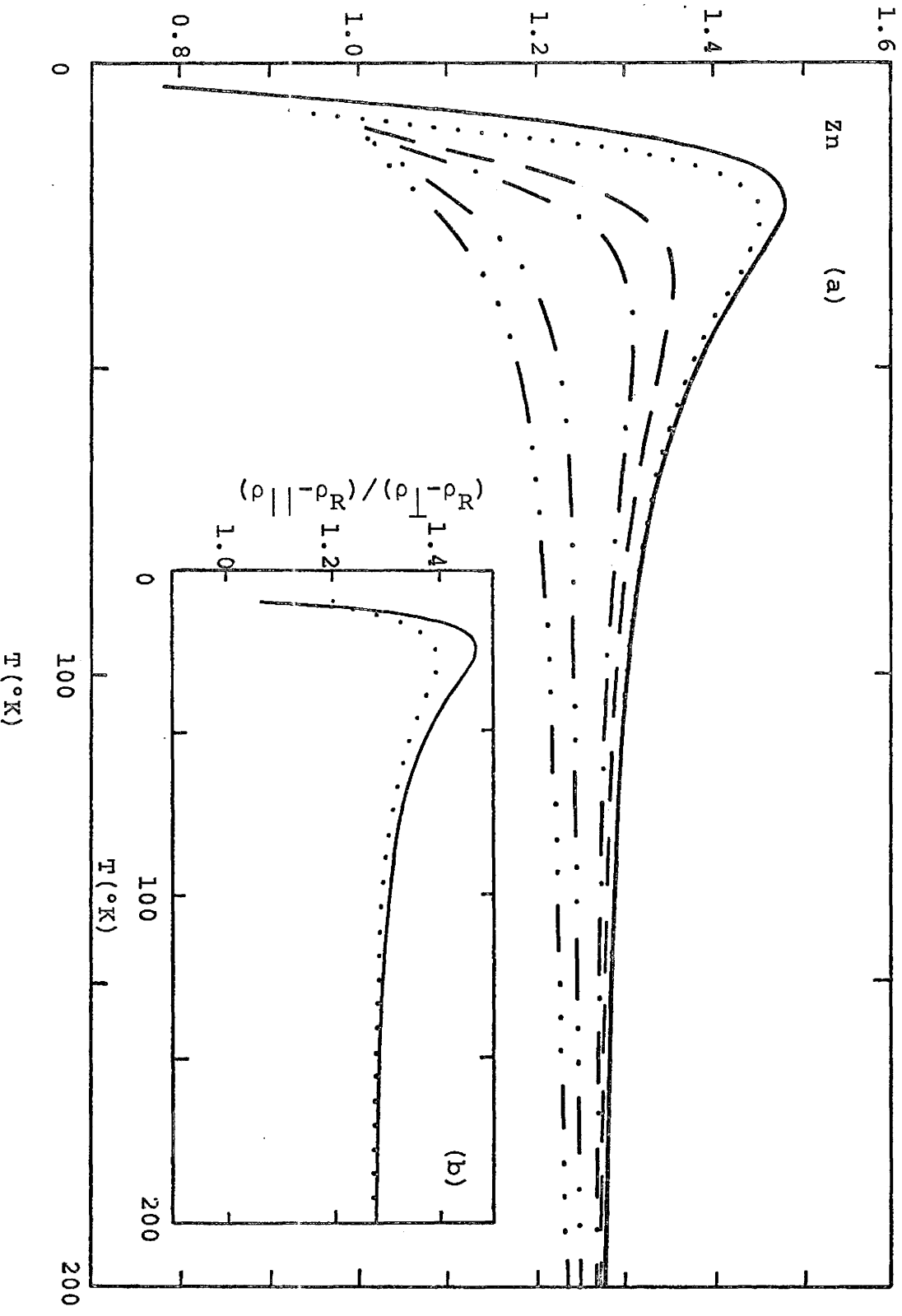
or less. Of course, τ_R should really be anisotropic; however, these very low temperature effects are not of great interest here and do not affect our arguments in an essential way. From Fig. 2(a) it is clear that the temperature variation of the ratio $\rho_{||}/\rho_{\perp}$ is affected in an important way by the addition of impurities, and also that the effect is large enough to be measured.

We stress that the changes in T variation of the ratio $\rho_{||}/\rho_{\perp}$ with impurity concentration shown in Fig. 2(a) are not simply the result of adding the residual resistivity ρ_R to the ideal resistivities to form the ratio

$$\frac{(\rho_{||}^{ideal}(T) + \rho_R)}{(\rho_{\perp}^{ideal}(T) + \rho_R)} \ .$$

This addition would assume Matthiessen's rule which we will show to be invalid; however, in order to avoid misinterpretation of our results, we subtract ρ_R from the alloy resistivities $\rho_{||}$ and $\rho_{\perp}$ and then form the resistivity ratio. If we had used Matthiessen's rule as mentioned above to form the alloy resistivities, this new ratio would be equal to the ideal ratio $\rho_{||}^{ideal}/\rho_{\perp}^{ideal}$ for all impurity concentrations. Our results are shown in Fig. 2(b) for the smallest and largest ρ_R considered in Fig. 2(a) (curves for the other ρ_R lie between the curves shown); we see from the figure that concentration dependence remains, and we note that these curves are qualitatively similar to those in Fig. 2(a).

Although we have used a very simple model for the electron-phonon interaction and for the electronic structure of Zn, there is some evidence that our model is quite reasonable for the present discussion. For example, we have calculated $\rho_{ideal}^{poly}(T)$ given by (6.11), and the results are shown in Fig. 3 where we compare with experimental data from Meaden [37]. The agreement over this considerable temperature range is quite good, and verifies that our model is reasonably adequate. We note that if the averaging procedure (6.7) is used instead of (6.8) the change (increase) in ρ_{ideal}^{poly} is less than 2% above 60°K and less than 3.5% below 60°K.

There has been much recent interest in deviations from Matthiessen's rule [16], and for this reason we have calculated $\Delta(c,T)$ given by our Eq. (6.12) for several impurity concentrations. These results are presented in Fig. 4 as a function of temperature and for several values of the residual resistivity. We note that if the averaging procedure (6.7) is used instead of (6.8), $\Delta(c,T)$ is decreased by roughly 20% to 25% but this is not crucial since we attach only qualitative significance to our results for $\Delta(c,T)$.

We are not aware of any experimental data to which we can compare Fig. 4 in any detail; the recent data of Salvadori et al. [36] on the resistivity of Zn alloys is given in terms of $(\rho_{alloy}^{poly} - \rho_R)$ rather than $\Delta(c,T)$, and is

Figure 3: The temperature variation of the Zn ideal polycrystalline resistivity $\rho_{ideal}^{poly}(T)$ in units of $\mu\Omega$-cm. The solid curve is the theoretical result and the experimental points (Δ) are from Meaden.
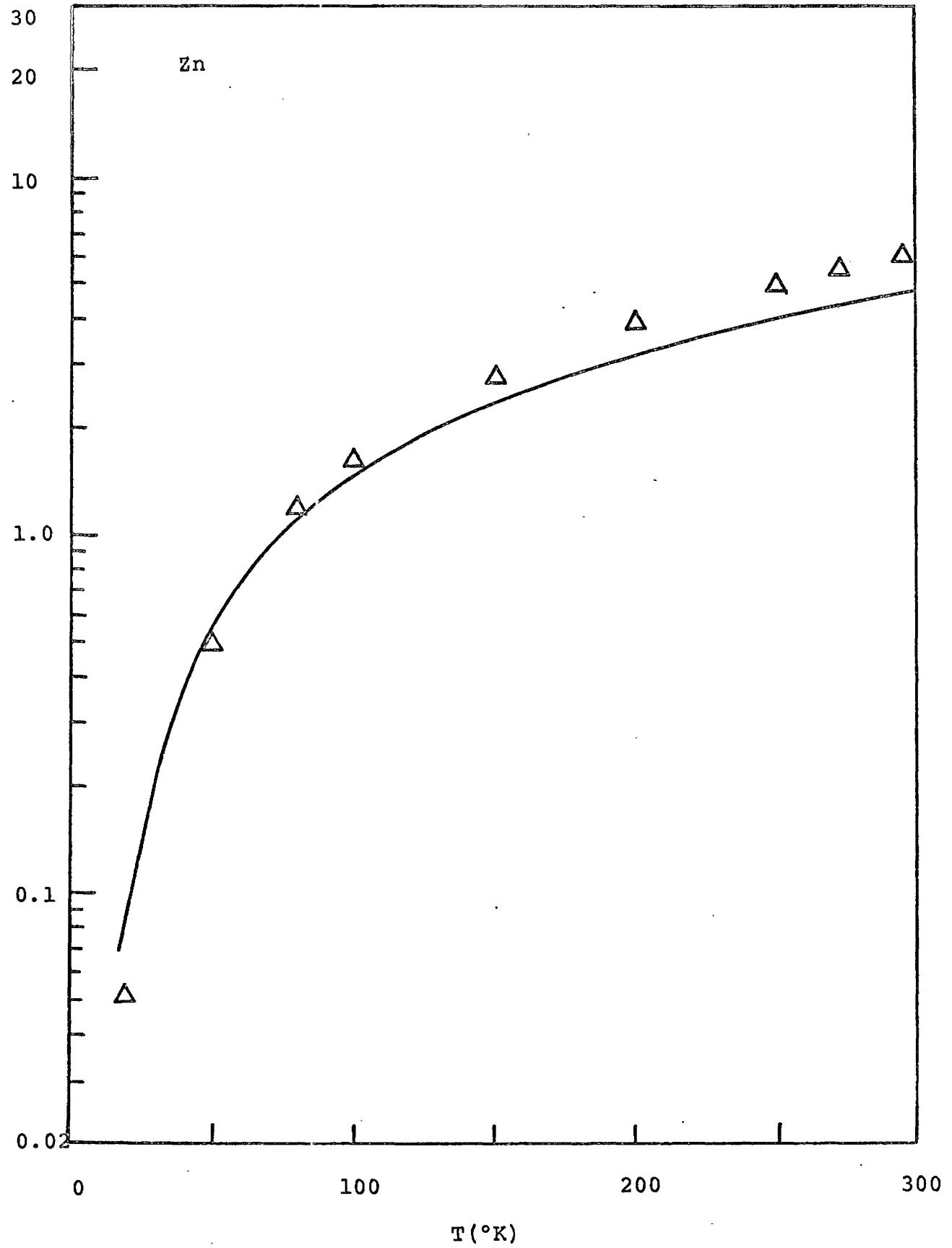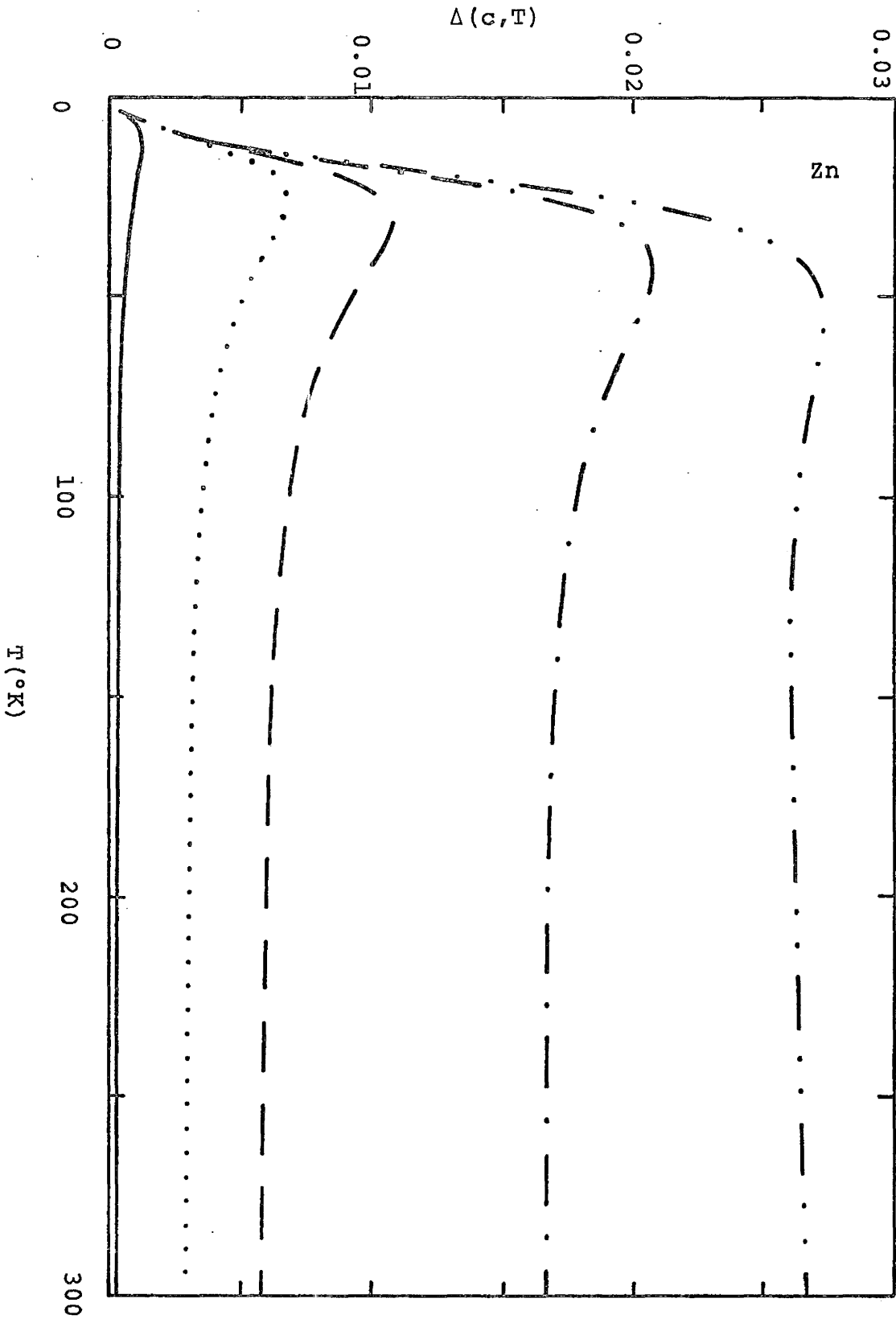
Figure 3

Zn

T(°K)

Figure 4: The theoretical deviations from Matthiessen's rule $\Delta(c,T)$ in $\mu\Omega$-cm. for Zn as a function of temperature T. The curves shown are (from bottom to top) for residual resistivities of 0.005, 0.05, 0.1, 0.3, and 0.5 $\mu\Omega$-cm.

Figure 4

Figure 4

unfortunately presented on a log-log plot. Nevertheless, it is of interest to compare our results with their data, and this is done in Fig. 5. The agreement with experiment is reasonable, although it is clear that such a plot is not very discriminating when it comes to the deviation from Matthiessen's rule $\Delta(c,T)$. If the averaging procedure (6.7) is used instead of (6.8) $(\rho_{alloy}^{poly} - \rho_R)$ increases by less than 1%.

In summary, we have calculated the effect of small amounts of impurities on the temperature dependence of the resistivity ratio $\rho_{||}/\rho_{\perp}$ in Zn, and important changes are predicted which should be observable. We have also calculated the deviations from Matthiessen's rule which should result in polycrystalline samples, and they are in reasonable agreement with the presently available experimental data. Although our calculations are carried out within a very simplified model for the electron-phonon interaction and the electronic structure of Zn, we believe that our results are qualitatively significant.

Figure 5: Comparison of the theoretical (a) and
experimental (b) temperature variation of
polycrystalline resistivities (units of $n\Omega$-cm.)
in Zn. In (a) the solid curve is $\rho_{ideal}^{poly}(T)$ and
the dotted curve is $(\rho_{alloy}^{poly}(T) - \rho_R)$ for a
residual resistivity $\rho_R = 1905.6$ $n\Omega$-cm. In (b)
the corresponding experimental results of
Salvadori et al. are shown.

Figure 5

92

Zn

(a)

(b)

10^3

10^2

10

1

10^{-1}

10^{-2}

1

10

100 1

10

100

T(°K)

T(°K)
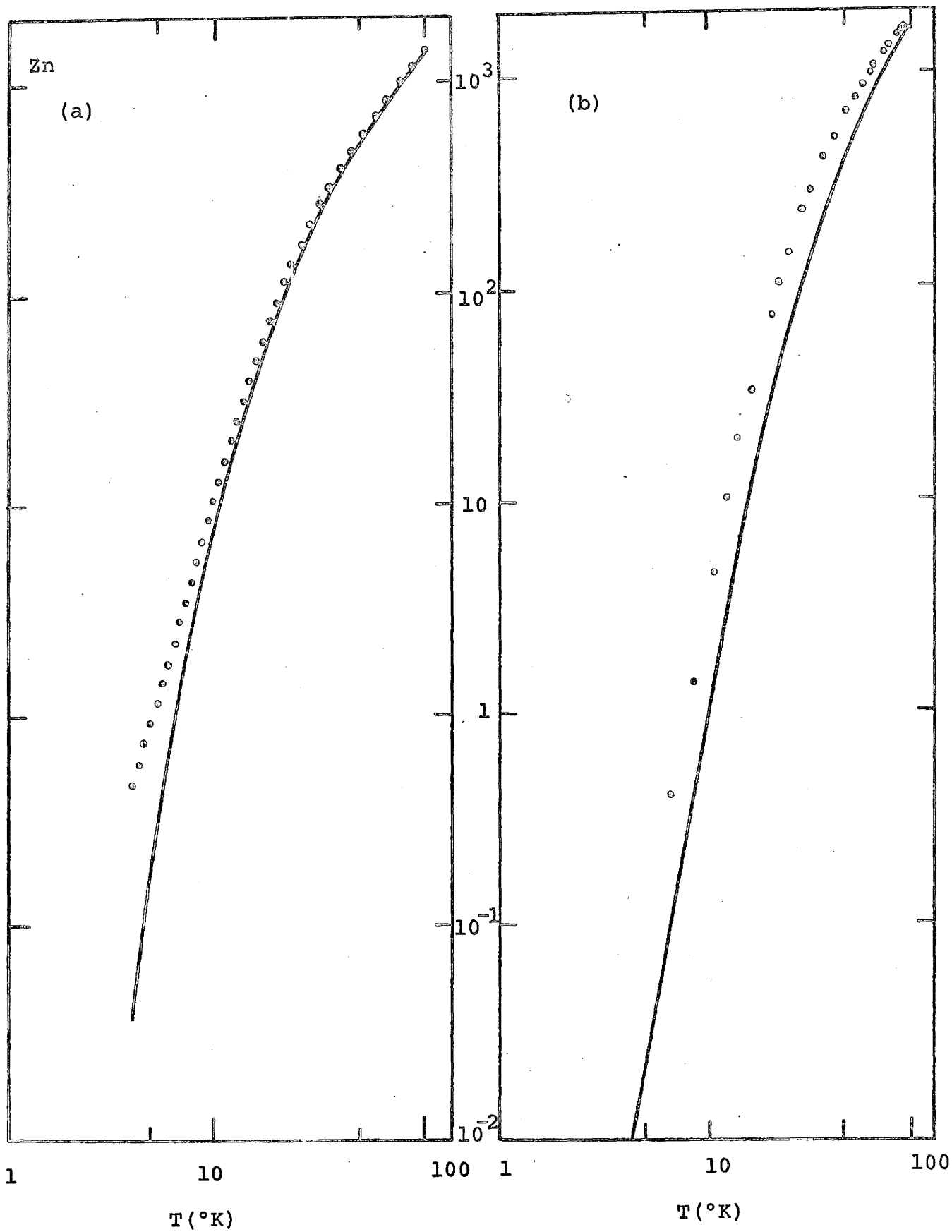
APPENDIX A

In order to derive the expression (4.38) for the conductivity tensor in the variational method, we begin with (4.35):

$$\underline{\underline{\sigma}}^{V} = \frac{1}{\Omega P_{11}} \underline{J}_1 \underline{J}_1 \tag{A.1}$$

where the V denotes the variational method expression. The trial function (4.36) may be written as

$$\phi_1(\underline{k}) = \underline{V}_{\underline{k}} \cdot \underline{u} \tag{A.2}$$

where $\underline{u}$ is a unit vector in the direction of $\underline{E}$, since $e\tau|\underline{E}|$ of (4.36) cancels in (A.1). Using the definition (4.21) of $\underline{J}_1$, we have

$$\underline{J}_1 = - \sum_{\underline{k}\sigma} e\underline{V}_{\underline{k}}\underline{V}_{\underline{k}} \cdot \underline{u} \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \quad . \tag{A.3}$$

Making the usual change from a sum to an integral [7],

$$\sum_{\underline{k}} \rightarrow \frac{\Omega}{(2\pi)^3} \int d^3k \quad , \tag{A.4}$$

93

and writing the integral as the product of an energy

integral and a surface integral over constant energy

surfaces in $\underline{k}$-space [19],

$$\int d^3k \rightarrow \int_0^\infty d\varepsilon_{\underline{k}} \int \frac{dS(\varepsilon_{\underline{k}})}{\hbar |\underline{V}_{\underline{k}}|} \quad , \tag{A.5}$$

(A.3) becomes

$$\underline{J}_1 = \frac{e\Omega}{4\pi^3} (-) \int_0^\infty d\varepsilon_{\underline{k}} \frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} [\int \frac{dS(\varepsilon_{\underline{k}})}{\hbar |\underline{V}_{\underline{k}}|} \underline{V}_{\underline{k}}\underline{V}_{\underline{k}} \cdot \underline{u}] \tag{A.6}$$

where the sum over spin gives a factor of 2. We note that
$f^0_{\underline{k}}$ depends on $\underline{k}$ only through $\varepsilon_{\underline{k}}$.

Making use of the well-known result [7, 8] for the

Fermi distribution function,

$$- \int_0^\infty d\varepsilon F(\varepsilon) \frac{\partial f^0(\varepsilon)}{\partial \varepsilon} = F(\mu) + \frac{\pi^2}{6} (k_B T)^2 F^{(ii)}(\mu) + \dots \tag{A.7}$$

where F is some function of energy ε, μ is the chemical

potential, and $^{(ii)}$ denotes the second derivative, (A.6)

becomes

$$\underline{J}_1 = \frac{e\Omega}{4\pi^3\hbar} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \underline{V}_{\underline{k}}\underline{V}_{\underline{k}} \cdot \underline{u} \tag{A.8}$$

where the integral is over the Fermi surface (F.S.) and we

have neglected derivatives of the quantity in square

brackets at the F.S..

Using (A.2) in the definition (4.28) we have

$$P_{11} = \beta \sum_{\underline{k}\sigma\underline{k}'} [\underline{V}_{\underline{k}} \cdot \underline{u} - \underline{V}_{\underline{k}'} \cdot \underline{u}]^2 \, \delta_{(\underline{k}'-\underline{k})_R, \underline{q}} \, P^{\underline{k}'}_{\underline{k};\underline{q}} \qquad (A.9)$$

where $P^{\underline{k}'}_{\underline{k};\underline{q}}$ is given by (4.3). We use (A.4) and (A.5) to change the sums in (A.9) to integrals. The energy delta function in $P^{\underline{k}'}_{\underline{k};\underline{q}}$ implies that $\varepsilon_{\underline{k}'} \simeq \varepsilon_{\underline{k}}$ and therefore $f^0_{\underline{k}}(1-f^0_{\underline{k}'}) \simeq f^0_{\underline{k}}(1-f^0_{\underline{k}})$, which is proportional to $\partial f^0_{\underline{k}}/\partial\varepsilon_{\underline{k}}$, and this is approximately a delta function peaked at the F.S. by (A.7). Thus we evaluate the surface integrals, electron velocities, and $g_{\underline{k}',\underline{k};j}$ at the F.S., and we are left with the energy integrals

$$\int_0^\infty d\varepsilon_{\underline{k}} \int_0^\infty d\varepsilon_{\underline{k}'} \, f^0_{\underline{k}}(1-f^0_{\underline{k}'}) \delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}} - \hbar\omega_j(\underline{q})) \qquad .$$

By means of the transformations

$$\eta = \beta(\varepsilon_{\underline{k}} - \mu)$$

and

$$z = \beta \hbar\omega_j(\underline{q}) \qquad ,$$

the above expression may be written as

$$\frac{1}{\beta} \int_{-\infty}^{+\infty} d\eta \; \frac{1}{e^{\eta}+1} \; \frac{1}{1+e^{-(\eta+z)}} \tag{A.10}$$

where the lower limit of the integral, $(-\mu/k_B T)$, has been approximated by $(-\infty)$, which is justified for the temperature range we will consider ($T \lesssim 300°K$). By Eq. (B.7) of Appendix B, (A.10) is

$$\frac{1}{\beta} \frac{z}{1-e^{-z}} \quad .$$

We now collect these results, using the periodicity in the reciprocal lattice of the phonon frequencies $\omega_j(\underline{q})$. Inserting an integration over ω with a delta function $\delta(\omega - \omega_j(\underline{k}'-\underline{k}))$, we obtain

$$P_{11} = -\frac{2\beta\Omega^2}{(2\pi)^5 \hbar^3} \int_0^{\infty} d\omega R(\omega) \; \{ \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|}$$

$$\times \; [\underline{V}_{\underline{k}} \cdot \underline{u} - \underline{V}_{\underline{k}'} \cdot \underline{u}]^2 \; \sum_j |g_{\underline{k}',\underline{k};j}|^2 \; \delta(\omega-\omega_j(\underline{k}'-\underline{k})) \} \tag{A.11}$$

where

$$R(\omega) = \frac{\hbar\omega}{(e^{\beta\hbar\omega}-1)(1-e^{-\beta\hbar\omega})} \quad .$$

Using (A.8) and (A.11) in (A.1), we obtain the expression (4.38).

APPENDIX B

Consider the function of (finite) z defined by the integral

$$I(z) = \int_{-\infty}^{+\infty} \frac{F(\eta)\,d\eta}{(e^{\eta}+1)(1+e^{-(\eta+z)})} \qquad (B.1)$$

where F is a polynomial in η. This may be written as

$$I(z) = \frac{1}{e^{-z}-1} \int_{-\infty}^{+\infty} \frac{[F(\eta) - F(\eta-z)]}{1 + e^{-\eta}}\,d\eta \quad . \qquad (B.2)$$

Define a function of η and z by

$$H(\eta;z) = \int_{\eta-z}^{\eta} F(\eta')\,d\eta' \qquad (B.3)$$

which is a polynomial in η with coefficients depending on z. Integrating (B.2) by parts, and using (B.3), we obtain

$$I(z) = \frac{-1}{e^{-z}-1} \int_{-\infty}^{+\infty} \frac{H(\eta;z)e^{-\eta}}{(1 + e^{-\eta})^2}\,d\eta \quad . \qquad (B.4)$$

The Fermi function $f^0(\eta)$ is defined by

$$f^0(\eta) = \frac{1}{e^{\eta}+1}$$

97

and has the property

$$\frac{\partial f^0}{\partial \eta} = -\frac{-e^{-\eta}}{(1 + e^{-\eta})^2} \quad .$$

Thus we may write (B.4) as

$$I(z) = \frac{-1}{1 - e^{-z}} \int_{-\infty}^{+\infty} H(\eta; z) \, \frac{\partial f^0}{\partial \eta} \, d\eta \quad . \tag{B.5}$$

As in (A.7) of Appendix A, the integral of H with the derivative of the Fermi function can be expanded [7, 8] to give

$$I(z) = \frac{1}{1 - e^{-z}} \{ H(0;z) + \frac{\pi^2}{6} H^{(ii)}(0;z) + \frac{7\pi^4}{360} H^{(iv)}(0;z)$$

$$+ \frac{31\pi^6}{15120} H^{(vi)}(0;z) + \dots \} \tag{B.6}$$

where the second, fourth, and sixth derivatives of H with respect to η are evaluated at $\eta = 0$.

We note the following special cases: $F(\eta) = 1$ gives

$$I(z) = \frac{z}{1 - e^{-z}} \quad , \tag{B.7}$$

$F(\eta) = \eta$ gives

$$I(z) = \frac{1}{1 - e^{-z}} \left(\frac{-z^2}{2} \right) \quad , \tag{B.8}$$

and $F(\eta) = \eta^2$ gives

$$I(z) = \frac{1}{1 - e^{-z}} \{\frac{z^3}{3} + \frac{\pi^2}{3} z\} \quad . \tag{B.9}$$

APPENDIX C

In order to derive the expression (4.59) for the thermal conductivity tensor in the variational method, we begin with (4.57):

$$\underline{\underline{\kappa}}^V = \frac{1}{\Omega T P_{22}} \, \underline{U}_2 \underline{U}_2 \tag{C.1}$$

where V denotes the variational method. The trial function (4.58) may be written as

$$\phi_2(\underline{k}) = (\varepsilon_{\underline{k}} - \mu) \underline{V}_{\underline{k}} \cdot \underline{u} \tag{C.2}$$

where $\underline{u}$ is a unit vector in the direction of ∇T, since $(- \tau \frac{|\nabla T|}{T})$ of (4.58) cancels in (C.1). Using the definition (4.25) of $\underline{U}_2$, we have

$$\underline{U}_2 = - \sum_{\underline{k}\sigma} \underline{V}_{\underline{k}} (\varepsilon_{\underline{k}} - \mu)^2 \, \underline{V}_{\underline{k}} \cdot \underline{u} \, \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \quad .$$

Using (A.4) and (A.5) of Appendix A we have

$$\underline{U}_2 = - \frac{\Omega}{4\pi^3 \hbar} \, (-) \int_0^\infty d\varepsilon_{\underline{k}} \, \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \, [\int \frac{dS(\varepsilon_{\underline{k}})}{|\underline{V}_{\underline{k}}|} \, \underline{V}_{\underline{k}} \underline{V}_{\underline{k}} \cdot \underline{u} (\varepsilon_{\underline{k}} - \mu)^2]$$

where a factor of 2 comes from the sum over spin σ. By (A.7)

of Appendix A this becomes

$$
\underline{U}_2 = \frac{\Omega (k_B T)^2}{12\pi\hbar} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \underline{V}_{\underline{k}}\underline{V}_{\underline{k}} \cdot \underline{u} \quad , \tag{C.3}
$$

where the integral is over the Fermi surface and we have neglected derivatives with respect to energy (evaluated at the Fermi energy) of the surface element and the electron velocities.

Using (C.2) in the definition (4.28), we have

$$
P_{22} = \beta \sum_{\underline{k}\sigma\underline{k}'} [(\epsilon_{\underline{k}}-\mu)\underline{V}_{\underline{k}} \cdot \underline{u} - (\epsilon_{\underline{k}'}-\mu)\underline{V}_{\underline{k}'} \cdot \underline{u}]^2 \, \delta_{(\underline{k}'-\underline{k})_R,\underline{q}} \, P^{\underline{k}'}_{\underline{k};\underline{q}} \tag{C.4}
$$

where $P^{\underline{k}'}_{\underline{k};\underline{q}}$ is given by (4.3). We use (A.4) and (A.5) of Appendix A to convert the sums in (C.4) to integrals, and by the same arguments as in Appendix A we evaluate surface integrals, electron velocities, and the electron-phonon coupling constant at the F.S., leaving us with energy integrals to be evaluated. Thus we have

$$
P_{22} = \frac{\beta\Omega^2}{16\pi^5\hbar^3} \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \, \delta_{(\underline{k}'-\underline{k})_R,\underline{q}} \sum_j |g_{\underline{k}',\underline{k};j}|^2 \, n^0_{\underline{q}j}
$$

$$
\times \int_0^\infty d\epsilon_{\underline{k}} \int_0^\infty d\epsilon_{\underline{k}'} [(\epsilon_{\underline{k}}-\mu)\underline{V}_{\underline{k}} \cdot \underline{u} - (\epsilon_{\underline{k}'}-\mu)\underline{V}_{\underline{k}'} \cdot \underline{u}]^2
$$

$$
\times f^0_{\underline{k}}(1-f^0_{\underline{k}'}) \delta(\epsilon_{\underline{k}'} - \epsilon_{\underline{k}} - \hbar\omega_j(\underline{q})) \quad . \tag{C.5}
$$

By means of the transformations

$$\eta = \beta(\epsilon_{\underline{k}}-\mu)$$

and

$$z = \beta\hbar\omega_j(\underline{q}) \quad,$$

the energy integrals in (C.5) may be written as

$$\frac{1}{\beta^3} \int_{-\infty}^{+\infty} d\eta \; \frac{[\eta\underline{V}_{\underline{k}}\cdot\underline{u} - (\eta+z)\underline{V}_{\underline{k}'}\cdot\underline{u}]^2}{(e^\eta+1)(1+e^{-(\eta+z)})} \qquad (C.6)$$

where $(-\mu/k_BT)$ has been replaced by $(-\infty)$ in the lower limit of the integral as in Appendix A. If we interchange $\underline{k}$ and $\underline{k}'$ in one term of (C.6) (noting that $|g_{\underline{k}',\underline{k};j}|^2$ and $\eta^0_{\underline{q}j}$ in (C.5) are invariant under this change), the squared factor in (C.6) may be written as

$$(\eta^2+\eta z)[2(\underline{V}_{\underline{k}}\cdot\underline{u})^2 - 2(\underline{V}_{\underline{k}}\cdot\underline{u})(\underline{V}_{\underline{k}'}\cdot\underline{u})] + z^2(\underline{V}_{\underline{k}}\cdot\underline{u})^2 \quad.$$
$$(C.7)$$

Using (C.7) in (C.6), and the results (B.7), (B.8), and (B.9) of Appendix B, (C.6) becomes

$$\frac{2\pi^2}{3\beta^3} \frac{z}{1-e^{-z}} \{(\underline{V}_{\underline{k}}\cdot\underline{u})^2[1 + \frac{z^2}{\pi^2}] - (\underline{V}_{\underline{k}}\cdot\underline{u})(\underline{V}_{\underline{k}'}\cdot\underline{u})[1 - \frac{z^2}{2\pi^2}]\} \quad. \quad (C.8)$$

Using (C.8) in (C.5), the periodicity of $\eta^0_{\underline{q}j}$, and inserting

an integration over ω with a delta function $\delta(\omega - \omega_j(\underline{k}' - \underline{k}))$,

$$P_{22} = \frac{\Omega^2}{24\pi^3 \hbar^3 \beta} \int_0^\infty d\omega R(\omega) \{ \int_{F.S.} \frac{dS_{\underline{k}}}{|\underline{V}_{\underline{k}}|} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} [(\underline{V}_{\underline{k}} \cdot \underline{u})^2$$

$$\times (1 + \frac{(\beta \hbar \omega)^2}{\pi^2}) - (\underline{V}_{\underline{k}} \cdot \underline{u})(\underline{V}_{\underline{k}'} \cdot \underline{u})(1 - \frac{(\beta \hbar \omega)^2}{2\pi^2})]$$

$$\times \sum_j |g_{\underline{k}',\underline{k};j}|^2 \, \delta(\omega - \omega_j(\underline{k}' - \underline{k}))\} \qquad (C.9)$$

where $R(\omega)$ is defined in Appendix A and by (4.39). Inserting (C.3) and (C.9) in (C.1), we obtain the expression (4.59).

APPENDIX D

In order to derive Eq. (5.4) of Section 5.1, we begin with Eq. (5.1):

$$\frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \underline{V}_{\underline{k}} \cdot e\underline{E} = \beta \sum_{\underline{k}'} (\Phi_{\underline{k}'} - \Phi_{\underline{k}}) f^0_{\underline{k}} (1 - f^0_{\underline{k}'}) W^{\underline{k}'}_{\underline{k}} \tag{D.1}$$

where $W^{\underline{k}'}_{\underline{k}}$ is given by (3.29). Using the deviation function given by (5.2)

$$\Phi_{\underline{k}} = e\underline{\Lambda}_{\underline{k}} \cdot \underline{E}$$

in (D.1), we obtain

$$\frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \underline{V}_{\underline{k}} \cdot \underline{u} = \beta \sum_{\underline{k}'} (\underline{\Lambda}_{\underline{k}'} \cdot \underline{u} - \underline{\Lambda}_{\underline{k}} \cdot \underline{u}) f^0_{\underline{k}} (1 - f^0_{\underline{k}'}) W^{\underline{k}'}_{\underline{k}} \tag{D.2}$$

where $\underline{u}$ is a unit vector in the direction of $\underline{E}$. We now integrate (D.2) over $\varepsilon_{\underline{k}}$.

The integral of the L.H.S. of (D.2) is

$$\int_0^\infty d\varepsilon_{\underline{k}} \frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \underline{V}_{\underline{k}} \cdot \underline{u} \quad ,$$

which, by (A.7) of Appendix A, may be written as

104

$$- \underline{V}_{\underline{k}} \cdot \underline{u}]_{\varepsilon_{\underline{k}}=\mu} \qquad (D.3)$$

where we have neglected derivatives with respect to energy of the electron velocity (evaluated at the Fermi energy).

Converting the sum over $\underline{k}'$ in (D.2) to an integral by means of (A.4) and (A.5) of Appendix A, the integral of the R.H.S. of (D.2) is

$$\frac{\beta\Omega}{8\pi^3\hbar} \int_0^\infty d\varepsilon_{\underline{k}} \int_0^\infty d\varepsilon_{\underline{k}'} \int \frac{dS(\varepsilon_{\underline{k}'})}{|\underline{V}_{\underline{k}'}|} [\underline{\Lambda}_{\underline{k}'} \cdot \underline{u} - \underline{\Lambda}_{\underline{k}} \cdot \underline{u}] f_{\underline{k}}^0 (1 - f_{\underline{k}'}^0) W_{\underline{k}}^{\underline{k}'} \quad . \quad (D.4)$$

Since the delta functions in $W_{\underline{k}}^{\underline{k}'}$ imply that $\varepsilon_{\underline{k}'} \simeq \varepsilon_{\underline{k}}$, we may use the same argument as in Appendix A to write (D.4) as

$$\frac{\beta\Omega}{4\pi^2\hbar^2} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} [\underline{\Lambda}_{\underline{k}'} \cdot \underline{u} - \underline{\Lambda}_{\underline{k}} \cdot \underline{u}] \sum_j |g_{\underline{k}',\underline{k};j}|^2 n_{\underline{q}j}^0 \delta(\underline{k}'-\underline{k})_{R'} \underline{q}$$

$$\times \int_0^\infty d\varepsilon_{\underline{k}} \int_0^\infty d\varepsilon_{\underline{k}'} f_{\underline{k}}^0 (1-f_{\underline{k}'}^0) \{\delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}} - \hbar\omega_j(\underline{q}))$$

$$+ e^{\beta\hbar\omega_j(\underline{q})} \delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}} + \hbar\omega_j(\underline{q}))\} \qquad (D.5)$$

where the surface integral is over the F.S., $\underline{k}$ is on the F.S., and we have used the expression (3.29) for $W_{\underline{k}}^{\underline{k}'}$. The first energy integral in (D.5) is the same as the one considered in Appendix A and its value is, by (A.11),

$$\frac{\hbar\omega_j(\underline{q})}{1 - e^{-\beta\hbar\omega_j(\underline{q})}} \quad .$$

It is obvious that the value of the second energy integral can be obtained from this result by replacing $[\hbar\omega_j(\underline{q})]$ by $[-\hbar\omega_j(\underline{q})]$ and multiplying by $e^{\beta\hbar\omega_j(\underline{q})}$; hence, the second integral has the same value as the first. Using the periodicity of $n^0_{\underline{q}j}$ and inserting an integration over ω with a delta function $\delta(\omega - \omega_j(\underline{k}'-\underline{k}))$, (D.5) becomes

$$\frac{\beta\Omega}{2\pi^2\hbar^2} \int_0^\infty d\omega R(\omega) \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} [\underline{\Lambda}_{\underline{k}'}\cdot\underline{u} - \underline{\Lambda}_{\underline{k}}\cdot\underline{u}] \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega-\omega_j(\underline{k}'-\underline{k}))$$

$$(D.6)$$

with $\underline{k}$ on the F.S. and $R(\omega)$ given by Eq. (4.39). The results (D.3) and (D.6) then lead to Eq. (5.4).

In order to derive Eq. (5.24) of Section 5.2, we begin with the Boltzmann equation (5.21):

$$-\frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} \frac{(\varepsilon_{\underline{k}}-\mu)}{T} \underline{V}_{\underline{k}} \cdot \nabla T = \beta \sum_{\underline{k}'} (\Phi_{\underline{k}'} - \Phi_{\underline{k}}) f^0_{\underline{k}}(1-f^0_{\underline{k}'}) W^{\underline{k}'}_{\underline{k}} \quad (E.1)$$

where $W^{\underline{k}'}_{\underline{k}}$ is given by (3.29). Using the deviation function given by (5.22),

$$\Phi_{\underline{k}} = -\frac{(\varepsilon_{\underline{k}}-\mu)}{T} \underline{\Lambda}^W_{\underline{k}} \cdot \nabla T \quad ,$$

in (E.1), we obtain

$$\frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} (\varepsilon_{\underline{k}}-\mu) \underline{V}_{\underline{k}} \cdot \underline{u} = \beta \sum_{\underline{k}'} [(\varepsilon_{\underline{k}'}-\mu)\underline{\Lambda}^W_{\underline{k}'} \cdot \underline{u} - (\varepsilon_{\underline{k}}-\mu)\underline{\Lambda}^W_{\underline{k}} \cdot \underline{u}] f^0_{\underline{k}}(1-f^0_{\underline{k}'}) W^{\underline{k}'}_{\underline{k}}$$

$$(E.2)$$

where $\underline{u}$ is a unit vector in the direction of ∇T. We now multiply (E.2) by $(\varepsilon_{\underline{k}}-\mu)$ and integrate over $\varepsilon_{\underline{k}}$.

The L.H.S. of (E.2) becomes

$$\int_0^\infty d\varepsilon_{\underline{k}} \frac{\partial f^0_{\underline{k}}}{\partial \varepsilon_{\underline{k}}} (\varepsilon_{\underline{k}}-\mu)^2 \underline{V}_{\underline{k}} \cdot \underline{u} \quad ,$$

which, by (A.7) of Appendix A, may be written as

$$- \frac{\pi^2}{3\beta^2} \, \underline{V}_{\underline{k}} \cdot \underline{u}]_{\varepsilon_{\underline{k}}=\mu} \qquad (E.3)$$

where we have neglected derivatives with respect to energy (evaluated at the Fermi energy) of the electron velocities.

When we convert the sum over $\underline{k}'$ to an integral by means of (A.4) and (A.5) of Appendix A, the R.H.S. of (E.2) becomes

$$\frac{\beta\Omega}{8\pi^3\hbar} \int_0^\infty d\varepsilon_{\underline{k}} \int_0^\infty d\varepsilon_{\underline{k}'} \int \frac{dS(\varepsilon_{\underline{k}'})}{|\underline{V}_{\underline{k}'}|} \, [(\varepsilon_{\underline{k}}-\mu)(\varepsilon_{\underline{k}'}-\mu)\underline{\Lambda}_{\underline{k}'}^W \cdot \underline{u} - (\varepsilon_{\underline{k}}-\mu)^2 \underline{\Lambda}_{\underline{k}}^W \cdot \underline{u}]$$

$$\times \, f_{\underline{k}}^0 (1-f_{\underline{k}'}^0) W_{\underline{k}}^{\underline{k}'} \qquad . \qquad (E.4)$$

Since the delta functions in $W_{\underline{k}}^{\underline{k}'}$ imply $\varepsilon_{\underline{k}'} \simeq \varepsilon_{\underline{k}}$, we may use the same argument as in Appendix A to write (E.4) as

$$\frac{\beta\Omega}{4\pi^2\hbar^2} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \sum_j |g_{\underline{k}',\underline{k};j}|^2 \, n_{\underline{q}j}^0 \delta(\underline{k}'-\underline{k})_{R'}\underline{q} \, \{\int_0^\infty d\varepsilon_{\underline{k}} \int_0^\infty d\varepsilon_{\underline{k}'}$$

$$\times \, [(\varepsilon_{\underline{k}}-\mu)(\varepsilon_{\underline{k}'}-\mu)\underline{\Lambda}_{\underline{k}'}^W \cdot \underline{u} - (\varepsilon_{\underline{k}}-\mu)^2 \underline{\Lambda}_{\underline{k}}^W \cdot \underline{u}] f_{\underline{k}}^0 (1-f_{\underline{k}'}^0)$$

$$\times \, [\delta(\varepsilon_{\underline{k}'}-\varepsilon_{\underline{k}}-\hbar\omega_j(\underline{q})) + e^{\beta\hbar\omega_j(\underline{q})} \delta(\varepsilon_{\underline{k}'}-\varepsilon_{\underline{k}}+\hbar\omega_j(\underline{q}))]\} \qquad (E.5)$$

where the surface integral is over the F.S., $\underline{k}$ is on the F.S., and we have used (3.29). By means of the transformations

$$\eta = \beta(\varepsilon_{\underline{k}}-\mu)$$

and

$$z = \beta \hbar \omega_j(\underline{q}) \quad ,$$

the first energy integral in the brackets of (E.5) may be written as

$$\frac{1}{\beta^3} \int_{-\infty}^{+\infty} d\eta \; \frac{[\eta(\eta+z)\underline{\Lambda}_{\underline{k}'}^W \cdot \underline{u} - \eta^2 \underline{\Lambda}_{\underline{k}}^W \cdot \underline{u}]}{(e^\eta+1)(1+e^{-(\eta+z)})}$$

where, as in Appendix A, the lower limit of integration, $(-\frac{\mu}{k_B T})$, has been replaced by $(-\infty)$. Using (B.8) and (B.9) of Appendix B, the value of this integral is

$$\frac{\pi^2}{3\beta^3} \frac{z}{1-e^{-z}} \{(1 + \frac{z^2}{\pi^2})(\underline{\Lambda}_{\underline{k}'}^W \cdot \underline{u} - \underline{\Lambda}_{\underline{k}}^W \cdot \underline{u}) - \frac{3z^2}{2\pi^2} \underline{\Lambda}_{\underline{k}}^W \cdot \underline{u}\} \quad .$$

$$(E.6)$$

It is easily seen that the second energy integral can be obtained from the first by replacing z by $(-z)$ and multiplying by e^z; hence, it also has the value given by (E.6). Using the periodicity of $n_{\underline{q}j}^0$ and inserting an integration over ω with the delta function $\delta(\omega-\omega_j(\underline{k}'-\underline{k}))$, (E.5) becomes, using the result (E.6),

$$\frac{\Omega}{6\hbar^2\beta} \int_0^\infty d\omega R(\omega) \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \{(1 + (\frac{\hbar\omega}{\pi k_B T})^2)(\underline{\Lambda}_{\underline{k}'}^W \cdot \underline{u} - \underline{\Lambda}_{\underline{k}}^W \cdot \underline{u})$$

$$- \frac{3}{2\pi^2}(\frac{\hbar\omega}{k_B T})^2 \underline{\Lambda}_{\underline{k}}^W \cdot \underline{u}\} \sum_j |g_{\underline{k}',\underline{k};j}|^2 \delta(\omega-\omega_j(\underline{k}'-\underline{k})) \qquad (E.7)$$

where $\underline{k}$ is on the F.S. and $R(\omega)$ is given by Eq. (4.39). The
results (E.3) and (E.7) then lead to Eq. (5.24).

APPENDIX F

We discuss here the approximation (6.5) of Section 6.2 for the (dilute) alloy transport scattering times:

$$\frac{1}{\tau(\underline{k},T)} = \frac{1}{\tau_0(\underline{k},T)} + \frac{1}{\tau_R} \, . \qquad\qquad (F.1)$$

We make the initial assumption that the scattering of a conduction electron from $\underline{k}$ to $\underline{k}'$ due to the presence of small amounts of impurities in a metal may be characterized by an intrinsic transition probability per unit time, denoted by $V_{\underline{k}}^{\underline{k}'}$. The detailed structure of $V_{\underline{k}}^{\underline{k}'}$ does not concern us here, but we do assume elastic scattering ($V_{\underline{k}}^{\underline{k}'}$ contains $\delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}})$) and the principle of microscopic reversibility [32, 33]

$$V_{\underline{k}}^{\underline{k}'} = V_{\underline{k}'}^{\underline{k}} \, . \qquad\qquad (F.2)$$

Then it follows that the term

$$\sum_{\underline{k}'} [f_{\underline{k}'}(1-f_{\underline{k}})V_{\underline{k}'}^{\underline{k}} - f_{\underline{k}}(1-f_{\underline{k}'})V_{\underline{k}}^{\underline{k}'}] \qquad\qquad (F.3)$$

should be added to the R.H.S. of the expression (3.11) for

111

$\dfrac{\partial f_{\underline{k}}}{\partial t}]_{scatt}$ when impurity scattering is included in addition

to the scattering due to the electron-phonon interaction.

Ziman [11] also combines the impurity and phonon scattering

effects in this way; however, this assumption that effects

of scattering by lattice vibrations and by impurities are

independent and additive is certainly not correct [16, 31, 34, 35]

There will be additional scattering due to (1) interference

between phonon and impurity scattering and (2) inelastic

electron-impurity scattering; these processes result from

the oscillations of the impurity ions about their

equilibrium positions. Thus in our approximation we ignore

dynamic effects of the impurities and retain only the

static effects.

Returning to the expression (F.3) we see that it may

be written as

$$\sum_{\underline{k}'} (f_{\underline{k}'} - f_{\underline{k}}) V_{\underline{k}}^{\underline{k}'} \tag{F.4}$$

using (F.2). The equilibrium situation argument (3.12) is

unaffected by the addition of (F.4) to the R.H.S. of (3.11)

since the electron-phonon and impurity terms are

independent; moreover, (F.4) automatically vanishes in the

equilibrium situation due to the elastic scattering delta

function in $V_{\underline{k}}^{\underline{k}'}$ ($f_{\underline{k}}^0$ depends only on energy $\varepsilon_{\underline{k}}$ at a given

temperature). Hence the expansion (3.15) may be used

exactly as in Section 3.2 and we have the additional term

due to (F.4):

$$\beta \sum_{\underline{k}'} (\phi_{\underline{k}'} - \phi_{\underline{k}}) f_{\underline{k}}^0 (1-f_{\underline{k}'}^0) V_{\underline{k}}^{\underline{k}'} \tag{F.5}$$

where $f_{\underline{k}'}^0 = f_{\underline{k}}^0$ by the energy delta function in $V_{\underline{k}}^{\underline{k}'}$. We note that at this point $\phi_{\underline{k}}$ is still unspecified and determined only by the definition (3.15). Assuming the phonons to be in equilibrium (no phonon drag effects) the linearized Boltzmann equation for the conduction electrons (3.28) in the absence of a temperature gradient (Eq. (5.1)) is now modified to

$$\frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \underline{V}_{\underline{k}} \cdot e\underline{E} = \beta \sum_{\underline{k}'} (\phi_{\underline{k}'} - \phi_{\underline{k}}) f_{\underline{k}}^0 (1-f_{\underline{k}'}^0) [W_{\underline{k}}^{\underline{k}'} + V_{\underline{k}}^{\underline{k}'}] \tag{F.6}$$

where $W_{\underline{k}}^{\underline{k}'}$ is given by (3.29).

We now use the approximation (6.2)

$$\phi_{\underline{k}} = e\tau(\underline{k},T)\underline{V}_{\underline{k}} \cdot \underline{E}$$

but, in order to make the correspondence with the previous analysis for pure crystals as clear as possible, we write this as

$$\phi_{\underline{k}} = e\underline{\Lambda}_{\underline{k}} \cdot \underline{E} \tag{F.7}$$

where the mean free path is approximated by

$$\underline{\Lambda}_{\underline{k}} = \tau(\underline{k},T)\underline{V}_{\underline{k}} \qquad \text{(F.8)}$$

with $\tau(\underline{k},T)$ the (dilute) alloy transport scattering time. As in Appendix D, the integration over $\varepsilon_{\underline{k}}$ of (F.6) leads to the result (5.4) with the additional term

$$\beta \int_0^\infty d\varepsilon_{\underline{k}} \sum_{\underline{k}'} (\underline{\Lambda}_{\underline{k}} - \underline{\Lambda}_{\underline{k}'}) f_{\underline{k}}^0 (1-f_{\underline{k}'}^0) V_{\underline{k}}^{\underline{k}'} \qquad \text{(F.9)}$$

due to $V_{\underline{k}}^{\underline{k}'}$ on the R.H.S., where $\underline{k}$ is on the F.S.. Converting the sum over $\underline{k}'$ to an integral by (A.4) and (A.5) of Appendix A, the integral over $\varepsilon_{\underline{k}'}$ is eliminated by the $\delta(\varepsilon_{\underline{k}'} - \varepsilon_{\underline{k}})$ in $V_{\underline{k}}^{\underline{k}'}$ and (F.9) becomes

$$- \frac{\Omega}{8\pi^3\hbar} \int_0^\infty d\varepsilon_{\underline{k}} \frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} \int \frac{dS(\varepsilon_{\underline{k}'})}{|\underline{V}_{\underline{k}'}|} (\underline{\Lambda}_{\underline{k}} - \underline{\Lambda}_{\underline{k}'}) V_{\underline{k}}^{\underline{k}'}$$

using

$$\frac{\partial f_{\underline{k}}^0}{\partial \varepsilon_{\underline{k}}} = - \beta f_{\underline{k}}^0 (1-f_{\underline{k}}^0) \quad .$$

By (A.7) of Appendix A we have, ignoring energy derivatives (evaluated at the Fermi energy) of the surface element, electron velocities, mean free path, and $V_{\underline{k}}^{\underline{k}'}$,

$$\frac{\Omega}{8\pi^3\hbar} \int_{\text{F.S.}} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} (\underline{\Lambda}_{\underline{k}} - \underline{\Lambda}_{\underline{k}'}) V_{\underline{k}}^{\underline{k}'} \qquad \text{(F.10)}$$

where $\underline{k}$ is on the F.S..

Using the approximation (F.8) and the expansion (5.5)

$$\underline{\Lambda}_{\underline{k}} - \underline{\Lambda}_{\underline{k}'} = \tau(\underline{k})[\underline{V}_{\underline{k}} - \underline{V}_{\underline{k}'}] + [\tau(\underline{k}) - \tau(\underline{k}')]\underline{V}_{\underline{k}'} \quad ,$$

we take the dot product of $\underline{V}_{\underline{k}}$ ($\underline{k}$ on the F.S.) with Eq. (5.4) as before and divide by $|\underline{V}_{\underline{k}}|^2$ to obtain Eq. (5.6) with the additional term on the R.H.S. (due to (F.10))

$$\frac{\Omega}{8\pi^3\hbar} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} \left\{\tau(\underline{k})[1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}] + [\tau(\underline{k}) - \tau(\underline{k}')]\frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}\right\} v_{\underline{k}}^{\underline{k}'} \quad .$$

Since we have a dilute alloy, the arguments following Eq. (5.6) are still approximately valid and we may drop the terms involving $[\tau(\underline{k}) - \tau(\underline{k}')]$. Thus as a first approximation we have

$$\frac{1}{\tau(\underline{k},T)} = \frac{4\pi}{k_B T} \int_0^\infty d\omega R(\omega) \beta_{tr}^2 F(\omega,\underline{k}) + \frac{\Omega}{8\pi^3\hbar} \int_{F.S.} \frac{dS_{\underline{k}'}}{|\underline{V}_{\underline{k}'}|} [1 - \frac{\underline{V}_{\underline{k}} \cdot \underline{V}_{\underline{k}'}}{|\underline{V}_{\underline{k}}|^2}] v_{\underline{k}}^{\underline{k}'}$$

where the first term is the result (5.10) for the pure crystal scattering time which we denote by $\frac{1}{\tau_0(\underline{k},T)}$. The term involving impurity scattering may be written simply as $\frac{1}{\tau_R(\underline{k})}$ in terms of an anisotropic residual scattering time. Assuming τ_R to be isotropic we then have

$$\frac{1}{\tau(\underline{k},T)} = \frac{1}{\tau_0(\underline{k},T)} + \frac{1}{\tau_R}$$

and we determine τ_R from the experimental value of the residual resistivity ρ_R by the relation

$$\rho_R = \frac{m}{ne^2 \tau_R} \quad .$$

REFERENCES

1) A. A. Maradudin, E. W. Montroll, G. H. Weiss, and
   I. P. Ipatova, <u>Theory of Lattice Dynamics in the
   Harmonic Approximation</u>, (Academic Press, New York,
   1971).

2) M. Born and K. Huang, <u>Dynamical Theory of Crystal
   Lattices</u>, (Oxford University Press, 1954).

3) M. Dresden, Rev. Mod. Phys. <u>33</u>, 265 (1961).

4) P. T. Truant and J. P. Carbotte, Can. J. Phys. <u>51</u>, 922
   (1973).

5) W. A. Harrison, <u>Pseudopotentials in the Theory of Metals</u>,
   (W. A. Benjamin, Inc., New York, 1966).

6) J. P. Carbotte and R. C. Dynes, Phys. Rev. <u>172</u>, 476
   (1968).

7) J. M. Ziman, <u>Principles of the Theory of Solids</u>,
   (Cambridge University Press, 1972).

8) J. M. Ziman, <u>Electrons and Phonons</u>, (Oxford University
   Press, 1960).

9) P. L. Taylor, <u>A Quantum Approach to the Solid State</u>,
   (Prentice-Hall, Inc., Englewood Cliffs, New Jersey,
   1970).

10) See reference (8), page 383.

11) See reference (8), Chapters VII and IX.

12) F. W. Sheard, J. Phys. F: Metal Phys. $\underline{3}$, 1963 (1973).

13) M. Kaveh and N. Wiser, Phys. Rev. Lett. $\underline{29}$, 1374 (1972).

14) B. Hayman and J. P. Carbotte, Can. J. Phys. $\underline{51}$, 1109 (1973).

15) See reference (9), pages 272-273.

16) J. Bass, Advan. Phys. $\underline{21}$, 431 (1972).

17) J. W. Ekin and B. W. Maxfield, Phys. Rev. B $\underline{6}$, 2071 (1972).

18) J. W. Ekin and A. Bringer, Phys. Rev. B $\underline{7}$, 4468 (1973).

19) C. Kittel, Introduction to Solid State Physics, (John Wiley and Sons, Inc., New York, 1971), pp. 210-211.

20) B. Hayman and J. P. Carbotte, Can. J. Phys. $\underline{49}$, 1952 (1971).

21) B. Hayman and J. P. Carbotte, J. Phys. F: Metal Phys. $\underline{2}$, 915 (1972).

22) P. B. Allen, Phys. Rev. B $\underline{3}$, 305 (1971).

23) P. T. Truant, Ph.D. Thesis, McMaster University, (unpublished), 1972.

24) J. W. Ekin, Phys. Rev. B $\underline{6}$, 371 (1972).

25) M. P. Greene and W. Kohn, Phys. Rev. $\underline{137}$, A513 (1965).

26) J. E. Robinson and J. D. Dow, Phys. Rev. $\underline{171}$, 815 (1968).

27) P. L. Taylor, Proc. Roy. Soc. (London) $\underline{A275}$, 200 (1963).

28) M. Tinkham, Group Theory and Quantum Mechanics, (McGraw-Hill Book Company, New York, 1964), page 279.

29) P. T. Truant and J. P. Carbotte, Sol. St. Comm. 11, 443 (1972).

30) F. W. Kus and J. P. Carbotte, J. Phys. F: Metal Phys. 3, 1828 (1973).

31) F. W. Kus, Ph.D. Thesis, McMaster University, (unpublished), 1973.

32) F. Reif, Fundamentals of Statistical and Thermal Physics, (McGraw-Hill, New York, 1965), page 384.

33) See reference (8), page 266.

34) Yu. Kagan and A. P. Zhernov, Soviet Phys. JETP 23, 737 (1966).

35) R. S. Seth and S. B. Woods, Phys. Rev. B 2, 2961 (1970).

36) P. Salvadori, E. Babić, R. Krsnik, and C. Rizzuto, J. Phys. F: Metal Phys. 3, L195 (1973).

37) G. T. Meaden, Electrical Resistance of Metals, (Plenum Press, New York, 1965).