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AN INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL RESISTIVITY OF CONCENTRATED STRONG-SCATTERING ALLOYS

A Thesis
Presented to
The Faculty of the Department of Physics
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Doctor of Philosophy

by
An-Ban Chen
August 1971

APPROVAL SHEET

This thesis is submitted in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy
in
Physics

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LIST OF FIGURES AND FIGURE CAPTIONS

ABSTRACT

A theoretical investigation is made of the temperature dependence of the electrical resistivity of concentrated strong-scattering, disordered alloys. First, the deformation potential theory and the semi-classical Boltzmann equation are used to study the effect of the collision rate on the electron-phonon coupling constant. The result indicates that the criterion on collision rates for the validity of the use of Born-Oppenheimer adiabatic approximation may be beyond the previously accepted limit. The theory also indicates that although it occurs in principle, in real alloys the electron-phonon interaction is never quenched by fast collisions. Thus, this mechanism fails to account for the quenched temperature dependence of the resistivity observed in many alloys. Second, a model calculation for the temperature dependence of the electronic density of states and the conductivity based on the Kubo linear response theory is made by introducing thermal disorder in the coherent potential approximation. Thermal disorder is found to smear and broaden the static alloy density of states. The electrical resistivity in weak scattering alloys always increases with the temperature. But in the strong-scattering case, the temperature coefficients of resistivity can be positive, zero, or negative, depending on the location of the Fermi energy.

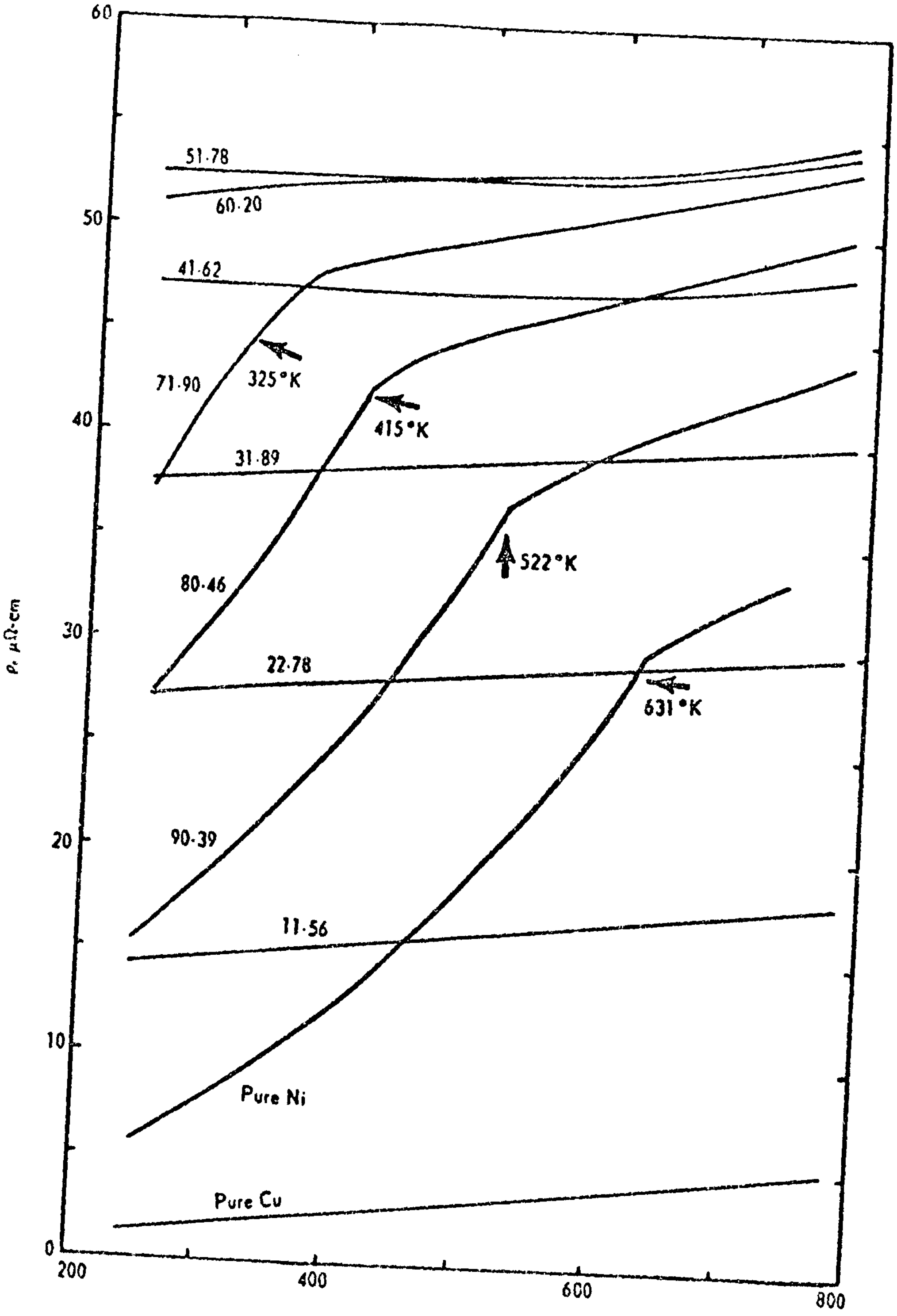
AN INVESTIGATION OF THE TEMPERATURE DEPENDENCE OF THE ELECTRICAL RESISTIVITY OF CONCENTRATED STRONG-SCATTERING ALLOYS

INTRODUCTION

The macroscopic electronic properties of alloys, such as the d.c. electrical resistivity and the Hall coefficients, have been fruitful subjects for experiments,[1,2] because useful devices, e.g. strain gauges, have been constructed which depend on these properties, they can be measured accurately, and the results of these experiments provide an insight into the microscopic behavior of the materials. The theoretical interpretation of these properties has lagged far behind the wealth of experimental information. For example, it is well known that constantan has a very constant resistivity over a wide range of temperature (See Fig. I). Because of a formidable combination of complexities, (a detailed discussion of this point is given at the end of Chap. 3), this fact remains a challenging theoretical problem. It is too early a stage in the development of alloy theory to give a first principles, quantitative description of the transport properties of concentrated, strong scattering, disordered systems, like constantan, since the easier and more basic electronic quantity, the static alloy density of states, is just beginning to be understood.[3,4,5,6] At present, even a qualitative or model description of the transport properties in such alloys is greatly needed.

Desiring to understand the temperature dependence of electrical resistivity, we started an investigation of the role of lattice motion in

Figure I. Electrical resistivity of Cu-Ni as a function of temperature (Ref. 2. p. 118). The numbers relate to the concentrations of Ni. The temperature indicated by the arrows are the Curie points. Those alloys containing about 40 to 45 at -% of Ni which have very low resistivity temperature coefficients are known as constantans.



ρ, μΩ-cm
0
10
20
30
40
50
60
200
400
600
800
51·78
60·20
41·62
71·90
325°K
415°K
31·89
80·46
522°K
22·78
631°K
90·39
11·56
Pure Ni
Pure Cu

Figure I

an alloy. The first simple question we ask is: can the nature of the electron-phonon interaction be affected by the high collision rate of electrons in an impure material? We approach this problem from deformation potential theory and the classical Boltzmann equation. Using the collision time approximation, we derive "collision time" dependent deformation potentials for longitudinal and transverse phonons. The conclusion is that the collision rates encountered in real alloys can never become large enough to affect the electron-phonon interaction. The characteristic collision time which must be reached before collisions change the deformation potential is much too fast to find even in the most disordered case. This characteristic time condition can be understood from the following point of view. The condition indicates that the Born-Oppenheimer adiabatic approximation[7] is valid as long as the diffusion length of an electron in a phonon period is greater than the Thomas-Fermi screening length. This is equivalent to the condition that the effective force on an electron due to collisions is smaller than the Coulomb force producing screening.

The second problem, the more important result of this research, is to investigate the temperature dependence of the electronic density of states and electrical resistivity of disordered alloys from a more rigorous theory. First, we set up the formalism for the density of states and d.c. conductivity of disordered systems in terms of the averaged Green's functions $\langle\langle G\rangle\rangle$ and $\langle\langle GG\rangle\rangle$. Then a general discussion of the temperature dependent aspects of the formulae is given along with a review of directly related work. After giving an outline of the formalism of the coherent potential approximation (CPA),[3,8,9] we present a model calculation based on CPA.

In the model calculation, we use a model Hamiltonian similar to that of Velický[3] et.al., but with thermal disorder added. A new interpretation of the basis and matrix elements which enter into the formalism is given, and this is then incorporated in the matrix manipulation of the averaged Green's function. The thermal disorder Hamiltonian takes the usual form containing one-phonon creation and annihilation operators. Working within this model, we reduce the CPA self-consistent operator equation to a scalar integral equation for the self-energy. In order to obtain the numerical results, we use simple forms for the input functions: a semi-ellipse for the pure crystal density of states, a velocity functional form proportional to the density of states, and a Gaussian distribution governing the thermal fluctuation of the random atomic energy levels. Following a detailed discussion of the numerical method of solving the integral equation, we present the results of numerical computations for some representative parameters. A systematic study of self-energies, the total density of states, the component density of states and the conductivity is exhibited in the form of three dimensional plots. Thermal disorder is found to smear and broaden the static alloy density of states. Disorder always increases the electrical resistivity in the weak scattering limit. However, in the strong scattering case, the conductivity may decrease, increase, or remain constant with temperature depending on the location of the Fermi energy.

The numerical results are followed by a discussion of the implications of the model calculation. The non-perturbation nature of the problem is briefly mentioned, then an interpretation of the selfenergy in the averaged Green's function is given. We show that the relaxation time, corresponding to the imaginary part of the self-energy appearing in the formulae for the density of states and the conductivity, is not the usual decay time of the Bloch states, but rather is the decay time for a different process. However, in the weak scattering limit, there is no distinction between these two relaxation times. We also attempt, by a proper choice of the relaxation time and the Fermi velocity, to reduce the CPA conductivity formula to the customary form which aids in the physical interpretation of the results. In the free electron case, this is particularly vivid.

Finally, a systematic analysis of the problems associated with a real transition metal alloy is given. From this, we can see how far we are from the goal of a quantitative theory of transition metal alloys.

THE INFLUENCE OF THE COLLISION RATE ON THE ELECTRON-PHONON INTERACTION

A. A Simple Illustration of a Saturated Collision Rate and the Temperature Dependence of the Electrical Resistivity.

The simplest formula for the d.c. electrical resistivity is[10]

$$\rho = \frac{m^*}{n_0 e^2}\frac{1}{\tau} , \qquad (2\text{-}1)$$

where m* is the effective mass of the carriers, n_0 is the number of carriers per unit volume and τ is the collision time.

The simplest approximation for τ in an impure metal at finite temperature is the Matthiessen's[11] rule,

$$\frac{1}{\tau} = \frac{1}{\tau_I} + \frac{1}{\tau_p} , \qquad (2\text{-}2)$$

where $1/\tau_I$ and $1/\tau_p$ are the contributions to the total collision rate $1/\tau$ due to impurity scattering and electron-phonon interaction respectively. Here $1/\tau_I$ is independent of temperature while $1/\tau_p$ is linear in temperature at high temperatures.

If the resistivity of certain concentrated alloys, such as constantan, were calculated using the Matthiessen's rule, then the temperature coefficients $\frac{d\rho}{dT}$ of the calculated resistivity would be greater than the observed value. (The observed $\frac{d\rho}{dT}$ for constantan is almost zero as seen from Fig. I). It is generally found that metals which exhibit small temperature-coefficients in resistivity also have rather large resistivities, so one question that may be asked is, can high collision rates modify the electron-phonon coupling constant in such a way that the temperature variation of the resistivity is quenched? The answer to this question is yes in principle, but not in practice. To serve as an introduction to the chapter, an outline of a theory will be developed to show how the resistivity variation can be quenched. A detailed theory could easily be constructed following this outline.

Suppose we have a collision-time dependent electron-phonon interaction which can be expressed as

$$H_{e.p} = H^{o}_{e.p}\, g(\tau)\,, \tag{2-3}$$

where the function $g(\tau)$ (See Fig. II) contains the effect of collisions and is a function whose magnitude starts at unity and decreases sharply as $1/\tau$ exceeds some critical value $1/\tau_c$. $H^{0}_{e.p}$ is the collision-time independent electron-phonon interaction Hamiltonian. A collision time τ_p' is associated with $H_{e.p}$ as τ_p is associated with $H^{0}_{e.p}$. As a consequence of 'golden rule' and Eq. (2-3), τ_p' is related to τ_p by

$$\frac{1}{\tau_p'} = |g(\tau)|^2 \frac{1}{\tau_p}\,. \tag{2-4}$$

Applying Matthiessen's rule in our case, we arrive at a self-consistent equation for τ,

$$\frac{1}{\tau} = \frac{1}{\tau_I} + \frac{1}{\tau_p'} = \frac{1}{\tau_I} + |g(\tau)|^2 \frac{1}{\tau_p}\,. \tag{2-5}$$

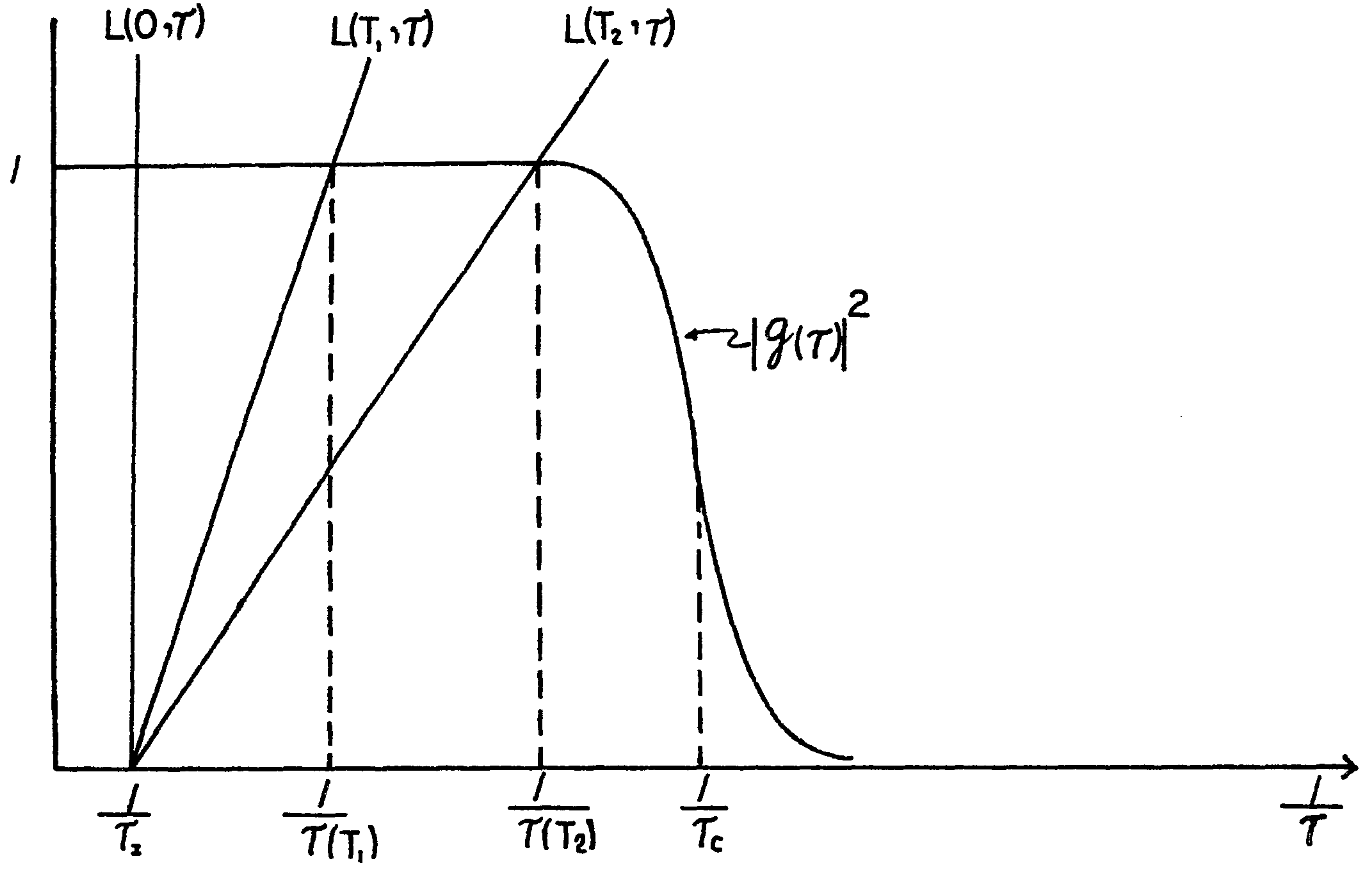
A graphical solution for $1/\tau$ from Eq. (2-5) is shown in Fig. II. We find that if $1/\tau_I < 1/\tau_c$, the collision rate increases with temperature and is saturated at $1/\tau_c$. If $1/\tau_I > 1/\tau_c$, a situation which never occurs in real metals as will be seen later, then the collision rate is constant, not varying with temperature, and $1/\tau \simeq 1/\tau_I$.

Figures II(a) - II(c). The sketches of the graphical solution for Eq. (2-5), i.e. $\frac{1}{\tau} = \frac{1}{\tau_I} + |g(T)|^2 \frac{1}{\tau_p(T)}$, or $L(T,\tau) \equiv \tau_p(T)\left(\frac{1}{\tau} - \frac{1}{\tau_I}\right) = |g(\tau)|^2$. As a function of $1/\tau$, $|g(\tau)|^2$ drops sharply when $1/\tau > 1/\tau_c$.

Figure II(a). For $1/\tau_I \ll 1/\tau_c$, the solutions, $1/\tau(T)$, increase linearly with $1/\tau_p(T)$.

Figure II(b). For $1/\tau_I \lesssim 1/\tau_c$, the solutions, $1/\tau(T)$, are quenched around $1/\tau_c$.

Figure II(c). For $1/\tau_I > 1/\tau_c$, the solutions, $1/\tau(T)$, are independent of T and approximately equal to $1/\tau_I$.



$L(0,\tau)$
$L(T_1,\tau)$
$L(T_2,\tau)$
1
$|g(\tau)|^2$
$\frac{1}{\tau_z}$
$\frac{1}{\tau(T_1)}$
$\frac{1}{\tau(T_2)}$
$\frac{1}{\tau_c}$
$\frac{1}{\tau}$

Figure II(a)

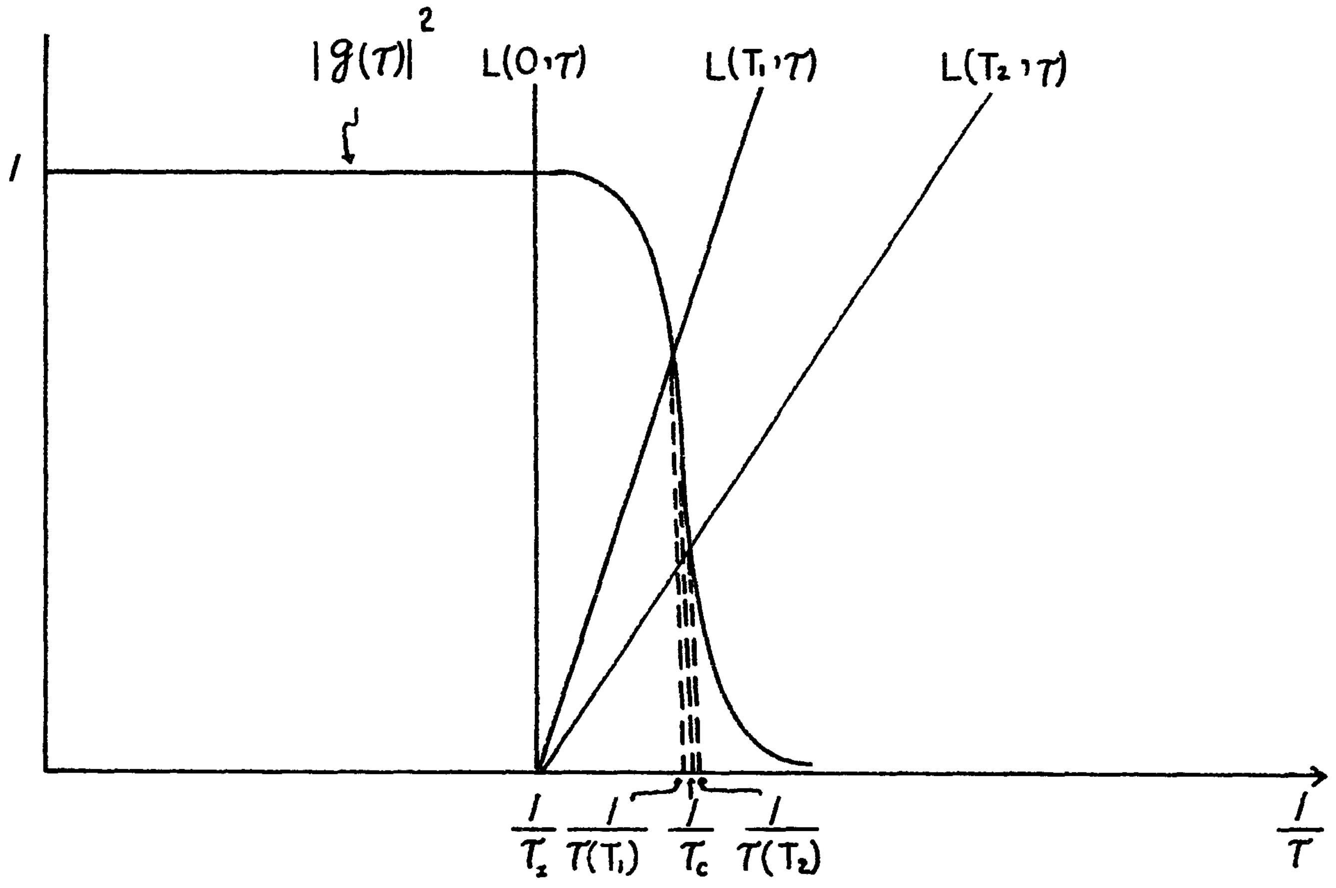

$|g(\tau)|^2$
$L(0,\tau)$
$L(T_1,\tau)$
$L(T_2,\tau)$
1
$\frac{1}{\tau_x}$
$\frac{1}{\tau(T_1)}$
$\frac{1}{\tau_c}$
$\frac{1}{\tau(T_2)}$
$\frac{1}{\tau}$

Figure II(b)

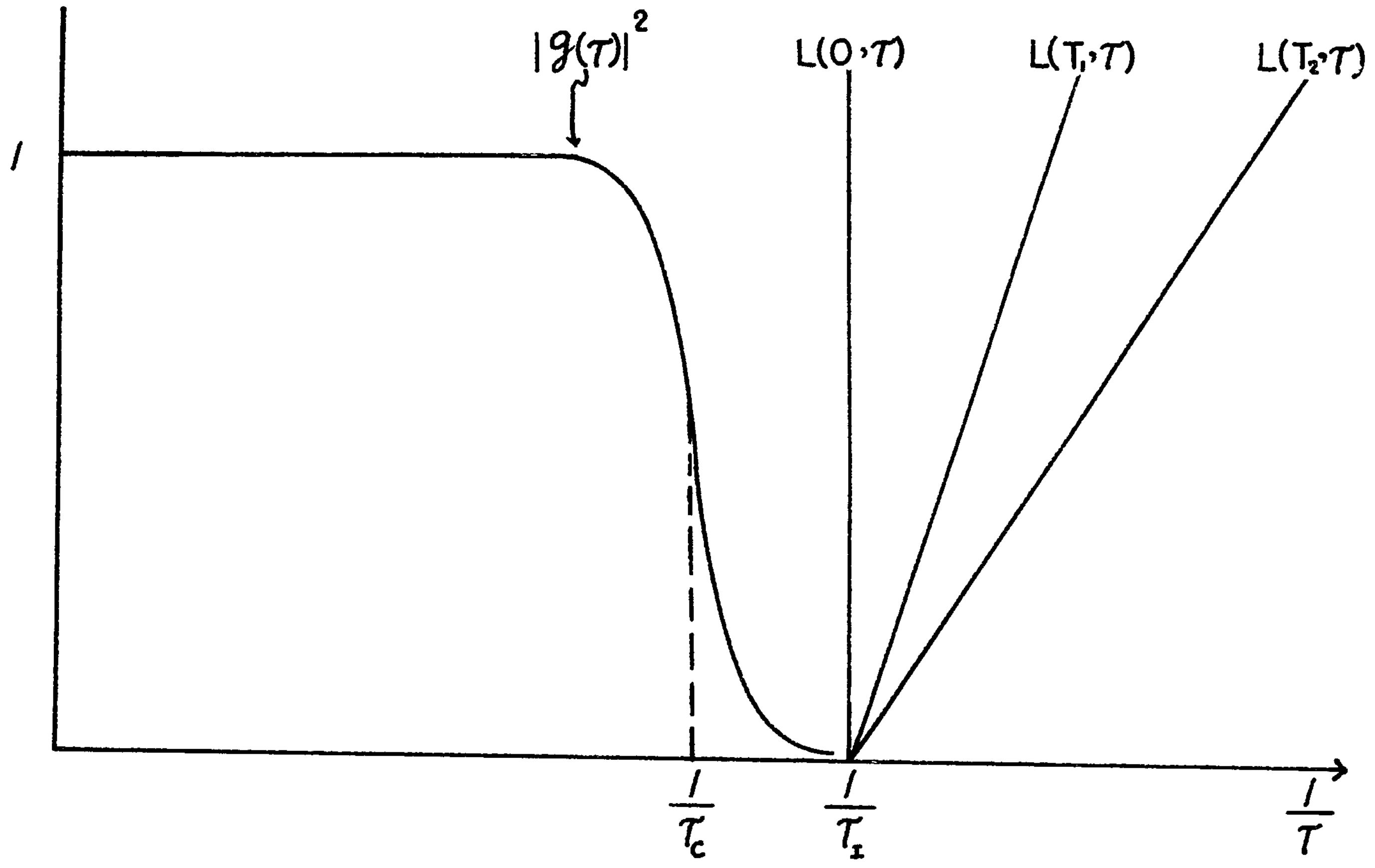


Figure II(c)

The next sections will give the details of how to calculate $H_{e.p}$ from the "bare" deformation potential. It will be seen later that the resulting $H_{e.p}$ for the longitudinal phonons does have the character represented by Eq. (2-3), but the critical collision rate $1/\tau_c$ is of order of $\omega(\frac{v_F}{v_s})^2 \simeq 10^{19}$ sec^{-1}, which can never be reached in a real alloy. Here ω is a typical phonon frequency, say the Debye frequency, v_s is the speed of sound, and v_F is the electron velocity at the Fermi level. For transverse phonons, $1/\tau_c$ corresponds to $\omega(\frac{v_F}{v_s}) \simeq 10^{16}$ sec^{-1}, but the saturation effect is only effective for long wave length phonons, which contribute very little to resistivity. So the saturated collision rate cannot account for the electrical resistivity of constantan.

B. Deformation Potential.

When the atomic lattice is subjected to smooth, longwave deformation, so that locally it can still be thought of as crystalline, a good description of the electron dynamics can be obtained from the band structure as a function of position. The deformation potential is the energy change of an electron per unit strain relative to its energy in the static crystal when the crystal is distorted by a phonon. In a metal the major contribution to the deformation potential arises because the electrons do not follow the motion of the ions perfectly. Consequently, in the Coulomb gauge, a longitudinal phonon produces an electrical potential and a transverse phonon produces a vector potential. A single electron moves in the electrical potential caused by all the other electrons and the distorted ion lattice. The energy of interaction constitutes an extra term in the one electron Hamiltonian. This charge shift plays a very important role in the determination of electron-phonon interaction in metals.[12] But in an alloy, the high collision rate of the electrons with defects, i.e. "impurities" and phonons, tends to drag the electrons along with the moving lattice in an equilibrium where the electrons move rigidly with the ions. Thus the charge shift, and as a consequence the electron-phonon interaction, can be modified by collisions.

We shall derive the collision time dependent deformation potential by generalizing arguments which have been developed for the theory of acoustic attenuation.[13,14,15] The acoustic attentuation theory is modified here in two ways; first, the effect of phonons on the band structure is formally introduced into the theory, and second, the solution method previously used, i.e. the Chambers trajectory method,[16] is replaced by one in which the physical approximations are more evident. The theory is semi-classical and in outline proceeds as follows. A Boltzmann equation for the temporal and spatial dependence of the electron distribution function, with a collision time approximation, is introduced. A phonon acts as an external driving force in this equation. The Boltzmann equation is solved self-consistently with Maxwell's equations to yield a deformation potential which is an explicit function of collision time.

It is well known that the deformation potential calculation outlined above is only justified for long wave phonons.[17] For short wave phonons, we have an inherently more difficult problem. Our method cannot yield accurate answers. However, it should indicate the general trends. We shall use three items as input for our calculation: the unperturbed band structure, the 'bare' deformation potential (to be discussed shortly) and the collision time which represents all the collisions. The point of interest is how collisions modify the deformation potential.

C. The Calculation of the Deformation Potential.

1. General Formalism

Consider a crystal with n_0 mono-valent atoms per unit volume at a finite temperature T so there are a number of phonons thermally excited. Let us focus on the electron interaction with one mode of the phonon spectrum, wave vector $\vec{q}$ and frequency ω. If the lattice is deformed smoothly, as is always assumed in the deformation potential formalism, the phonon is characterized by the atomic velocity field

$$\vec{u}(\vec{r},t) = \delta\vec{u}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} . \tag{2-6}$$

This field then generates forces on the electrons which shift the electron distribution. Also, the electrons collide with lattice defects which tend to force the electrons toward a new local equilibrium. In a steady state, we shall find the effective forces on the electrons and their energy shift by solving the Boltzmann equation.

Let $f(\vec{r},\vec{k},t)$ be the distribution function of the electrons. It is the density of electrons at location $\vec{r}$, with wave vector $\vec{k}$, at time t. The Boltzmann equation in the collision time approximation is:

$$\frac{\partial f}{\partial t} + \frac{\hbar\vec{k}}{m}\cdot\frac{\partial f}{\partial\vec{r}} + \frac{\vec{F}}{\hbar}\cdot\frac{\partial f}{\partial\vec{k}} = -\frac{f(\vec{r},\vec{k},t) - f_{l.e}(\vec{r},\vec{k},t)}{\tau} , \tag{2-7}$$

where $f_{\ell.e}$ is the local equilibrium distribution to which the electron collisions tend to drive the system, and $\vec{F}$ is the effective force on the electrons caused by the phonon. The Boltzmann equation, Eq. (2-7), has been written assuming that the effective electron mass equals the free electron mass. At any point in space, the electron density $n(\vec{r},t)$ is related to $f(\vec{r},\vec{k},t)$ by

$$n(\vec{r},t) = \int d^3k \, f(\vec{r},\vec{k},t) . \tag{2-8}$$

In thermal equilibrium and in the absence of phonons, the distribution function $f_e(\vec{k})$ is a Fermi distribution:

$$f_e(\vec{k}) = \frac{1}{4\pi^3} \frac{1}{e^{\beta(\mathcal{E}^0_{\vec{k}} - \mu_0)} + 1} , \tag{2-9}$$

where $\beta = 1/_{KT}$, K is the Boltzmann constant. The equilibrium electron density n_0 is

$$n_0 = \int d^3k \, f_e(\vec{k}) . \tag{2-10}$$

Eq. (2-10) determines μ_0, the Fermi energy. $\mathcal{E}^0_{\vec{k}}$ is the unperturbed energy of the electron, i.e., the unperturbed band structure.

The local equilibrium distribution into which the collisions tend to drive the distribution is a drifted, local Fermi distribution $f_{\ell.e}$

$$f_{\ell.e}(\vec{r},\vec{k},t) = \frac{1}{4\pi^3} \frac{1}{e^{\beta[\mathcal{E}_{\vec{k}}(\vec{r},t) - \mu(\vec{r},t) - m\vec{V}_{\vec{k}}\cdot\vec{u}(\vec{r},t)]}} . \tag{2-11}$$

Except for terms of order u^2, that we neglect, $f_{\ell.e}$ is simply a Fermi function in terms of the electron energies as seen by an observer riding the atoms at velocity $\vec{u}$.[18] The "drift" term $-m\vec{V}_{\vec{k}}\cdot\vec{u}(\vec{r},t)$ transforms the rest-frame energy to that measured in the moving frame.

The distribution Eq. (2-11) is called a "local" distribution, because the local Fermi energy $\mu(\vec{r},t)$ must be adjusted to match the local electron density,

$$n(\vec{r},t) = \int d^3k\, f_{l.e}(\vec{r},\vec{k},t) . \tag{2-12}$$

Finally, in Eq. (2-11), $\mathcal{E}_{\vec{k}}(\vec{r},t)$ is the energy of an electron with wave vector $\vec{k}$ in a crystal homogeneously strained with the strain tensor characterizing the neighborhood of the position $\vec{r}$ of the actual crystal at time t. The difference between $\mathcal{E}_{\vec{k}}(\vec{r},t)$ and $\mathcal{E}^{\circ}_{\vec{k}}$ is the "bare" deformation energy which is defined by

$$\delta\mathcal{E}_{\vec{k}}(\vec{r},t) \equiv \mathcal{E}_{\vec{k}}(\vec{r},t) - \mathcal{E}^{\circ}_{\vec{k}} = \mathcal{E}^{\alpha\beta}_{\vec{k}}\, Y_{\alpha\beta}(\vec{r},t) . \tag{2-13}$$

$\mathcal{E}^{\alpha\beta}_{\vec{k}}$ is called the deformation potential. $Y_{\alpha\beta}(\vec{r},t)$ is the instantaneous strain tensor, which is related to the velocity field $\vec{u}(\vec{r},t)$ by

$$Y_{\alpha\beta}(\vec{r},t) = \frac{-q^{\alpha}u^{\beta}(\vec{r},t)}{\omega} = \frac{-q^{\alpha}\delta u^{\beta}}{\omega}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} . \tag{2-14}$$

A detailed formal development of the calculation of $\mathcal{E}^{\alpha\beta}_{\vec{k}}$ may be found in Whitfield's[19] work, but $\mathcal{E}_{\vec{k}}(\vec{r},t)$ will be regarded as an input to this calculation.

The effective force on an electron, $\vec{F}$ in Eq. (2-7), is given by

$$\vec{F} = -\frac{\partial\mathcal{E}_{\vec{k}}(\vec{r},t)}{\partial\vec{r}} + e\left(\vec{E} + \frac{1}{c}\,\vec{v}_{\vec{k}} \times \vec{B}\right) . \tag{2-15}$$

The first term in Eq. (2-15) arises because the band energy in the presence of a phonon is position dependent. The second term is the electromagnetic Lorentz force due to the fields $\vec{E}$ and $\vec{B}$. These fields must be determined self-consistently from Maxwell's equations, with the charge density $\rho(r,t)$ defined by

$$\rho(\vec{r},t) = e\left[n(\vec{r},t) - n_I(\vec{r},t)\right] , \tag{2-16}$$

and the current density $\vec{J}(\vec{r},t)$ defined by

$$\vec{J}(\vec{r},t) = \vec{j}_e(\vec{r},t) - n_0 e \vec{u}(\vec{r},t) . \tag{2-17}$$

In Eq. (2-16), $n(\vec{r},t)$ is the electron density defined in Eq. (2-8) and $n_I(\vec{r},t)$ is the instantaneous ionic density around $\vec{r}$ at t. In Eq. (2-17) $\vec{j}_e$ is the electronic current density which is related to the distribution function $f(\vec{r},\vec{k},t)$ by

$$\vec{j}_e(\vec{r},t) = \int d^3k \; e \vec{v}_{\vec{k}} \, f(\vec{r},\vec{k},t) . \tag{2-18}$$

The second term in Eq. (2-17) is the current density due to the ionic motion.

The solution of the Boltzmann equation in the linear approximation is characterized by all variables oscillating about their equilibrium values with changes proportional to the spatial and temporal factor $e^{i(\vec{q}\cdot\vec{r}-\omega t)}$. Thus the various quantities can be written as

$$f(\vec{r},\vec{k},t) = f_e(\vec{k}) + \delta f(\vec{k}) \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} , \tag{2-19}$$

$$n(\vec{r},t) = n_0 + \delta n \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} , \tag{2-20}$$

$$n_I(\vec{r},t) = n_0 + \delta n_I \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} , \tag{2-21}$$

$$f_{l.e}(\vec{r},\vec{k},t) = f_e(\vec{k}) + \delta f_{l.e}(\vec{k}) \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} , \tag{2-22}$$

$$\varepsilon_{\vec{k}}(\vec{r},t) = \varepsilon_{\vec{k}}^{0} + \delta \varepsilon_{\vec{k}} \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} , \tag{2-23}$$

$$\mu(\vec{r},t) = \mu_0 + \delta\mu \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} , \tag{2-24}$$

$$\vec{E}(\vec{r},t) = \delta\vec{E}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)}, \tag{2-25}$$

$$\vec{B}(\vec{r},t) = \delta\vec{B}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)}. \tag{2-26}$$

Eqs. (2-6), (2-9), (2-11), (2-22), (2-23) and (2-24) combine to yield

$$\delta f_{l.e} = \frac{\partial f_e}{\partial \varepsilon^0_{\vec{k}}}\left(\delta\varepsilon_{\vec{k}} - \delta\mu - m\vec{v}_{\vec{k}}\cdot\delta\vec{u} \right). \tag{2-27}$$

Because the Fermi distribution cuts off sharply, we have

$$\frac{\partial f_e}{\partial \varepsilon^0_{\vec{k}}} \simeq -\frac{1}{4\pi^3}\,\delta(\varepsilon^0_{\vec{k}} - \mu_0), \tag{2-28}$$

with $\delta\mu$ fixed by

$$\delta n = \int d^3k\, \delta f_{l.e} = -D(\varepsilon_F)\left(\overline{\delta\varepsilon_F} - \delta\mu\right). \tag{2-29}$$

The quantity D(ε_F) , the density of states (including both spins) per unit volume at the Fermi level ε_F,is given by

$$D(\varepsilon_F) \equiv \frac{1}{4\pi^3}\oint \frac{dS^0_F}{\hbar\, v_{\vec{k}_F}}, \tag{2-30}$$

where d S^0_F is an element of area in k space on the unperturbed Fermi surface, and $v_{\vec{k}_F}$ is the speed of the electron with wave vector $\vec{k}_F$. In Eq. (2-29) $\overline{\delta\varepsilon_F}$ is the average of the change of the electron energy over the Fermi surface,

$$\overline{\delta\varepsilon_F} = \frac{1}{S^0_F}\oint \delta\varepsilon_{\vec{k}_F}\, dS^0_F . \tag{2-31}$$

In the linear approximation the driving term in Eq. (2-7) is approximated by

$$\frac{\vec{F}}{\hbar}\cdot\frac{\partial f}{\partial\vec{k}} \simeq \frac{\vec{F}}{\hbar}\cdot\frac{\partial f_e}{\partial\vec{k}} = \left(-i\,\delta\varepsilon_{\vec{k}}\,\vec{q}\cdot\vec{v}_{\vec{k}} + e\vec{v}_{\vec{k}}\cdot\delta\vec{E}\right)\frac{\partial f_e}{\partial\varepsilon^0_{\vec{k}}}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} . \tag{2-32}$$

Notice the magnetic part of the Lorentz force $\frac{e}{c}\vec{v}_{\vec{k}}\times\vec{B}$ makes no contribution in Eq. (2-32) since it is always perpendicular to $\vec{v}_{\vec{k}}$.

Now that all the quantities are defined, it is trivial to write down the linear solution to Eq. (2-7)

$$\delta f(\vec{k}) = \left(\frac{\partial f_e}{\partial \varepsilon^\circ_{\vec{k}}}\right) \frac{\delta\varepsilon_{\vec{k}}(i\vec{q}\cdot\vec{\Lambda}) - e\vec{\Lambda}\cdot\delta\vec{E} + \delta\varepsilon_{\vec{k}} - \overline{\delta\varepsilon_F} - \frac{\delta n}{D} - m\vec{V}_{\vec{k}}\cdot\delta\vec{u}}{1 - i\omega\tau + i\vec{q}\cdot\vec{\Lambda}}, \tag{2-33}$$

where $\vec{\Lambda} \equiv \vec{V}_{\vec{k}}\tau$ is the mean free path of the electron with velocity $\vec{V}_{\vec{k}}$. The factor $\frac{\partial f_e}{\partial \varepsilon^\circ_{\vec{k}}}$ in Eq. (2-33) guarantees that only electrons near the Fermi surface contribute to δf.

It is interesting to compare Eq. (2-33) with the result from acoustic attenuation theory. For the free electron gas, the "bare" deformation energy is zero, and the density of states per volume is simply

$$D(\epsilon_F) = \frac{m k_F}{\hbar^2 \pi^2} = \frac{3}{2}\frac{n_0}{\varepsilon_F}. \tag{2-34}$$

Thus Eq. (2-33) reduces to

$$\delta f(\vec{k}) = \left(-\frac{\partial f_e}{\partial \varepsilon^\circ_{\vec{k}}}\right) \frac{e\vec{\Lambda}\cdot\delta\vec{E} + m\vec{V}_{\vec{k}}\cdot\delta\vec{u} + \frac{2}{3}\varepsilon_F\frac{\delta n}{n_0}}{1 - i\omega\tau + i\vec{q}\cdot\vec{\Lambda}}, \tag{2-35}$$

which is exactly the same as Kittel's expression.[20]

Eq. (2-33) is still an implicit equation for δf, since the electric field $\delta\vec{E}$ is a function of δn and the current density $\vec{j}_e$ through Maxwell's equations, while δn and $\vec{j}_e$ are in turn functions of δf as seen from Eqs. (2-8) and (2-18). The results are different for different types of phonons. In the next two sections, longitudinal and transverse phonons are discussed separately.

2. Longitudinal Phonon

For a longitudinal phonon, the direction of the velocity field is the same as that of the wave vector, i.e. $\hat{u} = \hat{q}$. The electrical field $E(\vec{r},t)$ is connected to the particle densities by Poisson's equation,

$$\frac{\partial}{\partial \vec{r}} \cdot \vec{E}(\vec{r},t) = 4\pi e\left[n(\vec{r},t) - n_I(\vec{r},t) \right], \tag{2-36}$$

or

$$i\vec{q} \cdot \delta\vec{E} = 4\pi e\,(\delta n - \delta n_I). \tag{2-37}$$

Eq. (2-33) then becomes

$$\delta f(\vec{k}) = \left(\frac{\partial f_e}{\partial \varepsilon^0_{\vec{k}}}\right) \frac{\delta\varepsilon_{\vec{k}} + \frac{\mathfrak{q}^2}{q^2}\left(\frac{\delta n}{D} - \frac{\delta n_I}{D}\right) i\vec{q}\cdot\vec{\Lambda} + \delta\varepsilon_{\vec{k}} - \overline{\delta\varepsilon_f} - \frac{\delta n}{D} - m\vec{v}_{\vec{k}}\cdot\delta\vec{u}}{1 - i\omega\tau + i\vec{q}\cdot\vec{\Lambda}}, \tag{2-38}$$

where

$$\mathfrak{q} \equiv (4\pi e^2 D)^{1/2}. \tag{2-39}$$

The wave number $\mathfrak{q}$ is the reciprocal of the Fermi-Thomas shielding length. In what follows, we shall only treat a parabolic band. Eq. (2-38) relates two unknowns, $\delta f(\vec{k})$ and δn. But δn does not depend on $\vec{k}$, and, from Eqs. (2-8), (2-19) and (2-30), is related to $\delta f(\vec{k})$ through a simple integration,

$$\delta n = \int d^3k \; \delta f(\vec{k}). \tag{2-40}$$

If we integrate both sides of Eq. (2-38) over k space, we can solve for δn in terms of known quantities. After a little manipulation, we find (see Appendix A)

$$\delta n = \frac{\delta n_I - \overline{\delta\varepsilon_f}\, D \frac{q^2}{\mathfrak{q}^2} - i \frac{m v_{\vec{k}}\, \delta u}{q\Lambda} D \frac{q^2}{\mathfrak{q}^2}}{1 + (1 + I(\tau)) \frac{q^2}{\mathfrak{q}^2}}, \tag{2-41}$$

where

$$I(\tau) \equiv \frac{i\omega\tau}{1 - i\omega\tau - \dfrac{2iq\Lambda}{\ln\left(\dfrac{1 - i\omega\tau + iq\Lambda}{1 - i\omega\tau - iq\Lambda}\right)}}. \tag{2-42}$$

Now that δn is known, we can proceed to obtain the electrical potential ϕ(r,t) in a straightforward way. Let

$$\phi(\vec{r},t) = \delta\phi \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} . \tag{2-43}$$

Using Poisson's equation,

$$\nabla^2\phi = -4\pi e \left[n(\vec{r},t) - n_I(\vec{r},t) \right] , \tag{2-44}$$

we find

$$\delta\phi = \frac{4\pi e}{q^2} (\delta n - \delta n_I) . \tag{2-45}$$

Finally, the total deformation energy caused by the longitudinal phonon is

$$\mathcal{D}_{\vec{q}}(\vec{r},t) = e\phi(\vec{r},t) + \left[\mathcal{E}_{\vec{k}}(\vec{r},t) - \mathcal{E}^{\circ}_{\vec{k}} \right] = \delta D_{\vec{q}} \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} . \tag{2-46}$$

Thus $\delta D_{\vec{q}}$ can be expressed in terms of all the known quantities. The result is also derived in Appendix A:

$$\delta D_{\vec{q}} = \frac{\left(-\frac{\delta n_I}{D} + \delta\varepsilon_{\vec{k}} \frac{q^2}{\bar{q}^2}\right)\left[1 + I(\Upsilon)\right] + \delta\varepsilon_{\vec{k}} - \overline{\delta\varepsilon_F} - \frac{i m v \delta u}{q\Lambda}}{1 + \left[1 + I(\Upsilon)\right]\left(\frac{q^2}{\bar{q}^2}\right)} . \tag{2-47}$$

From this we can write down the final electron-longitudinal-phonon interaction Hamiltonian,

$$H_{e\cdot p} = \sum_{\vec{q}} \left[\delta D_{\vec{q}} \, e^{i(\vec{q}\cdot\vec{r}-\omega t)} + \delta D^{*}_{\vec{q}} \, e^{-i(\vec{q}\cdot\vec{r}-\omega t)} \right] . \tag{2-48}$$

Let's investigate $\delta D_{\vec{q}}$ to see where it changes character as $1/\Upsilon$ increases. To do this, we first express $\delta\varepsilon_{\vec{k}}$, $\overline{\delta\varepsilon_F}$ and δu in terms of δn_I, with the aid of some brief arguments involving the strain tensor defined in Eq. (2-14), as follows. Without losing generality, we can take $\hat{u}$ to be $\hat{z}$. In this case, the only nonvanishing component in the strain tensor is Y_{zz}, which according to Eq. (2-14) is

$$Y_{zz}(\vec{r},t) = \frac{-q\,\delta u}{\omega}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} \quad . \tag{2-49}$$

The dilatation $\Delta(\vec{r},t)$ is the trace of the strain tensor. Here it is just $Y_{zz}(\vec{r},t)$. Denote the dilatation by

$$\Delta(\vec{r},t) = \delta\Delta\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} , \tag{2-50}$$

and the zz component of deformation energy i.e. $\mathcal{E}^{zz}_{\vec{k}}$ in Eq. (2-13)

$$\mathcal{E}^{zz}_{\vec{k}} = U_{\vec{k}} \, . \tag{2-51}$$

Then it is a straightforward matter to write the following relations:

$$\delta n_I = -n_0\,\delta\Delta \, , \tag{2-52}$$

$$\delta\mathcal{E}_{\vec{k}} = U_{\vec{k}}\,\delta\Delta = -U_{\vec{k}}\,\frac{\delta n_I}{n_0} \, , \tag{2-53}$$

$$\overline{\delta\mathcal{E}_F} = \overline{U}_F\,\delta\Delta = -\overline{U}_F\,\frac{\delta n_I}{n_0} \, , \tag{2-54}$$

where U_F is U_k averaged over the unperturbed Fermi surface. Substituting Eqs. (2-51), (2-53) and (2-54) in Eq. (2-47) we find

$$\delta D_{\vec{q}} = \left(-\frac{\delta n_I}{n_0}\right) \frac{\left(\frac{n_0}{D} + U_{\vec{k}}\frac{q^2}{\ell^2}\right)[1+I(\tau)] + U_{\vec{k}} - \overline{U}_F + \frac{i\hbar k V_s}{q\Lambda}}{1 + [1+I(\tau)]\left(\frac{q^2}{\ell^2}\right)} \quad . \tag{2-55}$$

Note that except for the last term in the numerator, the dependence of $\delta D_{\vec{q}}$ on τ is through the function $I(\tau)$. Referring to the definition of $I(\tau)$, Eq. (2-42), we now examine the extreme cases: $q\Lambda >> 1$ and $q\Lambda << 1$, where $I(\tau)$ reduces to

$$I(\tau) = \begin{cases} \dfrac{-i\omega\tau}{\frac{2}{\pi}\,q\Lambda} \quad ; \quad q\Lambda >> 1 \; , \\[2ex] \dfrac{-3i\omega\tau}{q^2\Lambda^2} = \dfrac{-3i}{q\Lambda}\,\dfrac{V_s}{V_F} \quad ; \quad q\Lambda << 1 \; . \end{cases} \tag{2-56}$$

Thus $|I(\tau)|$ is small compared to unity until $q\Lambda$ becomes small enough so that $q\Lambda < \frac{v_s}{v_F}$.

It is interesting to consider the case when $q\Lambda >> 1$, which applies to most metals. In this case $\delta D_{\vec{q}}$ reduces to Ziman's result[21]

$$\delta D_{\vec{q}} = \left(-\frac{\delta n_s}{n_0}\right)\left[\frac{n_0}{D} + U_{\vec{k}} - \overline{U}_F + \frac{q^2}{q^2} U_{\vec{k}}\right] \Big/ \left(1 + \frac{q^2}{q^2}\right) . \qquad (2\text{-}57)$$

Using Eq. (2-34), Eq. (2-55) becomes

$$\delta D_{\vec{q}} = \left(-\frac{\delta n_s}{n_0}\right) \frac{\left(\frac{2}{3}\mathcal{E}_F + U_{\vec{k}} \frac{q^2}{q^2}\right)(1 + I(\tau)) + i \frac{2\mathcal{E}_F}{q\Lambda}\frac{v_s}{v_F}}{1 + [1 + I(\tau)]\left(\frac{q^2}{q^2}\right)} , \qquad (2\text{-}58)$$

and Eq. (2-57) becomes

$$\delta D_{\vec{q}} = \left(-\frac{\delta n_s}{n_0}\right)\left[\frac{\frac{2}{3}\mathcal{E}_F + U_{\vec{k}} \frac{q^2}{q^2}}{1 + \frac{q^2}{q^2}}\right] . \qquad (2\text{-}59)$$

The quantity in the bracket of Eq. (2-59) is the form factor of the electron-phonon interaction matrix element as discussed in Ziman's text.[22]

Notice that in Eqs. (2-57) and (2-59), $\delta D_{\vec{q}}$ is independent of τ. We shall show that $\delta D_{\vec{q}}$ remains steady over the range of collision times τ that are physically accessible. From Eq. (2-56) and Eq. (2-58), we see that collisions are most effective in changing $\delta D_{\vec{q}}$ when $q\Lambda$ is much smaller than one, because $I(\tau)$ increases as $\frac{1}{q\Lambda}$ and the last term in the numerator of Eq. (2-58) is proportional to $\frac{1}{q\Lambda}$. But in the limit $q\Lambda << 1$, there is a cancellation between the term $\frac{2}{3}\mathcal{E}_F I(\tau)$ and the last term in the numerator of Eq. (2-58), leaving the equation in the form

$$\delta D_{\vec{q}} = \left(-\frac{\delta n_s}{n_0}\right) \frac{\frac{2}{3}\mathcal{E}_F + U_{\vec{k}} \frac{q^2}{q^2} - i \frac{3v_s}{v_F}\frac{1}{q\Lambda} U_{\vec{k}} \frac{q^2}{q^2}}{1 + \left(1 - 3i \frac{v_s}{v_F}\frac{1}{q\Lambda}\right)\left(\frac{q^2}{q^2}\right)} . \qquad (2\text{-}60)$$

If we define a characteristic time τ_c such that

$$\frac{1}{\tau_c} \equiv \left(\frac{v_F}{v_s}\right)^2 \mathfrak{q}\, v_s \,, \tag{2-61}$$

then Eq. (2-60) becomes

$$\delta D_{\vec{q}} = \left(-\frac{\delta n_I}{n_0}\right) \frac{\frac{2}{3}\varepsilon_F + U_{\vec{k}}\frac{q^2}{\mathfrak{q}^2} - i\,3\left(\frac{\tau_c}{\tau}\right)\left(\frac{q}{\mathfrak{q}}\right) U_{\vec{k}}}{1 + \frac{q^2}{\mathfrak{q}^2} - i\,3\left(\frac{\tau_c}{\tau}\right)\left(\frac{q}{\mathfrak{q}}\right)} \,. \tag{2-62}$$

There are three factors in Eq. (2-62) which guarantee the steadiness of $\delta D_{\vec{q}}$ as a function of τ. First $U_{\vec{k}}$ is small compared to ε_F. For a smeared positive background and in the Hartree approximation U_k is zero. Second, the screening length $1/\mathfrak{q}$ is of the order of 10^{-7} to 10^{-8} cm, and the maximum phonon wave vector is roughly $\mathfrak{q}$, so $q/\mathfrak{q}$ has an upper limit of order one. Third, τ_c is a very short time of order 10^{-19} sec., which prevents τ from being important in the physical regime. A collision time of 10^{-19} sec. corresponds to a resistivity of $10^5 \mu\Omega$-cm, which is far bigger than the highest resistivity found in alloys.

3. Transverse Phonon

For a transverse phonon, the deformation potential can be obtained in a way similar to that for a longitudinal phonon. The difference is that there is no charge shift, because a transverse phonon does not produce a dilation in the crystal. There is, however, a current generated by the moving charges.

Using the same techniques as used in the previous section, we can let the electron current density be

$$\vec{j}_e(\vec{r},t) = \delta\vec{j}_e\, e^{i(\vec{q}\cdot\vec{r} - \omega t)} \,, \tag{2-63}$$

and the total current density be

$$\vec{J}(\vec{r},t) = \delta\vec{J}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} = (\delta\vec{j}_e - n_0 e\,\delta\vec{u})\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} \quad . \tag{2-64}$$

To solve for $\delta\vec{j}_e$, first we connect the current density $\delta\vec{J}$ with the effective field $\delta\vec{E}$ through Maxwell's equations. Without losing generality, we can let the directions of $\vec{q}$ and $\vec{u}$ be $\hat{z}$ and $\hat{x}$ respectively. Then the components of $\delta\vec{E}$ and $\delta\vec{J}$ are simply related by

$$\delta E_z = \frac{4\pi}{i\omega}\,\delta J_z \;, \tag{2-65}$$

and

$$\delta E_{x,y} = \frac{i\left(\frac{4\pi}{\omega}\right)\left(\frac{v_s}{c}\right)^2}{1-\left(\frac{v_s}{c}\right)^2}\,\delta J_{x,y} \simeq i\left(\frac{4\pi}{\omega}\right)\left(\frac{v_s}{c}\right)^2 \delta J_{x,y} \tag{2-66}$$

Then we relate $\delta\vec{j}_e$ and $\delta\vec{E}$ by

$$\delta\vec{j}_e = \int d^3k\; e\,\vec{v}_{\vec{k}}\;\delta f(\vec{k}) \,, \tag{2-67}$$

which is the result of the combination of Eq. (2-18), (2-19) and (2-63). Eqs. (2-65), (2-66) and (2-67) are then used to solve for $\delta\vec{j}_e$.

But we have to specify the "bare" deformation potential $\delta\mathcal{E}_{\vec{k}}$ in $\delta f(\vec{k})$ (See. Eq. (2-33)) before we can do the integration in Eq. (2-67). In our case, the only non-vanishing component of the strain tensor is γ_{zx} (See Eq. (2-14)). The corresponding $\delta\mathcal{E}_{\vec{k}}$ can be obtained from a combination of Eqs. (2-13), (2-14) and (2-23).

$$\delta\mathcal{E}_{\vec{k}} = -\,\mathcal{E}_{\vec{k}}^{zx}\left(\frac{q\,\delta u}{\omega}\right) , \tag{2-68}$$

where $\mathcal{E}_{\vec{k}}^{zx}$ is the zx component of the deformation energy per unit strain as defined by Eq. (2-13). If we used a general expression for $\mathcal{E}_{\vec{k}}^{zx}$, e.g. the one given by Whitfield[19], then integration of Eq. (2-67) would be quite difficult. Then the self-consistent solution of the current density $\delta\vec{j}_e$ would be so implicit that insight into the collisions' effect on the deformation potential would be lost. Instead, we shall restrict ourselves to the jellium model. In this case, $\delta \varepsilon_{k} = 0$, and $f(\vec{k})$ is simply

$$\delta f(\vec{k}) = \left(-\frac{\partial f_e}{\partial \varepsilon_{k}^{0}}\right)\left[\frac{e\vec{\Lambda}\cdot\delta\vec{E} + \frac{\delta n}{D} + m\vec{V}_{k}\cdot\delta\vec{u}}{1 - i\omega\tau + i\vec{q}\cdot\vec{\Lambda}}\right]. \tag{2-69}$$

Using $\delta f(\vec{k})$ from Eq. (2-69), we find the following results after a little manipulation (See Appendix A):

$$\delta n = 0 \quad , \tag{2-70}$$

$$(\delta j_e)_y = (\delta j_e)_z = 0 \, , \tag{2-71}$$

and

$$(\delta j_e)_x = n_0 e\,\delta u\left[\frac{1 + i\,3\left(\frac{q}{\not{q}}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{1}{q\Lambda}\right)}{1 + i\,4\left(\frac{q}{\not{q}}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{1}{q\Lambda}\right)\frac{1}{I_0}}\right], \tag{2-72}$$

where ($1/\not{q}$), again, is the Thomas-Fermi screening length, D is the electronic density of states per unit volume at the Fermi level ε_F, and I_0 is the integral

$$I_0 \equiv \int_{-1}^{1} d\eta \, \frac{(1-\eta^2)}{1 - i\omega\tau + iq\Lambda\eta} \; . \tag{2-73}$$

From Eqs. (2-65) and (2-66), we then obtain

$$\delta E_z = \delta E_y = 0 \tag{2-74}$$

and

$$\begin{aligned} \delta E_x &= i\,\frac{4\pi}{\omega}\left(\frac{v_s}{c}\right)^2 \delta J_x = i\,\frac{4\pi}{\omega}\left(\frac{v_s}{c}\right)^2\left[(\delta j_e)_x - n_0 e\,\delta u\right] \\ &= i\,\frac{4\pi}{\omega}\left(\frac{v_s}{c}\right)^2 n_0 e\,\delta u\left[\frac{i\left(\frac{q}{\not{q}}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{1}{q\Lambda}\right)(3 - 4/I_0)}{1 + i\,4\left(\frac{q}{\not{q}}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{1}{q\Lambda}\right)\frac{1}{I_0}}\right] \\ &= \frac{-\frac{4\pi}{\omega}\left(\frac{q}{\not{q}}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{1}{q\Lambda}\right)(3 - 4/I_0)\, n_0 e\,\delta u}{1 + i\,4\left(\frac{q}{\not{q}}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{1}{q\Lambda}\right)\frac{1}{I_0}} \; . \end{aligned} \tag{2-75}$$

This electric field produces an extra force on the electrons. The perturbing Hamiltonian H_{ep} for an electron can be obtained by the standard method:

$$\delta H_{e\cdot p} = \frac{1}{2m}(\vec{p} + \frac{e}{c}\vec{A})^2 - \frac{p^2}{2m} + e\phi . \tag{2-76}$$

It is natural to choose a gauge in which the electric potential is zero, since there are no unbalanced charge sources. Then the vector potential $\vec{A}$ is related to the electric field by

$$\vec{A}(\vec{r},t) = \delta\vec{A}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} = \frac{c}{i\omega}\delta\vec{E}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} . \tag{2-77}$$

From Eqs. (2-74) and (2-75) only A_x in nonzero, and $\nabla\cdot\vec{A} = 0$ is guaranteed in the Coulomb gauge, so Eq. (2-76) is just

$$\delta H_{e\cdot p}(\vec{r},t) = e^{i(\vec{q}\cdot\vec{r}-\omega t)} \frac{e}{mc} A_x p_x . \tag{2-78}$$

To lowest order in the fields, we can replace p_x by $mv_x(\vec{k})$. Let

$$\delta H_{e\cdot p}(\vec{r},t) = \delta H_{\vec{k}}\, e^{i(\vec{q}\cdot\vec{r}-\omega t)} . \tag{2-79}$$

Then, from Eqs. (2-75), (2-77) and (2-78), we can identify $\delta H_{\vec{k}}$ as

$$\delta H_{\vec{k}} = \left(\frac{e}{mc}\right)\left(\frac{c}{i\omega}\right)\left[\frac{-\frac{4\pi}{\omega}\left(\frac{q}{q}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{1}{q\Lambda}\right) n_0 e\,\delta u\,(3-4/I_0)}{1+i\,4\left(\frac{q}{q}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{1}{q\Lambda}\right)\frac{1}{I_0}}\right] m v_x(\vec{k}) \tag{2-80}$$

$$= \left(-\frac{4\pi e^2 n_0}{i m\omega^2}\right)\left[\frac{\left(\frac{q}{q}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{1}{q\Lambda}\right)(3-4/I_0)\, m v_x(\vec{k})\,\delta u}{1-4\left(\frac{q}{q}\right)^2\left(\frac{c}{v_s}\right)^2\frac{1}{i\omega\tau I_0}}\right].$$

But

$$\frac{4\pi e^2 n_0}{m\omega^2} = \frac{4\pi e^2 D}{m}\,\frac{n_0}{D}\,\frac{1}{\omega^2} = \frac{q_t^2}{m}\,\frac{2}{3}$$

$$= \frac{1}{3}\left(\frac{q_t^2}{q^2}\right)\left(\frac{v}{v_s}\right)^2. \qquad (2\text{-}81)$$

Putting Eq. (2-81) into Eq. (2-80), we find

$$\delta H_{\vec{k}} = \frac{-\frac{1}{3}\left(\frac{v}{v_s}\right)\left(\frac{1}{iq\Lambda}\right)(3-4/I_0)\; m\,v_x(\vec{k})\,\delta u}{1-4\left(\frac{q}{q_t}\right)^2\left(\frac{c}{v_s}\right)^2\frac{1}{i\omega\tau I_0}}$$

$$= \frac{m\,v_x(\vec{k})\,\delta u\left(\frac{4}{3i\omega\tau I_0}-\frac{1}{i\omega\tau}\right)}{1-4\left(\frac{q}{q_t}\right)^2\left(\frac{c}{v_s}\right)^2\frac{1}{i\omega\tau I_0}}\;. \qquad (2\text{-}82)$$

For $\vec{q}$ & $\vec{u}$ in general (perpendicular) directions, one should write Eq. (2-82) as

$$\delta H_{\vec{k}} = \frac{m\,\vec{v}_{\vec{k}}\cdot\delta\vec{u}\left(\frac{4}{3i\omega\tau I_0}-\frac{1}{i\omega\tau}\right)}{1-4\left(\frac{q}{q_t}\right)^2\left(\frac{c}{v_s}\right)^2\frac{1}{i\omega\tau I_0}}\;. \qquad (2\text{-}83)$$

Notice that, in Eq. (2-82), the entire effect of the collisions is contained in the factors $\frac{1}{i\omega\tau}$ and

$$F = i\omega\tau I_0\;. \qquad (2\text{-}84)$$

As the collision rate increases, F behaves as follows: when $q\Lambda \gg 1$, F has the constant value $i\pi\frac{v_s}{v_F}$; it remains very steady and goes to $(\pi-2)\frac{iv_s}{v_F}$ when $q\Lambda \simeq 1$; then it behaves like $i\frac{4}{3}q\Lambda\frac{v_s}{v_F}$ as $q\Lambda$ decreases further.

Define a characteristic wave number q_T by

$$q_T \equiv q_t\sqrt{\frac{v_s v_F}{c^2}} \simeq 10^{-4} q_t\,, \qquad (2\text{-}85)$$

which is of order of 10^{+4} cm^{-1}. For a fixed q, as a function of $1/\tau$, $\delta H_{\vec{k}}$ begins with the value

$$\delta H_{\vec{k}} \simeq \frac{-m\vec{v}_{\vec{k}}\cdot\delta\vec{u}\left(\frac{4i}{3\pi}\frac{v_F}{v_s}\right)}{1+i\frac{\pi}{4}\left(\frac{q}{q_T}\right)^2} \quad ; \quad q\Lambda >> 1 . \qquad (2\text{-}86)$$

As $1/\tau$ increases, δH_{k} stays very steady, until $\frac{1}{i\omega\tau}$ is comparable with $\frac{1}{i\omega\tau I_0}$, i.e. when $q\Lambda \sim 1$. We get

$$\delta H_{\vec{k}} \simeq \frac{-m\vec{v}_{\vec{k}}\cdot\delta\vec{u}\left[\frac{10-3\pi}{3(\pi-2)}\, i\, \frac{v_F}{v_s}\right]}{1+i\frac{4}{\pi-2}\left(\frac{q}{q_T}\right)^2} \quad ; \quad q\Lambda \sim 1 . \qquad (2\text{-}87)$$

As $1/\tau$ further increases, the two terms in the numerator tend to cancel each other, and the denominator gets larger. The cancellation is exact when $1/\tau \to \infty$.

Since the factor $i\omega\tau I_0$ is almost pure imaginary, there is never a singular behavior in $\delta H_{\vec{k}}$. Thus the increase of collision rate tends to diminish $\delta H_{\vec{k}}$, but this is unimportant until $q\Lambda \sim 1$. After that $\delta H_{\vec{k}}$ decreases very fast.

There is another quantity that must be noticed. The quantity $\left(\frac{q}{q_T}\right)^2$ in the denominator makes $\delta H_{\vec{k}}$ small except when $q \lesssim q_T \simeq 10^4 \text{cm}^{-1}$, i.e. in the extremely long wave length phonon regime. Thus, since a typical Debye wavenumber is 2 x 10^8 cm^{-1}, only one phonon out of 10^{13} is involved, and we can therefore ignore the transverse phonons altogether.

D. Conclusions

We have given the details of the calculation of the effect of collisions on the electron-phonon interaction based on the deformation potential theory and the semi-classical Boltzmann equation. The results for both longitudinal and transverse phonons do exhibit a decrease of the deformation potential, as intuitively suggested. In the limit of infinite collision rate $1/\tau$, the longitudinal deformation energy $\delta D_{\vec{q}}$ (Eq. (2-62)) goes to $-\frac{\delta n}{n_0} U_{\vec{k}}$, which is just the input "bare" deformation energy $\delta \mathcal{E}_{\vec{k}}$ (Eq. (2-53)). Similarly the extra transverse deformation energy $\delta H_{\vec{k}}$ goes to zero in the limit $1/\tau \to \infty$

However, we have also concluded that this phenomenon which yields a saturated collision time cannot be the cause of the observed saturated electrical resistivity of many high resistivity metals. In the longitudinal phonon case, this does not happen until a collision rate is reached which is too fast, while the transverse phonons are always negligible.

The results do, however, reveal that the adiabatic decomposition of the crystal energy into electrons and phonons seems to be valid far beyond the usual criterion. Instead of the old criterion,[7]

$$q\Lambda \gtrsim 1 \quad , \tag{2-88}$$

which Ziman derives from a transport equation result of Pippard for acoustic attenuation, we arrive at the new criterion, to be discussed shortly,

$$q d \gtrsim 1 \quad , \tag{2-89}$$

where $1/q$ is the shielding length of the electrons and d is the diffusion length of the electron in a phonon period $1/\omega$.

It is easy to show that the criterion in Eq. (2-89) is the condition that guarantees the independence of $\delta D_{\vec{q}}$ from collision time. From Eq. (2-60), we see that $\delta D_{\vec{q}}$ is independent of τ as long as

$$\frac{v_s}{v_F}\,\frac{1}{\mathbf{q}\Lambda}\,\frac{q^2}{\mathbf{q}^2} \lesssim 1 , \tag{2-90}$$

or

$$\frac{\mathbf{q}^2}{q^2}\,\mathbf{q}\Lambda\,\frac{v_F}{v_s} \gtrsim 1 . \tag{2-91}$$

But Eq. (2-91) can be rewritten as

$$\mathbf{q}^2\Lambda^2\,\frac{1}{\omega\tau} \gtrsim 1 , \tag{2-92}$$

or

$$\mathbf{q}\Lambda\sqrt{\frac{1}{\omega\tau}} \gtrsim 1 . \tag{2-93}$$

Now, except for a constant factor of order unity, $\Lambda\sqrt{\frac{1}{\omega\tau}}$ is the root mean square distance d that an electron diffuses in a time $t=\frac{1}{\omega}$. Thus we arrive at the criterion of Eq. (2-89).

The criterion of Eq. (2-89) agrees with the usual intuitive picture for the validity of the adiabatic approximation. As long as the electrons can diffuse a distance large compared to the shielding length in a period of the phonon disturbance, "they can adjust themselves to the ionic motion, increasing the negative charge density where the ions are compressed, restoring the Fermi level where this is disturbed, and so on."[23] Since the shielding length is short, roughly one interatomic distance, a violation of the condition, Eq. (2-89), means that the electrons cannot move far enough from "their ions" in one phonon period to set up the shielded distribution and the adiabatic condition is not satisfied. More specifically, the electrons are "rigidly" attached to the ions by collisions, so there is no electro-magnetic potential established by unbalanced sources.

It is worth mentioning why our criterion for the validity of the Born-Oppenheimer approximation is different from Ziman's. The mistake Ziman made stems from the fact that he reached his criterion by watching the change of character of the acoustic power absorbed as a function of the collision time, instead of the change of the coupling constant of electron-phonon interaction. In our notation, in the longitudinal phonon case, the acoustic power absorbed as a function of collision time is dominated by a term which is proportional to the imaginary part of I(τ) (see Eqs. (2-41) and (2-42)), which changes its character at $q\Lambda \sim 1$ as seen from Eq. (2-56). However, in our case, the magnitude of I(τ) (or $|\mathcal{I}_m I(\tau)|$, since I(τ) is almost pure imaginary) must be comparable with unity in order to change the character of δD_q (see Eq. (2-55)). Physically, the difference arises from the fact that the interaction Hamiltonian has a large τ-independent term which arises from the forces producing shielding, in competition with the terms from collisions. However, this competition does not exist in the expression for acoustic attenuation, hence the difference in behavior. We contend that the criterion for the validity of the Born-Oppenheimer approximation depends on the nature of the electron-phonon interaction, and other macroscopic quantities may not provide a proper measure.

But generally speaking, even though the Hamiltonian doesn't change its character, the use of Boltzmann equation for the transport properties of an alloy is still not valid since the condition

$$k_f \Lambda < 1 \tag{2-94}$$

can be reached in a concentrated transition metal alloy like constantan, and we have no right to assign a momentum to an electron when the uncertainty of the momentum exceeds the momentum. To investigate the problem of the electron-phonon interaction in such a system, the quantum-mechanical density matrix technique ought to be used. The broad computational path is essentially the same. For example, we can start with a "bare" electron-phonon interaction as an input, use Kubo's[24] linear response theory to find the charge density $\rho(\vec{r},t)$ and current density $\vec{J}(\vec{r},t)$, and then compute the extra electro-magnetic potential on the electrons. But we no longer use the simple collision time approximation or momentum basis states. Instead, we have to specify all the collision mechanisms in the Hamiltonian and try to carry out the trace required in the Kubo formula. This prescription is much too involved. The result we would expect is that the "bare" interaction would be subject to the usual static screening processes appropriate to the alloy. Collisions would not affect the screening until the criterion $q\ell \geq 1$ is violated.

But in order to obtain the correct transport coefficients, we ought to take the full linear response theory seriously, rather than simply using a Boltzmann equation. The next part of the thesis is devoted to this purpose.

THE TEMPERATURE DEPENDENCE OF THE ELECTRON DENSITY OF STATES AND D-C ELECTRICAL RESISTIVITY OF DISORDERED BINARY ALLOYS

A. Density of States, Conductivity and the Green's Function in a Disordered System.

Transport properties, such as electrical conductivity, are often obtained from solutions to the Boltzmann equation. But the semi-classical Boltzmann equation is not valid if the uncertainty in the momentum of the carrier is greater than the momentum itself. This is equivalent to the Landau-Peierls[25] criterion for the validity of Boltzmann equation:

$$\varepsilon_F \tau \geq \hbar \qquad (3\text{-}1)$$

To avoid this difficulty, we have to use a quantum mechanical approach to the transport properties. One approach is to use some quantum transport equation, such as Van Hove's[26] generalized master equation, but the application of this method is not well developed in the literature, since his integral equation is too difficult to solve. Other, more manageable transport equations, such as the Kohn-Luttinger type,[27,28] are perturbation-theoretic, and depend on the existence of a small parameter, such as a small impurity concentration or weak scattering; therefore, we cannot use such a method for a concentrated, strong-scattering alloy. Another, more popular approach will be used here, namely the density matrix method of the Kubo linear response theory,[24,29] which is both rigorous and convenient. A good comparison of the Kubo and Kohn-Luttinger methods is given by Moore.[30] Our starting point, the Kubo formula for the electrical conductivity, is obtained from a formal solution to the Liouville equation of the density matrix to first order in the external electrical field. The formal expression for the d-c electrical conductivity tensor $\sigma^{\alpha\beta}$ is[24]

$$\sigma^{\alpha\beta} = \frac{1}{\Omega}\int_0^\infty dt \int_0^{1/kT} d\lambda \langle J_\beta(-i\hbar\lambda) J_\alpha(t)\rangle \ , \tag{3-2}$$

where $J_\alpha(t)$ is the α-component of the total current operator in the unperturbed Heisenberg picture,

$$J_\alpha(t) = e^{i\mathcal{H}t/\hbar} J_\alpha e^{-i\mathcal{H}t/\hbar} \ , \tag{3-3}$$

and Ω is the volume of the system, K is Boltzmann's constant, and T is the temperature. In Eq. (3-3), $\mathcal{H}$ is the total Hamiltonian of the system before the field is turned on. The bracket $\langle\ \rangle$ in Eq. (3-2) means the ensemble average, i.e.

$$\langle A\rangle = \mathrm{Tr}\, \rho_e(\mathcal{H}) A \ , \tag{3-4}$$

where $\rho_e(\mathcal{H})$ is the equilibrium density matrix. The Hamiltonian generally includes all the subsystem Hamiltonians, e.g. electrons, phonons, spin waves, etc., and the interactions among them. We shall restrict ourselves to an alloy composed of N atoms and cN electrons. The appropriate Hamiltonian of the alloy is

$$\mathcal{H} = \sum_i H(\vec{r}_i ; \vec{R}_1, \vec{R}_2, \cdots, \vec{R}_N) + H_{ion}(\vec{R}_1, \cdots, \vec{R}_N) \ , \tag{3-5}$$

where the one electron Hamiltonian H takes the form

$$H(\vec{r}) = \frac{p^2}{2m} + V(\vec{r}\,;\vec{R}_1, \vec{R}_2, \cdots, \vec{R}_N)\,, \tag{3-6}$$

where $V(\vec{r}; \vec{R}_1, \vec{R}_2, \ldots, \vec{R}_N)$ is the appropriate screened ionic potential when the ions are located at positions $\vec{R}_1$ through $\vec{R}_N$. Notice that H depends on the locations of the ions. The eigenfunctions of H and eigenvalues are defined by

$$H(\vec{r}; \vec{R}_1, \cdots, \vec{R}_N)\,\psi_a(\vec{r}\,; \vec{R}_1, \cdots, \vec{R}_N) = \mathcal{E}_a \psi_a(\vec{r}\,; \vec{R}_1, \cdots, \vec{R}_N). \tag{3-7}$$

In a static alloy the positions of the ions are fixed so H commutes with H_{ion}, and the Kubo formula Eq. (3-2) can be reduced[31] to the Greenwood formula[32]

$$\sigma^{\alpha\beta} = \frac{2\pi e^2\hbar}{\Omega}\left\langle \sum_a \sum_b \left(-\frac{\partial f}{\partial \varepsilon_a}\right) \delta(\varepsilon_a - \varepsilon_b)\, v^{\alpha}_{ab}\, v^{\beta}_{ba} \right\rangle_c\,, \tag{3-8}$$

where a and b are quantum numbers defined in Eq. (3-7), and v_{ab} is electron velocity matrix element

$$v^{\alpha}_{ab} \equiv \frac{1}{m}\langle \psi_a | p^{\alpha} | \psi_b \rangle\,, \tag{3-9}$$

where p^{α} is the α-component of the electron momentum operator. In Eq. (3-8), $\langle\ \rangle_c$ means an average over all the substitutional arrangements of the ions, usually called the "configuration average". The function f in Eq. (3-8) is the Fermi-Dirac distribution

$$f(\varepsilon) = \frac{1}{e^{\beta(\varepsilon-\mu)} + 1}\,, \tag{3-10}$$

where $\beta = 1/kT$ as usual, and μ is the Fermi energy.

In general, the one electron Hamiltonian H does not commute with the ionic Hamiltonian H_{ion}. It is a rather difficult problem trying to carry out the trace by any kind of perturbation expansion in Eq. (3-2). However, we can approximate in the spirit of the Born-Oppenheimer adiabatic approximation at this point. Since the ionic motion is slow compared to the electron motion, i.e. $(\frac{v_{ion}}{v_{elec}}) \quad 10^{-3}$, we can freeze the ionic positions and solve for electronic states, i.e. Eq. (3-7). Then we can find the expectation value of the electronic quantities in this particular ionic configuration. Finally, we can average the expectation value over all possible positions of the ions in the given configuration, and then over all possible configurations to get the macroscopic expectation value. Applying this to the electrical resistivity, the Kubo-Greenwood formula (Eq. (3-8)) is merely modified by an extra average,

$$\sigma^{\alpha\beta} = \frac{2\pi e^2 \hbar}{\Omega} \left\langle\left\langle \sum_a \sum_b \left(-\frac{\partial f}{\partial \varepsilon_a}\right) \delta(\varepsilon_a - \varepsilon_b)\, v^{\alpha}_{ab}\, v^{\beta}_{ba} \right\rangle_p \right\rangle_c , \qquad (3\text{-}11)$$

where $\langle\ \rangle_p$ means an average over the ionic positions. We shall drop the indices from the double average in what follows.

When Eq. (3-11) is applied to a liquid metal, we do not need the configuration average. Then Eq. (3-11) is identical with the equation used by Edwards.[33] To be explicit, let us define the alloy electronic spectral density matrices ρ_1, ρ_2, etc., following Edwards,

$$\begin{aligned} \rho_1(\vec{r}, \vec{r}_1{}'; E) \equiv & \Big\langle \int \sum_a \psi_a^*(\vec{r}_1; \vec{R}_1, \cdots, \vec{R}_N)\, \psi_a(\vec{r}_1{}'; \vec{R}_1, \cdots, \vec{R}_N)\, \delta(\varepsilon_a - E) \\ & \quad P_c(\vec{R}_1, \cdots, \vec{R}_N) \prod_i d^3 R_i \Big\rangle_c \\ \equiv & \left\langle\left\langle \sum_a \psi_a^*(\vec{r}_1)\, \psi_a(\vec{r}_1{}')\, \delta(E - \varepsilon_a) \right\rangle\right\rangle , \end{aligned} \qquad (3\text{-}12)$$

and

$$\rho_2(\vec{r}_1,\vec{r}_1\,'; \vec{r}_2,\vec{r}_2\,'; E_1,E_2) \equiv \langle\!\langle \sum_a \sum_b \psi_a^*(\vec{r}_1)\,\psi_a(\vec{r}_1\,')\,\psi_b^*(\vec{r}_2)\,\psi_b(\vec{r}_2\,')\;\delta(E_1-\mathcal{E}_a)\;\delta(E_2-\mathcal{E}_b)\rangle\!\rangle , \tag{3-13}$$

where $P_c(\vec{R}_1,\ldots,\vec{R}_N)$ is the distribution function of ionic positions $(\vec{R}_1,\ldots,\vec{R}_N)$ in a particular ionic configuration, as indicated by the index c. Explicitly, P_c is

$$P_c = \sum_\gamma |\phi_\gamma^c(\vec{R}_1,\cdots,\vec{R}_N)|^2 e^{-\beta E_\gamma^c} \Big/ \sum_{c',\gamma'} e^{-\beta E_{\gamma'}^{c'}} , \tag{3-14}$$

where ϕ_γ^c is the eigenfunction of H_{ion} with the eigen value E_γ^c in a particular configuration c, so that

$$H_{ion}(\vec{R}_1,\cdots,\vec{R}_N)\,\phi_\gamma^c(\vec{R}_1,\cdots,\vec{R}_N) = E_\gamma^c\,\phi_\gamma^c(\vec{R}_1,\cdots,\vec{R}_N) . \tag{3-15}$$

Eqs. (3-12) and (3-13) serve to define the double average explicitly. They are also useful to connect the quantities of interest to us, i.e. density of states and electrical conductivity, to the Green's function, as follows.

The electronic density of states per atom is

$$\mathcal{N}(E) = \frac{1}{N}\int d^3r\, \rho_1(\vec{r},\vec{r}; E) . \tag{3-16}$$

The electrical conductivity is related to ρ_2 by

$$\sigma^{\alpha\beta} = \frac{2\pi e\hbar^3}{m^2\Omega}\int d\eta\left(-\frac{df}{d\eta}\right)\int d^3r_1\, d^3r_2\, \nabla_1'^{\alpha}\,\nabla_2'^{\beta}\,\rho_2(\vec{r}_1,\vec{r}_1\,';\vec{r}_2,\vec{r}_2\,';\eta,\eta)\Big|_{\substack{\vec{r}_1\,'=\vec{r}_1\\ \vec{r}_2\,'=\vec{r}_2}} . \tag{3-17}$$

Let us define a Green's function of complex argument z associated with H,

$$G(z) \equiv \frac{1}{z - H} = \sum_a \frac{|\psi_a\rangle\langle\psi_a|}{z - \varepsilon_a} , \tag{3-18}$$

which is analytic everywhere except for a line of poles $\{\varepsilon_a\}$, for large Ω equivalent to a branch cut along the real energy axis,where the spectrum of H lies.

Using the identity

$$\frac{1}{x \pm i0} = \mathbb{P}\,\frac{1}{x} \mp i\pi\delta(x), \tag{3-19}$$

we can easily show that Eq. (3-16) is equivalent to

$$\mathcal{N}(E) = \pm\frac{1}{N\pi}\,\mathrm{Im}\,\mathrm{Tr}\,\langle\!\langle G(E \mp i0)\rangle\!\rangle . \tag{3-20}$$

We can also rewrite Eq. (3-11) or Eq. (3-17) in the operator form

$$\sigma^{\alpha\beta} = \frac{2\pi e^2\hbar}{m\Omega}\int d\eta\,\left(-\frac{df}{d\eta}\right)\,\mathrm{Tr}\,\langle\!\langle p^\alpha\delta(\eta-H)\,p^\beta\delta(\eta-H)\rangle\!\rangle, \tag{3-21}$$

or, when the delta functions are expressed in terms of the Green's function through Eqs. (3-18) and (3-19), $\sigma^{\alpha\beta}$ becomes

$$\sigma^{\alpha\beta} = \frac{2\pi e^2\hbar}{m^2\Omega}\int d\eta\,\left(-\frac{df}{d\eta}\right)\,I_{p^\alpha p^\beta}(\eta,\eta), \tag{3-22}$$

where

$$I_{p^\alpha p^\beta}(\eta,\eta) \equiv \frac{1}{4\pi^2}\,\mathrm{Tr}\,p^\beta\big[K(\eta^+,p^\alpha,\eta^-) + K(\eta^-,p^\alpha,\eta^+) - K(\eta^+,p^\alpha,\eta^+) - K(\eta^-,p^\alpha,\eta^-)\big], \tag{3-23}$$

with

$$K(z_1, p^\alpha, z_2) \equiv \langle\!\langle G(z_1)\,p^\alpha\,G(z_2)\rangle\!\rangle . \tag{3-24}$$

In Eq. (3-23), $\eta^{\pm}$ means $\eta \pm i0$.

So far the formulae, Eqs. (3-20) and (3-22) are still very general, they can apply to any disordered system. Thus, to solve for the density of states, we need to average the one electron Green's function G; while for conductivity, we need, loosely speaking, an average of the product of two Green's functions <<GG>>.

However, the conductivity formula Eq. (3-22) is only an approximation to the exact Kubo formula Eq. (3-2). It is valid whenever the ionic motion can be treated classically, or, equivalently, when we can neglect the non-commutation of the ionic momenta and positions. Thus, it is valid to use Eq. (3-22) in liquid metals, and solid metals at high temperatures.[34]

Intuitively, we feel that Eq. (3-22) may still be a valid approximation for a solid alloy at low temperatures so long as the collision rate $1/\tau$ of the electrons is much faster than the Debye frequency ω_D of the ionic motion, i.e.,

$$\frac{1}{\tau} \gg \omega_D \, . \tag{3-25}$$

This means that the uncertainty in the electron energy is big compared to the maximum phonon energy, so that the conservation of energy in the scattering of one electron by a phonon is of little significance. Under this circumstance we can approximate the phonons as "static scatters" and treat the scattering as elastic as in Eq. (3-11).

B. A Survey.

As we have seen in the previous section, the averaged Green's functions <<G>> and <<GG>> determine the electronic properties of interest in the alloy: the electronic density of states $\mathcal{N}(E)$ and the electrical resistivity σ. Although there has been some contact between experiment and some aspects of the theory, as reviewed extensively by Mott[35], plausible approximation schemes for calculations in real disordered materials have not been worked out[36,37], but are rapidly being developed. In what follows, we shall survey the relevant areas of the field, and state our own problem and methods against this background.

In the averaging process, we must first know the ionic distribution function P_c in Eq. (3-14), the quantity that leads to the temperature dependence of the density of states $\mathcal{N}(E)$ (Eqs. (3-16) and (3-12)) and the conductivity σ (Eq. (3-21)). In a completely disordered system with no ionic correlations, $\langle P_c\rangle_c$ is the trivial uniform distribution

$$\langle P_c\rangle_c = \frac{1}{\Omega^N}. \tag{3-26}$$

In this case, there is no temperature variation in $\mathcal{N}(E)$, while the temperature dependence of σ is only characterized by the trivial Fermi distribution factor $(-\frac{df}{d\eta})$ in Eq. (3-21). This simply distribution is not true even in the most disordered materials like liquid alloys or amorphous material. The determination of the temperature coefficient in $\mathcal{N}(E)$ and σ of these material relies on a genuine understanding of P_c, which is always complicated. However, when the atomic potential is weak, our Eqs. (3-17) or (3-21) can be reduced[33,38] to the Faber-Ziman[39] type formula for the resistivity of liquid alloys. What we then need is the structure factor, which can be found from neutron diffraction experiments or can be calculated as in the work of Bathia and Thornton.[40]

In a crystalline alloy, the ions are restricted to vibrate around their lattice sites. Then the ionic motion can be described in terms of normal modes, or phonons. The average over ionic positions can be replaced by a thermal average over the phonon distribution. In a static disordered alloy, which is the most popular topic in the literature, the average is simply the configuration average $\langle\ \rangle_c$.

More difficult than the determination of P_c is the computation of the average in <<G>> and <<GG>>. The most trivial approximation to <<G>> is the one corresponding to <<H>>. This sometimes results in a rigid shift of the band, and then is called the "rigid band" model.[41] In the weak scattering limit, Edwards,[42] starting from Eq. (3-17), summed up certain diagrams in both the $\langle G\rangle_c$ and $\langle GG\rangle_c$ expansion series and was able to rederive the usual conductivity formula (the one arrived at from the Boltzmann equation). At low concentration, Langer[43] used the many body thermodynamic Green's function[44] and a perturbation expansion to get the conductivity to the first order in concentration. For strong scattering, but localized potentials, Beeby[45] neglected the statistical correlation between the atomic scattering matrices in the multiple scattering expansion of $\langle G\rangle_c$ and summed up the series to get the so called "average T matrix" approximation. This approximation produces an unphysical band gap[3] in the alloy density of states at all scattering potential strengths. Later, Ballentine[46] used a self-consistent method in the calculation of the band structure of liquid Al and Bi. This "self-consistent virtual crystal" approximation (see Reference 3), in contrast to the "averaged T matrix" approximation, gives no splitting of the alloy band no matter how big the potential strength is. The first good theory to deal with alloys of arbitrary concentrations and scattering strengths is the "Coherent Potential Approximation", or CPA for short. This approach to $\langle G \rangle_c$ was originated by Soven[8] and was greatly extended by Velický et al.[3]. Velický[9] further extended CPA to attack the problem of electronic transport in a static alloy, and discussed the numerical results for α in a model alloy.

So far, the CPA approximation is still the basic working approximation in the electronic theory of concentrated strong-scattering alloys. It is also a powerful tool for other alloy properties. For example, Taylor[47] used the same technique for the lattice vibration problem in alloys, and Onodera and Toyozawa[48] applied the same approximation to Frenkel excitons in mixed ionic crystals. Since we are going to use CPA in our model calculation of the temperature dependence of $\mathcal{N}(E)$ and α in a crystalline disordered alloy, the CPA formalism will be discussed in detail in the sections that follow.

The more recent developments in the theory of $\langle\langle G \rangle\rangle$ and $\langle\langle GG \rangle\rangle$ are either mathematical justifications, or generalizations of CPA. First, Yonezawa[49] carefully analyzed and generalized the expansion series in the self-energy of $\langle G \rangle_c$. Excluding "multiple occupancy" of a site by more than one atom, she concluded that the approximate self-energy obtainable by summing all terms involving multiple scattering at the same site was identical with the CPA result. Later, Ziman[50] conjectured that for a tight binding alloy, the "locator" expansion of Matsubara and Toyozawa[51] was superior to the usual band propagator expansion and used it to arrive at a different conclusion from CPA about the splitting of the band. But in a later paper Leath[52], using a diagram technique and taking into account the "multiple occupancy" correction, showed that Ziman's idea was not correct. Furthermore, he also showed that the diagrams of Edwards[42], Langer[43], and Verboven[31], when properly corrected for "multiple occupancy", led to Velický's[9] CPA electrical conductivity result. In an attempt to improve CPA by including random off-diagonal (hopping) matrix elements, Berk[53] restricted himself to the weak-scattering limit, to avoid the difficulty of the strong-scattering problem. His work is essentially a different version of the "self-consistent virtual crystal" approximation. An attempt at the same problem was made by Edwards and Loveluck.[54] They used an elaborate diagram method and summed up a large number of diagrams. But their result for the density of states still exhibits the unphysical "average T matrix" band gaps. They also concluded that the self-consistent method was too complicated for their case.

The most substantial generalization of CPA, namely CP$\tilde{n}$, was recently developed by Freed and Cohen.[55] They generalized the coherent potential theory from the single-site approximation to n-atom clusters. The cluster Green's function $G_{\underset{\sim}{n}}$ (in their notation) is self-consistently determined in a way similar to $\langle G\rangle_c$ in CPA but more involved. However, they showed that uniformly averaging a finite cluster Green's function to get the translational invariant alloy Green's function could not produce a different result from CPA. In order to get nontrivial results, one should go through a subtle averaging process, called ECP$\tilde{n}$ (extended CP$\tilde{n}$ approximation). The simplest version of ECP$\tilde{n}$ is Kohn's notion of periodically compact disordered clusters.[56] The most important results of CP$\tilde{n}$ is the demonstration of the existence of localized states (bound states), outside the CPA band, and in the regions obeying the localization theorem.[78]

Several interesting uses of CPA have appeared in the literature. CPA has not been restricted to the tight binding approximation. In an early, different version of CPA, Anderson and McMillan[57] used a self-consistent equation for the phase-shift to calculate the band structure of liquid iron. Using a similar method, Soven[58] has applied CPA to a muffin tin potential and has been able to deal with an alloy with constituents of different band-widths. CPA also serves as an approximate quantitative scheme. It has been used to yield the density of states in Cu-Ni alloys.[4,5] It was also applied to the magnetic properties of Cu-Ni alloys.[59] Velický and Levin[60] have also used CPA to discuss intraband optical constants in a simple tight binding band. Recently Levin and Ehrenreich[6] applied CPA along with a model Hamiltonian for Ag-Au alloys. By adjusting a concentration dependent d-level energy, they could make the concentration dependence of the optical absorption edge agree with experiment.

From this review, it can be seen that the self-consistent Green's function approach to the alloy problem, with CPA as the basic approximation, has been fruitful. Although CP$\tilde{n}$ should give better answers than CPA, at present, when even a model description of CP$\tilde{n}$ has yet to be developed, and the CP$\tilde{n}$ two Green's function average has not even been discussed in the literature, CPA is the only simple and practical method to use in an investigation of the temperature variation trends of $\mathcal{N}(E)$

and α in a concentrated, strong-scattering alloy. It is expected, however, that the method developed below can be generalized to CP$\tilde{n}$.

C. The Coherent Potential Approximation

Henceforth, we shall consider only crystalline disordered substitutional binary alloys. Let x and y be the fractional concentrations of the constituent A atoms and B atoms respectively, so that x is the probability of an A atom occupying a given site. The one-electron Hamiltonian H in Eq. (3-6) takes the form

$$H = H_0 + U = H_0 + \sum_n U_n , \tag{3-27}$$

where H_0 is the periodic part of H, and U contains the randomness due to both substitutional and thermal disorder. U_n is the contribution of the n-th site to U. The decomposition in Eq. (3-27) is not unique. However, a convenient decomposition can always be chosen for a given system.

Our object is to determine <<G>> and <<GG>>. Here the double average is a thermal average over the phonon ensemble in a given configuration, followed by an average over all configurations. The coherent potential approximation (CPA) is a technique for finding a self-consistent solution for the average Green's function. The method[61] is outlined below.

The average Green's function can be expressed as

$$\langle\langle G(z) \rangle\rangle \equiv \bar{\bar{G}} = \frac{1}{z - H_0 - \hat{\Sigma}} . \tag{3-28}$$

This defines $\hat{\Sigma}$, the self-energy operator, which has the full crystal symmetry since $\bar{\bar{G}}$ does. Thus $\hat{\Sigma}$ represents an effective potential for the averaged crystal. Expressing G from Eq. (3-18) in terms of $\bar{\bar{G}}$ yields:

$$G = \bar{\bar{G}} + \bar{\bar{G}}\, T\, \bar{\bar{G}} \ , \tag{3-29}$$

where

$$\begin{aligned} T &= (U-\hat{\Sigma})\left[1-\bar{\bar{G}}(U-\hat{\Sigma})\right]^{-1} = \left[1-(U-\hat{\Sigma})\bar{\bar{G}}\right]^{-1}(U-\hat{\Sigma}) \\ &= (U-\hat{\Sigma}) + (U-\hat{\Sigma})\bar{\bar{G}}\, T \ . \end{aligned} \tag{3-30}$$

Now taking the average on both sides of Eq. (3-29), we get

$$\langle\langle G \rangle\rangle = \bar{\bar{G}} + \bar{\bar{G}} \langle\langle T \rangle\rangle \bar{\bar{G}} \ , \tag{3-31}$$

which is solved by

$$\langle\langle T(\hat{\Sigma}) \rangle\rangle = 0 \ . \tag{3-32}$$

This, as can be seen from Eqs. (3-28) and (3-30), is the self-consistent equation which must be solved for $\hat{\Sigma}$. $\hat{\Sigma}$ can be expressed as a sum of self energy operators $\hat{\Sigma}_n$,

$$\hat{\Sigma} = \sum_n \hat{\Sigma}_n \ . \tag{3-33}$$

The choice of the operators $\hat{\Sigma}_n$ is not unique, the only restriction is that the sum over $\hat{\Sigma}_n$'s must add to the operator $\hat{\Sigma}$ which has the symmetry of the pure crystal. A particular choice will be useful such that each $\hat{\Sigma}_n$ is localized near its site n and places an equal contribution on each site.

Since the potential U is a sum of contributions from each site, i.e. $U = \sum_n U_n$, the scattering operator T can be expressed as

$$T = \sum_n Q_n = \sum_n \widetilde{Q}_n \ , \tag{3-34}$$

with

$$\begin{aligned} Q_n &= (U_n - \hat{\Sigma}_n)(1 + \bar{\bar{G}} T) = T_n (1 + \bar{\bar{G}} \textstyle\sum_{m(\neq n)} Q_n) \\ &= T_n + \sum_{m(\neq n)} T_n \bar{\bar{G}} T_m + \sum_{m(\neq n)} T_n \bar{\bar{G}} T_m \sum_{\ell(\neq m)} \bar{\bar{G}} T_\ell + \cdots , \end{aligned} \tag{3-35}$$

and

$$\begin{aligned} \tilde{Q}_n &= (1 + T \bar{\bar{G}})(U_n - \hat{\Sigma}_n) = (1 + \textstyle\sum_{m(\neq n)} \tilde{Q}_m \bar{\bar{G}}) T_n \\ &= T_n + \sum_{m(\neq n)} T_m \bar{\bar{G}} T_n + \sum_{\ell(\neq m)} T_\ell \bar{\bar{G}} \sum_{m(\neq n)} T_m \bar{\bar{G}} T_n + \cdots . \end{aligned} \tag{3-36}$$

The atomic scattering operator T_n is defined as:

$$\begin{aligned} T_n &= (U_n - \hat{\Sigma}_n)[1 - \bar{\bar{G}}(U_n - \Sigma_n)]^{-1} \\ &= (U_n - \hat{\Sigma}_n) + (U_n - \hat{\Sigma}_n) \bar{\bar{G}} T_n \end{aligned} \tag{3-37}$$

In multiple scattering language, Q_n, as seen from Eqs. (3-34) and (3-35) represents the contribution to the total scattering such that the last scattering happens at site n; while Q_n represents the contribution to T such that the first scattering is at site n. In terms of the T_n's, the scattering operator T has the customary form:

$$T = \sum_n T_n + \sum_{n,m\,(n\neq m)} T_n \bar{\bar{G}} T_m + \sum_{\substack{n,m,\ell \\ (n\neq m,\, m\neq \ell)}} T_n \bar{\bar{G}} T_m \bar{\bar{G}} T_\ell + \cdots . \tag{3-38}$$

The ensemble average of Eq. (3-34) along with Eq. (3-32) is:

$$\langle\langle T \rangle\rangle = 0 = \sum_n \langle\langle Q \rangle\rangle . \tag{3-39}$$

But from Eq. (3-35) we have

$$\langle\langle Q_n \rangle\rangle = \langle\langle T_n (1 + \bar{\bar{G}} \sum_{m(\neq n)} Q_m) \rangle\rangle . \tag{3-40}$$

The coherent potential approximation for $\hat{\Sigma}$ consists of two ingredients: (i) there exists a decomposition of $\hat{\Sigma}$ as in Eq. (3-33) such that we can neglect the statistical correlation between the atomic T matrix T_n and the effective waves coming from other sites, i.e.

$$\begin{aligned}\langle\langle Q_n \rangle\rangle &= \langle\langle T_n \left(1 + \bar{\bar{G}} \sum_{m(\neq n)} Q_m\right) \rangle\rangle \\ &\simeq \langle\langle T_n \rangle\rangle \left(1 + \bar{\bar{G}} \sum_{m(\neq n)} \langle\langle Q_m \rangle\rangle\right).\end{aligned} \tag{3-41}$$

This is a "single site approximation".

(ii) $\hat{\Sigma}_n$ satisfies

$$\langle\langle T_n(\hat{\Sigma}) \rangle\rangle = 0. \tag{3-42}$$

Eq. (3-42) is the CPA equation for $\hat{\Sigma}$, which entirely determines $\bar{\bar{G}}(z)$ and thus the density of states $\mathcal{N}(E)$.

For the electrical conductivity, we have to determine the operator K as defined in Eq. (3-24). Substituting G into K from the Eq. (3-29), and using the CP equation, Eq. (3-32), we can reduce K to the form

$$K(z_1, p^{\alpha}, z_2) = \bar{\bar{G}}(z_1)\left[p^{\alpha} + \Gamma(z_1, p^{\alpha}, z_2)\right]\bar{\bar{G}}(z_2), \tag{3-43}$$

where the vertex operator Γ is given by

$$\Gamma(z_1, p^{\alpha}, z_2) \equiv \langle\langle T(z_1)\bar{\bar{G}}(z_1)\, p^{\alpha}\, \bar{\bar{G}}(z_2) T(z_2) \rangle\rangle. \tag{3-44}$$

The vertex operator Γ may then be rewritten as the sum of contribution from all sites by using Eq. (3-34) for T and Eqs. (3-35) and (3-36) for Q_n and $\tilde{Q}_n$ respectively,

$$\begin{aligned}\Gamma &= \sum_n \sum_m \langle\langle Q_n \bar{\bar{G}}\, p^{\alpha} \bar{\bar{G}} \tilde{Q}_m \rangle\rangle \\ &= \sum_n \sum_m \langle\langle T_n \left(1 + \bar{\bar{G}} \sum_{p(\neq n)} Q_p\right) \bar{\bar{G}}\, p^{\alpha} \bar{\bar{G}} \left(1 + \sum_{s(\neq m)} \tilde{Q}_s \bar{\bar{G}}\right) T_m \rangle\rangle.\end{aligned} \tag{3-45}$$

CPA for K has a further single site approximation in addition to Eq. (3-41), i.e.

$$\begin{aligned}&\langle\langle T_n (1+\bar{\bar{G}}\textstyle\sum_{p(\neq n)} Q_n)\bar{\bar{G}}\, p^\alpha \bar{\bar{G}}(1+\sum_{s(\neq m)}\widetilde{Q}_s\bar{\bar{G}})T_m\rangle\rangle \\ &\simeq \langle\langle T_n \langle\langle (1+\bar{\bar{G}}\textstyle\sum_{p(\neq n)} Q_n)\bar{\bar{G}}\, p^\alpha \bar{\bar{G}}(1+\sum_{s(\neq m)}\widetilde{Q}_s\bar{\bar{G}})\rangle\rangle T_m\rangle\rangle ,\end{aligned} \tag{3-46}$$

which is zero for n ≠ m, since T_n and T_m are then independent, and each averages to zero, by Eq. (3-42). Thus we arrive at the following result

$$\begin{aligned}&\langle\langle Q_n\bar{\bar{G}}\, p^\alpha\bar{\bar{G}}\widetilde{Q}_m\rangle\rangle \simeq \langle\langle Q_n\bar{\bar{G}}\, p^\alpha\bar{\bar{G}}\widetilde{Q}_n\rangle\rangle\,\delta_{nm} \\ &\equiv \Gamma_n\,\delta_{nm} .\end{aligned} \tag{3-47}$$

This, in two resolvent language, means that we have neglected all the statistical correlations between two particles unless they are scattered at the same site. In other words, we have neglected the statistical correlation between the scattered waves from two different sites.

Using Eqs. (3-35), (3-36) and (3-46) we find

$$\begin{aligned}\Gamma_n &= \langle\langle Q_n\bar{\bar{G}}\, p^\alpha\bar{\bar{G}}\widetilde{Q}_n\rangle\rangle \\ &\simeq \langle\langle T_n\langle\langle (1+\bar{\bar{G}}\textstyle\sum_{p(\neq n)}Q_p)\bar{\bar{G}}\, p^\alpha\bar{\bar{G}}(1+\sum_{s(\neq n)}\widetilde{Q}_s\bar{\bar{G}})\rangle\rangle T_n\rangle\rangle \\ &= \langle\langle T_n\langle\langle \bar{\bar{G}}\, p^\alpha\bar{\bar{G}} + \bar{\bar{G}}(\textstyle\sum_{p(\neq n)}\langle\langle Q_p\bar{\bar{G}}\, p^\alpha\bar{\bar{G}}\widetilde{Q}_p\rangle\rangle)\bar{\bar{G}}\rangle\rangle T_n\rangle\rangle \\ &= \langle\langle T_n\bar{\bar{G}}(p^\alpha + \textstyle\sum_{p(\neq n}\Gamma_p)\bar{\bar{G}}T_n\rangle\rangle\end{aligned} \tag{3-48}$$

In Eq. (3-48) we have used the CPA results $\langle\langle Q_n\rangle\rangle = \langle\langle\widetilde{Q}_n\rangle\rangle = 0$.

Combine Eqs. (3-43), (3-45), (3-47), and (3-48) to obtain the closed equations for K,

$$K = \bar{\bar{G}}(p^\alpha + \textstyle\sum_n \Gamma_n)\bar{\bar{G}} , \tag{3-49}$$

and

$$\Gamma_n = \langle\langle T_n K T_n \rangle\rangle - \langle\langle T_n \bar{\bar{G}} \Gamma_n \bar{\bar{G}} T_n \rangle\rangle , \tag{3-50}$$

which yield the formal solution for Γ :

$$\Gamma = \sum_n \langle\langle T_n \bar{\bar{G}} \rho^{d} \bar{\bar{G}} T_n \rangle\rangle + \sum_{\substack{n,m \\ (n \neq m)}} \langle\langle T_n \bar{\bar{G}} \langle\langle T_m \bar{\bar{G}} \rho^{d} \bar{\bar{G}} T_m \rangle\rangle T_n \rangle\rangle + \cdots . \tag{3-51}$$

Eqs. (3-49) and (3-50) complete the CPA formalism. They are still formidable. We have to obtain the self-energy from Eq. (3-42) in order to get $\bar{\bar{G}}$, then try to sum the series in Eq. (3-51) to get Γ , and finally insert Γ into Eq. (3-43) to find K. In the next section a simple band model Hamiltonian will be used to reduce the operator equations to simple scalar equations.

D. Model Calculation

1. Simple Band Model

We shall use the simplest possible model electron Hamiltonian that includes both substitutional impurities and thermal disorder,

$$H = H_0 + D + \Theta , \tag{3-52}$$

where

$$H_0 = \sum_{n,m}' |n\rangle t_{nm} \langle m| \tag{3-53}$$

represents the part of the Hamiltonian off-diagonal in site indices, and the t_{nm} are assumed to be periodic, and independent of alloying and lattice distortion,

$$D = \sum_n |n\rangle \varepsilon_n \langle n| \tag{3-54}$$

represents the "impurity" Hamiltonian with ε_n either ε_A or ε_B, according to whether an A or B atom is on site n, and

$$\Theta = \sum_n |n\rangle \theta_n \langle n| \tag{3-55}$$

is the electron phonon interation. The phonon operator, θ_n depends on which ion occupies site n and on the phonon coordinates. This model is a generalization of the Koster-Slater one impurity case, and is identical with the model exploited by Velický et al.[3], with the addition of the phonon contribution.

A few words are appropriate here about some assumptions, definitions, and redefinitions that we are making. Some of the problems about which we shall be speaking are already present in the Koster-Slater case, although they are customarily (and unnecessarily) ignored. The heart of the problem is the definition of the site basis, and implications of the choice. Let us take $|n\rangle$ to be an atomic or Wannier function centered at $\vec{R}_n^0$. Following the convenient custom, we pretend that the $|n\rangle$ are not only very localized, as are atomic wave functions, but also orthogonal, as are Wannier functions. In other words, we assume that the difference between Wannier and atomic wave functions can be neglected, as is true in a good tight binding case. Now usually, in an exposition of the Koster-Slater model, the $|n\rangle$ are all taken to be one type of wave function, e.g. pure A crystal Wannier functions associated with a single atomic orbital, but this is highly unphysical - the true wave function can not generally be approximated well on such a basis, without multiplying the number of bands taken into account. Therefore, let us initially take $|n\rangle$ to be $|n_A\rangle$ or $|n_B\rangle$, the state appropriate to the type of atom at n , $|n\rangle$ being centered on the actual position $\vec{R}_n$, rather than the official lattice position $\vec{R}_n^0$. We assume that the tails of the atomic basis are almost the same, so that we can neglect differences in the off-diagonal matrix elements of energy and momentum, t_{nm} and $\vec{p}_{nm}$, and assume them to be independent of alloying. The phonon contribution is restricted to be diagonal only for the resulting mathematical convenience in the CPA formalism.[3]

Now let us redefine our point of view or notation. Using the basis described above, for a particular configuration let us convert all operators, such as G, K, etc., into matrices, and regard all the CPA equations as matrix equations. Equivalently, we could turn these matrices into operators by using an abstract periodic basis. The final results will not be affected, of course, but some very clumsy notation and language is being avoided, without pretending that Schrödinger's equation is insensitive to the potential (the literal use of one type of $|n\rangle$).

Let us apply the CPA formulation of the previous section to the simple band model. In the "mock periodic" crystal described by H_0, the Green's function is

$$G_0(z) = \frac{1}{z - H_0} = \sum_{\vec{k}} \frac{|\vec{k}\rangle\langle\vec{k}|}{z - \epsilon(\vec{k})} , \tag{3-56}$$

where the $|\vec{k}\rangle$ are the "mock Bloch states" of H_0 defined by

$$|\vec{k}\rangle \equiv \frac{1}{\sqrt{N}} \sum_n e^{i\vec{k}\cdot\vec{R}_n^0} |n\rangle ,$$

with energy $\epsilon(\vec{k})$ given by the usual expression

$$\epsilon(\vec{k}) = \sum_n e^{i\vec{k}\cdot\vec{R}_n^0} t_{n0} ,$$

and $\vec{k}$ is the usual wave vector in the Brillouin zone associated with the static crystal lattice. The Wannier or atomic states $|n\rangle$ of the site basis are then related to the "mock Bloch states" by

$$|n\rangle = \frac{1}{\sqrt{N}} \sum_{\vec{k}} e^{-i\vec{k}\cdot\vec{R}_n^0} |\vec{k}\rangle . \tag{3-57}$$

Since the site-diagonal matrix elements of G_0 are site-independent, i.e.

$$\begin{aligned} F_0(z) &\equiv \langle n| G_0(z) |n\rangle = \langle 0| G_0(z) |0\rangle \\ &= \frac{1}{N} \sum_{\vec{k}} \frac{1}{z - \epsilon(\vec{k})} , \end{aligned} \tag{3-58}$$

the pure crystal density of states per atom, $\mathcal{N}_0$, according to Eq. (3-20), is

$$\mathcal{N}_0(E) = \pm \frac{1}{\pi} \mathcal{I}m\, F_0(E \mp i0) . \tag{3-59}$$

Another useful relation between F_0 and $\mathcal{N}_0$, obtainable from Eq. (3-58), is

$$F_0(z) = \int dE \, \frac{\mathcal{N}_0(E)}{z - E} . \tag{3-60}$$

The averaged finite-temperature alloy described by $\bar{\bar{G}}(z)$ has the full crystal symmetry. Thus, corresponding to Eq. (3-58), we can define

$$F(z) \equiv \langle 0| \bar{\bar{G}}(z) |0\rangle = \frac{1}{N} \sum_{\vec{k}} \frac{1}{z - \epsilon(\vec{k}) - \Sigma(z,\vec{k})} . \tag{3-61}$$

Here we have used Eq. (3-28) and the general periodic property of the self-energy,

$$\hat{\Sigma}(z) = \sum_{\vec{k}} |\vec{k}\rangle \Sigma(z,\vec{k}) \langle \vec{k}| \, . \tag{3-62}$$

In the coherent potential approximation we obtain the self-energy from the solution of Eq. (3-42). A scalar solution for $\hat{\Sigma}$ can be found, so that the self-energy is a sum of site contributions, i.e.

$$\hat{\Sigma}_n = |n\rangle \Sigma \langle n| \, . \tag{3-63}$$

Thus, T_n (Eq. (3-37)) is site diagonal, and the operator equation, Eq. (3-42), becomes the scalar equation

$$\left\langle\!\!\left\langle \frac{\varepsilon_n + \theta_n - \Sigma}{1 - (\varepsilon_n + \theta_n - \Sigma) F} \right\rangle\!\!\right\rangle = 0 \, . \tag{3-64}$$

This equation for Σ reduces to Eq. (4-22) of reference 3, if $\theta_n \to 0$, i.e. in the static alloy. However, in the static alloy the equation for Σ is merely algebraic, whereas here, with phonons included, it is an integral equation.

Once we obtain Σ from Eq. (3-64), we can obtain F from Eq. (3-61), in terms of F_0 (see Eq. (3-58)),

$$F(z) = F_0(z - \Sigma) \, , \tag{3-65}$$

since Σ is independent of $\vec{k}$. The density of states per atom $\mathcal{N}(E)$ is then, from Eqs. (3-20) and (3-61),

$$\mathcal{N}(E) = \pm \frac{1}{\pi} \, \mathrm{Im} \, F(E \mp i0) \, . \tag{3-66}$$

To obtain an expression for the conductivity, we first prove that the vertex correction Γ in Eq. (3-51) vanishes. Each term in the series expansion, Eq. (3-51), contains a factor $T_n \bar{\bar{G}} p^\alpha \bar{\bar{G}} T_n$. Since T_n is site diagonal, $\Gamma = 0$, if $\langle n | \bar{\bar{G}} p^\alpha \bar{\bar{G}} | n \rangle = 0$. But we have

$$\langle n | \bar{\bar{G}} p^\alpha \bar{\bar{G}} | n \rangle = \sum_{\vec{k}} \frac{1}{N} \frac{m\, v^\alpha(\vec{k})}{(z_1 - \epsilon(\vec{k}) - \Sigma)\,(z_2 - \epsilon(\vec{k}) - \Sigma)} , \tag{3-67}$$

where $v^\alpha(\vec{k})$ is the α component of the velocity, defined by

$$v^\alpha(\vec{k}) \equiv \frac{1}{m} \langle \vec{k} | p^\alpha | \vec{k} \rangle . \tag{3-68}$$

Time reversal symmetry gives the relations

$$v^\alpha(-\vec{k}) = - v^\alpha(\vec{k}) , \tag{3-69}$$

and

$$\epsilon(-\vec{k}) = \epsilon(\vec{k}) . \tag{3-70}$$

Therefore, the summation in Eq. (3-67) vanishes identically. Thus, from Eq. (3-49),

$$K = \bar{\bar{G}} p^\alpha \bar{\bar{G}} . \tag{3-71}$$

Combining Eqs. (3-22), (3-23), (3-68), and (3-71), and defining $g(\vec{k},z)$ as

$$g(\vec{k},z) \equiv \langle \vec{k} | \bar{\bar{G}}(z) | \vec{k} \rangle = \frac{1}{z - \epsilon(\vec{k}) - \Sigma(z)} , \tag{3-72}$$

the conductivity becomes

$$\sigma^{\alpha\beta} = \frac{2e^2\hbar}{\pi\Omega} \int d\eta \left(-\frac{df}{d\eta}\right) \sum_{\vec{k}} v^\alpha(\vec{k})\, v^\beta(\vec{k}) \left[\mathrm{Im}\, g(\vec{k},\eta^+) \right]^2 . \tag{3-73}$$

Or, following Velický,[62] we have the alternate form

$$\sigma^{\alpha\beta} = \frac{2e^2\hbar}{\pi\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\int d\xi\left[\frac{\Delta(\eta)}{[\eta-\xi-\Lambda(\eta)]^2+\Delta^2(\eta)}\right]^2 \times\frac{1}{N}\sum_{\vec{k}} v^{\alpha}(\vec{k})\,v^{\beta}(\vec{k})\,\delta(\xi-\epsilon(\vec{k}))\ , \tag{3-74}$$

where Ω_c is the volume per atom and Λ and Δ are defined from the self-energy Σ ,

$$\Lambda(\eta) \equiv \mathcal{R}_e\,\Sigma(\eta \pm io)\ , \tag{3-75}$$

and

$$\Delta(\eta) \equiv |\,\mathcal{I}_m\,\Sigma(\eta \pm io)|\,. \tag{3-76}$$

We have now set down the expressions for the model Hamiltonian conductivity and density of states. In the next section, we shall discuss the phonon system and the phonon averaging process in the self-energy equation, Eq. (3-64).

2. Electron-Phonon Interaction and Distribution Function for θ_n.

In the harmonic approximation, the atomic motion of the alloy in a given configuration can be described by the Hamiltonian

$$H_{ph} = \sum_{s=1}^{3N}\hbar\omega_s\left(1/2 + b_s^{+}b_s\right)\ , \tag{3-77}$$

where b_s^{+} and b_s are the creation and destruction operators for a phonon in states, with frequency ω_s. However, in a concentrated alloy, the phonon quantum number s can no longer be identified with the crystal momentum. The electron-phonon interaction, which does not conserve crystal momentum, is represented in our model (Eq. (3-55)) by the local Hamiltonian

$$H_{e\cdot p} = \Theta = \sum_n |n\rangle \, \theta_n \langle n| . \tag{3-78}$$

We make the standard, excellent approximation[63]

$$\theta_n = \sum_s \left[\gamma_s(n)\, b_s + \gamma_s^*(n)\, b_s^+ \right], \tag{3-79}$$

where $\gamma_s(n)$ is the probability amplitude for an electron at the n'th site to absorb a phonon with quantum number s. Notice that $\gamma_s(n)$, b_s, and θ_n are configuration dependent. Notice also that since θ_n is an operator, the self-consistent equation, Eq. (3-64), is a phonon operator equation. However, we can reduce it to a scalar form, as follows.

The phonon average of any function $f(\theta_n)$ of the operator θ_n is

$$\langle f(\theta_n) \rangle_p = Tr_{ph} \left[\rho_{ph} \, f(\theta_n) \right] , \tag{3-80}$$

where

$$\rho_{ph} = \frac{e^{-\beta H_{ph}}}{Tr\,[\,e^{-\beta H_{ph}}]} , \tag{3-81}$$

and the trace is over all states of the lattice motion. The average $\langle f(\theta_n) \rangle_p$ can also be written in terms of the probability distribution $P_n(\eta)$ as

$$\langle f(\theta_n) \rangle_p = \int_{-\infty}^{\infty} f(\eta)\, P_n(\eta)\, d\eta , \tag{3-82}$$

where $P_n(\eta)$ is defined in terms of its characteristic function $\varphi_n(\chi)$,

$$P_n(\eta) = \frac{1}{2\pi}\int_{-\infty}^{\infty} d\chi\, e^{-i\chi\eta}\varphi_n(\chi) \,, \tag{3-83}$$

which in turn is defined as

$$\varphi_n(\chi) = Tr_{ph}\left[\rho_{ph}\, e^{i\chi\theta_n}\right]. \tag{3-84}$$

Explicitly, the characteristic function is

$$\begin{aligned} \varphi_n(\chi) &= Tr_{ph}\left\{\frac{e^{-\beta\sum_s \hbar\omega_s(1/2 + b_s^+ b_s)}\, e^{i\chi\sum_s(\gamma_s(n) b_s + \gamma_s^*(n) b_s^+)}}{Tr_{ph}\left[e^{-\beta\sum_s \hbar\omega_s(1/2 + b_s^+ b_s)}\right]}\right\} \\ &= Tr_{ph}\left[\left(\prod_s \rho_s\right)\left(\prod_s e^{i\chi(\gamma_s(n) b_s + \gamma_s^*(n) b_s^+)}\right)\right] \\ &= Tr_{ph}\left[\left(\prod_s \rho_s\right)\left(\prod_s e^{i\chi \hat{W}_s(n)}\right)\right] \\ &= \prod_s\left[Tr_{ph}\,\rho_s\, e^{i\chi\hat{W}_s(n)}\right] = \prod_s \varphi_n^{(s)}(\chi). \end{aligned} \tag{3-85}$$

In the above expression, we have defined

$$\rho_s \equiv e^{-\beta\hbar\omega_s(1/2 + b_s^{\dagger} b_s)} \Big/ \sum_{n_s=0}^{\infty} e^{-\beta\hbar\omega_s(1/2 + n_s)} \,, \tag{3-86}$$

and

$$\hat{W}_s(n) \equiv \gamma_s(n)\, b_s + \gamma_s^*(n)\, b_s^+ \,, \tag{3-87}$$

and have used the commutation relation

$$\left[\rho_s \,,\, \hat{W}_{s'}(n)\right] = 0 \,, \qquad s \neq s'. \tag{3-88}$$

Note $\varphi_n^{(s)}(\chi)$ is the characteristic function of $\hat{\mathbf{W}}_s(n)$, which is essentially the displacement of a one-dimensional quantum oscillator, so that we can use the standard result[64]

$$\varphi_n^{(s)}(\chi) = e^{-\frac{1}{2}\alpha_n^{(s)}\chi^2}, \tag{3-89}$$

where

$$\alpha_n^{(s)} = |\gamma_s(n)|^2 \coth(\tfrac{1}{2}\beta\hbar\omega_s). \tag{3-90}$$

Thus, in view of Eqs. (3-80), (3-89) and (3-90), $\varphi_n(\chi)$ becomes

$$\varphi_n(\chi) = e^{-\frac{1}{2}\alpha_n\chi^2}, \tag{3-91}$$

where

$$\alpha_n = \sum_s \alpha_n^{(s)} = \sum_s |\gamma_s(n)|^2 \coth(\tfrac{1}{2}\beta\hbar\omega_s). \tag{3-92}$$

Note that $\alpha_n^{(s)}$ is proportional to the Debye-Waller factor times the square of the electron-phonon coupling constant. Since the characteristic function $\varphi_n(\chi)$ is a Gaussian, its Fourier transform, the distribution function, is a Gaussian too. Thus the distribution function is

$$P_n(\eta) = \frac{1}{\sqrt{2\pi\alpha_n}} e^{-\eta^2/2\alpha_n}. \tag{3-93}$$

Applying Eqs. (3-82) and (3-93) to the self-consistent equation, Eq. (3-64), we have a scalar integral equation for Σ,

$$\int d\eta \left\langle \frac{1}{\sqrt{2\pi\alpha_n}} e^{-\eta^2/2\alpha_n} \left(\frac{\varepsilon_n + \eta - \Sigma}{1 - (\varepsilon_n + \eta - \Sigma)F} \right) \right\rangle_c = 0. \tag{3-94}$$

Let us define a local distribution $P_A(\eta)$, which is the average of $P_n(\eta)$ over all configurations with an A atom at the n'th site, and define $P_B(\eta)$ similarly. Then Eq. (3-94) becomes more explicit,

$$\int d\eta \left[x P_A(\eta) \left(\frac{\varepsilon_A + \eta - \Sigma}{1 - (\varepsilon_A + \eta - \Sigma)F} \right) + y P_B(\eta) \left(\frac{\varepsilon_B + \eta - \Sigma}{1 - (\varepsilon_B + \eta - \Sigma)F} \right) \right] = 0 \, . \quad (3\text{-}95)$$

The equation for Σ thus depends on the pure crystal density of states and the distribution function. In the next section we shall further simplify the model in order to get a qualitative idea of the temperature dependence of density of states and the conductivity.

3. Model Density of States, Velocity Dispersion and Local Distribution Functions.

Let us first review the procedure for calculating the self-energy Σ, the density of states $\mathcal{N}$, and the conductivity σ, and then describe some model functions that we have actually used in our computations.

To calculate the self-energy Σ, we need to

(i) obtain $F_0(z)$ from the dispersion relation $\epsilon(\vec{k})$, using Eq. (3-58), or from the pure crystal density of states $\mathcal{N}_0(E)$, using Eq. (3-60);

(ii) Express F as a function of Σ by Eq. (3-65);

(iii) Specify the electron-phonon parameter $\gamma_s(n)$, then get α_n from Eq. (3-92). Perform the configuration average on $P_n(\eta)$ to get $P_A(\eta)$ and $P_B(\eta)$.

(iv) Solve the integral equation, Eq. (3-95) for Σ. Once the self-energy is obtained, we compute the density of states $\mathcal{N}(E)$ from Eq. (3-66).

To compute the conductivity, we assume a cubic lattice, so that the averaged conductivity is isotropic,

$$\sigma^{\alpha\beta} = \sigma\,\delta_{\alpha\beta}\,, \tag{3-96}$$

where, according to Eq. (3-74),

$$\sigma = \frac{2e^2\hbar}{\pi\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\int d\xi\left\{\left[\frac{\Delta(\eta)}{(\eta-\xi-\Lambda(\eta))^2+\Delta^2(\eta)}\right]^2 \frac{1}{N}\sum_{\vec{k}}\frac{1}{3}\,v^2(\vec{k})\,\delta(\xi-\epsilon(\vec{k}))\right\}. \tag{3-97}$$

If we define the velocity dispersion $v(\epsilon)$ by

$$v^2(\epsilon) \equiv \frac{1}{N}\sum_{\vec{k}} v^2(\vec{k})\,\delta(\epsilon-\epsilon(\vec{k}))\Big/\mathcal{N}_0(\epsilon)\;, \tag{3-98}$$

then

$$\sigma = \frac{2e^2\hbar}{\pi\Omega_c}\int d\eta\left(-\frac{df}{d\eta}\right)\int d\xi\,\frac{v^2(\xi)\,\mathcal{N}_0(\xi)\,\Delta^2(\eta)}{[(\eta-\xi-\Lambda(\eta))^2+\Delta^2(\eta)]^2}. \tag{3-99}$$

Since we are investigating the general trends, it is neither convenient nor profitable to start our calculation from a detailed $\epsilon(\vec{k})$ and $\gamma_s(n)$. Instead we shall use simple model forms for $\mathcal{N}_0(E)$, $v^2(\epsilon)$, and local distributions P_A and P_B as follows.

For pure crystal density of states, we have adopted the Hubbard[65] ellipse model,

$$\mathcal{N}_0(E) = \begin{cases} \dfrac{2}{\pi}\sqrt{1-E^2} & , \quad |E| \le 1 \\ 0 & , \quad |E| > 1 \end{cases}\;, \tag{3-100}$$

where the energy unit is a half-bandwidth. This model is essentially an approximation to a simple cubic tight-binding s band density of states. It also behaves like a free electron density of states around the bottom of the band. This is a model that has been used extensively in calculations of electronic properties in alloys.[3]

Corresponding to Eq. (3-100), we have

$$F_0(z) = 2z - 2\sqrt{z-1}\,\sqrt{z+1} \;, \qquad (3\text{-}101)$$

so that

$$F(z) = F_0(z-\Sigma) = 2(z-\Sigma) - 2\sqrt{(z-\Sigma)-1}\,\sqrt{(z-\Sigma)+1} \;. \qquad (3\text{-}102)$$

The simplest form for the local distribution functions P_A and P_B can be obtained by assuming that the electron-phonon interaction is independent of configurations,

$$P_A(\eta) = P_B(\eta) = \frac{1}{\sqrt{2\pi\alpha}}\, e^{-\eta^2/2\alpha} \;. \qquad (3\text{-}103)$$

Instead, and intuitively more attractive, we take

$$P_{A,B}(\eta) = \frac{1}{\sqrt{2\pi\alpha_{A,B}}}\, e^{-\eta^2/2\alpha_{A,B}} \;, \qquad (3\text{-}104)$$

which could, for example, be obtained by taking a typical term in the configuration average leading to P_A and P_B. The input parameters α_A and α_B are linear in temperature at high temperatures. (see Eq. (3-92)).

The spectrum $\epsilon(\vec{k})$, and therefore $v^2(E)$,cannot be uniquely derived from $\mathcal{N}_0(E)$. Following Velický[9], we chose the form

$$v^2(\epsilon) = v_m^2(1-\epsilon^2) \qquad (3\text{-}105)$$

which corresponds well with our model $\mathcal{N}_0(E)$, and with the simple band structure we just mentioned. Here v_m is the maximum velocity in the band. Combining Eqs. (3-99), (3-100) and (3-105), we obtain

$$\alpha = \frac{2e^2\hbar}{\pi\Omega_c}\left(\frac{2}{3\pi}v_m^2\right)\int d\eta\left(-\frac{df}{d\eta}\right)\int_{-1}^{1} d\xi\,\frac{(1-\xi^2)^{3/2}\,\Delta^2(\eta)}{[(\eta-\xi-\Lambda(\eta))^2+\Delta^2(\eta)]^2}. \qquad (3\text{-}106)$$

For later convenience, let us define a function $\mathcal{L}(\eta)$ by

$$\mathcal{L}(\eta) \equiv \int_{-1}^{1} d\xi\,(1-\xi^2)\left[\frac{\Delta(\eta)}{(\eta-\xi-\Lambda(\eta))^2+\Delta^2(\eta)}\right]^2, \qquad (3\text{-}107)$$

or, after integration (see Appendix B),

$$\mathcal{L}(\eta) = \frac{\pi^4\mathcal{N}^3(\eta)}{16\,\Delta(\eta)}\left[1+\frac{6\,\Delta(\eta)}{\pi\mathcal{N}(\eta)}\right]. \qquad (3\text{-}108)$$

For a metal alloy, $\left(-\frac{df}{d\eta}\right)$ is a sharply peaked function of η at $\eta=\epsilon_F$, and we can then express α in the usual approximation,

$$\alpha = \frac{2e^2\hbar}{\pi\Omega_c}\left(\frac{2v_m^2}{3\pi}\right)\left[\mathcal{L}(\epsilon_F)+\frac{\pi^2}{3}\mathcal{L}''(\epsilon_F)(kT)^2+\cdots\right]. \qquad (3\text{-}109)$$

Since $\mathcal{L}(\eta)$ is a smooth function of η except at the singular points of the density of states, terms involving $\mathcal{L}''(\epsilon_F)$ and higher derivatives are small compared to $\mathcal{L}(\epsilon_F)$ and may be neglected. Thus, if ϵ_F is not too close to a band edge, or other singularity, it is sufficient to keep only the first term in the expansion of Eq. (3-109), so the conductivity becomes

$$\alpha = \frac{\pi^2}{12}\,\frac{e^2\hbar v_m^2}{\Omega_c}\,\frac{\mathcal{N}^3(\epsilon_F)}{\Delta(\epsilon_F)}\left[1+\frac{6\,\Delta(\epsilon_F)}{\pi\mathcal{N}(\epsilon_F)}\right]. \qquad (3\text{-}110)$$

The temperature dependence of the density of states and the conductivity can now be investigated. The details and results of numerical calculation will be presented in the next section. However, a quicker understanding of some features of this theory can be obtained by investigating the weak scattering limit. This topic is treated in Appendix C.

4. Calculational Procedures.

Let us review the input parameters needed for the computation. For a binary alloy A_xB_y at finite temperature T, x and y are the concentrations of A and B atoms, ε_A and ε_B are the strengths of static random potentials around A and B atoms respectively, and, α_A and α_B are the electron-phonon interaction parameters which are linear in temperature at high temperatures. Indeed, α_A and α_B can be thought of as the mean square of the thermal fluctuation in the atomic potential strengths ε_A and ε_B respectively. It is convenient to define the origin of energy and a scattering strength δ by

$$\begin{cases} \varepsilon_A = \frac{1}{2}\delta \\ \varepsilon_B = -\frac{1}{2}\delta \end{cases} . \tag{3-111}$$

Here all the energies are in units of the half-bandwidth.

To solve for Σ from the integral equation,Eq. (3-95), it is convenient to express it in a different form which is useful for iteration,

$$\Sigma = \left\langle\!\left\langle \frac{\varepsilon_n + \theta_n}{1-(\varepsilon_n+\theta_n-\Sigma)F} \right\rangle\!\right\rangle \Big/ \left\langle\!\left\langle \frac{1}{1-(\varepsilon_n+\theta_n-\Sigma)F} \right\rangle\!\right\rangle , \tag{3-112}$$

which can be simplified further, to

$$\Sigma = z - \frac{1}{4} F - 1 \Big/ \left\langle\!\!\left\langle \frac{1}{z - (\varepsilon_n + \theta_n) - \frac{1}{4} F} \right\rangle\!\!\right\rangle . \tag{3-113}$$

In deriving Eq. (3-113), we have used Eq. (3-102), which can be rewritten as

$$\Sigma = z - \frac{1}{F(z)} - \frac{1}{4} F(z) . \tag{3-114}$$

The iteration procedure is as follows. Start with some appropriate F, compute Σ from Eq. (3-113), which provides a new F from Eq. (3-102), and so on.

The convergence of Σ depends on a good choice for the initial F. Notice that F is the site diagonal matrix element of a translationally invariant Green's function. In iterating, good convergence tends to depend on starting out close to the final answer. Since the phonons usually have a small effect compared with the alloying, the best initial trial value to use for F is generally the static alloy $F^{(0)}$. The speed of convergence also depends on the energy. There is always better convergence at the band center than at the band edges. So, in the actual computation, we solve for the static alloy $F^{(0)}$ (to be discussed shortly), then we start iterating at an energy corresponding to the peak of the static density of states, iterating Eq. (3-113) to get the temperature dependent self-energy Σ at that energy. Then we use this Σ , or the corresponding F as the initial value for a neighboring energy, and continue this procedure to the tails of the band. In the case of split bands, we carry out the procedure for each subband separately. The self-energy $\Sigma^{(0)}$ and the corresponding $F^{(0)}$ of the static alloy have been discussed in detail in Ref. 3. Here we only quote the results of Ref. 3 whenever they are needed for our computation. It is convenient to solve for $F^{(0)}$, which satisfies a cubic equation,

$$\frac{1}{16}F^{(0)3} - \frac{1}{2}zF^{(0)2} + \left[z^2 - \frac{1}{4}(\delta^2 - 1)\right]F^{(0)} - (z + \bar{\epsilon}) = 0 , \tag{3-115}$$

where $\bar{\epsilon}$ is the averaged energy $x\,\mathcal{E}_A + y\,\mathcal{E}_B$. When Eq. (3-115) is solved for a real energy z = E in the band, there are three roots. We only choose the correct root corresponding to E = E + io, i.e., the imaginary part of $F^{(0)}$ must be negative in order to give a positive density of states (see Eq. (3-66).

In the process of iteration in Eq. (3-113), we always encounter the following average:

$$\begin{aligned} &\left\langle\!\!\left\langle \frac{1}{z - (\mathcal{E}_n + \theta_n) - \frac{1}{4}F} \right\rangle\!\!\right\rangle \\ &= \int d\eta \left[\frac{x\, e^{-\eta^2/2\alpha_A}}{\sqrt{2\pi\alpha_A}\,(z - \epsilon_A - \eta - \frac{1}{4}F)} + \frac{y\, e^{-\eta^2/2\alpha_B}}{\sqrt{2\pi\alpha_B}\,(z - \mathcal{E}_B - \eta - \frac{1}{4}F)} \right] \\ &= \int dt\, \frac{e^{-t^2}}{\sqrt{\pi}} \left[\frac{x}{z - \mathcal{E}_A - \sqrt{2\alpha_A}\,t - \frac{1}{4}F} + \frac{y}{z - \mathcal{E}_B - \sqrt{2\alpha_B}\,t - \frac{1}{4}F} \right] . \end{aligned} \tag{3-116}$$

In other words, we have to carry out the integral

$$W(z_{A,B}) \equiv \int dt\, \frac{e^{-t^2}}{z_{A,B} - t} , \tag{3-117}$$

where

$$z_{A,B} = \frac{1}{\sqrt{2\alpha_{A,B}}}\left(z - \mathcal{E}_{A,B} - \frac{1}{4}F\right) . \tag{3-118}$$

Since, for a real energy z = E in the band, F will have a negative imainary part, we have

$$\mathrm{Im}\, z_{A,B} > 0 . \tag{3-119}$$

Except for a constant, the integral in Eq. (3-117), is a complex error function. A discussion of this function and the tabulated values for certain ranges of the argument are given in Ref. 66. In the actual calculation, we used the series expansion[67] for $|\mathrm{Re}\, z_{A,B}| \leq 2.8$ and $|\mathrm{Im}\, z_{A,B}| \leq 1.4$, while outside this range we used the ten point Gaussian Hermite quadrature formula.[80] The convergence for most cases is very fast.

Once the self-energies inside the bands are obtained, F follows immediately, yielding in its turn the density of states from Eq. (3-66). It is then easy to obtain the conductivity as a function of the Fermi energy, since we have expressed the conductivity in terms of the density of states and self-energy. (see Eq. (3-110)). But if we want the conductivity as a function of temperature, we have to calculate the Fermi level at each temperature. This can be done by solving for ϵ_F in

$$C = 2\int_{-\infty}^{\infty} d\epsilon\, f(\epsilon)\, \mathcal{N}(\epsilon) \simeq 2\int_{-\infty}^{\epsilon_F} \mathcal{N}(\epsilon)\, d\epsilon \tag{3-120}$$

where c is the average number of electrons per alloy atom and is given by

$$C = x\, C_A + y\, C_B \tag{3-121}$$

Here C_A and C_B are numbers of electrons per atom for pure A and B crystals.

5. Results of the Numerical Calculations and Discussion

Because we do not have a definite alloy in mind, all the parameters are free to vary for different alloys. We shall only pick some representative values for each parameter for numerical illustrations. However, an understanding of salient features of these examples should give some insight into the nature of the model.

In Fig. III(a) to III(c), the self-energy is plotted as a function of energy. Each figure represents an alloy with a definite concentration x and scattering strength δ but at two different temperatures. The solid line represents the static alloy while the dashed line stands for the alloy at $T \neq 0$. Fig. III(a) represents an alloy in the virtual crystal limit, in which $x = 0.1$, $\delta = 0.5$. We shall refer to a situation as having "virtual crystal" character when δ is small, and Σ relatively slowly varying, (so that perturbation theory is reasonable). The scattering nature of the static alloy is characterized by the a hump of Δ at the top of the band. When thermal disorder is introduced, Δ increases in the whole range of energy inside the band. But the increase of Δ in the lower energy part of the band is greater than that around the hump of the static Δ . The real part of the self-energy Λ , of the static alloy is almost a constant in the lower part of the band, but has interesting structure in the "impurity" part of the band. The thermal disorder affects the "host" part and "impurity" part equally, so that we have a shift of the spectrum from the center of each component bands to both wings. This is reflected in the change of Λ . As we go from the lower energy region up to higher energy, we have a negative change in Λ , then a positive change, then the change in Λ tends to become negative when we enter the impurity part, and finally positive at the very top of the band. In Fig. III(b), where $x = 0.5$, $\delta = 0.8$,the alloy

Figure III. The real part (Λ) and the absolute value of the imaginary part (Δ) of the self-energy for the static alloy (solid line) and the alloy at a finite temperature (dashed line) characterized by $\alpha_A = \alpha_B = \alpha = 0.015$. The three figures are for three alloys with (a) $x = 0.1$, $\delta = 0.5$; (b) $x = 0.5$, $\delta = 0.8$; and (c) $x = 0.1$, $\delta = 1.0$.

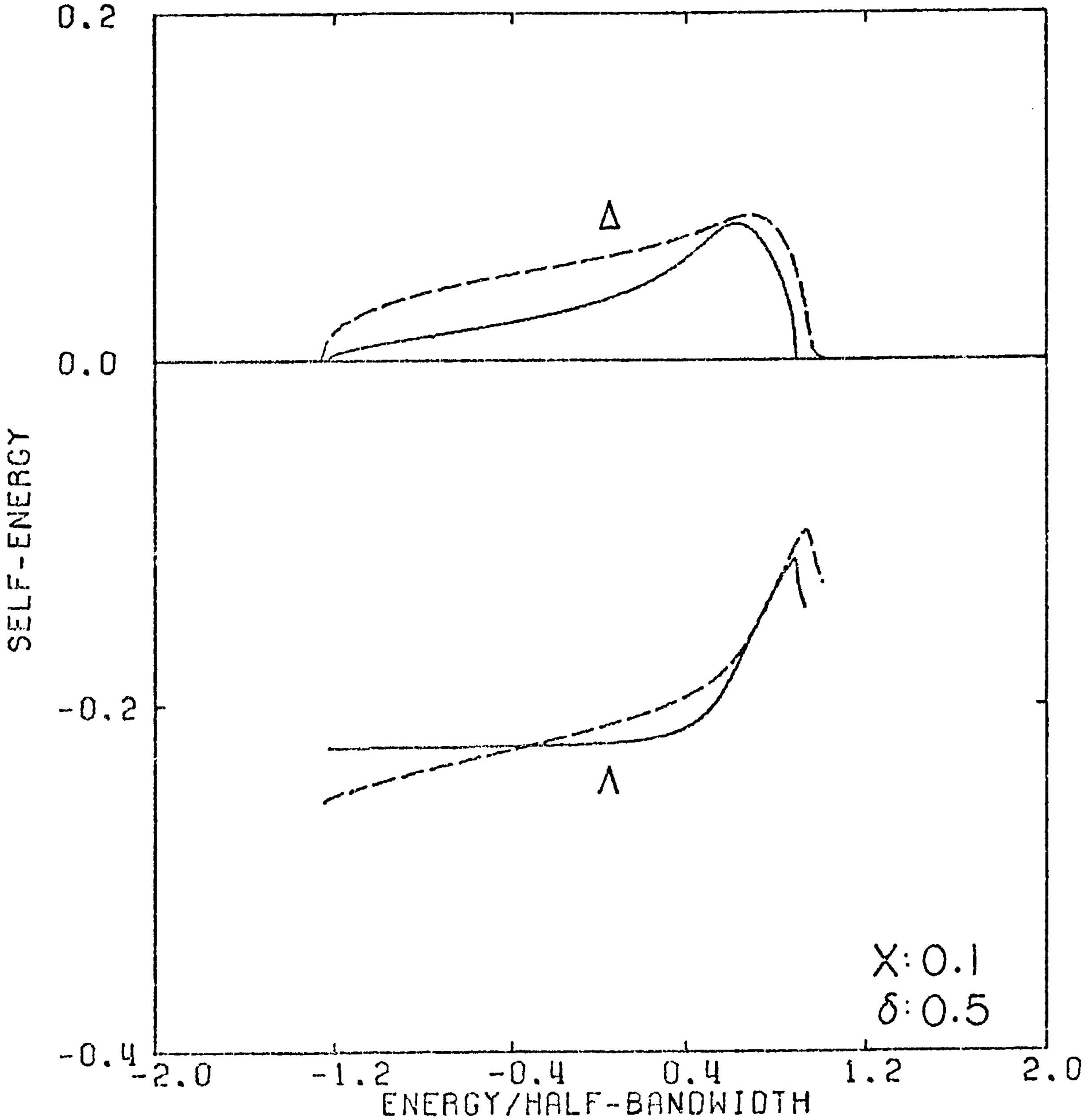

0.2
0.0
-0.2
-0.4
SELF-ENERGY
Δ
Λ
X: 0.1
δ: 0.5
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH

Figure III(a)

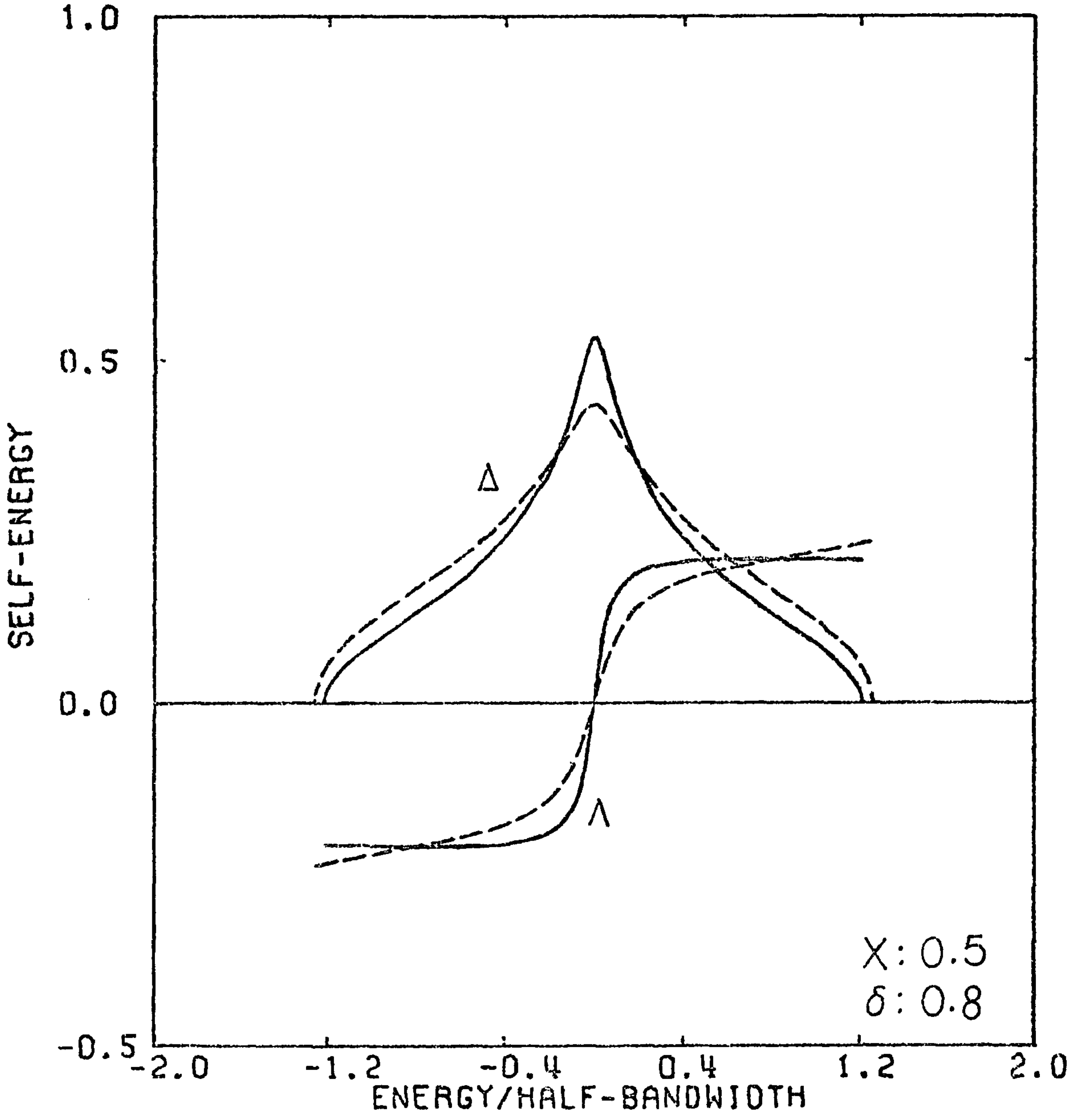

1.0
0.5
0.0
-0.5
SELF-ENERGY
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
Δ
Λ
X: 0.5
δ: 0.8

Figure III(b)

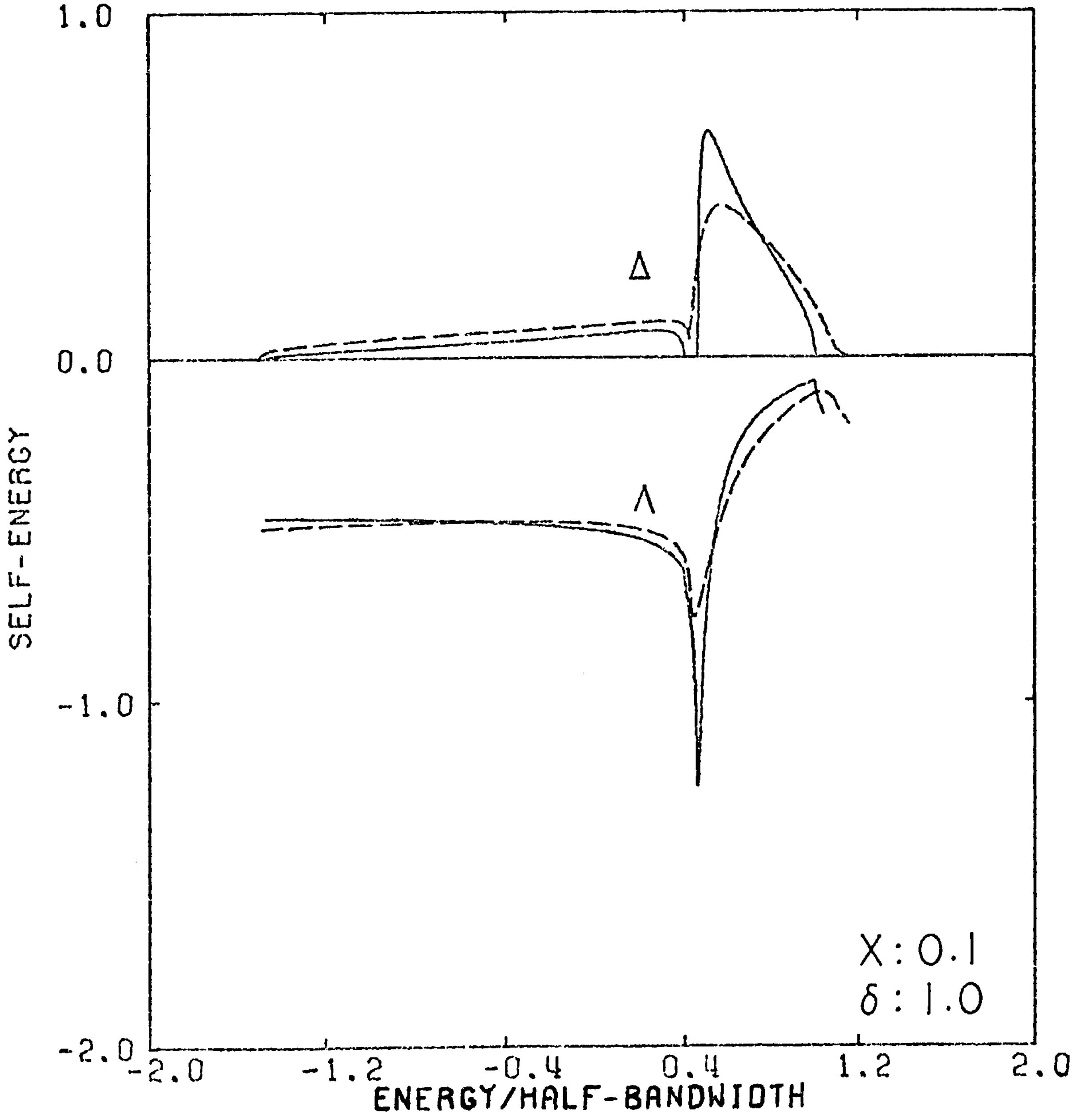

1.0
0.0
-1.0
-2.0
-2.0
-1.2
-0.4
0.4
1.2
2.0
SELF-ENERGY
ENERGY/HALF-BANDWIDTH
Δ
Λ
X : 0.1
δ : 1.0

Figure III(c)

is concentrated, and the scattering strength is moderately big. The static alloy Δ has a very sharp peak at the center of the band where the impurity scattering is most effective. The thermal disorder causes a positive change in both wings of the band and a negative change at the center. The decrease in Δ happens at the energies corresponding to the strongest damping in the static alloy. As will be clear from our later discussion of Σ , this implies that the highly scattered electrons in the warm alloy at these energies are in more nearly Bloch-like wavefunctions. The change in Λ has the same general character as in the first case discussed, and here again it shows the tendency towards a spreading of the spectrum. In Fig. III(c), $x = 0.1$, $\delta = 1.0$, the static alloy band is split. The static alloy is characterized by a virtual crystal Δ in the host subband, and a very high Δ in the impurity subband strongly peaked near the band gap. As expected from previous two cases, the thermal disorder increases Δ in the virtual crystal region, but decreases Δ at energies of very high damping. Since the static band is already split, the shift of the energy spectrum for each subband causes a stretching of the band.

The density of states as a function of temperature for the alloys of Fig. III are shown in Fig. IV. Several values of the temperature parameter α are represented in each plot. There is no visible structure in the density of states in Fig. IV(a), and increasing the temperature only stretches the band and smears its edges. Fig. IV(b) shows that the dip in the static density of states in gradually filled and disappears. The same long band tails appear for big values of α . In Fig. IV(c),

Figure IV. Density of states $\mathcal{N}(E)$ at five temperatures characterized by α = 0.0, 0.0075, 0.015, 0.05 and 0.1, and $\alpha_A = \alpha_B = \alpha$. The three figures are for three alloys with (a) χ = 0.1, δ = 0.5; (b) χ = 0.5, δ = 0.8 and (c) χ = 0.1, δ = 1.0.

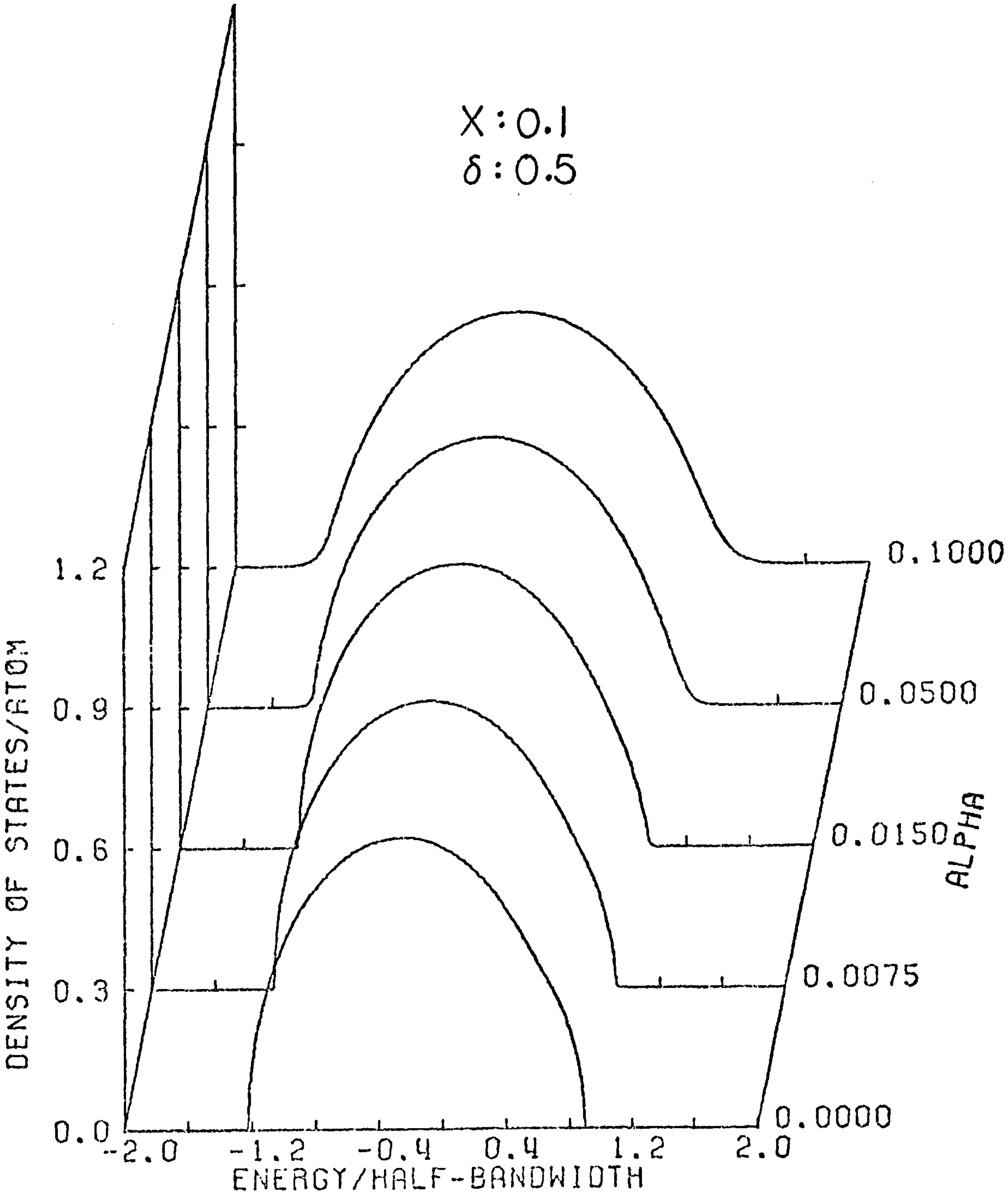

X:0.1
δ:0.5
DENSITY OF STATES/ATOM
1.2
0.9
0.6
0.3
0.0
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
0.1000
0.0500
0.0150
0.0075
0.0000
ALPHA

Figure IV(a)

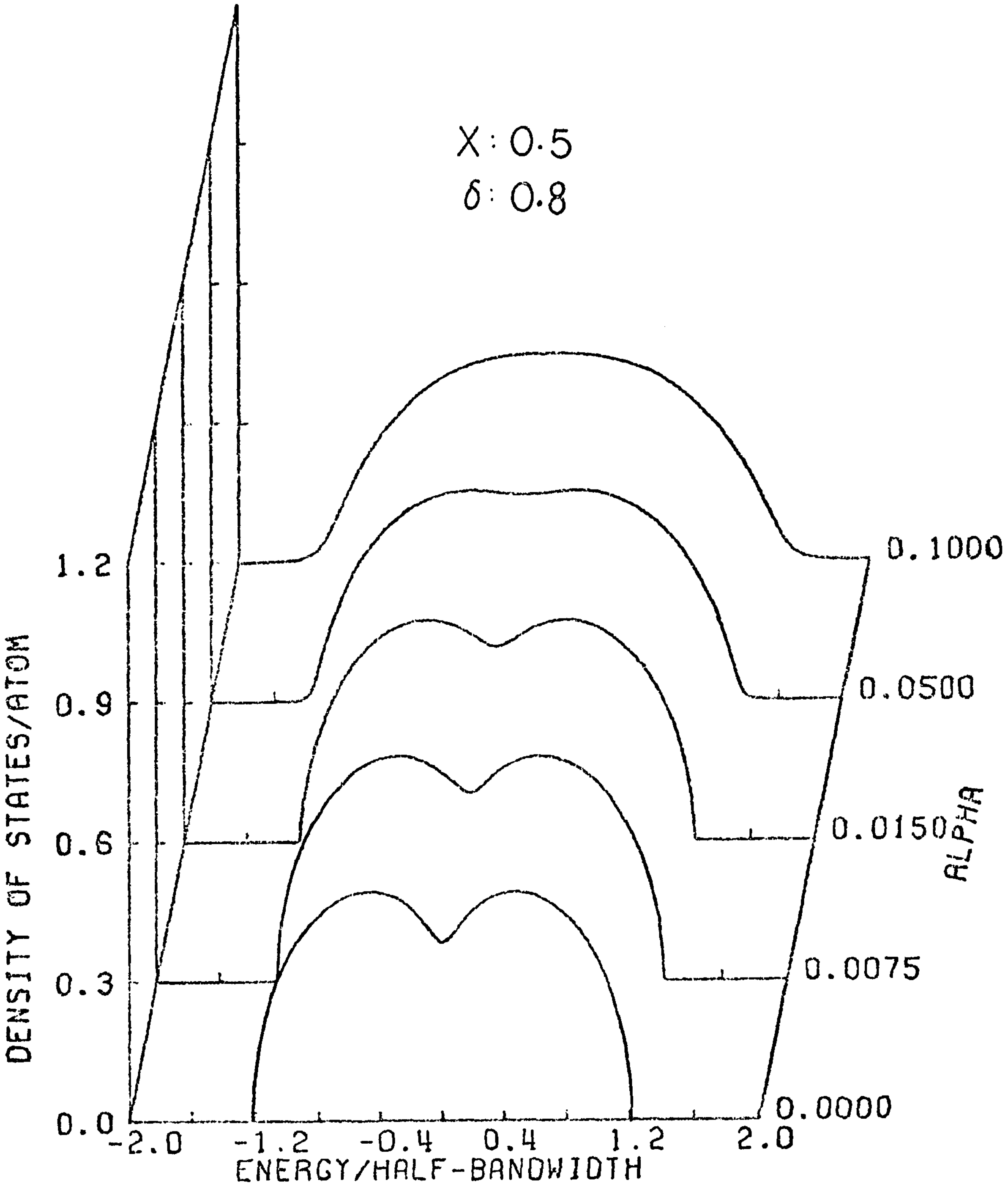

X : 0.5
δ : 0.8
DENSITY OF STATES/ATOM
0.0
0.3
0.6
0.9
1.2
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
ALPHA
0.0000
0.0075
0.0150
0.0500
0.1000

Figure IV(b)

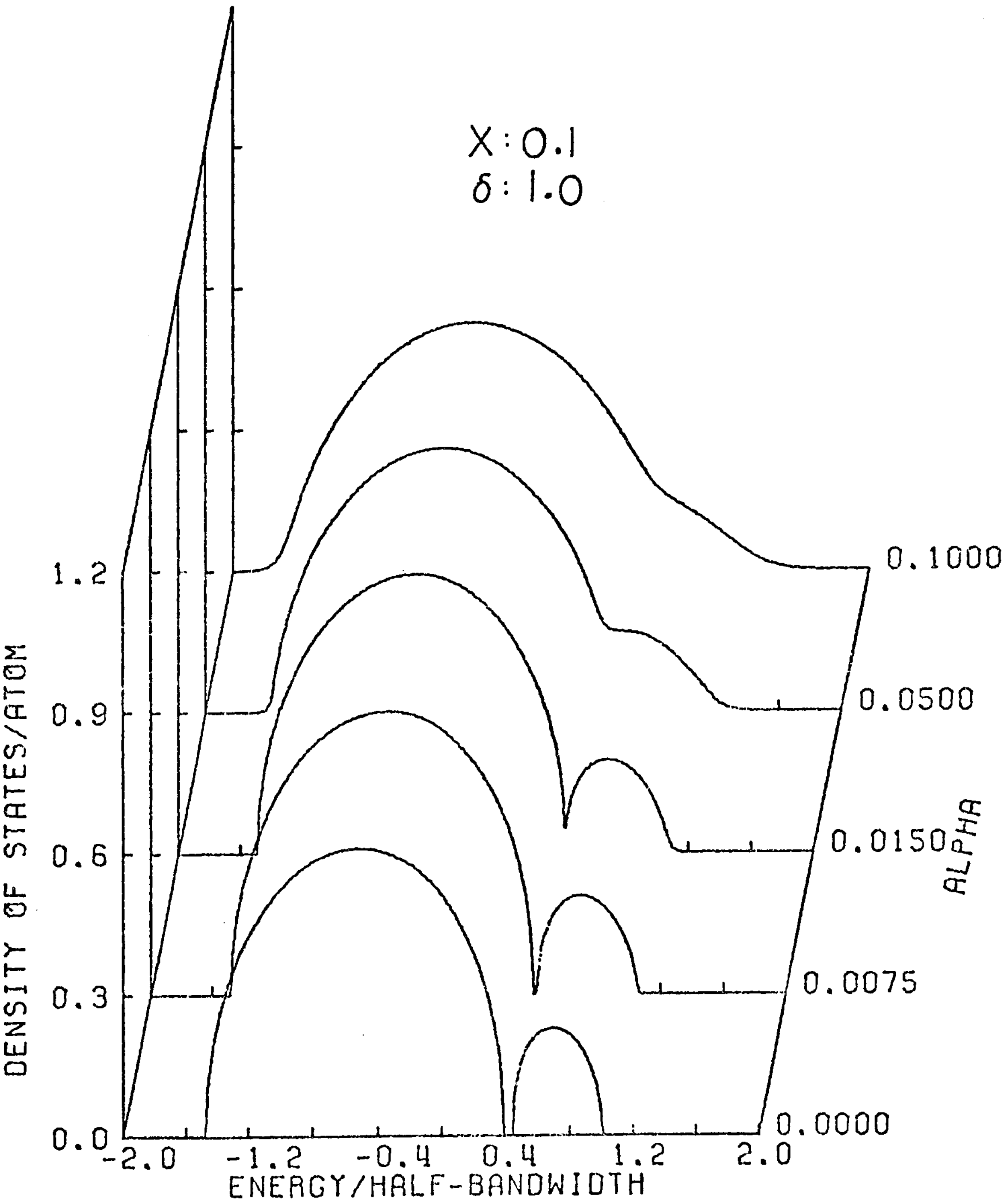

X : 0.1
δ : 1.0
DENSITY ØF STATES/ATØM
0.0
0.3
0.6
0.9
1.2
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
0.1000
0.0500
0.0150
0.0075
0.0000
ALPHA

Figure IV(c)

we start with a split static alloy band. But the band gap is very small, so the thermal fluctuation in the energy can easily close the band gap, and fill it up completely for big α values. The electron-phonon interaction, of course, can cause different fluctuations in the scattering strengths for A atoms and B atoms, so that $\alpha_A \neq \alpha_B$. Fig. V shows the plots corresponding to those in IV(b) and III(b). The only difference is that α_A is set to be four times as big as α_B, i.e. $\alpha_A / \alpha_B = 4$ and $\alpha_B = \alpha$. The effect on the self-energy is a bigger change in both Δ and Λ in the upper part of the band, with Σ in the lower part being almost like that in Fig. III(b). Similarly, the density of states is no longer symmetric, the upper energy part being stretched more than the lower energy part.

These results can be better visualized through the study of component densities of states. The self-consistent equation, Eq. (3-113), for Σ can be rewritten as a simpler expression for F by using the equality in Eq. (3-114),

$$F = \left\langle\!\left\langle \frac{1}{z - (\varepsilon_n + \theta_n) - \frac{1}{4}F} \right\rangle\!\right\rangle = \int d\eta \, P_A(\eta) \frac{x}{z - \varepsilon_A - \eta - \frac{1}{4}F} + \int d\eta \, P_B(\eta) \frac{y}{z - \varepsilon_B - \eta - \frac{1}{4}F} \, . \tag{3-122}$$

The quantities

$$F_{A,B}(\eta, z) \equiv \frac{1}{z - \varepsilon_{A,B} - \eta - \frac{1}{4}F} \tag{3-123}$$

have a special meaning. $F_A(\eta, z)$ means the diagonal matrix element of a restricted-averaged Green's function at the site zero. The restriction is that an A atom is definitely at site zero with a "phonon level shift η .

Figure V. (a) The self-energy for the alloy with $x = 0.5$, $\delta = 0.8$ and $\alpha_A = 4\,\alpha_B = 4\,\alpha$ at two temperatures characterized by $\alpha = 0.0$ (solid line) and $\alpha = 0.015$ (dashed line). (b) The density of states for the same alloy at four temperatures characterized by $\alpha = 0.0$, 0.0075, 0.015 and 0.05.

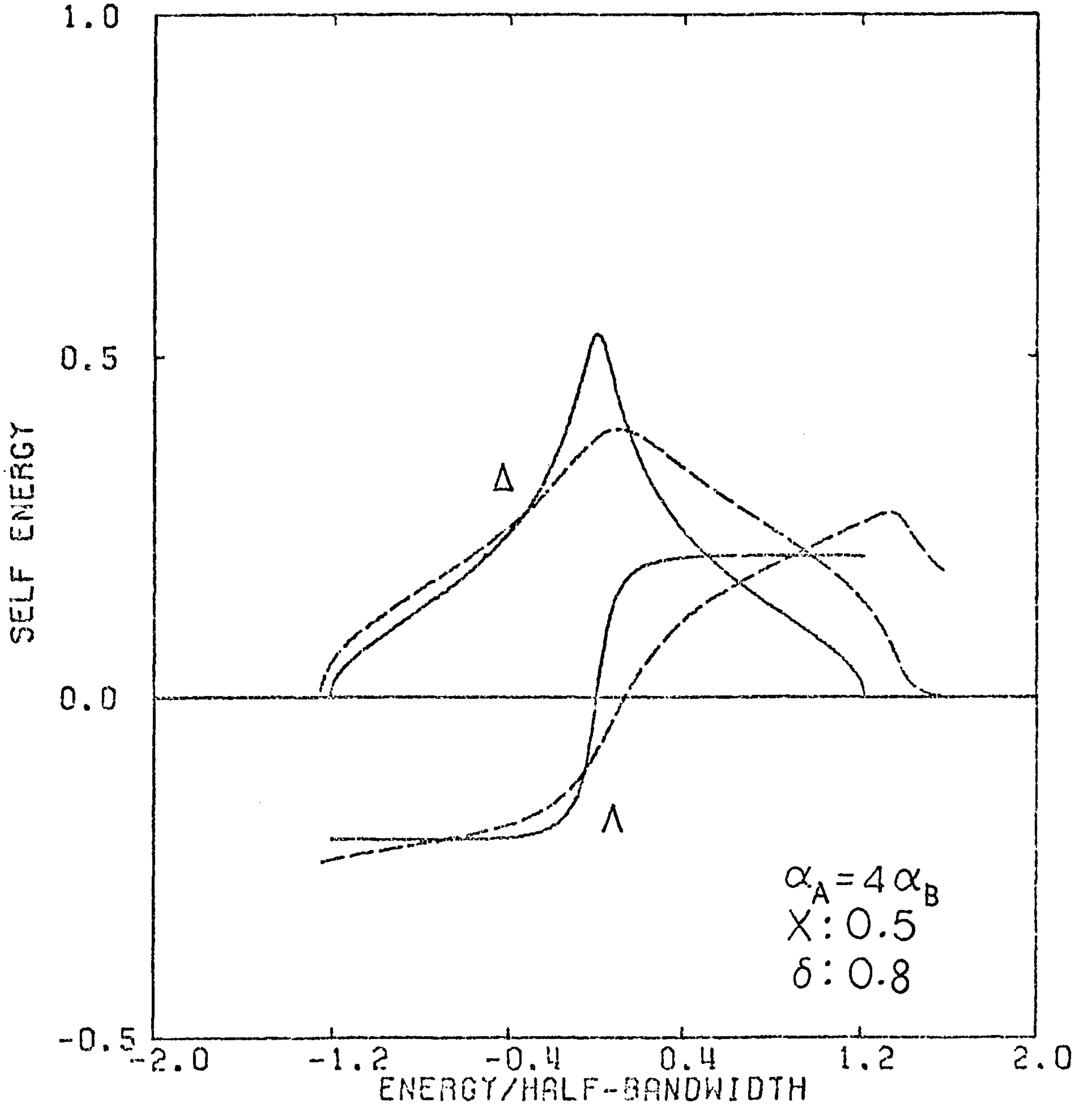

1.0
0.5
0.0
-0.5
SELF ENERGY
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
Δ
Λ
$\alpha_A = 4\alpha_B$
X: 0.5
δ: 0.8

Figure V(a)

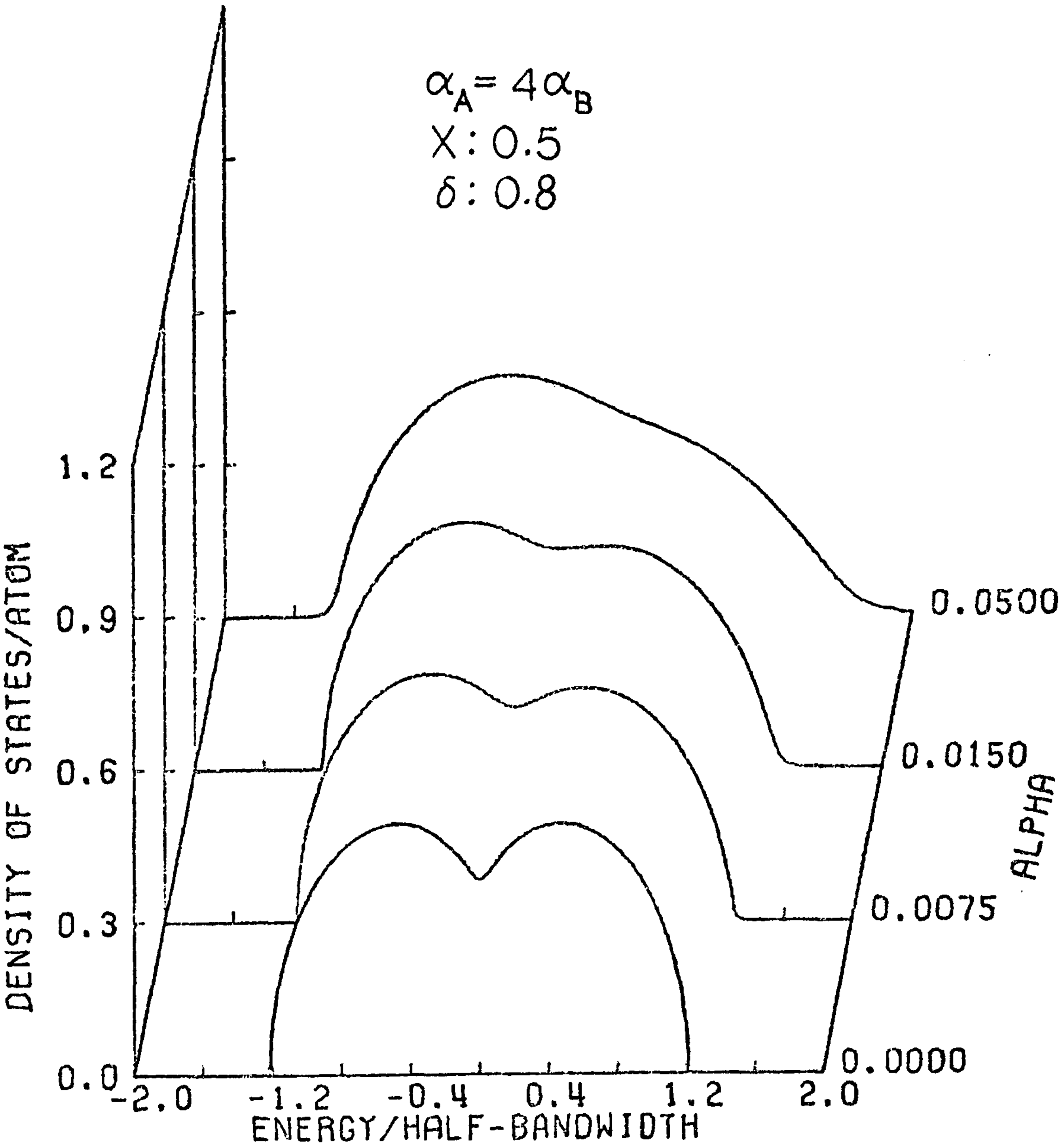

$\alpha_A = 4\alpha_B$
X : 0.5
δ : 0.8
DENSITY OF STATES/ATOM
0.0
0.3
0.6
0.9
1.2
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
0.0000
0.0075
0.0150
0.0500
ALPHA

Figure V(b)

In the CP$\tilde{n}$ language, this corresponds to a one atom cluster, i.e. CP$\tilde{_1}$(A, η). We are simply using the Green's function of a crystal characterized by the level $\varepsilon_A + \eta$ at site zero, and by Σ_{CPA} at all other sites, i.e.

$$\begin{aligned} F_A(\eta, z) &= \langle 0| \left[z - H_0 - \hat{\Sigma} - (|0\rangle \varepsilon_A + \eta \langle 0|) + (|0\rangle \Sigma \langle 0|) \right]^{-1} |0\rangle \\ &= \frac{F(z)}{1 - (\varepsilon_A + \eta - \Sigma) F} = \frac{1}{\frac{1}{F} - \varepsilon_A - \eta - \Sigma} \\ &= \frac{1}{z - \varepsilon_A - \eta - \frac{1}{4} F} \, . \end{aligned} \tag{3-124}$$

If we take the imaginary part of both sides of Eq. (3-124),and relate ImF to the density of states $\mathcal{N}$(E) through Eq. (3-66), we have

$$\mathcal{N}(E) = \int d\eta \, [\, x \, P_A(\eta) \, \nu_A(\eta, E) + y \, P_B(\eta) \, \nu_B(\eta, E) \,] \, , \tag{3-125}$$

where $\nu_{A,B}(\eta, E)$ are "local density of states" and are defined by

$$\nu_{A,B}(\eta, E) \equiv - \frac{1}{\pi} \, \mathrm{Im} \, F_{A,B}(\eta, E + i0) \, . \tag{3-126}$$

Or, after integration, Eq. (3-125) may be rewritten, in terms of what will be called "component densities of states", as

$$\mathcal{N}(E) = x \, \mathcal{N}_A(E) + y \, \mathcal{N}_B(E) \, . \tag{3-127}$$

Thus, the total density of states is the sum of the component densities of states $\mathcal{N}_A$(E) and $\mathcal{N}_B$(E) weighted by their concentrations. The component density of states $\mathcal{N}_{A,B}$(E) at finite temperature differs from the corresponding static component density of states $\mathcal{N}^{(0)}_{A,B}(E)$ by a smearing due to thermal fluctuations. The systematic changing of $\mathcal{N}_{A,B}(E)$ as a function of the temperature parameter α is shown in Fig. VI.

Note that in one special case, the algebra of our model forces a very simple kind of behavior. In a 50-50 alloy, with $\alpha_A = \alpha_B$, Λ should be antisymmetric and Δ symmetric in E. At the center of the band (E = 0), $\mathcal{N}$ and Δ will always go oppositely with a change of temperature, $\mathcal{N}$ increasing when Δ decreases, and vice-versa. This can be seen from the relation between $\mathcal{N}$ and Σ

$$\mathcal{N}(E) = \frac{1}{\pi}\int d\epsilon \frac{\mathcal{N}_0(\epsilon)\ \Delta(E)}{(E-\Lambda(E)-\epsilon)^2 + \Delta^2(E)} , \qquad (3\text{-}128)$$

which is a combination of Eqs. (3-60), (3-65) and (3-66).

Turning to the conductivity, once the density of states and the imaginary part of the self-energy are known, the conductivity as a function of the Fermi level is easily obtained from Eq. (3-110). Figs. VII(a)-(c) are the corresponding conductivity for alloys with the same parameters as shown in Figs. IV(a)-(c), while Fig. VII(d) is the one corresponding to Fig. V(b). In the virtual crystal (i.e. Figs. VII(a) and IV(a)), the change in density of states for small α is not visible, but the change in the conductivity is very big. Thus, in this case the electron-phonon interaction is the dominant mechanism for the resistivity at high temperatures. On the other hand, in the alloy with a high "impurity resistivity", (Fig. IV(b) and VII(b)), the relative change in the conductivity is not very large. In the split band limit, when the Fermi level is at the band edge or in the band gap, the degenerate Fermi

Figure VI. Component densities of states, $\mathcal{N}_A$ (solid line) and $\mathcal{N}_B$ (dashed line), as defined in Eqs. (3-125) and (3-127) at several temperatures characterized by different α values. The four figures are for alloys with (a) $x = 0.1$, $\delta = 0.5$, $\alpha_A = \alpha_B = \alpha$; (b) $x = 0.5$, $\delta = 0.8$, $\alpha_A = \alpha_B = \alpha$; (c) $x = 0.1$, $\delta = 1.0$, $\alpha_A = \alpha_B = \alpha$ and (d) $x = 0.5$, $\delta = 0.8$ but $\alpha_A = 4\alpha_B = 4\alpha$.

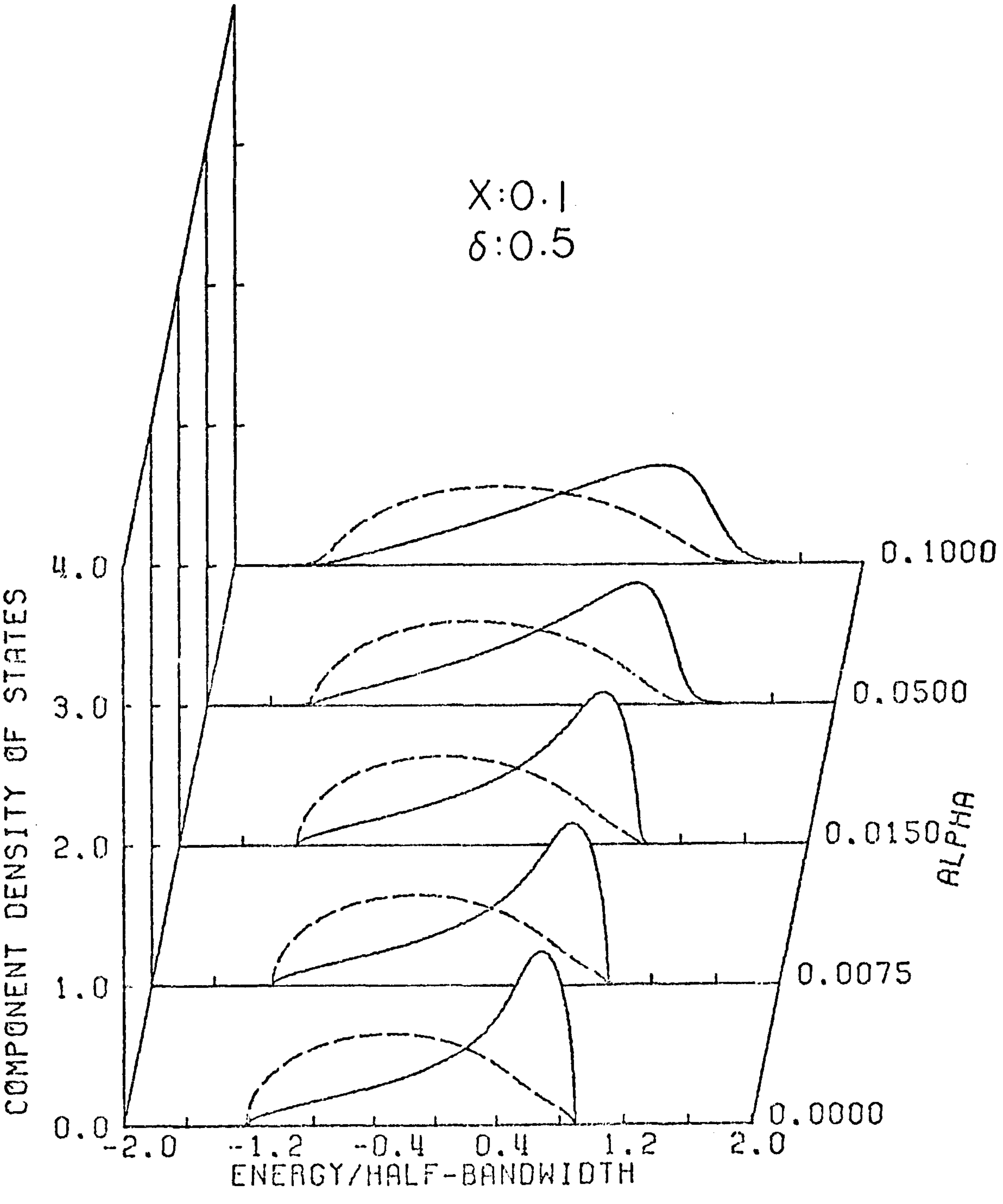

X:0.1
δ:0.5
COMPONENT DENSITY OF STATES
0.0
1.0
2.0
3.0
4.0
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
ALPHA
0.0000
0.0075
0.0150
0.0500
0.1000

Figure VI(a)

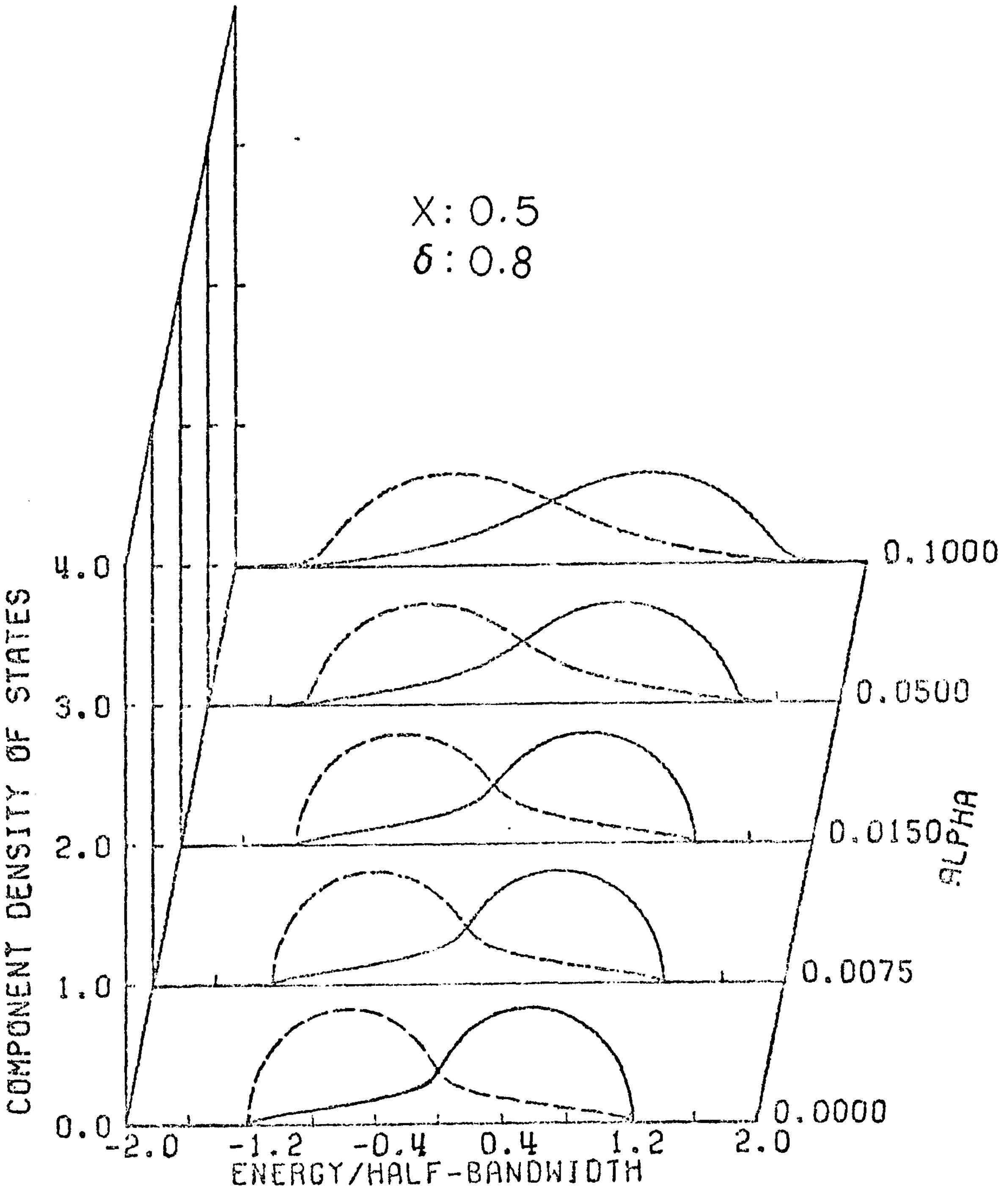
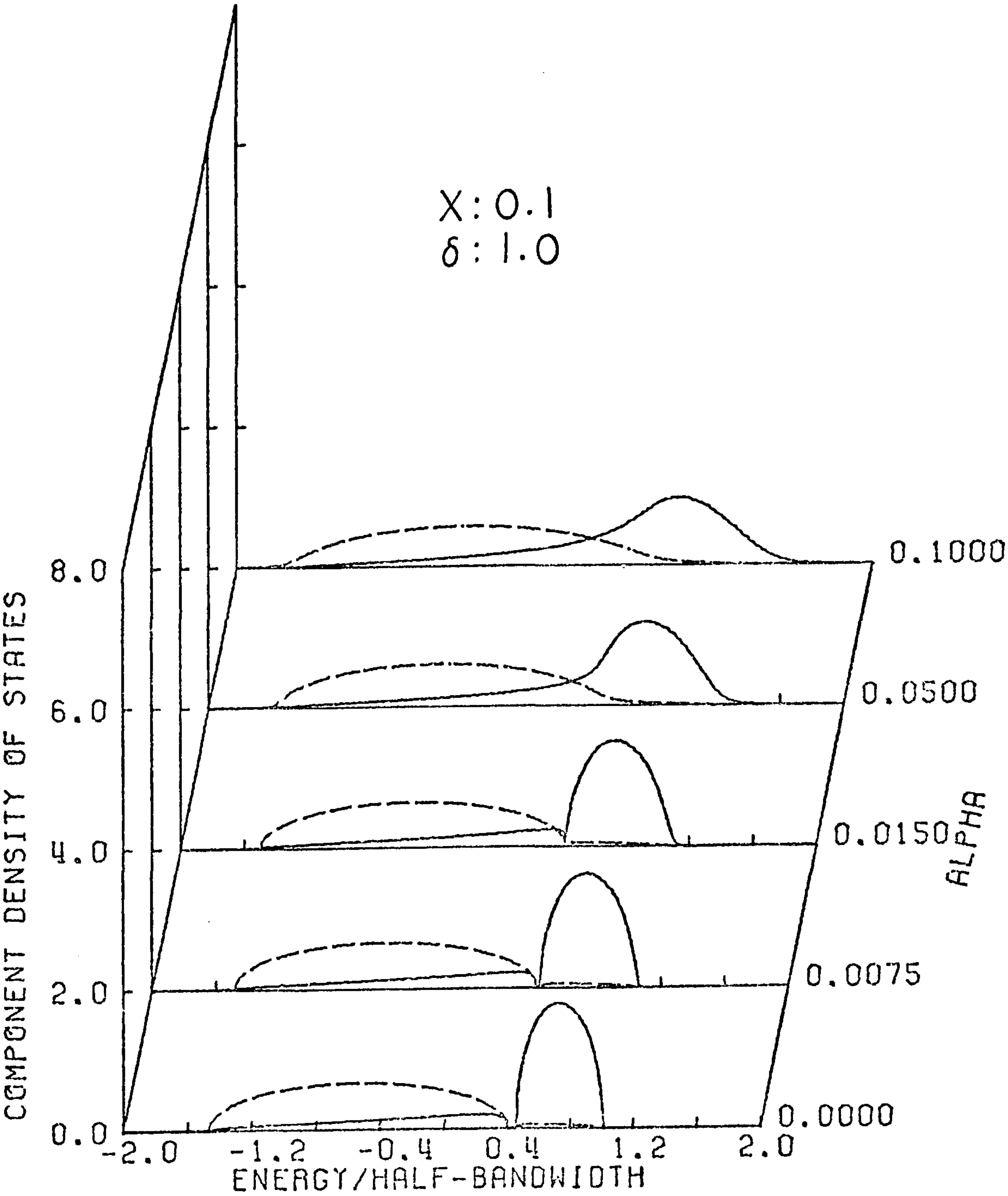

X: 0.5
δ: 0.8
COMPONENT DENSITY OF STATES
0.0
1.0
2.0
3.0
4.0
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
0.0000
0.0075
0.0150
0.0500
0.1000
ALPHA

Figure VI(b)


X: 0.1
δ: 1.0
COMPONENT DENSITY OF STATES
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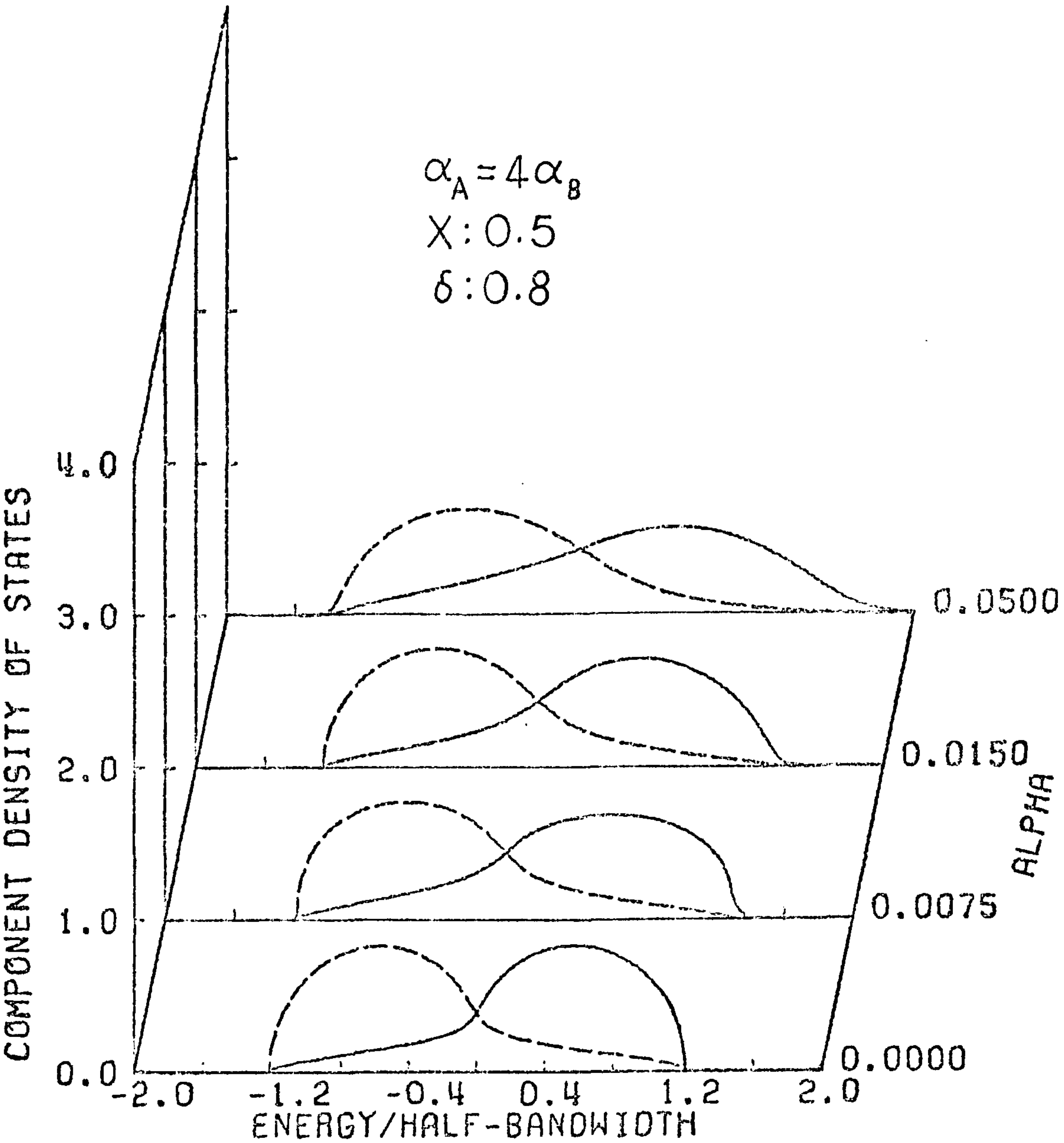
2.0
4.0
6.0
8.0
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
0.1000
0.0500
0.0150
0.0075
0.0000
ALPHA

Figure VI(c)


$\alpha_A = 4\alpha_B$
X : 0.5
δ : 0.8
COMPONENT DENSITY OF STATES
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1.0
2.0
3.0
4.0
-2.0
-1.2
-0.4
0.4
1.2
2.0
ENERGY/HALF-BANDWIDTH
ALPHA
0.0000
0.0075
0.0150
0.0500

Figure VI(d)

Figure VII. Electrical conductivity σ calculated from Eq. (3-110) as a function of the Fermi energy at different α values. The four figures are alloys with

(a) $x = 0.1$, $\delta = 0.5$, $\alpha_A = \alpha_B = \alpha$;

(b) $x = 0.5$, $\delta = 0.8$, $\alpha_A = \alpha_B = \alpha$;

(c) $x = 0.1$, $\delta = 1.0$, $\alpha_A = \alpha_B = \alpha$; and

(d) $x = 0.5$, $\delta = 0.8$, $\alpha_A = 4\alpha_B = 4\alpha$.

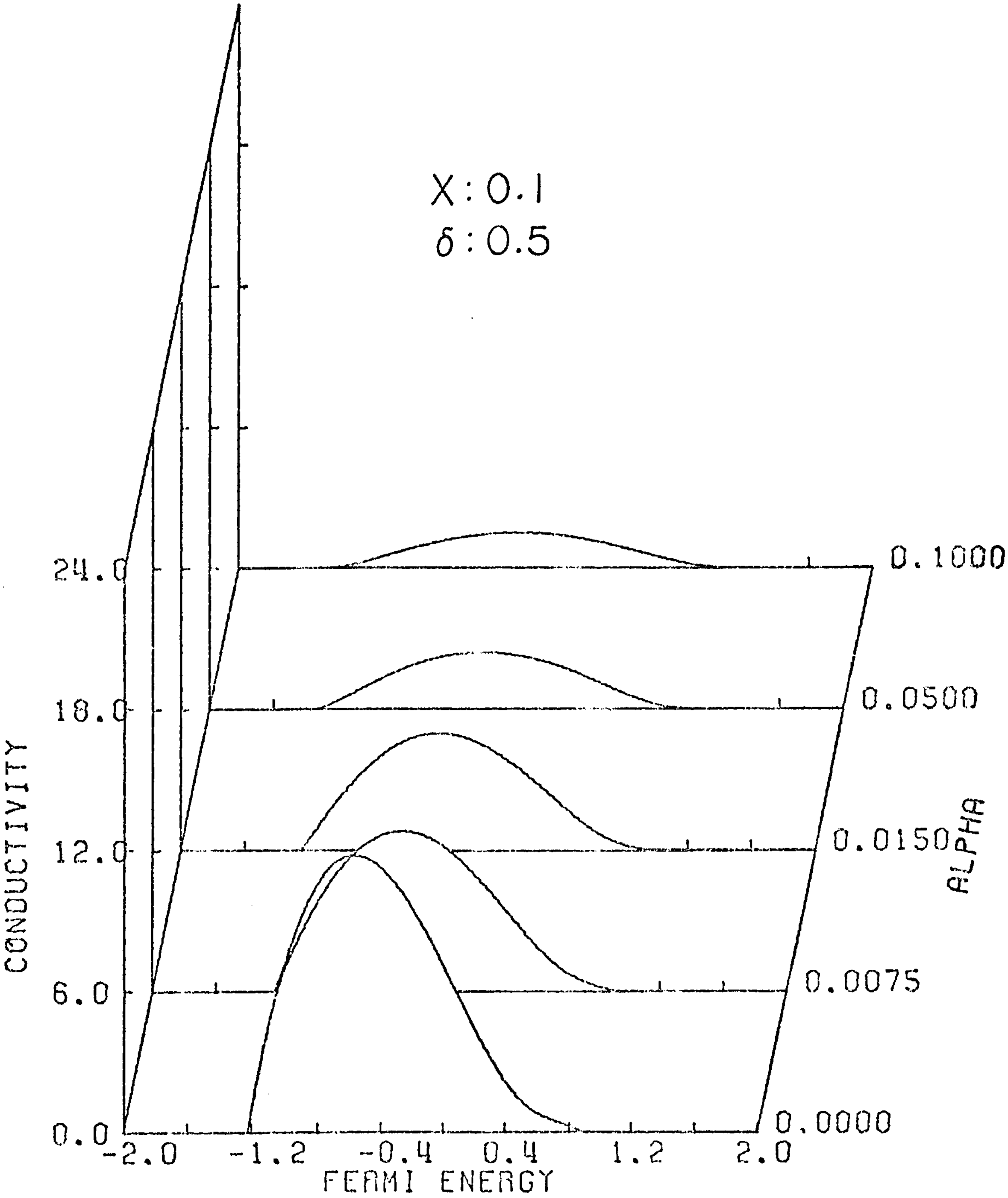
X : 0.1
δ : 0.5
CONDUCTIVITY
0.0
6.0
12.0
18.0
24.0
-2.0
-1.2
-0.4
0.4
1.2
2.0
FERMI ENERGY
ALPHA
0.0000
0.0075
0.0150
0.0500
0.1000

Figure VII(a)

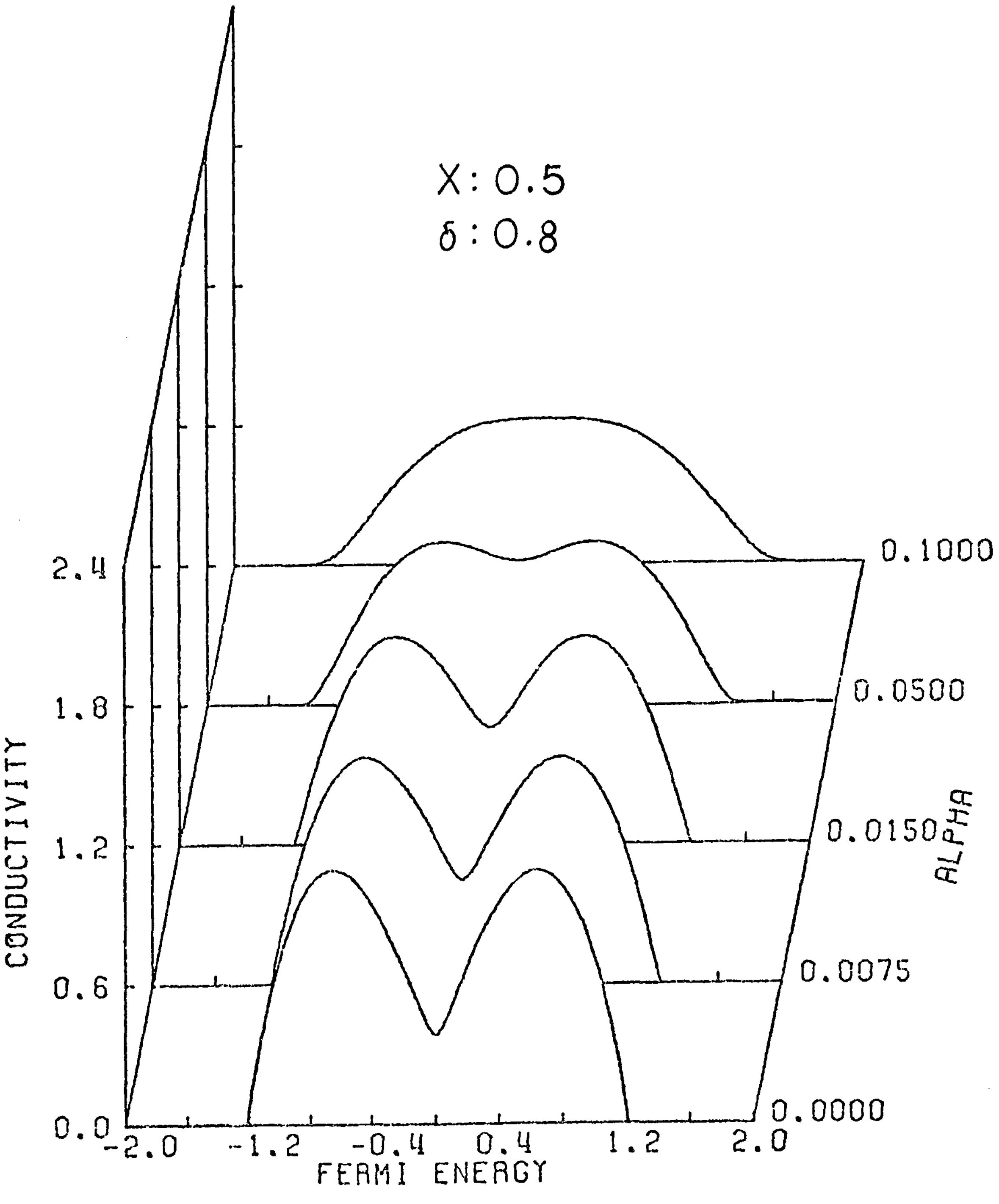
X: 0.5
δ: 0.8
CONDUCTIVITY
0.0
0.6
1.2
1.8
2.4
-2.0
-1.2
-0.4
0.4
1.2
2.0
FERMI ENERGY
ALPHA
0.0000
0.0075
0.0150
0.0500
0.1000

Figure VII(b)

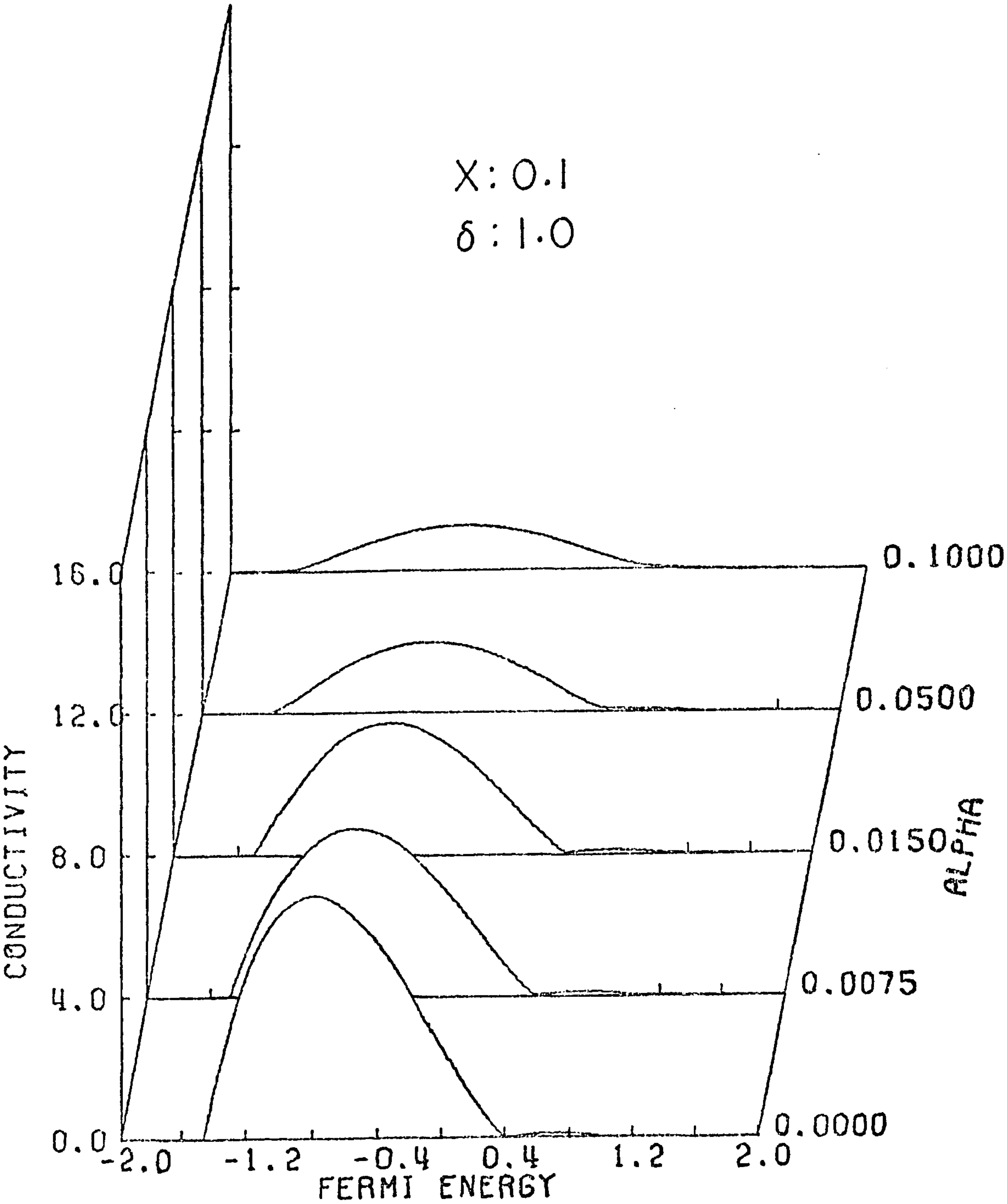
X: 0.1
δ: 1.0
CONDUCTIVITY
0.0
4.0
8.0
12.0
16.0
FERMI ENERGY
-2.0
-1.2
-0.4
0.4
1.2
2.0
ALPHA
0.0000
0.0075
0.0150
0.0500
0.1000

Figure VII(c)

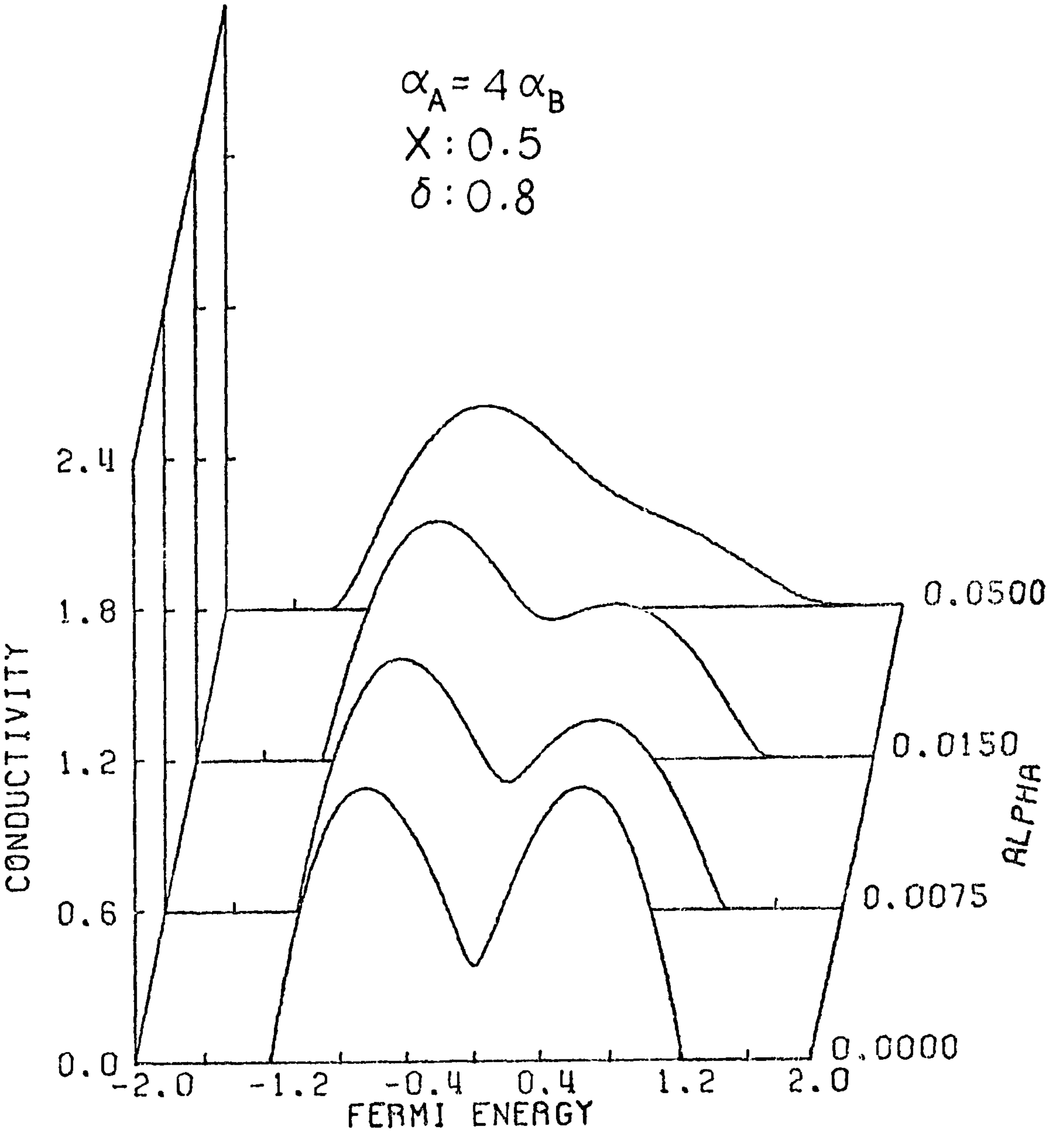
$\alpha_A = 4\alpha_B$
X : 0.5
δ : 0.8
CONDUCTIVITY
0.0
0.6
1.2
1.8
2.4
FERMI ENERGY
-2.0
-1.2
-0.4
0.4
1.2
2.0
ALPHA
0.0000
0.0075
0.0150
0.0500

Figure VII(d)

statistics leads to the zero conductivity that may be observed in the static alloy curve. When thermal disorder is introduced, the band gaps are filled so that the conductivity becomes non-zero. However, we cannot rely on CPA to describe the "impurity band" conductivity, since the cluster effect is very important in this case.[81]

In practice, the conductivity of an alloy is investigated as a function of temperature by fixing the average number of electrons per atom, C (see Eq. (3-120)), instead of fixing the Fermi level. Although it is difficult to experimentally adjust C, it is convenient and instructive to plot the conductivity as a function of C. In Fig. VIII we study this kind of plot for the case $x = 0.5$, $\delta = 0.8$. The solid line represents the static alloy, the other two dashed lines are the alloy with $\alpha = 0.0075$ and 0.015, respectively. It is interesting to see that the conductivity can either increase or decrease with temperature depending on the number of electrons per atom for the alloy. In other words, the temperature coefficients of conductivity are very sensitive to the location of the Fermi level. For the same band structure, the three different locations of Fermi energy, as shown by the arrows, give three qualitatively different results in $\frac{d\rho}{dT}$: At A it is positive; at B, zero; at C, negative. The corresponding resistivity vs temperature curves for these three cases are shown in Fig. IX. Finally, let us investigate the influence of different α_A and α_B on the temperature variation of the conductivity. The input parameters for Fig. X differ from those of Fig. VIII, only in that, in Fig. X, α_A is four times as big as α_B (in both figures, $\alpha_B = \alpha$). The conductivity is no longer symmetrical with respect to the center, the electron conductivity being bigger than the hole conductivity at finite temperatures.

Figure VIII. Electrical conductivity as a function of the numbers of electrons per atom per spin for the alloy with $x = 0.5$, $\delta = 0.8$, $\alpha_A = \alpha_B = \alpha$. The three curves represent the static alloy (solid) and the alloy with $\alpha = 0.0075$ (dashed line a) and $\alpha = 0.015$ (dashed line b). Arrows indicate three different temperature coefficients of electrical resistivity. At A, $\frac{d\rho}{dT}$ is positive; at B, zero; at C, negative.

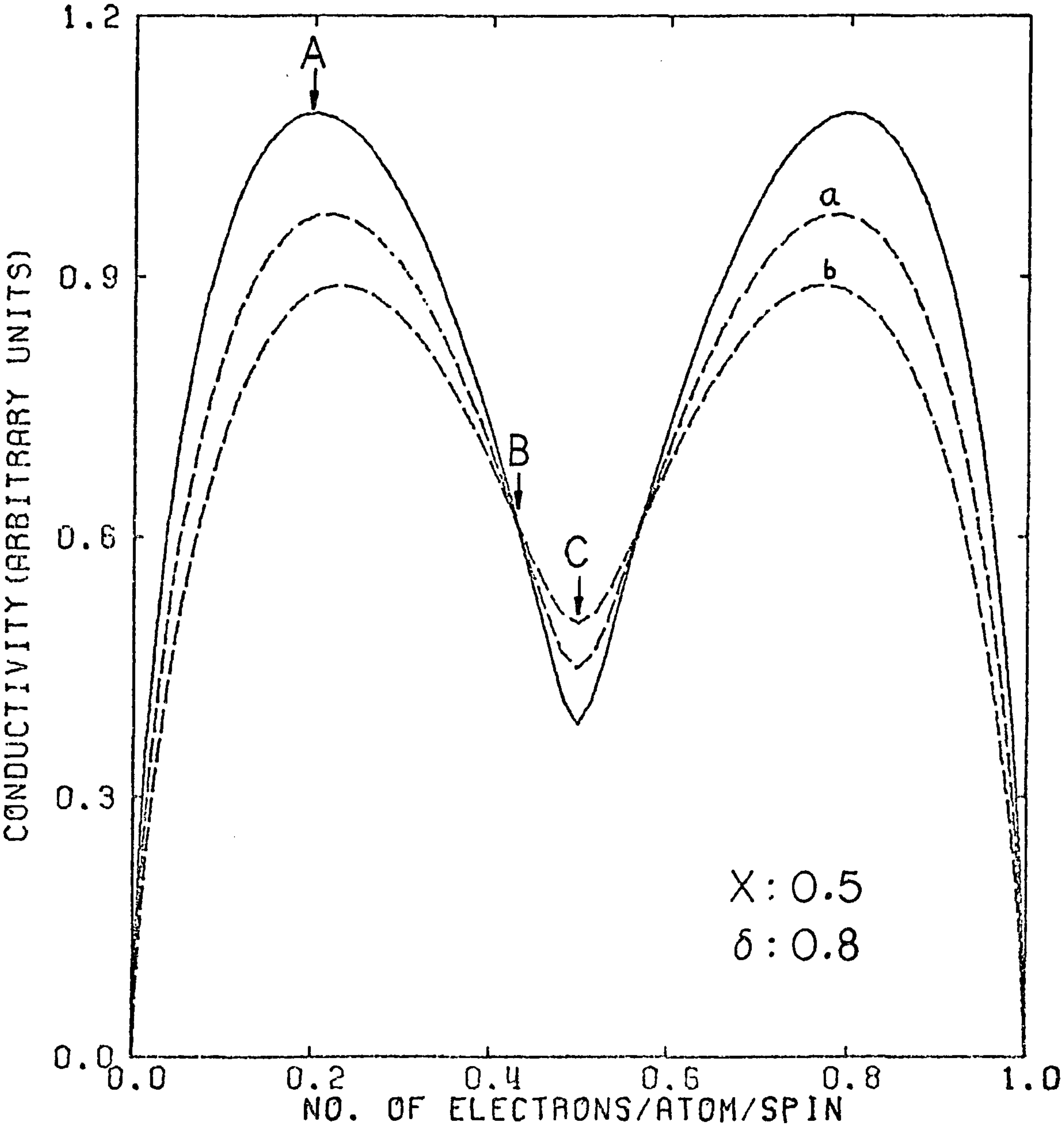
1.2
0.9
0.6
0.3
0.0
0.0
0.2
0.4
0.6
0.8
1.0
CONDUCTIVITY (ARBITRARY UNITS)
NO. OF ELECTRONS/ATOM/SPIN
A
B
C
a
b
X : 0.5
δ : 0.8

Figure VIII

Figure IX. The electrical resistivity as a function of temperature corresponding to the three cases indicated by the arrows in Fig. VIII. Here **o** is for case A, **x** for case B, and + for case C.

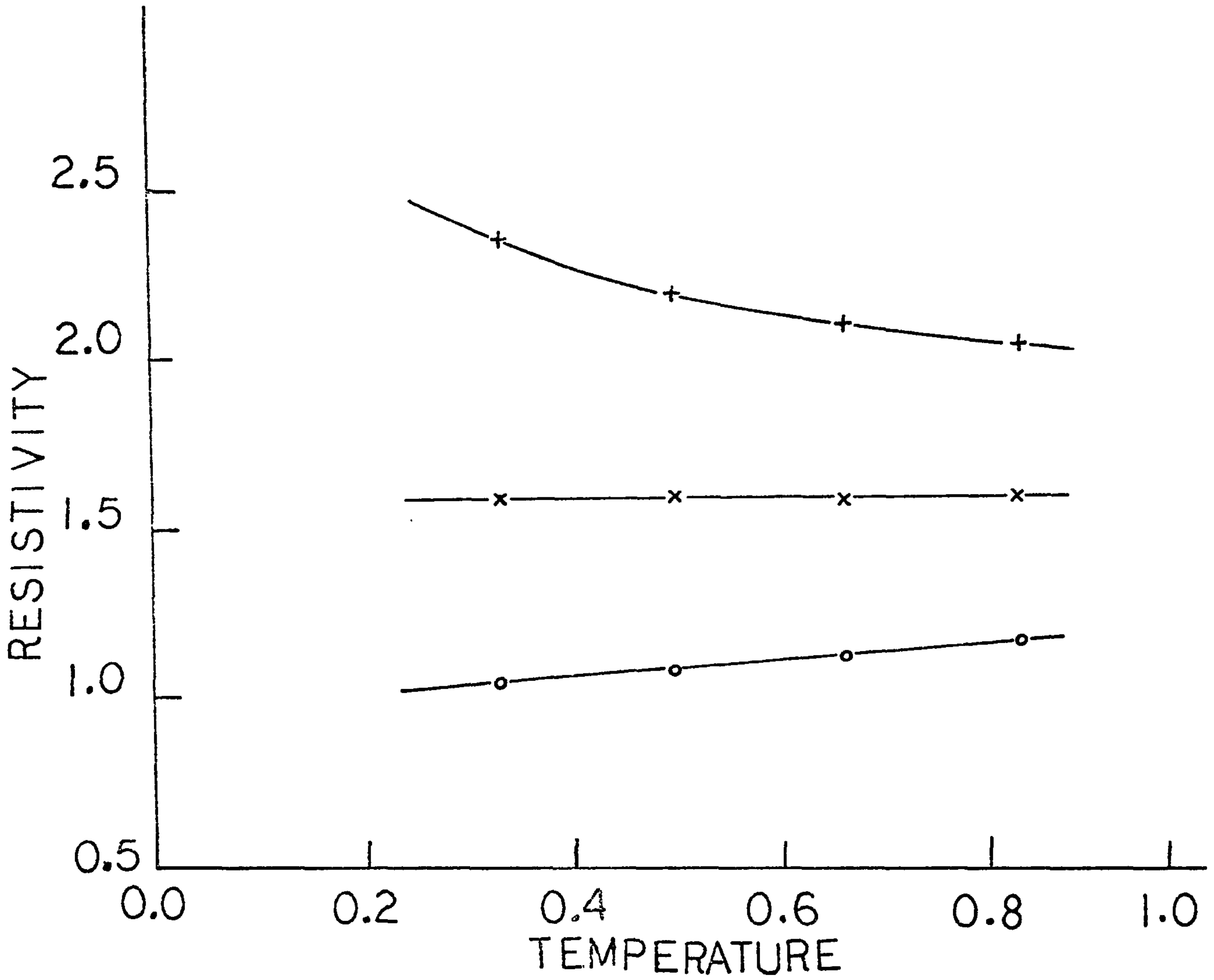

Figure IX

Figure X. Conductivity as a function of electrons per atom per spin for the alloy with $x = 0.5$, $\delta = 0.8$ and $\alpha_A = 4 \alpha_B = 4 \alpha$. The three lines are for three temperatures characterized by $\alpha = 0.0$ (solid line), $\alpha = 0.0075$ (dashed line a) and $\alpha = 0.015$ (dashed line b).

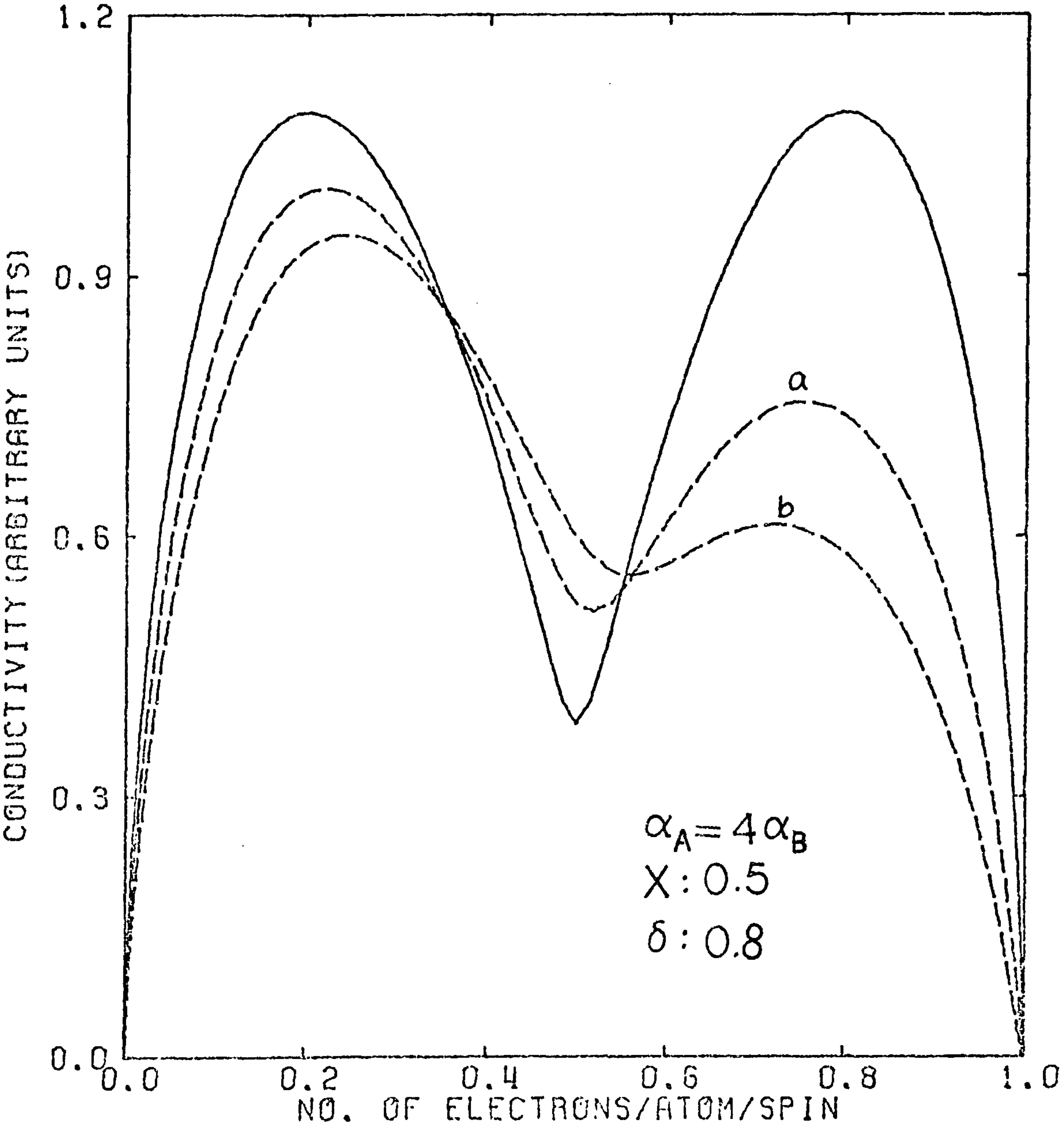
1.2
0.9
0.6
0.3
0.0
0.0
0.2
0.4
0.6
0.8
1.0
CONDUCTIVITY (ARBITRARY UNITS)
NO. OF ELECTRONS/ATOM/SPIN
a
b
$\alpha_A = 4\alpha_B$
X : 0.5
δ : 0.8

Figure X

E. Implications of the Model Calculation.

We have presented the main features of the model calculation. The most obvious conclusion that may be drawn from our data can be put in this way: The thermal disorder broadens and smears the electronic density of states in the alloy. It raises the electrical resistivity in the virtual crystal limit, but, in a strong scattering alloy, produces an increase or decrease in conductivity depending on the location of the Fermi energy. We can say more, outlined as follows. Since we have treated the density of states and conductivity adequately in a model which has many of the characteristics of an alloy, we should look for any physical ideas that might be suggested by our experience with the model. Along these lines, we will first ask what help perturbation theory can give us. Then, we compare the elementary expression for conductivity with the CPA formula, both generally and in a limiting case. In the process, we discover a need to re-examine the meaning of the self-energy. Finally, the complications inherent in real transition metal alloys are considered.

In a concentrated, strong scattering alloy, the electron-phonon interaction is small compared to the "impurity" scattering, but it is the essential mechanism governing the temperature dependence. (In our case it is the only mechanism.) It is believed that the lowest order contribution of the electron-phonon interaction to the resistivity, calculated by the usual perturbation theory, should give the correct answer. In our case this technique is prohibited by our poor knowledge of the nature of the static alloy. For example, let us expand the Green's function G (Eq. (3-18)) in terms of the static alloy Green's function G_S

$$G = G_s + G_s \Theta G_s + G_s \Theta G_s \Theta G_s + \cdots , \tag{3-129}$$

where G_S is defined as (see Eq. (3-52))

$$G_s \equiv \frac{1}{z - H_o - D} . \tag{3-130}$$

When we average on both sides on Eq. (3-129), we get

$$\langle\langle G \rangle\rangle = \langle G_s \rangle_c + \langle G_s \langle \Theta G_s \Theta \rangle_p G_s \rangle + \cdots \tag{3-131}$$

To use perturbation theory based on the static alloy, we need to know the three Green's function average $\langle G_s \langle \Theta G_s \Theta \rangle_p G_s \rangle_c$ very well, which is an unsolved problem to date. Therefore, we use the alternate method of the self-consistent CPA equations.

The Kubo Greenwood Formula for electrical conductivity in CPA and our model has been reduced to a very simple and explicit expression,

$$\alpha = \frac{\pi^2}{12} \frac{e^2 \hbar v_m^2}{\Omega_c} \frac{\mathcal{N}^3(\epsilon_F)}{\Delta(\epsilon_F)} \left(1 + \frac{6 \Delta(\epsilon_F)}{\pi \mathcal{N}(\epsilon_F)} \right) . \tag{3-132}$$

which is only a function of the density of states $\mathcal{N}$ and the absolute value of the imaginary part of the self-energy Δ at the Fermi energy The form of Eq. (3-132) makes for easy comparison with the elementary formula for resistivity,[68]

$$\rho = \frac{3}{e^2 v_F^2} \frac{1}{D(\epsilon_F)} \frac{1}{\tau} , \tag{3-133}$$

where $D(\epsilon_F)$ is the density of states per unit volume at the Fermi energy (including both spins), τ is the collision time, and v_F, the velocity of the electron at ϵ_F. We can identify

$$D(\epsilon_F) = \frac{2}{\Omega_c}\mathcal{N}(\epsilon_F), \tag{3-134}$$

and force

$$\begin{aligned} v_F^2\,\tau &= \frac{\pi^2}{4} v_m^2\,\mathcal{N}^2(\epsilon_F)\,\frac{\hbar}{2\Delta}\left(1+\frac{6\Delta}{\pi\mathcal{N}}\right) \\ &= \overline{v}^2(\epsilon_F)\,\frac{\hbar}{2\Delta}\left(1+\frac{6\Delta}{\pi\mathcal{N}}\right). \end{aligned} \tag{3-135}$$

In Eq. (3-135) we have defined a $\overline{v}^2(\epsilon_F)$ related to $\mathcal{N}(\epsilon_F)$ in the same way as $v^2(\epsilon)$ to $\mathcal{N}_0(\epsilon)$ in Eq. (3-105).

We could define a collision time τ either by $\frac{\hbar}{2\Delta}$ or $\frac{\hbar}{2\Delta}(1+\frac{6\Delta}{\pi\mathcal{N}})$, and let the remaining factor define v_F^2. But this is only meaningful if we understand the physical meaning of $\Delta(\epsilon_F)$, or the whole self-energy Σ.

The basic definition of the self-energy is Eq. (3-28), i.e.

$$\langle\langle G(z)\rangle\rangle = \frac{1}{z - H_0 - \hat{\Sigma}} . \tag{3-136}$$

We get a better feeling for Σ if we think of $\langle\langle G(z)\rangle\rangle$ as a propagator, and use the relation between the ensemble-averaged time evolution operator $\langle\langle U(t)\rangle\rangle$ and $\langle\langle G(z)\rangle\rangle$,

$$\langle\langle U(t)\rangle\rangle = \frac{-1}{2\pi i}\oint dz\, e^{-izt}\langle\langle G(z)\rangle\rangle . \tag{3-137}$$

The clockwise contour includes the real axis and surrounds the lower half z plane. Consider how an eigenstate of H_0, say a "mock Bloch state" $|\vec{k}\rangle$ in our case, evolves. Since $\hat{\Sigma}$ is diagonal in $|\vec{k}\rangle$, the probability amplitude for finding a state surviving after a time t is

$$a_{\vec{k}}(t) = \langle \vec{k} | \langle\langle U(t) \rangle\rangle | \vec{k} \rangle = \frac{-1}{2\pi i} \oint dz\, e^{-izt} \langle \vec{k} | \frac{1}{z - H_0 - \hat{\Sigma}} | \vec{k} \rangle$$

$$= \frac{-1}{2\pi i} \oint dz \, \frac{e^{-izt}}{z - \epsilon(\vec{k}) - \Sigma(z,\vec{k})}$$

$$= \frac{-1}{2\pi i} \oint dz\, e^{-izt} g(\vec{k},z) \; . \tag{3-138}$$

Or, after integration,

$$a_{\vec{k}}(t) = e^{-i z_1(\vec{k}) t} , \tag{3-139}$$

where $z_1(\vec{k})$ is the pole of $g(\vec{k},z)$ inside the contour. Thus, the real part of z_1 is the shifted spectrum corresponding to $\epsilon(\vec{k})$, and the imaginary part of z_1 measures the ensemble averaged decay of the "Bloch" states $|\vec{k}\rangle$. The decay time of the $|\vec{k}\rangle$ state is

$$\tau_{\vec{k}} = \frac{\hbar}{2(-\mathcal{I}m\, z_1(\vec{k}))} \; . \tag{3-140}$$

But the location of the pole at z_1 and the self-energy $\Sigma(z_1)$ are closely related by

$$\mathcal{R}e\, z_1(\vec{k}) = \epsilon(\vec{k}) + \mathcal{R}e\, \Sigma(z_1,\vec{k}) \; , \tag{3-141}$$

and

$$\mathcal{I}m\, z_1(\vec{k}) = \mathcal{I}m\, \Sigma(z_1,\vec{k}) \; . \tag{3-142}$$

Therefore, the self-energy at the poles of $g(\vec{k},z)$ has a very simple physical meaning: the real part of Σ is the shift of the energy level $\epsilon(\vec{k})$ in the alloy, the imaginary part is the uncertainty of this energy level in the ensemble.

However, the self-energies in the formulae for the density of states and conductivity (see Eqs. (3-20), (3-22), (3-23) and (3-24)) are at the energies $z = E \pm i0$. These are not necessarily the poles of $g(\vec{k},z)$. Thus, we have a physical interpretation for $\Sigma(z_1)$, but what we need is the meaning of $\Sigma(E \pm i0)$.

Suppose we construct states $|\psi_{\nu E}\rangle$ with a sharp energy E in a particular alloy and phonon configuration, and this state has the expression

$$|\psi_{E\nu}\rangle = \sum_{\vec{k}} A_\nu(E,\vec{k})\,|\vec{k}\rangle . \tag{3-143}$$

Then the average energy-momentum density of states, i.e. the spectral function, is

$$\left\langle\!\left\langle \sum_{\nu E'} |A_\nu(E',\vec{k})|^2 \delta(E-E') \right\rangle\!\right\rangle = \frac{1}{\pi}\,\frac{\Delta(E,\vec{k})}{[E-\epsilon(\vec{k})-\Lambda(E,\vec{k})]^2+\Delta^2(E,\vec{k})} , \tag{3-144}$$

as is well known from elementary Green's function theory. In our case, the self-energy is independent of $\vec{k}$, so we have

$$\left\langle\!\left\langle \sum_{\nu E'} |A_\nu(E',\vec{k})|^2 \delta(E-E') \right\rangle\!\right\rangle = \frac{1}{\pi}\,\frac{\Delta(E)}{[E-\epsilon(\vec{k})-\Lambda(E)]^2+\Delta^2(E)} . \tag{3-145}$$

Thus, if we take Eq. (3-145) as giving us the spectral density of a typical exact energy state of the alloy, then $\Delta(E)$ gives us a spectral width in terms of the pure perfect crystal spectrum $\epsilon(\vec{k})$. In other words, the alloy energy state is composed of "Bloch" states ranging over $\vec{k}$, with a spread $\Delta(E)$, in $\epsilon(\vec{k})$, so that the lifetime of coherence of the alloy wavefunction, when it is in a pure perfect crystal, is

$$\tau_c = \frac{\hbar}{2\Delta(E)} \quad . \tag{3-146}$$

Thus, our conductivity formula does not manifestly contain the usual collision time of a Bloch state. However, in the virtual crystal limit there is not much difference between these two relaxation times. The CPA result for the self-energy in this limit is (see Appendix C)

$$\Sigma(z) \simeq \bar{\epsilon} + (xy\delta^2 + x\alpha_A + y\alpha_B)\, F_0(z-\Sigma) . \tag{3-147}$$

In order to find the pole of $g(\vec{k},z)$, we need $z_1 - \Sigma = \vec{\epsilon}(\vec{k})$, so that Eq. (3-147) becomes

$$z_1 - \epsilon(\vec{k}) \simeq \bar{\epsilon} + (xy\delta^2 + x\alpha_A + y\alpha_B)\, F_0(\epsilon(\vec{k}) + i0) , \tag{3-148}$$

where we have set $\epsilon(\vec{k})$ to $\epsilon(\vec{k}) + i0$ in order to have a negative imaginary part for z_1. Using Eq. (3-140), we have

$$\frac{1}{\tau_{\vec{k}}} = \frac{2\pi}{\hbar}(xy\delta^2 + x\alpha_A + y\alpha_B)\, \mathcal{N}_0(\epsilon(\vec{k})) . \tag{3-149}$$

On the other hand, if we find the self-energy at $\bar{\epsilon} + \epsilon(k) \pm i0$, we have

$$\Sigma(\bar{\epsilon} + \epsilon(\vec{k}) \pm i0) \simeq \bar{\epsilon} + (xy\delta^2 + x\alpha_A + y\alpha_B)\, F_0(\epsilon(\vec{k}) \pm i0) , \tag{3-150}$$

so that

$$\Delta(\bar{\epsilon} + \epsilon(\vec{k})) = (xy\delta^2 + x\alpha_A + y\alpha_B)\, \pi\, \mathcal{N}_0(\epsilon(\vec{k})) , \tag{3-151}$$

The collision rate corresponding to the coherence time τ_c is

$$\frac{1}{\tau_c(\bar{\epsilon}+\epsilon(\vec{k}))} = \frac{2\,\Delta(\bar{\epsilon}+\epsilon(\vec{k}))}{\hbar} = \frac{2\pi}{\hbar}(xy\delta^2 + x\alpha_A + y\alpha_B)\mathcal{N}_0(\epsilon(\vec{k})), \qquad (3\text{-}152)$$

which is identical with $1/\tau_{\vec{k}}$ in Eq. (3-149). In this case, Eq. (3-135) takes on a more familiar form. When we drop terms of higher order than δ^2 and α, we can assign a collision time

$$\frac{1}{\tau} = \frac{1}{\tau_{\vec{k}}} = \frac{2\,\Delta(\epsilon_F)}{\hbar}\bigg|_{\epsilon_F = \epsilon(\vec{k})+\bar{\epsilon}} \qquad (3\text{-}153)$$

and the Fermi velocity

$$\begin{aligned} v_F^2 &= \frac{\pi^2 v_m^2}{4}\mathcal{N}^2(\epsilon_F) = \frac{\pi^2}{4}v_m^2\mathcal{N}^2(\bar{\epsilon}+\epsilon(\vec{k})) \\ &= \frac{\pi^2}{4}v_m^2\mathcal{N}_0^2(\epsilon(\vec{k})) = v^2(\epsilon(\vec{k}))\bigg|_{\epsilon(\vec{k}) = \epsilon_F - \bar{\epsilon}}. \end{aligned} \qquad (3\text{-}154)$$

These results, Eqs. (3-152)-(3-154), may be obtained also from perturbation theory. However, when perturbation theory is not valid, the contributing factors to the elementary conductivity formula, as well as the formula itself, tend to lose their simple meanings. If, for example, we identify the τ of the simple formula with our τ_c, then the corresponding Fermi velocity v_F is a function of the coherence time and density of states, as well as the pure crystal band structure.

It is interesting to apply the CPA result for the conductivity to a system composed of free electrons and randomly distributed strong scattering, short-ranged isotropic potentials. Since the potential is short-ranged and isotropic, the vertex correction can be neglected. Replacing Bloch waves by plane waves in Eq. (3-74), a little algebra suffices to rederive the elementary formula (see Appendix D)

$$\sigma = \frac{e^2}{3} v_F^2 D_F \tau , \tag{3-155}$$

where $D_F = 2 \mathcal{N}_F/\Omega_C$, τ is the coherence time, $\hbar/2\Delta_F$, and the Fermi velocity v_F^2 is related to the final density of states as the free electron velocity v_0^2 is related to the free electron density of states. That is, if

$$v_0^2(\vec{k}) = \frac{\hbar^2 k^2}{2m} \equiv A \mathcal{N}_0^2(\epsilon(\vec{k})) , \tag{3-156}$$

then

$$v_F^2 = A \mathcal{N}^2(\epsilon_F) \quad . \tag{3-157}$$

The formulae, Eqs. (3-155) and (3-157) provide useful information relating the density of states and the conductivity. Once the relaxation time is properly calculated, a measurement of the conductivity will give the density of states and vice-versa.

A word is in order here on the difficulties and complications that still separate a calculation like the present one from a realistic treatment of the transition metal alloys. In the first place, these metals have a complicated band structure.[69] At least six bands are involved, instead of one, none of the bands[70] having a true tight-binding character, and most of the bands (the d-bands) being extremely sensitive to small changes in the potential,[71] or crystal structure. This sensitivity implies that the self-consistent field (SCF) potential may be hard to take into account, the potential at one atomic cell being dependent on the configuration in its neighborhood, the electronic structure dependent on the potential, the electronic density on electronic structure, the potential on the electronic density, and so on, in a vicious circle. The change in band structure with temperature, due to expansion and other effects, may be difficult and important. In addition, not all configurations are equally likely, but rather there is some correlational clustering of atoms,[79] at best, and defects could be important in transition alloys made with a minimum of correlational clustering. Then, one may be extremely near a significant band-edge, as in constantan,[72] and generally transition metal conduction bands are jungles of singularities. Under such conditions, cluster effects are very important and CPA inadequate, as we have mentioned earlier. The electron-phonon interaction, also, is non-trivial in the transition metals, and all the more so in the alloys. Even the phonon spectrum itself changes significantly with alloying.[73] One of the most serious problems, along with the band structure complications mentioned above, is that all of the transition metals tend to have various magnetic properties. There are giant "polarization clouds" in at least some carefully made Cu-Ni alloys,[74,79] and a Kondo-like resistivity-minimum type effect[75] is probably extremely important, and should be explored in a semi-empirical way separately from all the other invluence that we have mentioned. One element of simplicity in the problem is that in Ni-Cu alloys, the "s-electrons" apparently carry most of the current. This idea, which has been present in the literature for many years on the basis of a vague hypothetical picture[41] of the transition-metal band structure, turns out to be accurate[76] for Cu-Ni (but probably not in some other transition alloys), as a result of an involved numerical balance among several competing effects. A hopeful sign is that some theoretical results based on fairly realistic atomic potentials should be available in the near future.[77] We have a long way to go, but some of the basic questions are now within reach.

Appendix A

The Derivation of Equations in Chapter Two

1. δ n in Eq. (2-41)

Putting δ f($\vec{k}$) from Eq. (2-38) into Eq. (2-40) and using the delta function approximation for $\frac{\partial f_e}{\partial \varepsilon^0_{\vec{k}}}$ (Eq. (2-28)), we first integrate the radial and the azimuthal part of d^3k and get

$$\delta n = -\frac{D}{2}\int_{-1}^{1} d(\cos\theta)\,\frac{\left[\overline{\delta\varepsilon}_F + \left(\frac{Q}{q}\right)^2\left(\frac{\delta n}{D} - \frac{\delta n_I}{D}\right)\right] iq\Lambda\cos\theta - \frac{\delta n}{D} - mv\delta u\cos\theta}{1 - i\omega\tau + iq\Lambda\cos\theta}, \qquad \text{(A-1)}$$

θ is the angle between $\hat{q}$ and $\hat{\Lambda}$, and D is the density of states per volume. It is understood that , Λ , and D are evaluated on the Fermi surface. We also have made the following approximation

$$\int d^3k\,\frac{\delta\varepsilon_{\vec{k}}\, i\vec{q}\cdot\vec{\Lambda}}{1 - i\omega\tau + i\vec{q}\cdot\vec{\Lambda}} \simeq \overline{\delta\varepsilon}_F \int d^3k\,\frac{i\vec{q}\cdot\vec{\Lambda}}{1 - i\omega\tau + i\vec{q}\cdot\vec{\Lambda}} . \qquad \text{(A-2)}$$

If we define the integral

$$I_1 \equiv \int_{-1}^{1} d\eta\,\frac{1}{1 - i\omega\tau + iq\Lambda\eta} = \frac{1}{iq\Lambda}\ln\left(\frac{1 - i\omega\tau + iq\Lambda}{1 - i\omega\tau - iq\Lambda}\right), \qquad \text{(A-3)}$$

then

$$\int_{-1}^{1} d\eta\,\frac{iq\Lambda\eta}{1 - i\omega\tau + iq\Lambda\eta} = 2 - (1 - i\omega\tau)\, I_1 \quad , \qquad \text{(A-4)}$$

and δn from Eq. (A-1) becomes

$$\delta n = -\frac{D}{2}\left\{\left[\overline{\delta\varepsilon_F} + \left(\frac{\mathfrak{q}}{q}\right)^2\left(\frac{\delta n}{D} - \frac{\delta n_I}{D}\right) - \frac{mv\delta u}{iq\Lambda}\right]\left[2-(1-i\omega\tau)I_1\right] - \frac{\delta n}{D} I_1\right\}. \qquad \text{(A-5)}$$

To solve for δn from Eq. (A-5), first we write

$$\delta n(2-I_1) = -D\left[\overline{\delta\varepsilon_F} + \left(\frac{\mathfrak{q}}{q}\right)^2\left(\frac{\delta n}{D} - \frac{\delta n_I}{D}\right) - \frac{mv\delta u}{iq\Lambda}\right]\left[2-(1-i\omega\tau)I_1\right], \qquad \text{(A-6)}$$

or

$$\frac{\delta n(2-I_1)\left(\frac{q}{\mathfrak{q}}\right)^2}{2-(1-i\omega\tau)I_1} = -D\,\overline{\delta\varepsilon_F}\left(\frac{q}{\mathfrak{q}}\right)^2 - iD\frac{mv\delta u}{q\Lambda}\left(\frac{q}{\mathfrak{q}}\right)^2 - (\delta n - \delta n_I), \qquad \text{(A-7)}$$

then group the δn terms on the left

$$\delta n\left[1 + \frac{2-I_1}{2-(1-i\omega\tau)I_1}\left(\frac{q}{\mathfrak{q}}\right)^2\right] = \delta n_I - D\,\overline{\delta\varepsilon_F}\left(\frac{q}{\mathfrak{q}}\right)^2 - i\frac{mv\delta u}{q\Lambda}\left(\frac{q}{\mathfrak{q}}\right)^2. \qquad \text{(A-8)}$$

The second term in the brackets can be expressed as

$$\frac{2-I_1}{2-(1-i\omega\tau)I_1} = 1 + \frac{i\omega\tau}{1-i\omega\tau-\frac{2}{I_1}} \quad . \qquad \text{(A-9)}$$

By the definition of I_1, we can identify the second term in (A-9) to be the I(τ) defined in Eq. (2-42). So finally Eq. (A-8) becomes

$$\delta n = \frac{\delta n_I - D\,\overline{\delta\varepsilon_F}\left(\frac{q}{\mathfrak{q}}\right)^2 - iD\frac{mv\delta u}{q\Lambda}\left(\frac{q}{\mathfrak{q}}\right)^2}{1 + \left[1 + I(\tau)\right]\left(\frac{q}{\mathfrak{q}}\right)^2} \quad . \qquad \text{(A-10)}$$

2. $\delta D_{\vec{q}}$ in Eq. (2-47)

From Eqs. (2-43) and (2-46), we can identify

$$\delta D_{\vec{q}} = e\,\delta\phi + \delta\varepsilon_{\vec{k}} \,. \tag{A-11}$$

But $\delta\phi$ is related to δ n by Eq. (2-45). Putting δ n from Eq. (A-10) into Eq. (A-11),we get

$$\begin{aligned}\delta D_{\vec{q}} &= \frac{4\pi e^2}{q^2}\left[\frac{\delta n_I - D\,\overline{\delta\varepsilon}_F\left(\frac{q}{\mathfrak{q}}\right)^2 - iD\,\frac{mv\delta u}{q\Lambda}\left(\frac{q}{\mathfrak{q}}\right)^2}{1+[1+I(\tau)]\left(\frac{q}{\mathfrak{q}}\right)^2} - \delta n_I\right] + \delta\varepsilon_{\vec{k}} \\ &= \frac{4\pi e^2}{q^2}\left[\frac{-\delta n_I(1+I(\tau))\left(\frac{q}{\mathfrak{q}}\right)^2 - D\,\overline{\delta\varepsilon}_F\left(\frac{q}{\mathfrak{q}}\right)^2 - iD\,\frac{mv\delta u}{q\Lambda}\left(\frac{q}{\mathfrak{q}}\right)^2}{1+[1+I(\tau)]\left(\frac{q}{\mathfrak{q}}\right)^2}\right] + \delta\varepsilon_{\vec{k}} \,.\end{aligned} \tag{A-12}$$

But $\mathfrak{q}^2 = 4\pi e^2 D$, so that we find

$$\begin{aligned}\delta D_{\vec{q}} &= \frac{\left(\frac{\mathfrak{q}}{q}\right)^2\left[-\frac{\delta n_I}{D}(1+I(\tau))\left(\frac{q}{\mathfrak{q}}\right)^2 - \overline{\delta\varepsilon}_F\left(\frac{q}{\mathfrak{q}}\right)^2 - i\,\frac{mv\delta u}{q\Lambda}\left(\frac{q}{\mathfrak{q}}\right)^2\right]}{1+[1+I(\tau)]\left(\frac{q}{\mathfrak{q}}\right)^2} + \delta\varepsilon_{\vec{k}} \\ &= \frac{-\frac{\delta n_I}{D}(1+I(\tau)) - \overline{\delta\varepsilon}_F + \delta\varepsilon_{\vec{k}} - i\,\frac{mv\delta u}{q\Lambda} + \delta\varepsilon_{\vec{k}}(1+I(\tau))\left(\frac{q}{\mathfrak{q}}\right)^2}{1+[1+I(\tau)]\left(\frac{q}{\mathfrak{q}}\right)^2} \\ &= \frac{\left[-\frac{\delta n_I}{D} + \delta\varepsilon_{\vec{k}}\left(\frac{q}{\mathfrak{q}}\right)^2\right][1+I(\tau)] + \delta\varepsilon_{\vec{k}} - \overline{\delta\varepsilon}_F - i\,\frac{mv\delta u}{q\Lambda}}{1+[1+I(\tau)]\left(\frac{q}{\mathfrak{q}}\right)^2} \,.\end{aligned} \tag{A-13}$$

3. $\delta \vec{j}_e$ in Eqs. (2-71) and (2-72)

Since we have specified $\hat{q} = \hat{z}$ and $\hat{u} = \hat{x}$, it is easy to show that the dilatation of the lattice is zero, so $\delta n_I = 0$. Then the Poisson's equation implies

$$\delta E_z = -i \frac{4\pi e}{q} \delta n \,. \tag{A-14}$$

A direct integration of Eq. (2-40) using $\delta f(\vec{k})$ defined in Eq. (2-69) gives

$$\delta n = \frac{1}{2} \delta n I_1 + \frac{1}{2} \frac{D e \Lambda \delta E_z}{i q \Lambda} \left[2 - (1 - i\omega\tau) I_1 \right] . \tag{A-15}$$

But δE_z is directly proportional to δn as seen in Eq. (A-14). A solution of Eq. (A-15) gives

$$\delta n = 0 \tag{A-16}$$

which implies $\delta E_z = 0$ from Eq. (A-14), so $(\delta j_e)_z = 0$, from Eq. (2-65). To find $(\delta j_e)_y$, we have to integrate $\int e v_y \delta f(\vec{k}) d^3k$. But because of symmetry, the only nonvanishing term in the integral is from the electric field term in $\delta f(\vec{k})$. This gives a function of τ times δE_y, which is proportional to $(\delta j_e)_y$ (see Eq. (2-66)). Thus $(\delta j_e)_y$ also has the solution $(\delta j_e)_y = 0$.

To obtain $(\delta j_e)_x$, we first use the result of Eq. (A-16), i.e. $\delta n = 0$, then use a method similar to that for the δn solution in Eq. (A-1) to integrate the radial and azimuthal part of d^3k to get

$$(\delta j_e)_x = \int d^3k \; e v_x \; \delta f(\vec{k})$$
$$= \frac{Dev}{4}(e\delta E\Lambda + mv\delta u)\int_{-1}^{1} d(\cos\theta)\,\frac{\sin^2\theta}{1-i\omega\tau+iq\Lambda\cos\theta}$$
$$= \frac{Dev I_0}{4}(e\delta E\Lambda + mv\delta u)\,, \qquad \text{(A-17)}$$

where I_0 is the integral defined in Eq. (2-73). Substituting Eq. (2-66) for δE (here $\delta E_x = \delta E$), Eq. (A-17) yields

$$(\delta j_e)_x = \frac{DevI_0}{4}\left\{e\Lambda\frac{4\pi i}{\omega}\left(\frac{v_s}{c}\right)^2[(\delta j_e)_x - n_0 e\delta u] + mv\delta u\right.\,, \qquad \text{(A-18)}$$

which may be rearranged in the form

$$(\delta j_e)_x\left(\frac{4}{DevI_0}\right)\left(\frac{-i\omega}{4\pi e\Lambda}\right)\left(\frac{c}{v_s}\right)^2 = \left(\frac{-i\omega}{4\pi e\Lambda}\right)\left(\frac{c}{v_s}\right)^2 mv\delta u + (\delta j_e)_x - n_0 e\delta u\,. \qquad \text{(A-19)}$$

Grouping the terms of $(\delta j_e)_x$ together, we obtain

$$(\delta j_e)_x = \frac{n_0 e\delta u\left[1+\left(\frac{i\omega}{4\pi e\Lambda}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{mv}{n_0 e}\right)\right]}{1+i\left(\frac{4}{DevI_0}\right)\left(\frac{\omega}{4\pi e\Lambda}\right)\left(\frac{c}{v_s}\right)^2}\,. \qquad \text{(A-20)}$$

Again, using $\not{q}^2 = 4\pi e^2 D$ and $\frac{n_0}{D} = \frac{2}{3}\epsilon_F = \frac{mv^2}{3}$, we may rewrite (A-20) as

$$(\delta j_e)_x = n_0 e\delta u\left[\frac{1+i3\left(\frac{q}{\not{q}}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{1}{q\Lambda}\right)}{1+i4\left(\frac{q}{\not{q}}\right)^2\left(\frac{v_s}{v}\right)\left(\frac{c}{v_s}\right)^2\left(\frac{1}{q\Lambda}\right)\frac{1}{I_0}}\right]. \qquad \text{(A-21)}$$

Appendix B

The Evaluation of $\mathcal{L}(\eta)$

The quantity $\mathcal{L}(\eta)$ is defined in Eq. (3-107) as:

$$\mathcal{L}(\eta) = \int_{-1}^{1} d\xi \, \frac{\Delta^{2}(\eta)\,(1-\xi^{2})^{3/2}}{[(\eta-\Lambda-\xi)^{2}+\Delta^{2}(\eta)]^{2}} \,, \tag{B-1}$$

where Λ , Δ are defined as the real and imaginary parts of the self energy

$$\Sigma(\eta+i0) \equiv \Lambda(\eta) - i\,\Delta(\eta) \tag{B-2}$$

It is convenient to define an auxiliary complex function

$$\begin{aligned} \Phi(z) &= \int_{-1}^{1} d\xi \, \frac{(1-\xi^{2})^{3/2}}{z-\xi} \\ &= (1-z^{2}) \int_{-1}^{1} d\xi \, \frac{(1-\xi^{2})^{1/2}}{z-\xi} + \int_{-1}^{1} d\xi \,(z+\xi)(1-\xi^{2})^{1/2} . \end{aligned} \tag{B-3}$$

Then in terms of Φ , $\mathcal{L}(\eta)$ may be rewritten as

$$\begin{aligned} \mathcal{L}(\eta) &= \frac{\Delta}{2}\frac{\partial}{\partial\Delta}\left(\frac{1}{\Delta}\,\mathrm{Im}\,\Phi(\eta+i0-\Sigma)\right) \\ &= -\frac{1}{2\Delta}\,\mathrm{Im}\left[\Phi(\eta+i0-\Sigma)\right] + \frac{1}{2}\,\mathrm{Im}\left[\frac{\partial}{\partial\Delta}\Phi(\eta+i0-\Sigma)\right] . \end{aligned} \tag{B-4}$$

Using Eqs. (3-60) and (3-100), Eq. (B-3) may be rewritten as

$$\Phi(z) = \frac{\pi}{2}(1-z^2)\int_{-1}^{1} d\xi \, \frac{\mathcal{N}_0(\xi)}{z-\xi} + \frac{\pi z}{2}\int_{-1}^{1} \mathcal{N}_0(\xi)\, d\xi$$

$$= \frac{\pi}{2}\left[z + (1-z^2) F_0(z) \right]. \tag{B-5}$$

There is no contribution to $\mathcal{L}(\eta)$ from the $\frac{\pi z}{2}$ term in Φ, since $-\frac{1}{\Delta}\,\mathrm{Im}(\eta+i0-\Sigma) + \frac{\partial}{\partial\Delta}\,\mathrm{Im}(\eta+i0-\Sigma) = 0$. If we define still another function,

$$\psi(z) \equiv (1-z^2) F_0(z) \;, \qquad z = \eta + i0 - \Sigma \;, \tag{B-6}$$

then, from Eq. (3-65), $\psi(z)$ can also be expressed as:

$$\psi(z) = (1-z^2)\, F(\eta+i0). \tag{B-7}$$

Then in terms of $\psi(z)$, $\mathcal{L}(\eta)$ becomes

$$\mathcal{L}(\eta) = \frac{\pi}{4}\left[\frac{-1}{\Delta}\,\mathrm{Im}\,\psi(z) + \frac{\partial}{\partial\Delta}\,\mathrm{Im}\,\psi(z) \right]. \tag{B-8}$$

Next evaluate Im $\psi(z)$,

$$\mathrm{Im}\,\psi(z) = -\pi\mathcal{N}(\eta) - (\mathrm{Re}\,z^2)(-\pi\mathcal{N}(\eta)) - (\mathrm{Im}\,z^2)(\mathrm{Re}\,F)$$

$$= -\pi\mathcal{N} - \left[(\eta-\Lambda)^2 - \Delta^2\right](-\pi\mathcal{N}) - 2\Delta(\eta-\Lambda)(\mathrm{Re}\,F) \tag{B-9}$$

$$= -\pi\mathcal{N}\left[1 - (\eta-\Lambda)^2 + \Delta^2 + \frac{2\Delta}{\pi\mathcal{N}}(\eta-\Lambda)\,\mathrm{Re}\,F \right],$$

and the derivative is:

$$\frac{\partial}{\partial\Delta}\,\mathrm{Im}\,\psi(z) = \mathrm{Im}\,\frac{\partial}{\partial\Delta}\psi(z) = \mathrm{Im}\left[\frac{\partial z}{\partial\Delta}\,\frac{d\psi(z)}{dz}\right]$$

$$= \mathrm{Im}\left[i\,\frac{d\psi(z)}{dz}\right] = \mathrm{Re}\left[\frac{d\psi(z)}{dz}\right]. \tag{B-10}$$

Using Eq. (B-6) and Eq. (3-101), we can write

$$\begin{aligned}\frac{d\psi(z)}{dz} &= \frac{d}{dz}\left[\,(1-z^2)(\,2z - 2\sqrt{z^2-1}\,)\right]\\ &= 2 - 3z(\,2z - 2\sqrt{z^2-1}\,)\\ &= 2 - 3zF_0(z) = 2 - 3zF(\eta+i0)\,,\end{aligned} \tag{B-11}$$

and the real part of Eq. (B-11) is

$$\begin{aligned}\mathrm{Re}\left[\frac{d\psi(z)}{dz}\right] &= 2 - 3(\mathrm{Re}\,z)(\mathrm{Re}\,F) + 3(\mathrm{Im}\,z)(\mathrm{Im}\,F)\\ &= 2 - 3(\eta-\Lambda)\,\mathrm{Re}\,F + 3\Delta(-\pi\mathcal{N})\\ &= \frac{\pi\mathcal{N}}{\Delta}\left[\frac{2\Delta}{\pi\mathcal{N}} - \frac{3\Delta}{\pi\mathcal{N}}(\eta-\Lambda)\,\mathrm{Re}\,F - 3\Delta^2\right].\end{aligned} \tag{B-12}$$

Substituting Eqs. (B-9), (B-10) and (B-12) into (B-8) yields the equation

$$\mathcal{L}(\eta) = \frac{\pi^2}{4}\,\frac{\mathcal{N}}{\Delta}\left[\,1 + \frac{2\Delta}{\pi\mathcal{N}} - 2\Delta^2 - (\eta-\Lambda)^2 - \frac{\Delta}{\pi\mathcal{N}}(\eta-\Lambda)\,\mathrm{Re}\,F\right]. \tag{B-13}$$

Then Eq. (3-114) can be used to connect Σ and F:

$$\Sigma(\eta^+) = \eta - \frac{1}{F(\eta^+)} - \frac{1}{4}F(\eta^+)\,, \tag{B-14}$$

or, taking the imaginary part of both sides of Eq. (B-14),

$$\Delta = \pi\mathcal{N}\left(\frac{1}{|F|^2} - \frac{1}{4}\right). \tag{B-15}$$

However, we know that

$$|F|^2 = (\mathrm{Re}\,F)^2 + \pi^2\mathcal{N}^2. \tag{B-16}$$

Solving Eqs. (B-15) and (B-16) for ReF,

$$(\mathrm{Re}\,F)^2 = \frac{1}{\frac{\Delta}{\pi\mathcal{N}} + \frac{1}{4}} - \pi^2\mathcal{N}^2. \tag{B-17}$$

The real part of (B-14) yields

$$(\eta - \Lambda) = \left(\frac{1}{|F|^2} + \frac{1}{4}\right)\mathrm{Re}\,F = \left(\frac{2\Delta}{\pi\mathcal{N}} + \frac{1}{2}\right)\mathrm{Re}\,F. \tag{B-18}$$

Substituting $\eta - \Lambda$ from Eq. (B-18) and $(\mathrm{ReF})^2$ from (B-17) into Eq. (B-13), and collecting terms, yields

$$\mathcal{L}(\eta) = \frac{\pi^4\mathcal{N}^3}{16\Delta}\left[1 + \frac{6\Delta}{\pi\mathcal{N}}\right]. \tag{B-19}$$

Appendix C

Virtual Crystal Limit

In the notation of Sec. D-4 of Chap. 3, the scattering strength is defined by $\varepsilon_A = \delta/2$, $\varepsilon_B = -\delta/2$. In the weak scattering limit $\delta \ll 1$ and α_A and $\alpha_B \ll 1$, and a perturbation expansion in powers of these parameters is useful. The CPA self-energy Σ can be expressed as

$$\Sigma = \langle\langle \varepsilon_n + \theta_n \rangle\rangle + \langle\langle (\varepsilon_n + \theta_n) F \tau_n \rangle\rangle , \tag{C-1}$$

where τ_n is the site diagonal matrix element of T_n (see Eq. (3-64), i.e.,

$$\begin{aligned} \tau_n &= \frac{\varepsilon_n + \theta_n - \Sigma}{1 - (\varepsilon_n + \theta_n - \Sigma) F} \\ &= \varepsilon_n + \theta_n - \Sigma + (\varepsilon_n + \theta_n - \Sigma) F (\varepsilon_n + \theta_n - \Sigma) + \cdots . \end{aligned} \tag{C-2}$$

Let us evaluate the first three $\Sigma^{(\ell)}$, defined as Σ correct to powers of δ^{ℓ} and $\sqrt{\alpha}^{\ell}$ in CPA. The first three moments of $\langle\langle (\varepsilon_n + \theta_n)^{\ell} \rangle\rangle$ are:

$$\begin{aligned} &\langle\langle \epsilon_n + \theta_n \rangle\rangle = (\chi - y)\, \delta/2 \equiv \overline{\epsilon} , \\ &\langle\langle (\varepsilon_n + \theta_n)^2 \rangle\rangle = \frac{\delta^2}{4} + \chi \alpha_A + y \alpha_B , \\ &\langle\langle (\varepsilon_n + \theta_n)^3 \rangle\rangle = (x - y) \frac{\delta^3}{8} + \frac{3\chi}{2} \delta \alpha_A - \frac{3y}{2} \delta \alpha_B . \end{aligned} \tag{C-3}$$

The first three self-energies are:

$$\Sigma^{(0)} = 0 ,$$

$$\Sigma^{(1)} = \langle\langle \varepsilon_n + \theta_n \rangle\rangle = \bar{\epsilon} ,$$

$$\begin{aligned}\Sigma^{(2)} &= \langle\langle \varepsilon_n + \theta_n \rangle\rangle + \langle\langle (\varepsilon_n + \theta_n)^2 \rangle\rangle F - \langle\langle (\varepsilon_n + \theta_n) \rangle\rangle \Sigma^{(1)} F \\ &= \bar{\epsilon} + \left(\frac{\delta^2}{4} + x\alpha_A + y\alpha_B \right) F - \bar{\epsilon}^2 F \\ &= \bar{\epsilon} + (xy\delta^2 + x\alpha_A + y\alpha_B) F. \end{aligned} \tag{C-4}$$

In Eq. (C-4), F must be correct to order of δ^{ℓ} and $\sqrt{\alpha}^{\,\ell}$. The density of states per atom $\mathcal{N}$(E) is then approximated by

$$\begin{aligned}\mathcal{N}(E) &= -\frac{1}{\pi} \operatorname{Im} F(E + i0) = \frac{-1}{\pi} \operatorname{Im} F_0(E + i0 - \Sigma(E+i0)) \\ &\simeq -\frac{1}{\pi} \operatorname{Im} F(E - \bar{\epsilon} + i0) = \mathcal{N}_0(E - \bar{\epsilon}) ,\end{aligned} \tag{C-5}$$

which is just the "rigid band model" result. To the lowest order, according to Eq. (3-110), the conductivity is

$$\sigma = \frac{\pi^2}{12} \left(\frac{e^2 \hbar v_m^2}{\Omega_c} \right) \left(\frac{\mathcal{N}_0^{\,3}(\epsilon_F - \bar{\epsilon})}{\Delta(\epsilon_F)} \right) , \tag{C-6}$$

and the resistivity is

$$\begin{aligned}\rho &= \frac{12}{\pi^2} \left(\frac{\Omega_c}{e^2 \hbar v_m^2} \right) \left(\frac{\Delta(\epsilon_F)}{\mathcal{N}_0^{\,3}(\epsilon_F - \bar{\epsilon})} \right) \\ &\simeq \frac{12}{\pi} \left(\frac{\Omega_c}{e^2 \hbar v_m^2} \right) \frac{(xy\delta^2 + x\alpha_A + y\alpha_B)}{\mathcal{N}_0^{\,2}(\epsilon_F - \bar{\epsilon})} .\end{aligned} \tag{C-7}$$

Eq. (C-7) exhibits Matthiessen's rule,

$$\rho = \rho_I + \rho_P \quad , \tag{C-8}$$

with

$$\rho_I = \frac{12\,\Omega_c}{\pi e^2 \hbar\, v_m^2}\;\frac{x y \delta^2}{\mathcal{N}_0^{\,2}(\epsilon_f - \bar{\epsilon})} \quad , \tag{C-9}$$

and

$$\rho_P = \frac{12\,\Omega_c}{\pi e^2 \hbar\, v_m^2}\;\frac{x \alpha_A + y \alpha_B}{\mathcal{N}_0^{\,2}(\epsilon_f - \bar{\epsilon})} \quad . \tag{C-10}$$

The "impurity" contribution ρ_I then obeys the Nordheim rule[82], because $\rho_I \propto x y \delta^2$. The "electron-phonon" contribution to resistivity, ρ_P , has a slope as a function of T which lies between those of the pure crystals.

Appendix D

The CPA Density of States and Conductivity in Terms of the Self-Energy in the Free Electron Model

In the free electron model, the unperturbed density of states per atom, $\mathcal{N}_0(E)$, is simply

$$\mathcal{N}_0(E) = \frac{1}{\sqrt{2}} \frac{\Omega}{N\pi^2} \frac{m^{3/2}}{\hbar^3} \sqrt{E} \equiv A\sqrt{E} \; . \tag{D-1}$$

The CPA density of states per atom, $\mathcal{N}(E)$, in terms of the self energy $\Sigma(E)$, is

$$\begin{aligned} \mathcal{N}(E) &= \frac{1}{\pi N} \sum_{\vec{k}} \frac{\Delta(E)}{[E - \Lambda(E) - \epsilon(\vec{k})]^2 + \Delta^2(E)} \\ &= \frac{1}{\pi} \int d\epsilon \, \frac{\mathcal{N}_0(\epsilon)\, \Delta(E)}{[E - \Lambda(E) - \epsilon]^2 + \Delta^2(E)} \; , \end{aligned} \tag{D-2}$$

where $\Sigma(E \pm i0) = \Lambda(E) \mp i\,\Delta(E)$ as usual. Using Eq. (D-1), we can rewrite $\mathcal{N}(E)$ as

$$\mathcal{N}(E) = A \, \frac{\Delta(E)}{\pi} \, Y(E) \; , \tag{D-3}$$

where $Y(E)$ is the integral

$$Y(E) \equiv \int_0^\infty \frac{\sqrt{\epsilon}\, d\epsilon}{[E - \Lambda(E) - \epsilon]^2 + \Delta^2(E)} \; . \tag{D-4}$$

This integral is easily carried out using a contour sketched in Fig. XI(a). Let us define $\beta = E - \Lambda(E)$, $\rho = \sqrt{\beta^2 + \Delta^2}$, and $\theta = \tan^{-1}\frac{\Delta}{\beta}$ (see Fig. XI(b)). Then in terms of residues,

$$
\begin{aligned}
Y(E) &= \pi i \, [\, \mathrm{Res}\,(\beta + i\Delta) + \mathrm{Res}\,(\beta - i\Delta)] \\
&= \pi i \, [\, \frac{(\beta + i\Delta)^{1/2}}{2i\Delta} + \frac{(\beta - i\Delta)^{1/2}}{-2i\Delta}] \\
&= \frac{\pi}{2\Delta} \rho^{1/2} [\, \frac{e^{i\theta/2}}{2i\Delta} + \frac{e^{i(2\pi-\theta)/2}}{-2i\Delta}] \\
&= \frac{\pi}{2\Delta} \rho^{1/2} \, 2\cos(\tfrac{\theta}{2}) = \frac{\pi}{\Delta}\sqrt{\tfrac{1}{2}(1 + \beta/\rho)}\, \rho^{1/2} \\
&= \frac{\pi}{\Delta}\sqrt{\tfrac{1}{2}(\rho + \beta)}\ . \qquad \text{(D-5)}
\end{aligned}
$$

Thus

$$
\mathcal{N}(E) = \frac{A}{\sqrt{2}}\sqrt{[(E - \Lambda(E))^2 + \Delta^2]^{1/2} + E - \Lambda(E)}\ . \qquad \text{(D-6)}
$$

The CPA conductivity, α, according to Eq. (3-97), is

$$
\alpha = \frac{2e^2\hbar}{\pi\Omega_c}\int d\eta\,(-\frac{df}{d\eta})\int d\xi\,[\frac{\Delta(\eta)}{[\eta - \xi - \Lambda(\eta)]^2 + \Delta^2(\eta)}]^2 \frac{1}{N}\sum_{\vec{k}} \frac{1}{3} v^2(\vec{k})\,\delta(\xi - \epsilon(\vec{k}))\,. \qquad \text{(D-7)}
$$

Since the velocity dispersion $v^2(\vec{k})$ is simply

$$
v^2(\vec{k}) = \frac{\hbar^2 k^2}{2m} = \frac{2\epsilon(\vec{k})}{m} = \frac{2}{mA^2}\mathcal{N}_0^2(\epsilon(\vec{k}))\,, \qquad \text{(D-8)}
$$

the conductivity is

$$\alpha = \frac{2ek}{\pi\Omega_c}\left(\frac{2}{3m}\right)\int d\eta\left(-\frac{df}{d\eta}\right)\int d\xi\,\frac{\mathcal{N}_0(\xi)\;\xi\;\Delta^2(\eta)}{[(\eta-\Lambda(\eta)-\xi)^2+\Delta^2(\eta)]^2}\,. \tag{D-9}$$

Using Eq. (D-1) for $\mathcal{N}_0(\xi)$,

$$\begin{aligned}\alpha &= \frac{2e^2k}{\pi\Omega_c}\left(\frac{2A}{3m}\right)\int d\eta\left(-\frac{df}{d\eta}\right)I_2(\eta)\;\Delta^2(\eta)\\ &\simeq \frac{2e^2k}{\pi\Omega_c}\left(\frac{2A\,\Delta^2(\epsilon_F)}{3m}\right)I_2(\epsilon_F)\,,\end{aligned} \tag{D-10}$$

where

$$I_2(\epsilon_F) \equiv \int_0^\infty d\epsilon\,\frac{\epsilon^{3/2}}{[(\epsilon_F-\Lambda(\epsilon_F)-\epsilon)^2+\Delta^2(\epsilon_F)]^2}\,. \tag{D-11}$$

Using the same contour as in Fig. XI(a), and the notation of Eq. (D-5), we can write

$$I_2 = \pi i\,[\,\mathrm{Res}(\beta+i\Delta)+\mathrm{Res}(\beta-i\Delta)]\,. \tag{D-12}$$

But now the residues are of the double poles, and

$$\mathrm{Res}(\beta+i\Delta) = \frac{3}{2}\,\frac{(\beta+i\Delta)^{1/2}}{(2i\Delta)^2}-\frac{2(\beta+i\Delta)^{3/2}}{(2i\Delta)^3}\,. \tag{D-13}$$

Similarly, for Res $(\beta-i\Delta)$, so that

$$\begin{aligned} I_2 &= \pi i \Big[\tfrac{3}{2}\left(\tfrac{-1}{4\Delta^2}\right) \rho^{1/2} e^{i\theta/2} + \tfrac{1}{4\Delta^3 i}\, \rho^{3/2} e^{i3\theta/2} \\ &\qquad + \tfrac{3}{2}\left(\tfrac{-1}{4\Delta^2}\right) \rho^{1/2} e^{i(\pi-\theta/2)} - \tfrac{1}{4\Delta^3 i}\, \rho^{3/2} e^{i(3\pi-3\theta/2)} \Big] \\ &= \pi i \Big[\tfrac{-3}{8\Delta^2}\, \rho^{1/2} (2i \sin\theta/2) + \tfrac{1}{4\Delta^3 i}\, \rho^{3/2}\, 2\cos(3\theta/2) \Big] \\ &= \frac{3\pi}{4\Delta^2}\, \rho^{1/2} \sin\theta/2 + \frac{\pi}{2\Delta^3}\, \rho^{3/2} \cos(3\theta/2) \,. \end{aligned} \tag{D-14}$$

Since

$$\sin\frac{\theta}{2} = \sqrt{\tfrac{1}{2}(1-\beta/\rho)} \,, \tag{D-15}$$

and

$$\begin{aligned} \cos(3\theta/2) &= \cos\theta \cos\theta/2 - \sin\theta \sin\theta/2 \\ &= \frac{\beta}{\rho}\sqrt{\tfrac{1}{2}\left(1+\tfrac{\beta}{\rho}\right)} - \frac{\Delta}{\rho}\sqrt{\tfrac{1}{2}\left(1-\tfrac{\beta}{\rho}\right)} \,, \end{aligned} \tag{D-16}$$

the integral, I_2, becomes

$$\begin{aligned} I_2 &= \frac{3\pi}{4\Delta^2}\sqrt{\tfrac{1}{2}(\rho-\beta)} + \frac{\pi}{2\Delta^3}\Big[\beta\sqrt{\tfrac{1}{2}(\rho+\beta)} - \Delta\sqrt{\tfrac{1}{2}(\rho-\beta)} \\ &= \frac{\pi}{4\Delta^2}\sqrt{\tfrac{1}{2}(\rho-\beta)} + \frac{\pi}{2\Delta^3}\,\beta\sqrt{\tfrac{1}{2}(\rho+\beta)} \,. \end{aligned}$$

Thus

$$\begin{aligned} \sigma &= \frac{2e^2}{3\Omega_c}\left(\frac{2A}{3m}\right)\left(\frac{\hbar}{2\Delta}\right)\Big[\beta\sqrt{\tfrac{1}{2}(\rho+\beta)} + \tfrac{1}{2}\Delta\sqrt{\tfrac{1}{2}(\rho-\beta)}\Big] \\ &= \frac{2e^2}{3\Omega_c}\left(\frac{2A}{3m}\right)\left(\frac{\hbar}{2\Delta}\right)\sqrt{\tfrac{1}{2}(\rho+\beta)}\Big[\beta + \frac{\Delta}{2}\sqrt{\frac{\rho-\beta}{\rho+\beta}}\Big] \,. \end{aligned}$$

Using the result of Eqs. (D-4) and (D-5), we can see that $\mathcal{N} = A\sqrt{\frac{1}{2}(\rho+\beta)}$. Then α becomes

$$\alpha = \frac{2e^2}{3\Omega_c}\left(\frac{2}{m}\right)\left(\frac{\hbar}{2\Delta}\right)\mathcal{N}(\epsilon_F)\left[\beta + \frac{\Delta}{2}\,\frac{\rho-\beta}{\sqrt{\rho^2-\beta^2}}\right]$$

$$= \frac{2e^2}{3\Omega_c}\left(\frac{2}{m}\right)\left(\frac{\hbar}{2\Delta}\right)\mathcal{N}(\epsilon_F)\left[\beta + \frac{\Delta}{2}\,\frac{\rho-\beta}{\Delta}\right]$$

$$= \frac{2e^2}{3\Omega_c}\left(\frac{2}{m}\right)\left(\frac{\hbar}{2\Delta}\right)\mathcal{N}(\epsilon_F)\left[\frac{\rho}{2} + \frac{\beta}{2}\right]$$

$$= \frac{2e^2}{3\Omega_c}\left(\frac{\hbar}{2\Delta}\right)\mathcal{N}(\epsilon_F)\,\frac{2}{mA^2}\,\mathcal{N}^2(\epsilon_F)\,. \tag{D-17}$$

If we define a Fermi velocity v_F which has the same relation to the density of states $\mathcal{N}(\epsilon_F)$ as that of v_0 to $\mathcal{N}_0(E)$ in Eq. (D-8), i.e.

$$v_F^2 \equiv \frac{2}{mA^2}\,\mathcal{N}^2(\epsilon_F)\,, \tag{D-18}$$

then we arrive at the elementary formula

$$\alpha = \frac{2e^2}{3\Omega_c}\left(\frac{\hbar}{2\Delta}\right)\mathcal{N}(\epsilon_F)\,v_F^2 = \frac{e^2}{3}\,v_F^2\,D_F\,\tau\,, \tag{D-19}$$

where D_F is defined in Eq. (3-134) and τ is $\frac{\hbar}{2\Delta(\epsilon_F)}$.

Figure XI(a). The contour for the integrations in Eq. (D-4) and (D-11).

(b). The relations among ρ, β, Δ, E, Λ and θ as used in Eqs. (D-5) and (D-12).

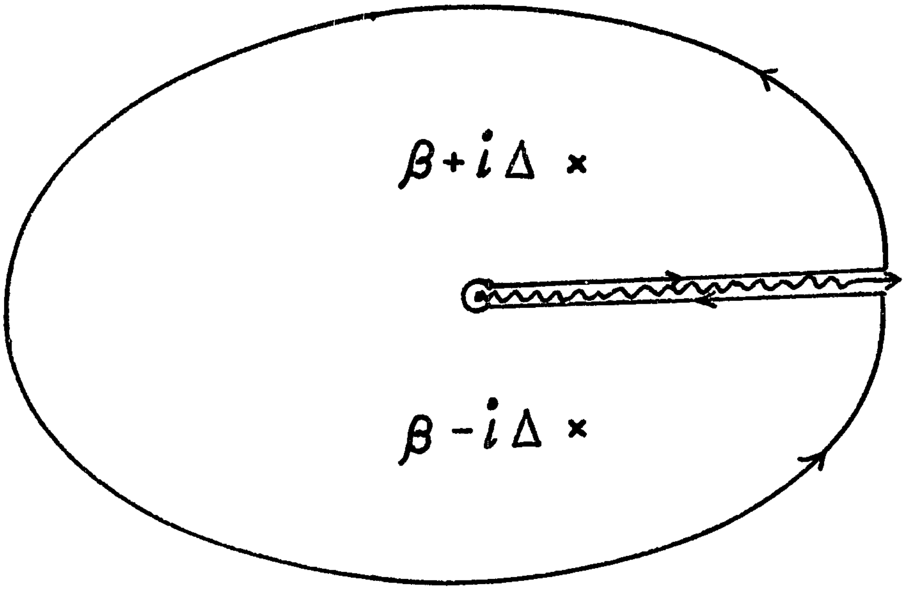

Figure XI(a)

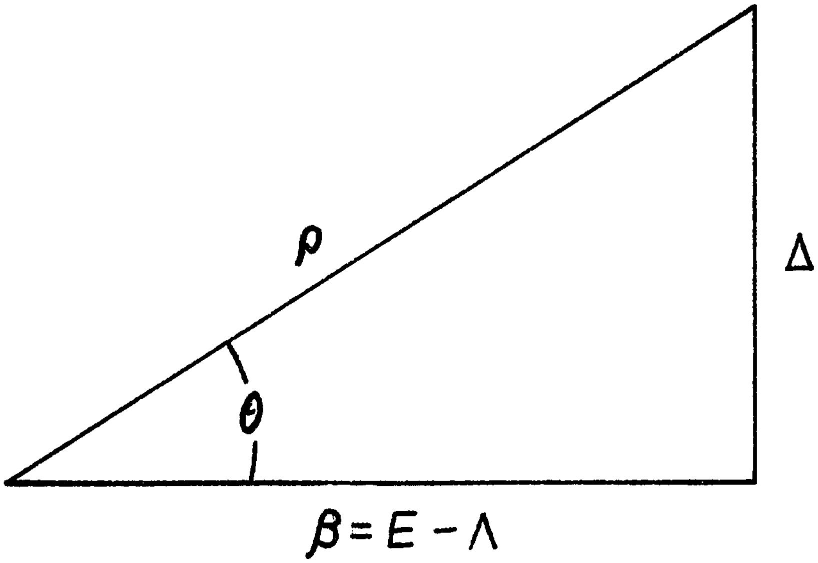

Figure XI(b)

REFERENCES

1. A collection of experimental data for thermal properties of alloys can be found in *Thermophysical Properties of High Temperature Solid Materials*. (Purdue Univ. 1967; Y. S. Touloukian, Editor) Vols. II and III.
2. For example. G. T. Meaden, *Electrical Resistance of Metals* (Plenum Press, 1965).
3. B. Velický, S. Kirkpatrick and H. Ehrenreich, Phys. Rev. 175, 747 (1968).
4. S. Kirkpatrick, B. Velický and H. Ehrenreich, Phys. Rev. B1, 8 (1970).
5. G. W. Stocks, R. W. Williams and J. S. Faulkner, Phys. Rev. Letters 26, 253 (1971).
6. K. Levin and H. Ehrenreich, Phys. Rev. B2, 4172 (1971).
7. J. M. Siman, Electrons and Phonons (Oxford, 1960) Secs. 5-1 and 5-12.
8. Paul Soven, Phys. Rev. 156, 809 (1967).
9. B. Velický, Phys. Rev. 184, 614 (1969).
10. C. Kittel, *Introduction to Solid State Physics*, 3rd Ed. (John Wiley and Sons, 1967) p.216, Eq. (60).
11. A. Matthiessen, Rep. Brit. Ass. 32, 144 (1862), or Ref. 7, pp. 286 and 337.
12. Ref. 7, p. 194.

13. A. B. Pippard, Phil. Mag. 46, 1104 (1955); "Dynamics of Conduction Electrons" in Low-Temperature Physics (Gordon and Breach), pp. 110-129.

14. M. H. Cohen, M. J. Harrison and W. Harrison, Phys. Rev. 117, 937 (1960).

15. L. Kleinman, Phys. Rev. 182, 686 (1969).

16. R. G. Chambers, Proc. Phys. Soc. (London) A65, 458 (1962); A238, 344 (1967).

17. L. J. Sham and J. M. Ziman, "The Electron-Phonon Interaction" in Solid State Physics (edited by F. Seitz and D. Turnbull, Academic Press, 1963), Vol. 15.

18. T. Holstein, Phys. Rev. 113, 479 (1959).

19. G. D. Whitfield, Phys. Rev. 121, 721 (1961).

20. C. Kittel, Quantum Theory of Solids (John Wiley & Sons, 4th Printing, 1967) p. 329, Eq. (18).

21. Ref. 7, Eq. (5, 6, 10).

22. J. M. Ziman, Principles of the Theory of Solids (Cambridge, 1965) p. 176, Eq. (6, 89).

23. The sentence inside the quotation marks is from Ref. 7, p. 214.

24. R. Kubo, J. of Phys. Soc., Japan, 12, 570 (1957).

25. R. E. Peierls, Quantum Theory of Solids (Clarendon Press, Oxford, 1955) pp. 139-142.

26. L. Van Hove, Physica 21, 517 (1955); 23, 441 (1957).

27. W. Kohn and J. M. Luttinger, Phys. Rev. 108, 590 (1957).

28. J. M. Luttinger and W. Kohn, Phys. Rev. 109, 1892 (1958).

29. R. Kubo, Lectures in Theoretical Physics (Interscience Publishers, Ind., New York) 1, 128 (1958).

30. E. J. Moore, Phys. Rev. Vol. 160 No. 3 607 (1967).

31. E. Verboven, Physica, <u>36</u>, 1091 (1960).

32. D. A. Greenwood, Proc. Phys. Soc. <u>71</u>, 585 (1958).

33. S. F. Edwards, Advances in Physics <u>16</u>, 359 (1967).

34. G. V. Chester and A. Thellung, Proc. Phys. Soc. <u>73</u>, 745 (1959).

35. N. F. Mott, Advances in Physics <u>16</u>, 49 (1967).

36. M. H. Cohen, J. Non-Cry. Solid <u>41</u>, 391 (1970).

37. M. H. Cohen, Physics Today, (May 1971), p. 26.

38. S. F. Edwards, Phil. Mag. <u>6</u>, 617 (1961).

39. T. E. Faber and J. M. Ziman, Phil. Mag. <u>11</u>, 153 (1965).

40. A. B. Bathia and D. E. Thornton, Phys. Rev. <u>B2</u>, 3004 (1970).

41. N. F. Mott and H. Jones, <u>Theory of the Properties of Metals and Alloys</u> (Dover Publications, Inc., New York, 1958).

42. S. F. Edwards, Phil. Mag. <u>3</u>, 1020 (1958).

43. J. S. Langer, Phys. Rev. <u>120</u>, 714 (1960); <u>124</u>, 1003 (1961); <u>127</u>, 5 (1962).

44. For example; A. A. Abrikosov, L. P. Gorkov and I. Ye Dzyaloshinskii <u>Quantum Field Theoretical Methods in Statistical Physics</u>, 2nd ed. (Pergamon Press, 1965).

45. J. L. Beeby and S. F. Edwards, Proc. R. Soc. <u>A274</u>, 395 (1963).

46. L. E. Ballentine, Canad. J. Phys., <u>44</u>, 2533 (1966).

47. D. W. Taylor, Phys. Rev. <u>156</u>, 1017 (1967).

48. Y. Onodera and Y. Toyozawa, J. Phys. (Japan), <u>24</u>, 341 (1968).

49. F. Yonezawa, Progr. Theoret. Phys. (Kyoto), <u>40</u>, 734 (1968).

50. J. M. Ziman, J. Phys. <u>C2</u>, 1230 (1969).

51. T. Matsubara and Y. Toyozawa, Progr. Theoret. Phys. (Kyoto), <u>26</u>, 739 (1961).

52. P. L. Leath, Phys. Rev. B2, 3078 (1970).

53. N. F. Berk, Phys. Rev. B1, 1336 (1970).

54. S. F. Edwards and J. M. Loveluck, J. Phys. C: Metal Phys. Supp. No. 3, S261 (1970).

55. K. F. Freed and M. H. Cohen, Phys. Rev. B3, 3400 (1971).

56. W. Kohn, Proceedings of the Third IMR Symposium on Electronic Density of States, Natl. Bur. Std. Special Publ. No. 323 (U. S. GPO, Washington, D. C., 1970).

57. P. W. Anderson and W. L. McMillan, in Theory of Magnetism in Transition metals, Proceedings of the International School of Physics "Enrico Fermi", Course 37, edited by H. Suhl (Academic Press, Inc., New York, 1967), p. 60.

58. Paul Soven, Phys. Rev. B2, 4715 (1970).

59. S. Kirkpatrick, B. Velicky, N. D. Lang and H. Ehrenreich, J. Applied Phys. 40, 3 809 (1967).

60. B. Velický and K. Levin, Phys. Rev. B2, 4, 938 (1970).

61. The formalism of CPA in this section follows closely to that given in Ref. 3 and 9.

62. Ref. 9, Eq. (118). Note the difference in the definition of .

63. Ref.19, Sec. 2, where there is a demonstration of some cancellation between the multiple phonon processes and the Debye-Waller factor. This allows us to use the one-phonon interaction Hamiltonian and ignore multiple phonon processes.

64. A. Messiah, Quantum Mechanics (John Wiley & Sons, Inc., 1966) Vol. 1, p. 448.

65. J. Hubbard, Proc. Roy. Soc. (London) A281, 401 (1964).

66. Handbook of Mathematical Functions (National Bureau of Standards), Edited by M. Abramowritz and I. A. Stegun. p. 297.

67. Ref. 66, Eq. (7.1.8).

68. J. M. Ziman, The Physics of Metals (Cambridge Univ. Press, 1969), Vol. 1, Chap. 5; Adv. in Phys. 16, 551 (1967).

69. L. F. Mattheis, Phys. Rev. 134, A970 (1964).

70. V. Heine, Phys. Rev. 153, 673 (1967).

71. R. E. Watson, H. Ehrenreich, and L. Hodges, Phys. Rev. Letters 24, 829 (1970).

72. See the density of states curve in L. Hodges, H. Ehrenreich and N. D. Lang, Phys. Rev. 152, 505 (1966).

73. Paul Soven, private communication.

74. T. J. Hicks, B. Rainford, J. S. Kouvel, and G. G. Low, Phys. Rev. Letters 22, 531 (1969).

75. See the review paper by J. Kondo in Solid State Physics (edited by F. Seitz and D. Turnbull, Academic Press) 23, 183 (1969).

76. G. Weisz, private communication.

77. K. S. Chang, private communication.

78. I. M. Lifshitz, Soviet Phys. USPEKHI. 7, 549 (1965).

79. J. S. Kouvel and J. B. Comly, Phys. Rev. Letters 24, 598 (1970).

80. V. I. Krylov, Approximate Calculation of Integrals (MacMillan, New York/London, 1962), pp. 129-130 and 343-346.

81. Paul Soven, Phys. Rev. 178, 1136 (1969).

82. L. Nordheim, Ann. Phys. (5), 9, 607 (1931).