MASTER

STUDIES IN THE THEORY OF SOLIDS

BY

HAROLD PAUL HJALMARSON

B.S., University of North Dakota, 1972
M.S., University of North Dakota, 1974

THESIS

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy in Physics
in the Graduate College of the
University of Illinois at Urbana-Champaign, 1979

Urbana, Illinois

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Urbana, Illinois

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STUDIES IN THE THEORY OF SOLIDS

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Chapter I: We show that the surface arrangement of atoms in a solid controls the energetically slowly varying features of a LEED spectrum. Because of inelastic collisions within the solid, the LEED electrons mainly sample a surface sandwich of atoms. Thus, the surface sandwich reflectivity, computed by using a method which considers only single reflections of the electron by sheets of atoms in the solid, can be directly compared with the slowly varying, surface dependent features in the data. To concentrate on these features of the data, the approximate surface sandwich reflectivity is compared with data which has been smoothed to remove energetically rapidly varying features which do not depend on surface structure. The spectra, defined as a function of momentum transfer, are smoothed by averaging over momentum shorter than a momentum transfer characteristic of a surface distance. The method, especially adapted to layered materials, was used to determine that the surface of TiS_2 is ideal whereas the surface sandwich of TiSe_2 expands outward slightly. For the final determinations, the smoothing method was used on both the data and a theory which includes multiple scattering to confine the comparison to just the slowly varying surface dependent features.

Chapter II: We show that energies of deep traps associated with impurities in semiconductors are controlled by the S and P orbital energies of the impurity atoms. First, the qualitative physics of a deep trap is worked out using a defect molecule model. For very deep traps the

trap energy is defined by a pinning energy which is determined by the energies of the nearest neighbors of the impurity. The quantitative theory is worked out using a tight binding Koster-Slater calculation. Using band-structure at symmetry points to define matrix elements of the host crystal Hamiltonian and a table of atomic energies to define the impurity potential, predictions of energies of deep traps caused by impurities are made for fourteen different semiconductors. The theory is compared with the data for GaP and the alloy $\text{GaAs}_{1-x}\text{P}_x$ before developing a phenomenological model which depends mainly on the energy centers of the valence and conduction band density of states as well as atomic energies of impurities. Finally, this phenomenological model is used to make predictions of deep trap energies in Si.

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CHAPTER ONE

Surface Dependent Features in LEED Spectra

I. INTRODUCTION

Indirect determination of surface structure by Low Energy Electron Diffraction (LEED) involves comparisons of data with computationally difficult multiple-scattering theory--which uses proposed models of surface structure as input. Direct determinations by simple single-scattering approximations (such as the Born approximation) are not attempted, especially since the development of multiple-scattering theories,^{1-3/} because the cross sections of the atomic constituents of many solids are large enough compared with the unit cell area that multiple-scattering effects must be included in quantitative calculations. One alternative to the cumbersome multiple scattering methods is to use data reduction methods,^{4,5/} such as "kinematical averaging" which is intended to recover the "single scattering" portion of the data for comparison with the simpler theory.^{2,6/} Unfortunately, such phenomenological methods involve substantial computational and experimental effort with no guarantee of success. Thus, a computationally simple theory of LEED intensities is needed.

In this work we propose a conceptually and computationally simple method which concentrates on the distinction between surface and bulk features in LEED data--this distinction is then used to extract the surface structure from the data. The conceptual isolation of surface from bulk structure is accomplished by regarding the solid as a stack of chemically identical sandwiches, each sandwich containing a few two-dimensional sheets of identical atoms (see Fig. 1). The sandwiches must be chosen large enough that all surface atomic rearrangement occurs within the outermost sandwich.^{*/} The LEED electrons pick out mainly structural information

*For monatomic materials each sandwich must contain more than one sheet of atoms; such a sandwich is analogous to a supercell. For the layered dichalcogenides which we shall consider later, each sandwich is simply a sheet of unit cells perpendicular to the surface.

Fig. 1 The solid is decomposed into sandwiches consisting of sheets of atoms; in the case shown here each sandwich contains three sheets of atoms. Because of absorption by inelastic collisions, the measured electrons with wavevector $\vec{k}_f$ originate mostly from the surface sandwich.

Solid Composed of Sheets of Atoms

from the outer sandwich of a solid because the short mean free path (about $5-10\text{\AA}^{2/}$) of the elastically scattered electrons limits their penetration into the surface. This fact, which makes LEED a useful tool for surface analysis, allows us to relate the intensity-energy spectra $I(E)$ (reflectivity) of just the outer sandwich--ignoring the rest of the solid--to the data.

Features in the data which vary slowly with energy compared to bulk structure Bragg peaks depend on the surface structure of the solid. To illustrate the distinction between surface and bulk features we schematically show typical LEED data in Fig. 2--a plot of the intensity of specularly reflected electrons as a function of energy. If the electrons interacted weakly with the solid, like X-rays,^{2/} the intensity spectrum would become a series of discrete Bragg peaks in the LEED data depending on interatomic distances long compared to separations between atoms near the surface; they are relics of bulk structure whose positions give no information about surface structure. The surface structure can be thought of as modulating the heights of the Bragg peaks; and in general it controls the energetically slowly varying features in the data.

The basic approximation in application of the method is to neglect contributions to the electron-solid scattering which correspond to scattering of the electrons by two or more atoms in different sandwiches; thus the electron-solid scattering amplitude becomes a sum of single sandwich scattering amplitudes. The validity and usefulness of this approximation rests on three facts: (i) for many solids, the elastic scattering cross section is smaller than the geometric cross section of a unit cell, and (ii) multiply-scattered electrons must travel at least two interatomic distances further than singly-scattered electrons and so are much more likely to be inelastically scattered out of the LEED beam, and (iii) in

Fig. 2 Comparison of schematic LEED data to the discrete peaks expected if inelastic collisions did not cause violation of the Bragg condition perpendicular to the surface. The peak widths are proportional to inelastic scattering cross-sections.

certain solids, such as the transition metal dichalcogenides, the atoms naturally occur in sandwiches and the inter-sandwich scattering is weaker than the intra-sandwich scattering.

To demonstrate the single sandwich reflection method, we employ it to determine the surface structures of the weak-scattering layered dichalcogenides, TiS_2 and TiSe_2 . The single reflection analysis of each solid, which was checked by a full multiple-scattering calculation, shows that both TiS_2 and TiSe_2 have nearly ideal unrelaxed surfaces.^{*/}

^{*/}For a relaxed surface the separation between sheets of atoms near the surface is different than the separation in the bulk.

II. INTRODUCTION TO LEED

A. Qualitative Physics

In 1927 Davisson and Germer^{7/} performed the first LEED experiment while verifying the wavelike properties of an electron. Soon the basic physics, energy and momentum conservation and consequent beam-like nature of the reflected electrons, was worked out. The electrons were found to have a short mean free path which made them sensitive to surface structure; by 1937 Slater^{8/} had worked out a phenomenological kinematic theory (single-scattering) in which the finite electron mean free path damps the electron beam and thus smears the Bragg peaks associated with reciprocal lattice vectors whose components are nonzero.

A LEED experiment, conceptually a simple scattering experiment, easily produces information about the planar arrangement of surface atoms. Because of sensitivity to surface contamination, the LEED experiment is done inside a vacuum chamber which usually is held at better than 10^{-10} Torr pressure. The basic experiment is shown in Fig. 3; electrons, which have been accelerated by a voltage V ($E=eV$) to energies within 10-300 eV by an electron gun, reflect from the surface of the sample and then collect in a Faraday cup detector. A retarding grid on the detector repels electrons which have been inelastically scattered; thus only the elastically scattered current $I(E)$ is measured by the experimenter.

The basic physics of the LEED problem, independent of the detailed nature of the electron-solid interaction, dictates that the electrons emerge as discrete plane-wave beams with well-defined momentum $\hbar\mathbf{K}_f$ and energy $E = \hbar^2\mathbf{K}_f^2/2m$. Consideration of the structure of a solid produces a conservation law for momentum. In particular, the equilibrium positions of atoms within the solid are denoted by

Fig. 3 The LEED experiment, performed inside a vacuum chamber, involves measurement of the current I reflected when a beam of electrons with energy E strikes the sample.

$$\begin{aligned}
\vec{R}_n &\equiv \vec{R}_{n||, n\perp} \\
&= \vec{\rho}_{n||} + \vec{z}_{n\perp}
\end{aligned} \tag{1}$$

with positions within atomic sheets parallel to the surface given by

$$\begin{aligned}
\vec{\rho}_{n||} &\equiv \vec{\rho}_{hk} \\
&= h \vec{A}_1 + k \vec{A}_2
\end{aligned} \tag{2}$$

and positions of atomic sheets perpendicular to the surface given by

$$\vec{z}_{n\perp} = n \vec{A}_3 \tag{3}$$

in which $\vec{A}_3$ points into the solid. A three-dimensional reciprocal lattice can be associated with this space lattice R_n :

$$\vec{G}_{lmn} = l \vec{a}_1 + m \vec{a}_2 + n \vec{a}_3 \tag{4}$$

with

$$\vec{a}_1 = 2\pi \frac{\vec{A}_2 \times \vec{A}_3}{\vec{A}_1 \cdot \vec{A}_2 \times \vec{A}_3} \tag{5}$$

and permutation of indices gives $\vec{a}_2$ and $\vec{a}_3$, $\vec{a}_1$ and $\vec{a}_2$ are parallel to the surface. Because a perfect surface has two-dimensional translational periodicity the electron's momentum parallel to the surface must be conserved modulo $\vec{G}_{||}$:

$$\vec{k}_{f||} = \vec{k}_{i||} + \vec{G}_{||} \tag{6}$$

with

$$\vec{G}_{||} \equiv \vec{g} = n \vec{a}_1 + k \vec{a}_2 \tag{7}$$

Also, because the experimenter measures only elastically scattered electrons

the energy of the scattered electrons is conserved; these two conservation laws uniquely define the allowed outgoing beams $\vec{k}_f = \vec{k}(g)$

$$\begin{aligned}\vec{k}(g) &= (\vec{k}(g)_{||}, \vec{k}(g)_{\perp}) \\ &= \left(\vec{k}_{i||} + \vec{g}, -\sqrt{\frac{2mE}{\hbar^2} - (K(g)_{||})^2} \right)\end{aligned}\quad (8)$$

which can be labelled $\vec{k}(h,k)$ to define the Miller indices h,k of the spots they produce on a fluorescent screen. Measurement of the direction and energy of an emerging beam defines its reciprocal lattice vector; then the positions of atoms on the surface can be determined.

B. Quantitative Measurements

The LEED experimenter measures the electron-solid reflectivity,

$$I_g(E) = \frac{\vec{j}_s(\vec{k}_f)_{\perp}}{\vec{j}_i(\vec{k}_i)_{\perp}} \quad (9)$$

which is the ratio of scattered electron current $\vec{j}_s$ with outgoing wavevector $\vec{k}_f = \vec{k}(g)$ to incident electron current $\vec{j}_i$ with wavevector $\vec{k}_i$. The experimenter produces plots of $I_g(E)$ versus energy E , with

$$E = \frac{\hbar^2}{2m} \vec{k}_i^2 \quad (10)$$

for each measured beam with wavevector $\vec{k}_f$; such plots of the reflectivity are called Intensity versus Energy spectra.

Quantitative measurements of intensity versus energy spectra of the reflected beams can be analyzed to give detailed information about positions of atoms near the surface. The electron scattering depends on both the scattering properties of each atom in the solid and also the positions of these atoms. Thus to extract structural information from the data one

needs a microscopic model of the electron-atom interactions. To be useful, the model must be good enough that the error in the predicted intensities produced by its deficiencies are less than the resolution required to distinguish between different surface structure models. The model of the electron-solid interaction has three distinct components and can be formulated as an interaction Hamiltonian H with^{2/}

$$H = K + H_{e-I} + H_{e-e} \quad (11)$$

The first term represents the kinetic energy of the LEED electron; the other two represent the electron's interaction with charges in the solid. The electron-ion term, H_{e-I} , represents the interaction with the ion's nuclear charge and tightly bound ion core electrons. This interaction produces elastic scattering because electrons are so tightly bound to the massive nucleus that intermediate excitation or ionization effects are small. Beyond the classical atomic radius the atoms appear neutral so the cross-section is comparable with the geometric area of the atom. The electron-electron term, H_{e-e} , represents interaction with the delocalized electrons in the solid and it produces spatially isotropic scattering. When the LEED electron is outside the sample, this interaction creates an image force whose effect on the electrons is slight; usually its effect is neglected because it acts like a step potential which slightly refracts the electrons trajectory. Within the solid, part of the interaction is equivalent to the ordinary contact potential which has a complicated many-electron origin.

The many-body electron-electron interaction effectively reduces the energy of the free electron while in the solid and gives it a finite lifetime at this energy. In other words, this interaction produces an inelastic nearly isotropic scattering: correlation and exchange lower the energy of the electron; plasmon creation and Auger processes contribute to a finite

lifetime of the electron at any given energy. Thus, in the actual calculation we will replace the electron-electron interactions by an optical model^{2/} approximation and assume a complex, constant self energy $\Sigma(E)$.

The vibrational properties of the solid have been omitted in the microscopic Hamiltonian. Thus, we shall do a calculation strictly valid only at $T = 0$. Because the finite temperature calculation produces no new insight into the ordinary LEED experiment which we consider, we shall include temperature effects phenomenologically in the microscopic theory to be discussed later.

Attempts at quantitative LEED analysis were made as early as 1930 when Morse^{9/} produced a wavefunction matching approach based on the Bloch wave approach developed by Bethe^{10/}; wavefunctions for free electrons (without damping) were matched at the surface to outgoing waves assuming a unit amplitude incoming wave. Later, Slater^{8/} introduced the electron damping as a complex, optical potential to reproduce the width of the Bragg-like peaks in the data.

Multiple-scattering of the electrons was included in calculations made after the resurgence of LEED experiments in the late 60's, mainly spurred by availability of good vacuum systems. McRae^{11/} attempted a multiple-scattering calculation by applying Darwin's theory of X-rays to calculate the self-consistent multiply-scattered electron wavefunction.^{12/} Unfortunately, neither his theory nor Beeby's transition matrix approach to the theory included inelastic collisions so both approaches overestimated multiple-scattering effects.^{13/} The effect of inelastic collisions in the wavefield approach of McRae was introduced by Capart; similarly, inelastic collisions were incorporated into Beeby's theory by Duke and Tucker.^{14,15/} Progress in the field since then has been extensively reviewed in the last ten years.^{1-3/}

III. THEORY

A. The Model

The overall goal in the section is to relate the electron-solid reflectivity $I_g(E)$, which depends on the scattered current $\vec{J}_s(\vec{k}_f)$, to a microscopic model of the electron-solid interaction. We shall produce a multiple-scattering theory which depends on not only structural information, mainly the positions of single atoms at the surface, but also on non-structural information, mainly single-atom scattering phase shifts and the electron mean free path. During this development we shall generate the qualitative physics; which has already been discussed, and a single-scattering kinematic theory which is similar in spirit to the sandwich single reflection model. The scattered current can be related to the microscopic Hamiltonian via the transition operator as follows. The current,

$$\vec{J}_s = \langle \psi_s | -\frac{i\hbar}{m} \nabla | \psi_s \rangle, \quad (12)$$

depends on the state $|\psi_s\rangle$ to which the electron scatters. This state is given by Lippmann-Schwinger equation:^{16/}

$$|\psi\rangle = |\phi\rangle + G(E)V|\psi\rangle, \quad (13)$$

where

$$G(E) = \lim_{\epsilon \rightarrow 0^+} (E - H_0 + i\epsilon)^{-1}. \quad (14)$$

The state $|\psi\rangle$ at energy E is a sum of the initial unperturbed state $|\phi\rangle$ controlled by Hamiltonian H_0 plus the state $G(E)V|\psi\rangle$ scattered by the interaction V . Actually, the incoming electron is represented by $|\phi\rangle$ and the outgoing scattered electron is given by $G(E)V|\psi\rangle$. In most scattering experiments the transition amplitude $\langle\phi|T|\phi\rangle$, defined as $\langle\phi|V|\psi\rangle$, governs the physics. For instance, it appears in the well-known Golden Rule ^{16/}

$$1/\tau = \frac{2\pi}{\hbar} |\langle \psi_f | V | \phi_i \rangle|^2 \delta(E_f - E_i) \quad (15)$$

used to calculate transition probability $1/\tau$ of transition from an initial state $|\phi_i\rangle$ to a final state $|\psi_f\rangle$. By formally solving Eq. (13) we have

$$|\psi_f\rangle = (1 - GV)^{-1} |\phi\rangle \quad (16)$$

then

$$\begin{aligned} \langle \phi | V | \psi \rangle &= \langle \phi | V (1 - GV)^{-1} | \phi \rangle \\ &\equiv \langle \phi | T | \phi \rangle \end{aligned} \quad (17)$$

which defines

$$T = V(1 - GV)^{-1} = V + GVT \quad (18)$$

Formally $T|\phi\rangle = V|\psi\rangle$ so the reflected portion of the initial state $|\phi\rangle$ is $|\psi_s\rangle = GT|\phi\rangle$.

The Hamiltonian H which controls the electron-solid interaction can be separated into non-directional scattering term H_0 and a directional scattering term V . The terms in the Hamiltonian H have been discussed and defined in Equation (11) which is

$$H = K + H_{e-I} + H_{e-e} \quad (19)$$

The kinetic energy K and electron-electron interaction H_{e-e} effectively cause the electron to behave as a free particle, with energy E and a finite lifetime, controlled by a Hamiltonian H_0 defined as

$$H_0 = T + H_{e-e} \quad (20)$$

Because LEED scattering usually does not depend on detailed properties of H_{e-e} , it is always replaced by a complex K -independent, spatially uniform

self energy $\Sigma(E)$. Thus, for an electron with initial kinetic energy E , its energy within the solid becomes $E - \Sigma(E)$. The interaction which causes directional scattering is due to the static crystal potential and can be written as a sum of potentials centered at atomic sites R_n :

$$V = \sum v(r - R_n) \equiv \sum v_n \quad (21)$$

Throughout the theoretical development we consider the atoms to be fixed at equilibrium positions ($T = 0$); later we shall introduce the effect of lattice vibrations in an ad hoc way via a Debye-Waller factor originating from an isotropic scattering model.^{3/}

Having defined the LEED problem, we now proceed to solve it in essentially two stages. First, we calculate the electron-solid reflectivity assuming no inter-site electron scattering--the kinematic or single scattering model. The salient points in the derivation are: (i) Momentum conservation and consequences of energy conservation follow naturally from the model; (ii) the single-site transition matrix is determined by single-atom phase shifts, and (iii) reflection boundary conditions are explicitly introduced. Second, we go beyond the single-site approximation and compute the inter-site multiple scattering contributions to the single-site transition matrices--this produces equations which we must solve iteratively by computer.

B. Single Scattering

To a very good approximation, the incident beam of electrons can be regarded as a free-particle state $|\vec{k}_i\rangle$ with experimentally specified initial wavevector $\vec{k}_i$. It is convenient to compute the transition matrix in such a plane-wave basis because the outgoing wave $|\psi_s\rangle = GT|\vec{k}_f\rangle$ also has a well defined wavevector. Thus, we concentrate on decomposing T into plane-wave components centered at individual lattice sites.

The translation operator U_n allows us to express the individual site transition operator terms with respect to a single origin so that later portions of the calculation can be done with an angular momentum defined at unique origin. We define U_n by its action in the coordinate representation

$$U_n |r\rangle = |r - R_n\rangle \quad (22)$$

with the lattice vectors R_n defined by Eqs. (1)-(3) in terms of components $\parallel$ and $\perp$ to the surface.

We develop some properties of the translation operator which will be used later. First, we define an operator O to be at the origin if

$$O = \int d^3r, d^3r' |\vec{r}\rangle \langle \vec{r}| O |\vec{r}'\rangle \langle \vec{r}'| \quad (23)$$

Then the operator centered at the lattice site R_n is

$$O_n = U_n O U_n^\dagger \quad (24)$$

Also, by using the definition

$$\langle \vec{r} | \vec{k} \rangle = (2\pi)^{-3/2} e^{i\vec{k} \cdot \vec{r}} \quad (25)$$

we can easily obtain

$$U_n |\vec{k}\rangle = e^{i\vec{k} \cdot \vec{R}_n} |\vec{k}\rangle \quad (26)$$

Now we can write the transition operator as a sum of contributions from each site in crystal. Because the potential is a sum of identical potentials centered at the various lattice sites

$$V(r) = \sum v_n \quad (27)$$

we can rewrite Eq. (18) as:

$$T = \sum_n v_n + \sum_n v_n G T. \quad (28)$$

From this equation we can unambiguously define

$$T = \sum_n T_n \quad (29)$$

with

$$T_n = v_n + v_n G T. \quad (30)$$

We shall attempt to express the n^{th} transition operator for the solid in terms of the transition operator τ_n of an isolated atom defining:

$$\tau_n = v_n + v_n G \tau_n \quad (31)$$

or

$$\tau_n = (1 - v_n G)^{-1} v_n \quad (32)$$

We find that τ_n sums up all multiple scatterings at the atom located at a single lattice site R_n . It gives the exact elastic scattering properties of an isolated atom at position R_n . Now let us rewrite Eq. (30) as

$$T_n = v_n + v_n G T_n + \sum_{\substack{n' \\ n' \neq n}} v_n G T_{n'} \quad (33)$$

Then

$$(1 - v_n G) T_n = v_n + v_n \sum_{\substack{n' \\ n' \neq n}} G T_{n'} \quad (34)$$

or

$$T_n = \tau_n + \tau_n \sum_{\substack{n' \\ n' \neq n}} G T_{n'} \quad (35)$$

In this equation, the first term represents the complete intra-site scattering at the atom sitting at R_n ; the second term represents the complete

inter-site scattering from all other atoms at sites $R_{n'}$, propagated by G , and rescattered by the atom at R_n . At this point we can assemble the elements of the transition operator in a plane wave basis. The incident wave will be labelled by $\vec{k}_i$; the final state plane waves elements will be related to $\vec{k}_i$. Using Eqs. (1)-(3), (24), (26) and (29) we can write

$$\begin{aligned} \langle \vec{k} | T | \vec{k}_i \rangle &= \sum_n \langle \vec{k} | U_{n\parallel} T_{n\perp} U_{n\parallel}^\dagger | \vec{k}_i \rangle \\ &= \sum_n \langle \vec{k} | e^{+i(\vec{k}-\vec{k}_i) \cdot \vec{\rho}_{n\parallel T_{n\perp}}(n_{\parallel})} | \vec{k}_i \rangle \end{aligned} \quad (36)$$

in which we translate to an origin within each sheet of atoms but $(n_{\parallel})$ distinguishes between atoms in a sheet. Now we use two-dimensional periodicity of the system: atoms in a sheet labelled by $n_{\perp}$ are assumed chemically identical. Therefore, we can extract

$$\sum_n e^{i(\vec{k}-\vec{k}_i) \cdot \vec{\rho}_{n\parallel}} = \frac{(2\pi)^2}{A} \delta(\vec{k}_{\parallel} - \vec{k}_{i\parallel} - \vec{g}) \quad (37)$$

in which δ is the Dirac delta function and A is the unit cell area. This lattice sum is zero unless

$$\vec{k}_{\parallel} = \vec{k}_{i\parallel} + \vec{g}, \quad (38)$$

$\vec{g}$ is the two-dimensional reciprocal lattice vector defined in Eq. (7). This equation means that electron momentum parallel to the surface is conserved modulo $\vec{g}$. Finally, we can write

$$\langle \vec{k} | T | \vec{k}_i \rangle = \sum_{n_{\perp}} \langle \vec{k} | T^{(n_{\perp})} | \vec{k}_i \rangle e^{i(\vec{k}-\vec{k}_i) \cdot \vec{z}_{n_{\perp}}} \frac{(2\pi)^2}{A} \delta(\vec{k}_{\parallel} - \vec{k}_{i\parallel} - \vec{g}) \quad (39)$$

in which all the atoms have been translated to a common center but atoms in different sheets are assumed different so and their single-site transition matrices are labelled by $(n_{\perp})$.

The outgoing scattered wave depends on the boundary conditions assumed for the propagator G , and one must distinguish between Fraunhofer and Fresnel diffraction conditions.^{17/} Quite often in solid-state physics one assumes Fraunhofer diffraction conditions--the dimensions of the diffracting object are small compared to the wavelength of the scattered particle, λ , and the distance, d , to the observer. More precisely, if an area with radius R scatters coherently, Fraunhofer conditions are applicable when $R^2 \ll \lambda d$; otherwise one must use Fresnel conditions.

For Fraunhofer diffraction conditions one has

$$\langle \vec{r} | G | \vec{r}' \rangle \rightarrow \frac{e^{i\mathbf{K} \cdot (\vec{r} - \vec{r}')}}{|\vec{r} - \vec{r}'|} \quad (40)$$

where $\vec{r}'$ ranges over the physical extent of the target; thus far from the target the scattered current will have the form

$$\frac{|f(\theta)|^2}{r^2} \quad (41)$$

with $\cos\theta = \hat{\mathbf{K}}_f \cdot \hat{\mathbf{K}}_i$. For LEED, the coherent patches of a crystalline solid surface are usually large enough that Fresnel boundary conditions apply. For $E \sim 100\text{eV}$, $\lambda \sim 10^{-10}\text{m}$ and a typical observer distance of $d = 0.25\text{m}$. Fresnel conditions apply if $R \geq 0.5 \times 10^{-5}\text{m}$.

Although a good sample area of this size can easily be prepared it is not guaranteed; one must make sure the coherently scattering portion of the sample, that which has no steps or other defects, is as large as possible to avoid ambiguity about boundary conditions used in the theory.

In agreement with LEED convention, we choose Fresnel boundary conditions on the outgoing scattered wave.^{18/} Thus when computing the scattered state we must explicitly retain the translational periodicity of the surface. The scattered state can be written as

$$G(E) T|\vec{k}_i\rangle = \int d^3\vec{q} \frac{|\vec{q} \times \vec{q}| T|\vec{k}_i\rangle}{E - \frac{\hbar^2 q^2}{2m} - \Sigma(E)} \quad (42)$$

by using Eq. (14) to write the propagator as

$$G(E) = \int d^3\vec{q} \frac{|\vec{q} \times \vec{q}|}{E - \frac{\hbar^2 q^2}{2m} - \Sigma(E)} \quad (43)$$

in which we have replaced H_{e-e} by $\Sigma(E)$. For convenience we define

$$\frac{\hbar^2 K^2}{2m}(E) \equiv E - \Sigma(E) \quad (44)$$

Inserting Eq. (39) into (42) we obtain

$$G(E) T|\vec{k}_i\rangle = \frac{2m}{\hbar^2} \frac{(2\pi)^2}{A} \sum_{\vec{g}} \int d\vec{q}_{\perp} \frac{\langle \vec{k}_{i\parallel} + \vec{g}, \vec{q}_{\perp} | T^{(n_{\perp})} e^{i(\vec{k}_i - \vec{q}) \cdot \vec{z}_{n_{\perp}}} | \vec{k}_{i\parallel}, \vec{k}_{i\perp} \rangle}{K^2(E)_{\perp} - q_{\perp}^2} \quad (45)$$

Evaluation of the integral gives

$$G(E) T|\vec{k}_i\rangle = \sum_{\vec{g}} \sum_{n_{\perp}} |\vec{k}^-(\vec{g})\rangle T^{(n_{\perp})}(\vec{k}^-(\vec{g}), \vec{k}^+(0)) e^{i(\vec{k}^+(0) - \vec{k}^-(\vec{g})) \cdot \vec{z}_{n_{\perp}}} \quad (46)$$

in which we define the sheet reflection amplitude by

$$T^{(n_{\perp})}(\vec{k}^-(\vec{g}), \vec{k}^+(0)) \equiv \frac{i(2\pi)^3 m}{\hbar^2 A K(\vec{g})_{\perp}} \langle \vec{k}^-(\vec{g}) | T^{(n_{\perp})} | \vec{k}^+(0) \rangle \quad (47)$$

with

$$\begin{aligned} \vec{k}^{\pm}(\vec{g}) &\equiv (\vec{k}(\vec{g})_{\parallel}, \pm \vec{k}(\vec{g})_{\perp}) \\ &\equiv \left(\vec{k}_{i\parallel} + \vec{g}_{\perp}, \pm \sqrt{\frac{2m}{\hbar^2} (E - \Sigma(E)) - \vec{k}(\vec{g})_{\parallel}^2} \right) \end{aligned} \quad (48)$$

The experimenter measures the electron-solid reflectivity, which is a ratio of outgoing to incoming current densities normal to and just outside the surface (See Eq. (9)):

$$I_g(E) = \frac{J_s(\vec{k}^-(g))_{\perp}}{J_i(\vec{k}^+(0))_{\perp}} \quad (49)$$

By using Eqs. (12), (46), and (47), the reflectivity can be rewritten as:

$$I_g(E) = \frac{K^{\text{ext}}(g)_{\perp}}{K^{\text{ext}}(0)_{\perp}} |R(E, g)|^2 \quad (50)$$

with the reflection amplitude

$$R(E, g) = \sum_{n_{\perp}} T^{(n_{\perp})}(\vec{k}^-(g), \vec{k}^+(0)) e^{i\vec{Q}(g) \cdot \vec{z}_{n_{\perp}}} \quad (51)$$

defined as a sum of atomic sheet reflection amplitudes times a factor which depends on the atomic sheet position and momentum transfer

$$\vec{Q}(g) = \vec{k}^-(g) - \vec{k}^+(0) \quad (52)$$

The normal momentum external to the surface is

$$K^{\text{ext}}(g)_{\perp} = \left(\frac{2mE}{\hbar^2} - K_{\parallel}^2(g) \right)^{\frac{1}{2}} \quad (53)$$

Implicitly we have here ignored electron reflection by the abrupt change in crystal potential at the surface; other workers have found that considering the effect of this barrier has little effect on the LEED spectra.^{19/}

Before solving for the complete transition matrix, we shall approximate it by neglecting all inter-site scattering; this is called the kinematical or single-scattering approximation. The scattering properties of each atom will be introduced via elastic scattering phase shifts $\delta_l(E)$ which depend on angular momentum $\hbar l$. The angular momentum representation $|KL\rangle$ with $L = (l, m)$ is related to the plane-wave representation $|\vec{k}\rangle = |\hat{k}K\rangle$ by

$$|\vec{k}\rangle = \sum_L |KL\rangle Y_L(\hat{k}) \quad (54)$$

in which $\hat{K}$ is the direction of $\vec{K}$.^{16/} Then, making the approximation $T_n \approx \tau_n$ in Eq. (52), we replace $\langle \vec{K}^-(\vec{g}) | T^{(n)} | \vec{K}^+(0) \rangle$ by

$$\langle \vec{K}_f | \tau | \vec{K}_i \rangle = \sum_{LL'} Y_L^*(\hat{K}_f) \langle K_f L | \tau | K_i L' \rangle Y_{L'}(\hat{K}_i) \quad (55)$$

in which we have suppressed the label $n_{\perp}$ for chemically different atoms and renamed the plane-wave states. Using the normalization condition^{16/}

$$\langle K_f L | K_i L' \rangle = \delta_{LL'} \frac{2}{K_i} \delta(K_f^2 - K_i^2), \quad (56)$$

we can get

$$\langle K_f L | \tau | K_i L' \rangle = \frac{\hbar^2}{m K_i} \delta(E - E') \langle L | \tau | L' \rangle. \quad (57)$$

Next, from the relationship^{14/}

$$\langle L | S - 1 | L' \rangle = (e^{2i\delta_L(E)} - 1) \delta_{LL'} = -2\pi i \delta(E - E') \langle L | \tau | L' \rangle \quad (58)$$

between the S-matrix and the single-site transition matrix we obtain, using Eqs. (55) and (57)

$$\langle \vec{K}_f | \tau | \vec{K}_i \rangle = - \frac{\hbar^2}{4\pi m} f(\theta) \quad (59)$$

where the scattering amplitude has the usual definition

$$f(\theta) = \frac{1}{2iK(E)} \sum_L (2L+1) (e^{2i\delta_L(E)} - 1) P_L(\cos\theta) \quad (60)$$

and

$$\cos\theta = \hat{K}_f \cdot \hat{K}_i \quad (61)$$

Inserting Eqs. (47), (51) and (59) into Eq. (50) we obtain the electron-solid reflectivity, $I_g(E)$, in terms of the atomic scattering amplitudes $f^{(n_{\perp})}(\theta)$ and atomic sheet positions $Z_{n_{\perp}}$

$$I_{\vec{g}}(E) = \frac{K_{\text{ext}}(\vec{g})_{\perp}}{K_{\text{ext}}(0)_{\perp}} \left| \sum_{\vec{n}_{\perp}} \frac{2\pi i f(\vec{n}_{\perp})(\theta)}{K(E)A} \exp(i\vec{Q}(\vec{g}) \cdot \vec{Z}_{\vec{n}_{\perp}}) \right|^2 \quad (62)$$

This completes the discussion of the most important physics in the LEED calculation; now we discuss the computer solution for the complete transition matrix T .

C. Multiple Scattering

To make the calculation feasible, the transition matrix equation to be solved will be formulated in terms of layer transition matrices. The alternative is to solve Eq. (35)

$$T_n = \tau_n + \sum_{n' \neq n} \tau_n G \tau_{n'}$$

in one step; the matrices required for an accurate calculation become too large to be handled on the average size computer. Thus to reduce the size of the matrices which must be handled, Eq. (35) is broken into two equations by introducing an intermediary, the transition matrix t_n for two-dimensional layers of atoms. Now we have to solve the pair of equations

$$T_{n_{\parallel}, n_{\perp}} = t_{n_{\parallel}, n_{\perp}} + \sum_{\substack{n' \\ n'_{\perp} \neq n_{\perp}}} t_{n_{\parallel}, n_{\perp}} G T_{n'_{\parallel}, n'_{\perp}} \quad (63)$$

and

$$T_{n_{\parallel}, n_{\perp}} = \tau_{n_{\parallel}, n_{\perp}} + \sum_{n'_{\parallel} \neq n_{\parallel}} \tau_{n_{\parallel}, n_{\perp}} G t_{n'_{\parallel}, n_{\perp}} \quad (64)$$

The first matrix expresses the single-site transition matrix T , with all multiple-scattering included, as a sum of all scattering between layers of atoms in the solid; the second equation expresses each layer transition matrix t as a sum of all intra-layer scattering between identical atoms within that layer.

Let us solve for the layer transition matrix first; ultimately, we need it in a plane-wave basis but the atomic transition matrices are in an angular-momentum basis; thus we first translate to a common origin by using the translation operator U_n . Then Eq. (65) can be written as

$$t = \tau + \sum_{n'' \neq n} \tau U_{n''}^+ G U_{n''} t U_{n''-n}^+ \quad (65)$$

in which the layer index (n) is implicit. By operating on both sides with $\langle \vec{K} |$ and $| \vec{K}_1 \rangle$ and canceling identical spherical harmonic terms, we can write the equation in angular momentum representation

$$\tilde{t} = \tilde{\tau} + \tilde{\tau} \tilde{G} \tilde{t} \quad (66)$$

with

$$\tilde{t} = \sum_{L,L'} |L\rangle t_{L,L'} \langle L'| \quad (67)$$

$$\begin{aligned} \tilde{\tau} &= \sum_{L,L'} |L\rangle \tau_{L,L'} \langle L'| \\ &= \sum_{L,L'} |L\rangle \frac{i\hbar^2}{2\pi m K(E)} (e^{2i\delta_L(E)} - 1) \delta_{L,L'} \langle L'| \end{aligned} \quad (68)$$

and

$$\tilde{G} = \sum_{L,L'} |L\rangle G_{L,L'}'' \langle L'| \quad (69)$$

The sum over atoms and the phase factor from $U_{n''-n}^+$ have been absorbed into the intra-sheet propagator

$$G_{L,L'}'' = \sum_{n'' \neq n} \int d^3K d^3K' \langle KL | U_{n''}^+ G U_{n''} | K'L' \rangle e^{i\vec{K} \cdot (\vec{\rho}_{n''} - \vec{\rho}_{n'})} \quad (70)$$

and G is the electron propagator defined in Eq. (43).

In Eq. (70), the integral can be performed analytically and the sum converges very rapidly because the finite mean free path of the electron causes successive terms to drop off exponentially. Then we have

$$G_{L,L'}'' = \sum_{L''} \sum_{\substack{n \\ n \neq 0}} i^{\ell''} h_{\ell''}^{(1)}(\vec{k}(E) \cdot \vec{\rho}_n) \times C(L L'' L') Y_{L''}(\hat{\rho}_n) \exp(i\vec{k}' \cdot \vec{\rho}_n) \quad (71)$$

where $h_{\ell}^{(1)}$ is a Hankel function of the first kind and $C(L L'' L')$ is a Slater coefficient.^{1/} Given phase shifts $\delta_{\ell}(E)$ and the positions of atoms within the layer, Eq. (67) can be solved by computer to give the layer transition matrix $t_{L,L'}$, defined in Eq. (68).

Knowing the layer matrices and atomic sheet separations, the transition matrix for the entire solid can be computed. Because the quantity actually needed in Eq. (47) is $\sum_n G T_{n,n}$ we multiply Eq. (63) throughout by G and sum over atoms to produce:

$$\sum_n G T_{n,n} = \sum_n G t_{n,n} + \sum_n G t_{n,n} \sum_{\substack{n' \\ n' \neq n}} G T_{n',n'} \quad (72)$$

This can be expressed as a matrix equation by using Eq. (46) and defining matrix elements of GT and Gt in which $\vec{k}', \vec{k} \in \{\vec{k}^{\pm}(\vec{g})\}$

$$T^{(n_{\perp})}(\vec{k}', \vec{k}) = \frac{i(2\pi)^3 m}{\hbar^2 A} \frac{\langle \vec{k}' | T^{(n_{\perp})} | \vec{k} \rangle}{K'} \quad (73)$$

and

$$\begin{aligned} t^{(n_{\perp})}(\vec{k}', \vec{k}) &= \frac{i(2\pi)^3 m}{\hbar^2 A} \frac{\langle \vec{k}' | t^{(n_{\perp})} | \vec{k} \rangle}{K'} \\ &= \frac{i(2\pi)^3 m}{\hbar^2 A} \sum_{L'L} \frac{Y_{L'}^*(\hat{k}') t_{L'L} Y_L(\hat{k})}{K'} \end{aligned} \quad (74)$$

in terms of the layer transition matrix elements defined in Eq. (67).

By canceling phase factors resulting from translations perpendicular to the surface we obtain

$$T^{(n_{\perp})}(\vec{k}, \vec{k}') = t^{(n_{\perp})}(\vec{k}, \vec{k}') + \sum_{\vec{k}'' \in \{\vec{k}^+(g)\}} \sum_{n_{\perp}' \neq n_{\perp}} t^{(n_{\perp})}(\vec{k}, \vec{k}'') T^{(n_{\perp})}(\vec{k}'', \vec{k}') \times e^{i\vec{k}'' \cdot (\vec{z}_{n_{\perp}'} - \vec{z}_{n_{\perp}})} \quad (75)$$

a matrix equation which must be solved by use of a computer.

The fundamental equations we have produced (Eqs. (47), (50) and (51)) relate the observed LEED spectrum to the transition matrix of the solid:

$$I_{\vec{g}}(E) = \frac{k_{\text{ext}}(\vec{g})_{\perp}}{k_{\text{ext}}(0)_{\perp}} \left| \frac{(2\pi)^3 \text{im}}{\hbar^2 \vec{k}(\vec{g})_{\perp}} A \sum_{n_{\perp}} \langle \vec{k}^-(\vec{g}) | T^{(n_{\perp})} | \vec{k}^+(0) \rangle e^{i\vec{Q}(\vec{g}) \cdot \vec{z}_{n_{\perp}}} \right|^2 \quad (76)$$

There are three fundamental levels of solution of this equation:

(i) the kinematic approximation in Eq. (62)--only intra-atomic scattering is included so $T^{(n_{\perp})} \rightarrow t^{(n_{\perp})}$; (ii) the single-reflection approximation to be discussed separately--all intra-layer scattering is included but inter-layer scattering is neglected so $T^{(n_{\perp})} \rightarrow t^{(n_{\perp})}$; and (iii) the computer solution of Eqs. (63) and (64) to be discussed next--all intra-atomic and inter-atomic scattering is included.

The transition-matrix equations which include all inter-site multiple scattering involve such large matrices that they can only be solved by use of a computer. Equation (66), for the layer transition matrix, has matrices of dimension 30×30 which can be solved exactly, within computer accuracy, by the computer once the single-site matrices are specified. The second, Eq. (75) for the total transition matrix for the solid in terms of layer transition matrices, usually is solved by iterative techniques because its size makes it difficult to solve directly. This matrix has dimension $N \times N \times M$, N is the number of plane waves used, about 50, and

M is the number of layers used in the thick slab approximation to the solid, about 10. Thus, unless one uses iterative methods, one must handle a three-dimensional matrix with 25,000 elements. Two frequently used iterative methods, which we used for the multiple scattering calculation, are Layer Doubling and Renormalized Forward Scattering.^{1/}

The reflectivity of a solid composed of sheets of atoms can be computed two sheets at a time until enough sheets are included that it converges. The method, called Layer Doubling, is illustrated by application to two identical sheets of atoms, separated by a distance d, characterized by reflection, $\mathcal{R}$, and transmission, $\mathcal{T}$, amplitudes

$$\mathcal{R}_{g',g} = t^{(n_1)}(\vec{k}(\vec{g}), \vec{k}(\vec{g})) e^{i(\vec{k}(\vec{g}') - \vec{k}(\vec{g}))d/2} \vec{k}(\vec{g}') \cdot \vec{k}(\vec{g}) < 0 \quad (77)$$

$$\mathcal{T}_{g',g} = \left[t^{(n_1)}(\vec{k}(\vec{g}'), \vec{k}(\vec{g})) + \delta_{\vec{g}', \vec{g}} \right] e^{i(\vec{k}(\vec{g}') - \vec{k}(\vec{g}))d/2} \vec{k}(\vec{g}) \cdot \vec{k}(\vec{g}') > 0 \quad (78)$$

The reflection amplitude $\mathcal{R}^{(2)}$ (see Fig. 4) of these two sheets is

$$\begin{aligned} \mathcal{R}^{(2)} &= \mathcal{R} + \mathcal{T} \mathcal{R} \mathcal{T} + \mathcal{T} \mathcal{R} \mathcal{R} \mathcal{R} \mathcal{T} \\ &= \mathcal{R} + [1 - \mathcal{R} \mathcal{R}]^{-1} \mathcal{T} \end{aligned} \quad (79)$$

This method is exact for the number of atomic sheets included but it is desirable to approximate it because several steps (4 to 5), each involving inversion of $N \times N$ matrices ($M \sim 50$), are required.

A useful approximation, called Renormalized Forward Scattering, allows the electron to scatter a finite number of times between a finite number of atomic sheets until the reflection amplitude converges. The method works because the mean free path of the electron attenuates long distance contributions to the reflection amplitude.

Fig. 4 By computing the reflection amplitude 2 sheets at a time we can successively double the thickness of the slab used to represent a solid. In principle, this method is exact for a slab of finite thickness but in practice it is much more time-consuming than more approximate methods such as Renormalized Forward Scattering.

$$R^{(2)} = R + TRT + TRRTT$$

$$R^{(4)} = R^{(2)} + \dots$$

.....

In the calculation, the electron beam amplitude between atomic sheets is computed iteratively in successive passes into and out of the solid. The beam amplitudes between atomic sheets numbered i and $i+1$ for beams labelled $\vec{g}$ can be denoted by $a_i(\vec{g})$. Initially,

$$a_i(\vec{g}) = 0 \quad (80)$$

and

$$a_0(0) = 1, \quad (81)$$

which denotes an incoming beam of unit amplitude. The amplitude between sheets i and $i+1$ will be a sum of transmitted amplitude $T(\vec{g}, \vec{g}') a_i(\vec{g}')$ from the i^{th} sheet plus the reflected amplitude $R(\vec{g}, \vec{g}') a_{i+1}(\vec{g}')$ from the $i+1^{\text{th}}$ sheet. Calculation of incoming beam amplitude is halted at the I^{th} sheet when $a_I(\vec{g}) \leq \epsilon$, $\epsilon = 10^{-3}$. Following the beam out of the solid, the amplitudes $a_i(\vec{g})$, $i \leq I$ can be recomputed; the inward and outward calculations are repeated until the new $a_0(\vec{g})$ is different by less than ϵ .

We solve the inter-sheet multiple scattering equation (see Eq. (75)) with a method which combines the exactness of Layer Doubling with the rapidity of Renormalized Forward Scattering. First the exact transition matrix of a sandwich of atoms is computed by successive application of Layer Doubling; then Renormalized Forward Scattering is used between sandwiches. These sandwiches are chosen large enough that Renormalized Forward Scattering accurately converges.

At this point the LEED problem is completely defined in terms of atomic scattering properties, via the phase shifts, and atomic positions. Next, we define the model used to obtain phase shifts, at LEED electron energies, from Hartree-Fock wavefunctions.

D. Phase Shifts

Scattering phase shifts of the single-site portion of the crystal potential $V(r)$ determine each single-site transition matrix. In general, the elastic scattering of any particle, such as an electron, by any "finite range" potential can be characterized by phase shifts $\delta_l(E)$; then the current of elastically scattered particles is proportional to the target's cross-section,

$$\frac{d\sigma}{d\Omega} = |f(\theta)|^2 \quad (82)$$

where we have

$$f(\theta) = \frac{1}{k_f} \sum_l (2l+1) \exp(i\delta_l(E)) \sin(\delta_l(E)) P_l(\cos\theta) \quad (83)$$

and

$$\cos\theta = \hat{k}_f \cdot \hat{k}_i \quad (84)$$

Here the particle has initial momentum $\hbar\vec{k}_i$ and scatters into a state with momentum $\hbar\vec{k}_f$.

The phase shifts are determined by the asymptotic behavior of the scattered electron wavefunction $\psi(\vec{r})$. By solving the Schrödinger equation $H_0\psi(\vec{r}) = E\psi(\vec{r})$ with

$$H_0 = -\frac{\hbar^2 \nabla^2}{2m} + v(r) \quad (85)$$

one obtains the wavefunction $\psi(\vec{r})$ of an electron in a central potential $v(r)$. At large r where $v(r) = 0$, the radial wavefunction of an electron with angular momentum $\hbar l$ can be written as:

$$\lim_{r \rightarrow \infty} \psi(r) = \exp(iKr - l\pi/2 + \delta_l(E))/Kr \quad (86)$$

compared to a free-electron wavefunction, the electrons have a phase shift of $\delta_l(E)$.

The crystal potential $V(\vec{r})$ is a sum of potentials $v(\vec{r})$ generated from free atom wavefunctions. In principle, a self-consistent calculation should be done to obtain the one-electron potential which scatters the LEED electron; in practice no one does that. Because ion-cores of atoms do most of the scattering in LEED, any potential which accurately reproduces the very attractive ion-core portion of the crystal potential can be used for LEED calculations. Furthermore, other workers^{2,20/} have shown that the LEED results are insensitive to charge redistribution due to bonding of atoms in the solid. Thus, to be consistent with our spirit of simplicity, we ignore the valence-charge redistribution and construct the crystal potential as a sum of neutral atom potentials, which overlap each other, obtained from tabulated free atom wavefunctions.^{21/} In addition, we write the crystal potential as a sum of non-overlapping muffin-tin potentials.

For LEED calculations the non-overlapping muffin-tin potential is superior to the overlapping potential because fewer phase shifts are required to describe its scattering properties. Classically, the maximum angular momentum $\hbar l_{\max}$ partial wave scattered at energy $E = \hbar^2 K^2 / 2m$ by a potential of range R is $l_{\max} \leq KR$. Thus, because the non-overlapping potential has the shorter range, $l_{\max}$ for this potential will be smaller.

Inclusion of high order phase shifts should be avoided, if possible, because such phase shifts are most affected by errors in the large- r region of the potential. The quasi-classical approximation^{22/} to the phase shift demonstrates how the potential controls the phase shifts. The approximate phase shift is

$$\begin{aligned}
\delta_{\ell}(E) &= \int_{r_1}^{R_{\text{muff}}} [E - \ell(\ell+1)/r^2 - v(r)]^{1/2} dr - \int_{r_0}^{R_{\text{muff}}} [E - \ell(\ell+1)/r^2]^{1/2} dr \\
&\approx \int_{r_1}^a [E - \ell(\ell+1)/r^2 - v(r)]^{1/2} dr - \int_{r_0}^a [E - \ell(\ell+1)/r^2]^{1/2} dr \\
&\quad - \int_a^{R_{\text{muff}}} \frac{v(r) dr}{[E - \ell(\ell+1)/r^2]^{1/2}}
\end{aligned} \tag{87}$$

and the second form allows us to examine the effect of the potential in the large- r limit: $a \leq r \leq R_{\text{muff}}$ with $a > r_0 > r_1$ and r_0 is the classical turning point without the potential and r_1 is the turning point with $v(r)$. In the large ℓ limit the last term in the eikonal controls the phase shift because $[E - \ell(\ell+1)/r^2] \rightarrow 0$ for large ℓ . Thus, for large ℓ the uncertain region of the potential determines the phase shift; therefore, large ℓ phase shifts should be avoided because they are (i) sensitive to approximations and (ii) time-consuming to include in the calculation.

An exchange potential between the scattered electron and the atom was not included in the one-electron potential $v(r)$ we used. For an external electron with wavefunction $\psi(r)$ and an atomic electron with wavefunction $\phi(r)$ the usual Hartree-Fock exchange potential,

$$V_{\text{HF}} = \iint \phi(\vec{r}') \psi(\vec{r}) \frac{1}{|\vec{r} - \vec{r}'|} \phi(\vec{r}) \psi(\vec{r}') d\vec{r} d^3\vec{r}',$$

is small because the free LEED and tightly bound atomic electrons do not overlap very much. A local-density exchange potential $\sim \rho(\vec{r})^{1/3}$ with $\rho(\vec{r}) = |\phi(\vec{r})|^2$, such as the Slater exchange potential,^{23/} is certainly not valid because it is derived by approximating the electronic system as a free-electron gas near equilibrium i.e. all states up to the Fermi energy

are occupied. This could only be valid if the LEED electron energy were similar to bound electron energies. Most importantly, neither the Hartree-Fock nor the local density exchange potentials have much effect on LEED electron phase shift.^{20/}

The actual procedure we used for calculation of phase shifts from tabulated wavefunctions is presented in Appendix A.

IV. SURFACE SANDWICH REFLECTIVITY

A. Motivation

At this point we return to the central theme--Relating the surface dependent features, which vary slowly with energy, in LEED experimental and theoretical spectra. The surface sandwich reflectivity spectrum contains all the surface dependent features in the theoretical spectra; it is calculated exactly in the first step of our multiple scattering method. However, we actually use the single reflection approximation to calculate the surface sandwich reflectivity, because it rapidly provides physical insight about atomic sheet spacing within the surface sandwich. To compare surface dependent features with the surface sandwich reflectivity, a smoothing method which averages over short momentum transfer components in the spectra is applied to the experimental data. The smoothing method and a quantitative test of the quality of fits between theory and data are described in the data analysis section.

The layered transition-metal-dichalcogenides, TiS_2 and TiSe_2 , both have a natural sandwich structure (See Fig. 5). In particular, TiS_2 consists of covalently, thus strongly, bonded three-sheet S-Ti-S sandwiches joined by a weak van der Waals band. Atoms within each sheet are hexagonally arranged but successive sheets displace so that each Ti atoms sits in an octahedral environment produced by the nearest S atoms. The bulk crystal structure is 1T (D_{3d}^3 space group) for both compounds. The bulk Ti-S sheet separation is $a = 1.442 \text{ \AA}$; the inter-sandwich Ti-Ti separation is $b = 5.6904 \text{ \AA}$.^{24,25/} The same discussion applies to TiSe_2 which has a bulk Ti-S₂ sheet separation of $a = 1.502 \text{ \AA}$ and an inter-sandwich separation of $b = 6.008 \text{ \AA}$.^{24,26/}

Fig. 5 The unit cells of TiS_2 stack to form sandwiches of thickness $2a$ separated by a distance b (Van der Waals gap). At the surface the sandwich thickness is $2a'$ and the sandwich separation is b' .

Surface sandwich
Van der Waals gap

From comparison of surface sandwich with van der Waals bond strength one would expect layered transition metal dichalcogenide surfaces would not distort from an ideal surface. All the sandwiches are strongly bonded compared with the weak van der Waals bond joining them, thus the absence of a van der Waals bond on the outside of the surface sandwich should have negligible effect on it. Such a surface, with no atomic rearrangement after it is created by removing sheets of atoms, is called ideal.

Based on a microscopic model, the surface sandwich thickness of TiSe_2 has been predicted to be very related to charge density wave formation near the surface.^{27/} Using a self-consistent ab initio method, the sandwich thickness was shown to be related to formation of a charge density wave via the sandwich thickness dependence of the Fermi surface, which is thought to control the ability to form a charge density wave. The calculation indicates that a contraction of the surface sandwich should be associated with the observed charge density wave. Thus, it is worthwhile to obtain the surface structure from the LEED data, taken at room temperature, to determine whether the surface sandwich thickness at room temperature differs from its predicted contracted thickness below the charge density wave transition temperature $T_c \approx 195\text{K}$. Thus this analysis would be a first step in the investigation of the temperature dependence of the surface sandwich for temperatures ranging from room temperature to below T_c .

Do TiS_2 and TiSe_2 have the same surface structure? Certainly as shown by Zunger's calculation, there should be a very sensitive relation between surface structure and surface electronic properties.^{27/} Because charge density waves extending to the surface have been observed in TiSe_2 but not in TiS_2 ,^{28/} one would expect their electronic properties to be slightly different and thus they may have slightly different expansion or

contraction of the surface sandwich.

To compare the two

we analyzed LEED data taken above T_c in the same way for both compounds.

The TiS_2 data was taken by B. J. Mrstik^{29/} and the TiSe_2 data was taken by W. Fabian and F. C. Brown.^{28,30/}

B. Single Reflection

The electron-solid reflectivity $I_{\vec{g}}(E)$ for electrons at energy E in a beam labelled by a surface reciprocal lattice vector $\vec{g}$ is given by Eq. (50):

$$I_{\vec{g}}(E) = \frac{K_{\vec{g}}^{\text{ext}}(E)}{K_{\vec{g}}^{\text{ext}}(0)} |R(E, \vec{g})|^2 \quad (88)$$

in terms of the reflection amplitude $R(E, \vec{g})$ of the solid which we approximate as a sum of single reflection amplitudes from the sheets of atoms in the solid.

The reflection amplitude is a function of atomic distances and sheet reflection amplitudes. To be specific we discuss TiS_2 but the model for TiSe_2 is equivalent. The Ti-S atomic distance, which fixes the sandwich thickness, is $\vec{a}'$ in the surface sandwich and the Ti-Ti atomic distance, which fixes the sandwich separation, is $\vec{b}'$ for the two outer sandwiches. The bulk Ti-S and Ti-Ti distances are denoted by $\vec{a}$ and $\vec{b}$, respectively. The Ti-sheet reflection amplitude is

$$R_{\text{Ti}}(\vec{g}) = \sum_{L, L'} \frac{Y_L^*(\hat{K}^-(g)) t_{L, L'} Y_L(\hat{K}^+(0))}{AK(g)_{\perp}} \quad (89)$$

in which $t_{L, L'}$, which is the exact transition matrix for the Ti sheet, has been obtained from the Ti atom phase shifts by solving Eq. (66). Similarly, from the S-atom phase shifts we obtain $R_S(\vec{g})$.

The reflection amplitude for the solid is a sum of two contributions; the first one from the surface sandwich and the second one from the rest of the solid together with a phase factor. Thus

$$R(E, \vec{g}) = R(\vec{g}, \vec{a}') + \exp(i\vec{Q}(\vec{g}) \cdot \vec{b}) [1 - \exp(i\vec{Q}(\vec{g}) \cdot \vec{b})]^{-1} R(\vec{g}, \vec{a}) \quad (90)$$

with

$$R(\vec{g}, \vec{a}) = \exp[i\vec{Q}(\vec{g}) \cdot \vec{a}/z] \{R_{T1}(\vec{g}) + 2R_s(\vec{g}) \cos[\vec{Q}(\vec{g}) \cdot \vec{a}]\} \quad (91)$$

where $R(\vec{g}, \vec{a})$ is the single-reflection approximation to the sandwich reflection amplitude in terms of the momentum transfer,

$$\vec{Q}(\vec{g}) = \vec{K}^+(\vec{g}) - \vec{K}^+(\vec{0}) \quad , \quad (92)$$

when an incoming electron of wavevector $\vec{K}^+(\vec{0})$ scatters to a reflected beam with wavevector $\vec{K}^+(\vec{g})$.

For the surface sandwich, the scattered intensity,

$$|f_{\vec{g}}(E, \vec{a}')|^2 = \frac{K_{\perp}^{\text{ext}}(\vec{g})}{K_{\perp}^{\text{ext}}(\vec{0})} |R(\vec{g}, \vec{a}')|^2 \quad (93)$$

depends on the sandwich thickness $a' = \vec{a}'_{\perp}$ but not on the larger "bulk" distances $\vec{b}$ or $\vec{b}'$. Furthermore, pronounced inelastic collision effects via a short mean free path attenuate the exponential phase factors in Eq. (90); thus, the surface sandwich controls the reflection amplitude and we have approximately

$$I_{\vec{g}}(E) \approx |f_{\vec{g}}(E, \vec{a}')|^2 \quad (94)$$

Realistic inelastic collision effects result in mean free paths short enough that the slowly varying envelope of $I_{\vec{g}}(E)$ corresponds to the outer sandwich reflectivity

$$|f_{\vec{g}}(E, \vec{a}')|^2 \quad (95)$$

The single reflection method becomes especially simple when applied to an ideal surface, with a surface sandwich identical to those of the bulk. The ideal surface model has $\vec{a}' = \vec{a}$ and $\vec{b}' = \vec{b}$ so the LEED reflectivity factors into two pieces

$$I_{\vec{g}}(E) = |f_{\vec{g}}(E, \vec{a})|^2 S_{\vec{g}}(E, \vec{b}) \quad (96)$$

in terms of the form factor $f_{\vec{g}}(E, \vec{a})$ and the structure factor

$$S_{\vec{g}}(E, \vec{b}) = |1 - \exp(i\vec{Q}(\vec{g}) \cdot \vec{b})|^{-2} \quad (97)$$

which depends only on the sandwich separation $\vec{b}$. As a function of energy, S consists of Bragg peaks broadened as a result of the finite electron mean free path. The sandwich form factor f depends on forces and atoms within a single sandwich and varies more slowly with energy than the structure factor S (see Fig. 6). Such separations of scattering rates into structure and form factors are characteristic of single scattering approximations and are well known in neutron, X-ray, and high energy electron scattering.^{17/}

The essential insight from this simple analysis is that surface structural information controls the surface sandwich reflectivity $|f|^2$, an envelope factor which modulates the bulk-Bragg peaks; most of the essential physics of surface atom rearrangement can be deduced by quantitatively comparing calculations of the surface sandwich reflectivity $|f|^2$ with the modulating envelope of an experimental spectrum. Before discussing the specific application to TiS_2 and TiSe_2 , we develop a quantitative method for comparing the envelopes of LEED spectra.

Fig. 6 The ideal surface single reflection LEED intensity $I(E) = |f(a)|^2 S(b)$ together with $|f(a)|^2$ and $S(b)$. Peak positions depend on the rapidly varying structure factor $S(b)$ while peak heights depend on slowly varying $|f(a)|^2$.

C. LEED Data Analysis

Using the insight gained from the single reflection analysis, we realize that a procedure for comparing LEED theory with data must compare the surface structure dependent features, which are energetically slowly varying, in the spectra. Unfortunately such a fitting scheme does not already exist; some approaches compare least square differences in Bragg peak positions^{18/} while others actually concentrate on energetically rapidly varying details in the spectra by comparing derivatives of intensities.^{31,32/} Our approach will be to emphasize moments, or integrals, of intensities to compare LEED spectra. Before describing the method, let us consider an example which demonstrates the pitfalls of concentrating on the fine-structure details in a LEED fit.

The purpose of a test of a fit of LEED theory to data is to determine when one has chosen the correct surface structure model. However, the fit also depends on non-structural information which we assume to be correct but in practice is often not very well known. Suppose that we use the correct surface structure but an electron mean free path which is too short in a fit to LEED data. For such a case both the theory and data, schematically shown in Fig. 7(a), consist of a series of uniformly spaced rectangles with the same area but the theory "peaks" are wider than the data "peaks."

The error in the fit, $\Delta I(q)$, is the difference between the theoretical and experimental intensities; it is plotted in Fig. 7(b). Clearly, $\Delta I(q)$ has large derivatives because of the rapidly varying details but the slowly varying difference is zero. A conventional test which considers details in the fit would reject this surface structure. Obviously, in the absence of a theory which guarantees complete knowledge of non-structural properties such as the mean free path, we need a new way of fitting LEED theory to data.

- Fig. 7
- (a) "Data", $I(q)$, fitted by theory which uses a model with correct surface structure but too short an electron mean-free path.
- (b) The difference between data and theory, when plotted as a function of momentum transfer q , varies rapidly compared with the spacing between peaks.

Extraction of surface structure from LEED data requires quantitative comparisons of smoothed LEED theoretical and experimental spectra. Maintaining the emphasis on single-scattering features in the spectra, we transform all spectra to functions of momentum transfer $q = Q(\vec{g})_{\perp}$ rather than energy (when convenient we will omit the beam label g).

Now an average over distances long compared to a characteristic surface distance X_s corresponds to an average over momentum transfer shorter than $1/X_s$. The normalized smoothed spectrum, $\langle I(q) \rangle_{X_s}$, is defined by

$$\langle I(q) \rangle_{X_s} = 2X_s \int_{q-1/X_s}^{q+1/X_s} I(q') dq' \quad (98)$$

The mean or average intensity involves an average over all distances; therefore, $X_s = 0$ and $I_{ave} = \langle I(q) \rangle_0$.

A quantitative comparison of theoretical and experimental spectra is necessary because LEED spectra contain so much information that a visual comparison cannot be used to judge the overall fit. Thus, we define a quantitative least squares test which we call the discrepancy index:

$$D_{X_s} = \langle \langle I_e(q) - I_t(q) \rangle_{X_s}^2 \rangle_0 / \langle (\langle I_e(q) \rangle_{X_s} - \langle I_e(q) \rangle_0)^2 \rangle_0 \quad (99)$$

It is a measure of the average squared difference between the smoothed experimental, $I_e(q)$, and theoretical, $I_t(q)$, spectra. The term in the denominator normalizes D_{X_s} so that $0 \leq D_{X_s} \leq 4$. Ideally, one adjusts the surface structure model until $D_{X_s} = 0$; in practice this is never attained so we must investigate the behavior of D_{X_s} as one approaches a good fit to the data.

To motivate the understanding of the behavior of D_{X_s} when applied to LEED analysis, we treat a simple solvable model first. We shall analyze

the behavior of D_{X_S} when applied to the calculation of the LEED spectrum of a surface sandwich consisting of two atomic sheets separated by a distance d . Ignoring the slowly varying angle dependent factor and energy dependence of the sheet reflection amplitudes r , we can write the scattered intensity as

$$I_e(q) \cong 2 + 2 \cos qd \quad (100)$$

Suppose we attempt to fit this data with a surface model which has a sheet spacing of $d+\Delta$; thus, the error in the structure model is Δ . If the experiment and the theory are compared over a range $q_i < q < q_f$, the discrepancy index will be

$$D(\Delta) = 2 \left[1 - \frac{\sin q_f \Delta - \sin q_i \Delta}{(q_f - q_i) \Delta} \right] \quad (101)$$

This index, which is plotted in Fig. 8, starts at $D(0) = 0$, overshoots $D = 2$ and finally oscillates about the asymptotic value $D(\infty) = 2$. For this simple model one can determine Δ in one trial if $\Delta \leq \pi/q_f$ because q_f is determined by the range of the data. However, the quantitative test alone cannot distinguish between different surface structure models when $\Delta > \pi/q_f$. Thus differences between poor fits, which can be ascertained by visual inspection, cannot be quantitatively distinguished.

The simple two-sheet model simulates very well the behavior of D_{X_S} as a function of Δ , the error in Ti-S (or Ti-Se for TiSe_2) sheet spacing in the surface sandwich of TiS_2 . For this case, $D_{X_S}(\Delta)$ cannot be analytically computed, just as LEED intensities cannot, because of its dependence on: (i) multiple-scattering effects; (ii) attenuation due to the electron mean free path; and (iii) energy dependent sheet reflection coefficients. However, D_{X_S} will have the same asymptotic behavior and similar oscillatory

Fig. 8 The discrepancy index $D(\Delta)$ varies rapidly for small Δ ; at large Δ it asymptotically approaches $D(\infty) = 2$. The parameters, $q_i = 4$ and $q_f = 7$, for the case shown here represent the momentum transfer range of a typical LEED experiment.

behavior as $D(\Delta)$ for the two-sheet model. Thus for $\Delta \leq \pi/q_f$ the index D_{X_S} will be useful in assigning bounds on Δ because in the region D_{X_S} will rapidly vary with changes in Δ i.e., surface structure model. For LEED work we adopt a pragmatic approach to the analysis which requires two steps: (i) visually compare the spectra to reject theoretical spectra which obviously do not fit the data, and (ii) use the discrepancy index D_{X_S} to distinguish the best from the good theoretical fits. From experience, satisfactory LEED fits require $D_{X_S} < 1$.

V. RESULTS

In this section we apply the sandwich single reflection method to surface structure determination of TiS_2 and TiSe_2 . In both cases the surface sandwich reflectivity $|f|^2$ for the undistorted or ideal surface is compared to the experimental data using the simple scaling with sandwich thickness of the surface sandwich spectrum for each beam. The surface model is adjusted to fit the surface sandwich reflectivity $|f_g(E)|^2$ to the envelope of the data. The surface dependent features, which are then quantitatively compared, are extracted from both theoretical and experimental spectra by a smoothing method. By quantitative comparison of both the surface sandwich spectra and also the conventional multiple-scattering spectra to the data, we find that for both TiS_2 and TiSe_2 the nearly ideal, with a perhaps slightly expanded surface sandwich, surface model fits the data better than models for which the sandwich expands or contracts significantly.

A. TiS_2

The surface sandwich reflectivity for TiS_2 is compared with data for the first order beams in Fig. 6. The slowly varying reflectivity $|f(a)|^2$, which depends only on sandwich thickness a , and the (10) beam data are in excellent agreement (Fig. 9a); for this beam the comparison can be made directly because the data vary relatively slowly with energy. For the (01) beam the data and $|f(a)|^2$ show a more typical agreement (Fig. 9b); the data exhibit some Bragg peaks, such as the double peak near 50 eV, but the modulation envelope of the data agrees well with $|f(a)|^2$.

To determine the surface structure of a solid, one must compare the surface sandwich reflectivity $|f(a)|^2$ of various relaxed-surface models with the envelope of the data. The effect of surface relaxation in TiS_2 on the (10) beam spectrum can be seen in Fig. 10, which compares $|f(a)|^2$

Fig. 9 Comparison of form factors squared $|f|^2$ with data for the (a) (10) and (b) (01) beams. Note that the modulating factors $|f(a)|^2$ contain the principal spectral features.

Fig. 10 Dependence of form factor squared $|f|^2$ on surface structure models. The surface sandwich Ti-S separation a is varied by $\pm 5\%$. Note that compression of the surface lattice constant leads to "expansion" of the energy dependence of $|f|^2$.

for models with $\pm 5\%$ relaxation of the surface sandwich with that for the ideal surface. The sheet reflection coefficients vary sufficiently slowly with energy that the form factor peak positions still have a smooth scaling with energy; expansion of the sandwich moves the peaks closer together and to lower energy.

To illustrate extraction of the surface structure features from data we apply the bulk-average $\langle I(q) \rangle_{X_S}$ to the TiS_2 (01) beam data already shown in Fig. 9b; all features dependent on distances larger than $X_S = 3a_0$ are averaged out. A comparison of the spectra, as a function of momentum transfer q , in Fig. 11 shows that all the slowly varying features in the averaged data agree with features in $|f(a)|^2$. In particular, the double peak in the data, at about 50 eV, has been replaced by a single peak, in agreement with the corresponding single peak in $|f(a)|^2$.

The surface sandwich reflectivity, corresponding to several different models involving changes in the surface sandwich thickness a' and van der Waals distance d' , was compared to the smoothed data with $X_S = 3a_0$ to remove features corresponding to distances longer than X_S . Most of the fits could be rejected by visual comparison; the remainder were quantitatively tested by computing the discrepancy index D_{X_S} , essentially a sum of the squared difference between the two sets of curves, after the data were smoothed. Figure 12 shows D_{X_S} plotted for the three surface models shown in Fig. 10 (ideal sandwich and $\pm 5\%$ expansion). The sum of the D_{X_S} for the first, second, and third order beams considered exhibits a minimum for the ideal sandwich model; the values of D_{X_S} for the individual beams have minima for slightly different surface sandwich expansion (0% or -5%) and different shifts in the constant potential $\text{Re } \Sigma$, shown in the figure. Often the best fits of different beam spectra occur for different surface structure models; we will also find this to be the case for TiSe_2 . From the author's

Fig. 11 Comparison of the smoothed TiS_2 (01) beam theoretical and experimental spectra as a function of momentum transfer. Smoothing does not affect the appearance of this spectrum because it, like the other TiS_2 beam spectra, had few rapidly varying features associated with bulk structure.

Fig. 12 Discrepancy index D_{X_S} as a function of TiS_2 surface sandwich thickness for the three first and second order beams compared with the surface sandwich reflectivity $|f(a)|^2$. The total discrepancy index for the five first, second, and third order beams is also shown. The constant shift in energy required to minimize the discrepancy index for each case is listed next to its corresponding data point.

experience with LEED analysis this agreement between theory and experiment for TiS_2 is excellent.

To verify the surface structure and to validate the surface single reflection approach to TiS_2 we present in Fig. 13 a comparison between it and a full multiple-scattering calculation. Clearly, they agree very well. Characteristic of all such comparisons, the multiple scattering spectra have slightly rounded features mainly due to multiple scattering which occurs even away from the "Bragg" peaks. Finally, the multiple scattering spectra for the three models discussed previously are quantitatively compared with the data; Fig. 14 shows that the agreement is similar to the agreement of single reflection spectra to the data. Both calculations agree with an ideal surface as the correct surface model.

B. TiSe_2

The power of the surface sandwich method was needed to compare LEED spectra for TiSe_2 . The data exhibited details which drastically varied from one experimental trial to another while the theoretical spectra contained details which varied with different non-structural input such as Debye temperature, phase shifts, and mean free path. Fortunately, the smoothed portions of the data, which contained surface structure dependent features, were very reproducible. Also, the smoothed theoretical curves followed quite nicely the appearance of their form factors $|f(a)|^2$. Thus one could meaningfully compare the sandwich reflectivity with the averaged experimental spectra.

To analyze the TiSe_2 spectra we first compare the surface sandwich reflectivity to the smoothed experimental data. Figure 15 shows, as a function of momentum transfer for the three lowest-order beams, data

Fig. 13 Comparison between a full multiple scattering calculation, and the single reflection calculation (which has intra-sheet multiple scattering). The agreement demonstrates that the fast single reflection calculation is ideal for selecting a model of surface relaxation.

Fig. 14 Discrepancy index D_{X_S} as a function of surface sandwich thickness for the three first and second order beams compared with the multiple scattering theory. Otherwise similar to Fig. 12. Both the surface sandwich reflectivity and complete multiple-scattering theory pick 0% expansion to be the correct surface structure model.

Fig. 15 Comparison of smoothed data and theory. Both the surface sandwich reflectivity $|f(a)|^2$ and the full multiple scattering theory are compared with the data.

(a) Comparison for the (10) beams.

Fig. 15 (b) Comparison for the (01) beams.

compared with a theory which assumes the surface is ideal. To diagnose the atomic sheet spacing from the figure we should think to each spectrum as a portion, about one period, of a periodic function such as $\sin^2 qa$ with a the outer sandwich sheet spacing. Can we modify a to match all the peaks and valleys in the two spectra? By inspection of Fig. 15 (a) and (b), the answer is no for the two first order beams because a must be increased for the (01) beam but must be decreased or not changed to fit the (10) beam data. However, this simple analysis suggests that we should increase a , that is, expand the surface sandwich, in order to fit the large peak at about $Q = 4.5$ (75 eV) in the (01) beam data. When the spectrum of a surface sandwich expanded by 5% was compared to the data, we found, just as expected, that all peaks moved closer together and to lower energy; in particular the theory and data peaks at ~ 75 eV became more in agreement than in Fig. 15 (b). Unfortunately, then the (10) beam spectra disagreed more for this model than for the ideal surface model. Thus, based on visual comparison, both the ideal and the expanded surface sandwich models fit the data about equally well.

To attempt a choice between the two surface models, we quantitatively analyzed the fit of the surface sandwich spectrum for four models, the sandwich expanded by 0%, $\pm 5\%$, and 10%. At the same time we quantitatively compare the multiple scattering to the data for these models. Figure 16 shows a plot of the discrepancy indices as a function of surface sandwich expansion. The surface sandwich and multiple scattering indices for each beam are very similar; however, their minima correspond to slightly different surface sandwich thicknesses. The minimum discrepancy index of the surface sandwich model corresponds to 0% expansion of the surface sandwich while the minimum for the full multiple scattering calculation

Fig. 16 Discrepancy index as a function of surface sandwich thickness for the three first and second order beams compared with a multiple scattering calculation for TiSe_2 . The sum of discrepancy indices for these beams is also shown. The constant shift in energy required to minimize the discrepancy index for each case is listed next to its corresponding data point.

corresponds to 5% expansion of the surface sandwich. Also, discrepancy indices for different beams have minima corresponding to different surface sandwich expansions. Thus, one cannot unambiguously distinguish between the 0 and 5% expansion models; the plots of discrepancy index suggest that the outer sandwich slightly expands, by about 2.5%. Furthermore, considering the ambiguity in this quantitative test, the error bars on the fit should be $\sim \pm 5\%$.

VI. DISCUSSION

A. The Surface Structure

We have used the sandwich single reflection method to determine that both TiSe_2 and TiS_2 have a nearly ideal surface structure. In each case, the correct surface model was verified quantitatively by using the discrepancy index, a test which quantitatively compares the slowly varying features in the spectra. For TiS_2 , the ideal surface model produced the best fit to the spectra. The results for TiSe_2 were not as conclusive as for TiS_2 ; the nearly-ideal surface model with a surface sandwich expansion of 5% best fit the data. We estimate the error to be $\pm 5\%$ which corresponds to an error in distance of approximately $0.08 \text{ \AA}$. We base this rough estimate on two points: (i) The average discrepancy $D_3 = 1.41$ between different trials of the experiment was greater than the overall discrepancy $D_3 = 1.3$ between the theory and the data, and (ii) discrepancy indices for different beam spectra have minima at either 0% or 5% expansion of the surface sandwich.

The essence of our results for both TiS_2 and TiSe_2 is that essentially no atomic rearrangement occurs on either surface. However, the TiSe_2 data suggest that the surface sandwich expands slightly. Taken with the prediction^{27/} that a contraction of the surface sandwich must be associated with the observed charge density wave,^{29/} this suggests that surface atoms must dramatically rearrange as the surface sandwich cools from just above the charge density wave transition temperature $T_c \sim 200\text{K}$ to just below T_c . To test this hypothesis investigators could analyze LEED measurements made just above and below the transition temperature.

B. Comments About LEED Strategies

Having successfully applied the surface sandwich method to analysis of LEED data we continue examining what it can tell us about the LEED problem. First, we examine the microscopic theory to point out that uncertainty in the microscopic model for the electron mean free path greatly affects the features controlled by multiple scattering between atoms. Thus, to make reliable structural determinations one should concentrate on compounds which have mainly single-scattering features in their LEED spectra. Second, we point out what appears to be a previously unemphasized fact--experimenters should be very careful to obtain the spectral features which vary slowly with energy. Then, finally we compare our procedure with the methods of other workers who in general concentrate on all the features in a LEED spectrum.

To predict when the sandwich single reflection method will work we examine the term (see Eq. (35)), $G\tau$, which gives the amplitude of the wave scattered by a single atom in the solid. Using Eq. (40) for G and Eq. (59) for τ , the coordinate space amplitude of the wave at a nearest neighbor atom a distance $R = |\vec{r}_2 - \vec{r}_1|$ away from the first atom is essentially

$$A(\theta) = \frac{f(\theta)e^{-R/\ell}}{R} e^{iKR} \quad (102)$$

in which the real part of the complex wavevector depends on energy, $E = \frac{\hbar^2 k^2}{2m}$, and the imaginary part, $1/\ell$, depends on electron mean free path $\ell/2$.

Inspection of the multiple-scattering equation, Eq. (35), shows that multiple-scattering effects will be negligible compared with single-scattering effects if $A(\theta) \ll 1$ for all angles θ .

A correct model for the inelastic scattering becomes very important when multiple scattering effects are large compared to single scattering

effects. In this case the transition matrix for the solid will be essentially a sum of single-site terms each of which includes contributions

$$T(\theta) = f(\theta)/(1-A(\theta)) \quad (103)$$

from nearest neighbors; $T(\theta)$ is a schematic way of writing the contribution to the transition matrix from multiple scattering between nearest neighbors. Rather than attempt to examine the total transition matrix we concentrate on $T(\theta)$ which ultimately controls the multiple scattering transition matrix.

The multiple-scattering amplitude $A(\theta)$ is controlled by two factors:

i) the elastic scattering amplitude $f(\theta)$ and ii) the inelastic-scattering mean free path $\ell/2$. Clearly, multiple-scattering effects become less important if the scattering amplitude, $f(\theta)$, or the mean free path, $\ell/2$, are short compared with the distance R between atoms.

At energies which produce multiple scattering peaks, $A(\theta) \sim 1$ for some angles θ ; and the multiple scattering essentially affects $T(\theta)$ in a multiplicative way. Define $m = (1-A(\theta))^{-1}$; then

$$T(\theta) = m f(\theta) \quad (104)$$

Using the multiple scattering theory discussed previously $T(\theta)$ can be quantitatively calculated. However, suppose that ℓ , which is short, has an error $\Delta\ell \sim \ell$. To be specific we choose $A(\theta) = 0.9$, then $m = 10$; then the error $\Delta T(\theta)$ in the transition matrix will be, if $R = 5a_0$ and $\ell = 16a_0$ (mean free path $4 \text{ \AA}$),

$$\frac{\Delta T(\theta)}{T(\theta)} \approx m R \Delta\ell / \ell^2 \sim 3 \quad (105)$$

This error, due to mean free path error, is 3 times greater than the error made by neglecting multiple scattering!

Our analysis shows that reliable LEED surface structure determinations can be made only on materials which have scattering amplitudes which are small compared with interatomic distance R . For materials with large cross-sections, $|f(\theta)|^2$, multiple scattering dominates single scattering but, because of our present day imperfect models for electron mean free path, errors due to mean free path errors wash out the multiple scattering effects. The only recourse is to concentrate on solids with small atomic cross-sections for which single scattering, or single reflection, controls the intensity versus energy spectrum.

By examining electron-atom cross-sections one can assess the probability of success in a LEED surface structure determination. To make reliable structure determinations with an imperfect model for the mean free path requires that $f(\theta)/R$ be small for each of the atoms in the solid. For instance, knowing that $f(\theta)$ is proportional to the atomic radii, which decrease along rows in the Periodic Table, one would assign low reliability to a surface structure determination of an alkali metal compared with a transition metal. Similarly, a surface structure determination of a compound composed of chemically different atoms with greatly differing ionic radii might be unreliable because of the multiple-scattering induced errors made in calculating the reflection amplitude of the sheets containing the large atoms.

Having chosen the compound to investigate and knowing which features in LEED data are important, one can make some comments about data collection strategies. Usually the experimenter must take data rapidly because the sample surface deteriorates within an hour, the time needed to take a LEED spectrum. Rather than take the data while systematically incrementing the beam energy, one should take data over a wide range of energy points in

order to correctly measure the slowly varying features. Then the remaining data points should be collected until the sample shows effects of deterioration. Close attention should be directed to insuring that the equipment does not have an energy dependent current response which masks the true energy dependence of the data. Conventional data collection procedures do not emphasize the energetically slowly varying features because of their focus on peak positions.

C. Comparison With Other Approaches

The single reflection sandwich method shall be compared with two other approaches to the LEED problem. One, the Bragg envelope energy averaging method developed by Duke and Tucker, attempts to average out multiple scattering features, called multiple scattering fine structure, in the $I(E)$ spectrum. The end result is an average,^{25/}

$$M_{hk} = \int_{E_0 - \Delta/2}^{E_0 + \Delta/2} I_{hk}(E) dE \quad (106)$$

with $E_0 = 140$ eV and $\Delta = 80$ eV, of the extra beams, labelled by (hk) , produced by ordered adsorbate atoms. This average is to be compared with a similar average over a kinematic (single-scattering) theoretical spectrum. Compared with our method we see that this method, no longer used by any LEED workers, corresponds to removing information about all distances longer than $\sim 0.25a_0$ from the spectrum. No interatomic distances are this short so the method should give no information about surface structure but rather serves as a check of the absolute normalization of the beam spectrum.

Most conventional tests of the fit of LEED spectra compare Bragg peak positions rather than the modulating envelope of the Bragg peaks. One

method measures the sum of the squared differences in peak positions;^{18/}
another employs a variety of measures such as counting the number of peaks
in the two spectra which match to within a defined tolerance and computing
the mean deviation between peak positions.^{33/} A more recent method computes
the sum of the squared difference between the first energy derivatives of
the two spectra, all weighted by a factor which depends on the second
derivative.^{31,32/} Our point is that all of these features, some of which
depend on bulk positions, should match if the microscopic theory and the
data collection procedure were both correct; unfortunately, they are not
so we concentrate on extracting only the "low frequency" surface information
and ignore the noise in the spectrum.

VII. CONCLUSION

We have developed the relationship between the surface structure of a solid and its control of the energetically slowly varying features in a LEED spectra. Thus we compare LEED theory with data by comparing the reflectivity of the surface sandwich with the slowly varying envelope of the data. The surface sandwich reflectivity for the layered dichalcogenides is calculated within the single reflection approximation; thus the calculation can be done very rapidly (50 times faster than a multiple scattering calculation) and one has physical insight about the scaling of the features as the surface sandwich thickness is varied. Because this calculation is a subset of the multiple scattering calculation, the surface structure model is easily refined and verified at the end by comparing smoothed experimental and theoretical spectra.

To analyze data we developed a quantitative test which essentially measures the squared difference between smoothed spectra. The spectra, as a function of momentum transfer, are smoothed by averaging over short momentum components which correspond to reciprocals of distances long compared to surface atomic sheet separations. The overall test involves qualitative comparison of spectra to reject those which obviously do not agree and then a quantitative test to pick the surface structure model which produces the theoretical spectrum which fits the data the best.

These ideas were introduced via a discussion of an analysis of LEED data for TiS_2 and TiSe_2 , two members of the layered dichalcogenide class of compounds. We found that both of these compounds have a nearly ideal surface structure with perhaps slight expansion of the surface sandwich of TiSe_2 .

APPENDIX A

Calculation of the Potential and Phase Shifts

We describe the calculation of phase shifts from neutral atom wavefunctions. The first step is generation of the atomic potential $v_o(r)$ from tabulated atomic wavefunctions. To compress the single-site potentials into non-overlapping spheres (muffin-tins) the spherically symmetric portion of the potential due to nearest neighbor atoms is added to $v_o(r)$; the resultant potential $v(r)$ differs slightly from the atomic potential near the muffin-tin radius R_m . Then for a given energy E , the Schrödinger equation

$$H_o \psi(r) = E \psi(r) \quad (A1)$$

with

$$H_o = -\frac{\hbar^2 \nabla^2}{2m} + v(r) \quad (A2)$$

is solved for the wavefunction $\psi(r)$. Finally, $\psi(r)$ is compared to the free electron wavefunction outside the range of the potential to determine phase shifts $\delta_l(E)$. In the remainder of this section we discuss each of these steps in more detail.

The Hartree interaction potential $v_o(r)$ between an external electron and the atom is generated from tabulated wavefunctions. The atomic Hartree-Fock wavefunction is a product of Hartree-Fock orbital wavefunctions^{21/}

$$\phi_{n\ell m}(\vec{r}) = \frac{1}{r} \rho_{n\ell}(r) Y_{\ell m}(\theta, \phi) \quad (A3)$$

labelled by principal (n), azimuthal (ℓ), and magnetic (m) quantum numbers. The local electron density to be used for computation of the one-electron potential can be written as^{23/}

$$\rho(\vec{r}) = \sum_{n\ell} N_{n\ell} |\phi_{n\ell m}(\vec{r})|^2 \quad (A4)$$

with

$$N_{nl} = 2(2l+1) \quad \text{for closed orbitals} \quad (\text{A5})$$

= occupation number for open orbitals

For closed shells $\rho(\vec{r})$ is spherically symmetric; for open shells $\rho(\vec{r})$ must be symmetrized. Using Poisson's law we can write

$$v_o(\vec{r}) = e^2 \int \frac{\rho(\vec{r}')}{|\vec{r}-\vec{r}'|} d^3\vec{r}', \quad (\text{A6})$$

the interaction potential $v_o(r)$ produced by a symmetrized electron density

$$\rho(r) = \frac{1}{4\pi} \int \rho(\vec{r}) d\Omega. \quad (\text{A7})$$

The resulting symmetric potential, which now includes the potential $-e^2 z/r$ due to the nucleus, can be written in terms of an effective charge $z(r)$:

$$v_o(r) = -e^2 z(r)/r \quad (\text{A8})$$

with

$$z(r) = z - \int_0^r \sigma(x) dx - r \int_r^\infty \frac{\sigma(x)}{x} dx \quad (\text{A9})$$

and

$$\sigma(r) = 4\pi r^2 \rho(r). \quad (\text{A10})$$

The effective charge has the following asymptotic behavior:

$$\text{i) } \lim_{r \rightarrow 0} z(r) = z, \quad \text{the nuclear charge} \quad (\text{A11})$$

and

$$\text{ii) } \lim_{r \rightarrow \infty} z(r) = Q, \quad \text{the net charge of the atom} \quad (\text{A12})$$

(Q=0 in our work).

The integrals in Eq. (A9) could be analytically performed because the wavefunctions were expressed as a sum of Slater-type orbitals:

$$\phi_{n\ell m}(\mathbf{r}) = \sum_p \chi_{p\ell m}(\vec{r}) c_{n\ell p} \quad (\text{A13})$$

with

$$\chi_{p\ell m}(r, \theta, \phi) = R_{\ell p}(r) Y_{\ell m}(\theta, \phi) \quad (\text{A14})$$

and

$$R_{\ell p}(r) = [(2n_{\ell p})!]^{-1/2} (2\xi_{\ell p})^{n_{\ell p} + 1/2} r^{n_{\ell p} - 1} \exp(-\xi_{\ell p} r) \quad (\text{A15})$$

The wavefunctions for each atomic orbital were specified by the tabulated numbers $n_{\ell p}$, $\xi_{\ell p}$ and $c_{n\ell p}$.

The speed and accuracy of the calculation of the potential (and the phase shifts) can be improved by using a non-linear radial mesh grid adjusted to each atom. This grid has closely spaced points ($h \approx .002a_0$, a_0 is the Bohr radius) near the origin where the effective charge varies rapidly; it becomes uniform with more widely spaced points ($h \approx 0.190$) far from the origin ($r > R_{TF}$ with $R_{TF} \sim .5a_0$) where the potential varies slowly. In between these extremes the grid spacing h doubles every N ($N = 10$) grid points. With such a grid the potential out to about $3a_0$ can be represented by about 70 grid points.

The non-overlapping muffin-tin potentials were computed by associating with each atomic site a symmetric potential which is a sum of the potential from the atom at that site plus the symmetric portion of the potential from the nearest neighbor atoms. Thus the effective charge $z(r)$ at the site of an atom with effective charge $z_0(r)$ is

$$z(r) = z_0(r) + \frac{N}{R} \int_{R-r}^{R+r} z_n(x) dx \quad r < R \quad (\text{A16})$$

in which the second term is the effective charge due to N nearest neighbors each with an effective charge $z_n(r)$, a distance R away from the atom.

The Numerov method is a three-point iterative method for solving a second order differential equation.^{34/} We apply it to solve the radial Schrödinger equation, with units $\hbar = 2m = \frac{e^2}{2} = 1$, for a central potential

$$v(r) = -2z(r)/r \quad (A17)$$

$$\frac{d^2 \chi_\ell}{dr^2} + \left[E + \frac{2z(r)}{r} - \frac{\ell(\ell+1)}{r^2} \right] \chi_\ell = 0 \quad (A18)$$

for

$$R_\ell(r) = \chi_\ell(r)/r, \quad (A19)$$

the radial wavefunction with energy E and azimuthal quantum number ℓ . This equation can be rewritten as

$$\frac{d^2 \chi_\ell}{dr^2}(r) = f_\ell(r) \chi_\ell(r) \quad (A20)$$

with

$$f_\ell(r) = \frac{\ell(\ell+1)}{r^2} - \frac{2z(r)}{r} - E. \quad (A21)$$

By Taylor expansion of $\frac{d^2 \chi_\ell}{dr^2}$ and χ_ℓ on a grid with points separated by distance h we can get the basic Numerov equation:

$$[1-T_\ell(r+h)]\chi_\ell(r+h) + [1-T_\ell(r-h)]\chi_\ell(r-h) = [2+10T(x)]\chi_\ell(r) - \frac{h^6}{240} \frac{d^6 \chi_\ell}{dr^6} + \dots \quad (A22)$$

with

$$T_\ell(r) = \frac{h^2}{12} f(r) \quad (A23)$$

Neglecting the sixth-order error term, the radial wavefunction $\chi_\ell(r)$ can be obtained for all points on a grid by iteration after specification of starting conditions at r_0 and r_0+h .

The starting conditions for integration of the Schrödinger equation from the origin are obtained by a Taylor series expansion of the potential near the origin. Because phase shifts are computed for continuum states of specified energy E the Schrödinger equation behaves stably when integrated outward in contrast to the behavior when bound state wavefunctions are computed.

The starting values of $\chi_\ell(r)$ near the origin are obtained by a power series solution of the radial equation.^{34/} The effective charge can be expanded as $z(r) = z + v_c r + O(r^3)$ in which $v_c = \lim_{r \rightarrow 0} [z(r) - z]/r$. Near the origin,

$$\chi_\ell(r) = N r^{\ell+1} \left[1 - \frac{N}{\ell+1} r + \alpha r^2 - \beta r^3 + O(r^4) \right] \quad (A24)$$

with

$$\alpha = \{2z^2 - (\ell+1)[2v_c - E]\} / 2(2\ell+3)(\ell+1) \quad (A25)$$

$$\beta = z\{2z^2 - (3\ell+4)[2v_c - E]\} / 6(\ell+1)(\ell+2)(2\ell+3) \quad (A26)$$

and N is a normalization constant. The starting conditions $\chi_\ell(h)$ and $\chi_\ell(2h)$ are obtained from this solution.

The phase shifts $\delta_\ell(E)$ at each energy are determined by the logarithmic derivative $\gamma_\ell = \frac{dR_\ell(r)/dr}{R_\ell(r)}$ evaluated at $r = a$ outside the range of the potential. This is a standard way of relating the radial wavefunction to the general free particle solution

$$rR_\ell(r) = A_\ell [\cos \delta_\ell j_\ell(Kr) - \sin \delta_\ell n_\ell(Kr)] \quad (A27)$$

Then

$$\tan \delta_\ell = \frac{Kj'_\ell(Ka) - \gamma_\ell j_\ell(Ka)}{Kn'_\ell(Ka) - \gamma_\ell n_\ell(Ka)}, \quad \text{with } K = \sqrt{E} \quad (A28)$$

contains derivatives of the regular, $j'_\ell(Ka)$, and irregular, $n'_\ell(Ka)$, spherical Bessel functions at $r = a$. The derivative of the radial wavefunction

$R_\ell(r)$ is evaluated with the Numerov technique:

$$h\chi'_\ell(r) = [1-T_\ell(r+h)]\chi_\ell(r+h) - [1-T_\ell(r-h)]\chi_\ell(r-h) + \frac{7h^5}{360} \frac{d^5\chi_\ell}{dr^5} \quad (A29)$$

The computer routine has been tailored to calculation of phase shifts due to electron-atom scattering. The radial grid is optimized for each calculation; the energy grid usually ranges from 50 to 250 ev with a spacing of 2 ev. In addition the routine has been tested by computing phase shifts caused by the following potentials:

$$\begin{aligned} \text{i) square well} \quad v(r) &= -V_0 \quad r \leq a \\ v(r) &= 0 \quad r > a \end{aligned} \quad (A30)$$

and

$$\text{ii) Hultén} \quad v(r) = -V_0 / [\exp(Kr) - 1] \quad (A31)$$

The computer generated phase shifts agree with the analytic values to within 0.5% of the total phase shift.

APPENDIX B

Computer Routines

This section describes the procedure, using the computer routines listed here, required to reproduce the LEED calculations. Omitted are the routines MSMAT, XMAT, SPHRM4, ZGE, and ZSU which were used to generate sheet reflection coefficients from atomic phase shifts; these routines are listed in the Appendix of Pendry's book on LEED theory.^{1/}

The basic calculation uses tabulated Hartree-Fock wavefunctions for atoms in the solid as the primary input to compute the theoretical LEED spectra which are to be compared with experimental spectra. Beginning with an atomic potential for isolated atoms generated by routine ZOFR from the Hartree-Fock wavefunctions, the potential for atoms in the solid is generated by routine ZOFNB which incorporates the effect of charge overlap of nearest-neighbor atoms. Phase shifts describing electron scattering from this potential are calculated using the routine PHS; these phase shifts are used in the routines listed in Pendry's book to compute reflection amplitudes of sheets of these atoms.

The stored reflection amplitudes are read by the routine LEED which calls SREF to calculate the surface sandwich reflectivity. The alternative, a full multiple scattering calculation, can be done by calling the routine PERTA which uses Renormalized Forward Scattering to compute multiple scattering between sandwiches of atoms whose reflection amplitudes are computed by the routine LRPT. Finally, the smoothed theoretical and experimental spectra are quantitatively compared by the routine FIT.

```

C      ROUTINE ZOFR
C      THIS ROUTINE GENERATES A POTENTIAL  $V(R)=Z(R)/R$  FROM
C      SLATER ORBITALS. NDEGN,NLP,ZETA AND C ARE OBTAINED
C      FROM A TABLE SUCH AS CLEMENTI OR BAGUS, GILBERT AND
C      Roothaan.
C
C      Z(R)=EFFECTIVE CHARGE.
C      R=RADIAL GRID CHARACTERIZED BY HFRST AND HLST.
C      RMUFF=R(NMUFF), THE MUFFIN-TIN RADIUS.
C      ZNUC=NUCLEAR CHARGE.
C      ZCOUL=TOTAL CHARGE OF THE ATOM.
C      RHO=UNIFORM CHARGE DENSITY.
C
C      IMPLICIT REAL*8 (A-H,O-Z)
C      DIMENSION C(4,4,10),ZETA(4,10),NLP(4,10),NDEGN(4,4)
C      DIMENSION R(200),Z(200)
C      DIMENSION PHS(6)
C      OPEN(UNIT=20,FILE='PRMTI.DAT',DIALOG)
C      OPEN(UNIT=21,FILE='ZOUT.DAT',DIALOG)
C      NMESH=200
C      MXN=4
C      NMX=4
C      MXF=10
C      Q2=2.E+0
C      Q3=3.E+0
C      Q4=4.E+0
C      QPI=3.14159265E+0
C      READ(20,6) NMUFF,ZNUC,HFRST,HLST,ZCOUL
1      FORMAT(8I2)
2      FORMAT(8F8.5)
4      FORMAT(4I2)
111     FORMAT(F9.5,6E11.5)
C
C
C      DEFINE RADIAL GRID
C      ECHAR=4.E+0
C      ESQT=SQRT(2.E+0*ECHAR)
C      AMU=.88534138E+0/ZNUC**(.1.E+0/3.E+0)
C      DH=.005E+0*AMU
C      DH=1.968503937E-3
C      DH=HFRST
C      H=DH
C      R(1)=DH
C      NF=NMESH
C      NMIN=2
10     NMAX=NMIN+9
20     DO 20 I=NMIN,NMAX
30     R(I)=R(I-1)+H
C      NMIN=NMIN+10
C      IF(NMIN+10-NMESH) 30,30,50
C      IF (HLST-H) 60,60,40

```

```

40    H=H+H
      GO TO 10
60    NF=NMIN-1
50    DO 70 I=NMIN,NMESH
70    R(I)=R(I-1)+H
      RMUFF=R(NMUFF)
C
C
113   FORMAT(8F11.5)
6     FORMAT(I8,F8.5,2E17.10,2F8.5)
8     FORMAT(10I2)
9     FORMAT(10F8.5)
11    FORMAT(7H NMUFF=,I8,7H RMUFF=,F8.5,6H ZNUC=,F8.5,
17H ZCOUL=,F8.5,5H RHO=,F8.5)
      DO 7 N=1,MXN
        READ(20,8) (NDEGN(N,L),L=1,N)
        READ(20,8) (NLP(N,INDX),INDX=1,MXP)
        READ(20,9) (ZETA(N,INDX),INDX=1,MXP)
        DO 7 L=1,N
          READ(20,9) (C(N,L,INDX),INDX=1,MXP)
7     CONTINUE
      CALL ZOFR(ZNUC,Z,R,C,ZETA,NLP,NDEGN,NMX,MXP)
C
C    INSERT A UNIFORM CHARGE DENSITY RHO INSIDE SPHERE OF
C    RADIUS RMUFF TO MAKE THE ATOM HAVE TOTAL CHARGE ZCOUL.
C
      ZDEFCT=Z(NMESH)-ZCOUL
      PRINT *,ZDEFCT
      RHO=Q3*ZDEFCT/(Q4*QPI*RMUFF**3)
      DO 100 I1=1,NMUFF
        RR=R(I1)
100    Z(I1)=Z(I1)-QPI*RHO*Q2*(RMUFF**2-RR**2/Q3)*RR
        NP1=NMUFF+1
        DO 101 I1=NP1,NMESH
101    Z(I1)=Z(I1)-ZDEFCT
        WRITE(3,11) NMUFF,RMUFF,ZNUC,ZCOUL,RHO
        WRITE(3,995)
103    WRITE(3,997) (Z(I),R(I),I=1,150)
        WRITE(21,998) HFRST,HLST
        WRITE(21,999) (Z(I),I=1,NMESH)
995    FORMAT(14H Z(R) VERSUS R )
997    FORMAT(8E13.5)
998    FORMAT(2E17.10)
999    FORMAT(8E12.5)
      CLOSE(UNIT=20)
      CLOSE(UNIT=21)
123   STOP
      END
C
      SUBROUTINE ZOFR(ZNUC,Z,R,C,ZETA,NLP,NDEGN,NMAX,PMAX)
C    IMPLICIT REAL*8 (A-H,Q-Z)
C

```

```

C      THIS ROUTINE GENERATES Z(R) FROM SLATER ORBITALS.
C
      INTEGER P1,P2,PMAX,P1D,P2D
      DIMENSION R(200),Z(200)
      DIMENSION SNORM(4,4,10)
      DIMENSION C(4,4,10),ZETA(4,10),NLP(4,10),NDEGN(4,4)
      COMMON /GAMMA/GAMA(11)
      DO 8 I=1,200
8      Z(I)=0.E+0
      GAMA(1)=1.E+0
      DO 1 I=1,10
1      GAMA(I+1)=GAMA(I)*FLOAT(I)
      DO 10 N=1,NMAX
      DO 10 LP1=1,NMAX
      DO 10 P1=1,PMAX
10      SNORM(N,LP1,P1)=C(N,LP1,P1)*(2.E+0*ZETA(LP1,P1))**
      1NLP(LP1,P1)*SQRT(2.E+0*ZETA(LP1,P1)/GAMA(2*NLP(LP1,P1)+1))
      DO 6 INDX=1,200
      XX=R(INDX)
      DO 5 N=1,NMAX
      DO 5 LP1=1,N
      DEGN=FLOAT(NDEGN(N,LP1))
      TOTAL=0.E+0
      DO 4 P1=1,PMAX
      DO 2 P2=1,P1
      NPWR=NLP(LP1,P1)+NLP(LP1,P2)
      ZZETA=ZETA(LP1,P1)+ZETA(LP1,P2)
      CALL SLTINT(XX,NPWR,ZZETA,RR)
      HNORM=SNORM(N,LP1,P1)*SNORM(N,LP1,P2)
2      TOTAL=TOTAL+2.E+0*RR*HNORM
4      TOTAL=TOTAL-RR*HNORM
5      Z(INDX)=Z(INDX)+DEGN*TOTAL
6      Z(INDX)=-Z(INDX)*XX+ZNUC
      RETURN
      END

C
C
C      REAL FUNCTION ZINT(X,N,A)
C      IMPLICIT REAL*8 (A-H,Q-Z)
C      COMMON/GAMMA/GAMA(11)
C      COMPUTES R**N*EXP(-A*R)/R> TO GIVE V(R)/  THUS
C      ONE OBTAINS Z(X)=X*V(X)
      FN=N
      NMIN=N-1
      ZINT=0.E+0
      IF(NMIN-1) 3,1,1
1      DO 2 I=1,NMIN
2      ZINT=ZINT+X**(N-I)/A**(I+1)*(1.E+0/GAMA(N-I)
1-FN/GAMA(N-I+1))
      ZINT=GAMA(N)*EXP(-A*X)*ZINT
3      ZINT=ZINT+GAMA(N+1)/A**(N+1)*(1.E+0-EXP(-A*X))
      RETURN

```

```

END
SUBROUTINE SLTINT(X,N,A,SINT)
C   IMPLICIT REAL*8 (A-H,O-Z)
C   COMPUTES INTEGRALS OF THE FORM:
C   INTEGRAND=X**N*EXP(-A*X)*R<**L/R>**<(L+1)>*DX
COMMON /GAMMA/ GAMA(11)
ZERO=0.E+0
IF (A-1.0E-2) 50,10,10
10  L=0
    QEXP=EXP(-A*X/2.E+0)
    K=L+1
    SINT1=ZERO
    NN=N+K
    DO 20 I=1,NN
20  SINT1=SINT1-GAMA(N+K)*X**(N-I)/(GAMA(N+K+1-I)*A**I)
    SINT1=SINT1*QEXP
    SINT1=SINT1*QEXP
    SINT1=SINT1+GAMA(N+K)/(A**(N+K)*X**K)
    KK=N-K+1
    SINT2=ZERO
    DO 30 I=1,KK
30  SINT2=SINT2+GAMA(N-K+1)*X**(N-I)/(GAMA(N-K+2-I)*A**I)
    SINT2=SINT2*QEXP
    SINT2=SINT2*QEXP
40  SINT=SINT1+SINT2
50  RETURN
END
@

```



```

C      ROUTINE ZOFNB
C      INFUT
C      ZNUC =NUCLEAR CHARGE
C      VCONST=CONST, MADLNG POTL
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON R(200),Z(200),ZOUT(1000)
      COMMON ZR(2,200),ZX(2,1000)
      DIMENSION NTYP(5),A(5),FNBR(5),NXPT(5)
      DATA NTYP/2,1,0,0,0/
      DATA A/4.5D+0,6.684D+0,0.D+0,0.D+0,0.D+0/
      DATA FNBR/3.D+0,6.D+0,0.D+0,0.D+0,0.D+0/
      OPEN(UNIT=20,DIALOG,DEVICE='DSK',FILE='ZSE20.DAT')
      OPEN(UNIT=21,DIALOG,DEVICE='DSK',FILE='ZTI20.DAT')
      OPEN(UNIT=22,DIALOG,FILE='ZNB.DAT')
      NMESH=200
      NMSHX=1000
      Q4=4.D+0
      ECHAR=4.D+0
      HX=.01D+0
      HXB3=HX/3.D+0
      Q0=0.D+0
      ZCONST=Q0
      DO 2 I=1,NMSHX
2      ZOUT(I)=Q0
      DO 3 I=1,NMESH
3      Z(I)=Q0
      READ(5,4) NTYP
      READ(5,5) A
      READ(5,5) FNBR
      WRITE(5,6) NTYP,A,FNBR
      READ(20,998) HFRST,HLST
      READ(21,998) HFRST,HLST
      READ(20,999) (ZR(2,I),I=1,NMESH)
      READ(21,999) (ZR(1,I),I=1,NMESH)
4      FORMAT(5I8)
5      FORMAT(5F8.5)
6      FORMAT(17H TYPE OF NEIGHBOR ,5I8,/,21H DISTANCE TO
1 NEIGHBOR ,5F8.5,/,21H NUMBER OF NEIGHBORS ,5F8.5)
998  FORMAT(2E17.10)
999  FORMAT(8E12.5)
      ESQT=DSQRT(2.D+0*ECHAR)
      DH=1.968503937D-3
      DH=HHFRST
      H=DH
      R(1)=DH
      NF=NMESH
      NMIN=2
10     NMAX=NMIN+9
      DO 20 I=NMIN,NMAX
20     R(I)=R(I-1)+H

```

```

      NMIN=NMIN+10
      IF(NMIN+10-NMESH) 30,30,50
30     IF (HLST-H) 60,60,40
40     H=H+H
      GO TO 10
60     NF=NMIN-1
50     DO 70 I=NMIN,NMESH
70     R(I)=R(I-1)+H
      DO 90 I=1,3
      DO 80 INC=1,NMSHX
      XX=DFLOAT(INC)*HX
      IF (A(I)-XX) 90,90,80
80     CONTINUE
90     NXPT(I)=INC
      NMAX=NXPT(1)-75
      DO 120 I=1,2
      DO 120 INC=1,NMSHX
      XX=DFLOAT(INC)*HX
      DO 100 MAX=1,NMESH
      IF(XX-R(MAX)) 110,100,100
100    CONTINUE
110    MIN=MAX-1
      ZX(I,INC)=ZR(I,MIN)+(ZR(I,MAX)-ZR(I,MIN))*(XX-R(MIN))
      1/(R(MAX)-R(MIN))
120    CONTINUE
C      WRITE(3,999) (ZX(1,I1),I1=1,1000)
C      WRITE(3,999) (ZX(2,I1),I1=1,1000)
      DO 130 N1=1,1
      N=NTYP(N1)
      NXPTF=NXPT(N1)
      Q2XA=2.D+0*A(N1)
      ZTOT=ZX(N,NXPTF)*HX*FNBR(N1)/A(N1)
      ZOUT(1)=ZOUT(1)+ZTOT
      ZCONST=ZCONST+FNBR(N1)/A(N1)*ZX(N,NXPTF)
      ZTOT=Q0
      DO 130 INC=3,NMAX,2
      MAX=NXPTF+INC-1
      MIN=NXPTF-INC+1
      ZTOT=ZTOT+HXB3/Q2XA*(ZX(N,MAX)+ZX(N,MIN)+ZX(N,MAX-2)+ZX(N,MIN+2)
      1+Q4*(ZX(N,MAX-1)+ZX(N,MIN+1)))*FNBR(N1)
      ZOUT(INC-1)=ZOUT(INC-1)+ZTOT
130    CONTINUE
      DO 135 I=3,NMSHX,2
135    ZOUT(I)=(ZOUT(I-1)+ZOUT(I+1))/2.D+0
      NHBYHX=IDINT(HX/DH)
      DO 140 I=1,NHBYHX
140    Z(I)=R(I)*ZCONST
      MP1=NHBYHX+1
      DO 160 INC=MP1,NMESH
      NM1=NMSHX-2
      DO 150 MIN=1,NM1
      XX=DFLOAT(MIN)*HX

```

```
IF(R(INC)-XX) 155,150,150
150 CONTINUE
155 MAX=MIN+1
Z(INC)=ZOUT(MIN)+(ZOUT(MAX)-ZOUT(MIN))*(R(INC)-XX)/HX
160 CONTINUE
WRITE(3,999) (Z(J),R(J),J=1,100)
DO 200 I=1,NMESH
200 Z(I)=(Z(I)+ZR(1,I))
WRITE(22,999) (Z(I),I=1,NMESH)
DO 210 I=1,700
210 ZOUT(I)=-2.D+0*(ZOUT(I)+ZX(1,I))/(HX*DFLOAT(I))
WRITE(3,999) (ZOUT(I),I=1,700)
CLOSE(UNIT=20,DEVICE='DSK',FILE='ZSE20.DAT')
CLOSE(UNIT=21,DEVICE='DSK',FILE='ZTI20.DAT')
CLOSE(UNIT=22,FILE='ZNB.DAT')
STOP
END
```

@

```

C      ROUTINE PHS
COMMENT MAIN PROGRAM FOR PHASE SHIFTS.
C      THIS ROUTINE CALCULATES PHASE SHIFTS PHS(L) FOR A POTL
C      V(R) AS A FUNCTION OF E AND L. ALSO THE SCATTERED WAVE
C      IS COMPUTED AND STORED IN WAVE(L,I) WITH X(I) THE GRID.
C      PHS=PHASE SHIFT AT ENERGY E ANG. MOM. L.
C      E=ENERGY IN RYD.
C      L=ANG. MOM.
C      Z(R)=EFFECTIVE CHARGE; POTL V(R)=Z(R)/R.
C      R(I)=RADIAL GRID; HERMAN AND SKILLMAN GRID SET BY
C      HFRST AND HLST.
C
      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION C(4,4,10),ZETA(4,10),NLP(4,10),NDEGN(4,4)
      COMMON R(200),P(200),Z(200),V(200),HF(200)
      DIMENSION PHS(6),WAVE(6,200)
      DATA AREA/38.783D+0/
C      EEMIN=50.D+0,NEND=51
      NMESH=200
      MXN=4
      NMX=4
      MXF=10
      EEMIN=50.D+0
      EEINC=2.D+0
      NEND=51
      NPHS=6
      Q2=2.D+0
      Q3=3.D+0
      Q4=4.D+0
      OPEN(UNIT=20,FILE='ZOUT.DAT',ACCESS='SEQUIN',DIALOG)
      OPEN(UNIT=21,FILE='PSDUM.DAT',DIALOG)
      OPEN(UNIT=22,FILE='WAVE.DAT',DIALOG)
      QPI=3.14159265D+0
      DO 8 I=1,NMESH
8      V(I)=0.D+0
1      FORMAT(8I2)
2      FORMAT(8F8.5)
3      FORMAT(I4,2F8.5,I4,F8.5)
4      FORMAT(4I2)
7      FORMAT(7H NMUFF=,I4,7H RMUFF=,F8.5,6H ZNUC=,F8.5,7H VMDLG=
1,F8.5,8H VCONST=,F8.5)
111  FORMAT(7E12.5)
C
C      NMUFF=POTENTIAL GOES TO VCONST AT R(NMUFF).
C      ZNUC=NUCLEAR CHARGE
C      EEMIN=FIRST ENERGY POINT IN ELECTRON VOLTS.
C      NEND=NUMBER OF ENERGY POINTS.
C      VMDLG=EXTERNAL CONSTANT POTENTIAL APPLIED TO THE SYSTEM.
C
      READ(5,3) NMUFF,ZNUC,EEMIN,NEND,VMDLG
C

```

```

C
NEPT=NEND
WRITE(21,997) NEPT,NPMS,AREA
READ(20,998) HFRST,HLST
READ(20,999) (Z(I),I=1,NMESH)
997  FORMAT(2I4,F8.5)
998  FORMAT(2E17.10)
999  FORMAT(8E12.5)
C
C
C  DEFINE RADIAL GRID
DH=HFRST
H=DH
R(1)=DH
NF=NMESH
NMIN=2
10  NMAX=NMIN+9
DO 20 I=NMIN,NMAX
20  R(I)=R(I-1)+H
    NMIN=NMIN+10
    IF(NMIN+10-NMESH) 30,30,50
30  IF (HLST-H) 60,60,40
40  H=H+H
    GO TO 10
60  NF=NMIN-1
50  DO 70 I=NMIN,NMESH
70  R(I)=R(I-1)+H
    RMUFF=R(NMUFF)
C
C  TEST ROUTINE BY SETTING NEND<0.
IF(NEND>0) GO TO 6
CALL TEST(ZNUC,VMDLG,NMUFF,RMUFF,EEMIN,NMESH,NEND)
6  CONTINUE
C
C
C  OUTPUT THE POTENTIAL
DO 75 I1=1,NMESH
RR=R(I1)
75  V(I1)=-2.D+0*Z(I1)/RR+VMDLG
    WRITE(3,112)
    WRITE(3,113) (V(I1),R(I1),I1=1,150)
112  FORMAT(3X,'V(R)',10X,'R(I)')
113  FORMAT(1X,8E12.5)
120  FORMAT(1X,7H ENERGY,30X,13H PHASE SHIFTS,/)
121  FORMAT(1X,7E13.5)
122  FORMAT(4H Z0=,E12.5,4H Z1=,E12.5,7H ALPHA=,E12.5,
16H BETA=,E12.5)
123  FORMAT(4H NF=,I4,7H NMUFF=,I4,5H NDV=,I4)
C
C
C  COMPUTE VCONST
C  VCONST ADJUSTED SO THE POTL IS ZERO AT R=RMUFF AND VCONST

```

```

C      FOR R>RMUFF.
      VCONST=2.D+0*Z(NMUFF)/R(NMUFF)
      VCONST=VCONST-VMDLG
      WRITE(3,7) NMUFF,RMUFF,ZNUC,VMDLG,VCONST
      WRITE(5,7) NMUFF,RMUFF,ZNUC,VMDLG,VCONST
C
C      PWR SERIES EXPANSION OF POTL AT R=0
C      NUCLEAR CHARGE INCLUDED
C      Z(R)=Z0+Z1*R+Z3*R*R*R+... SEE HARTREE
C      POWER SERIES EXPANSION IS INCORRECT FOR ALL TESTS SO
C      DO NOT EXPECT MUCH ACCURACY.
C      Z1=Z1-VCONST BECAUSE OF CONSTANT EXTERNAL POTL
C
      Z0=ZNUC
      Z1=(8.D+0*Z(1)-Z(2)-7.D+0*Z0)/(6.D+0*DH)
      Z1=Z1-2.D+0*(VCONST+VMDLG)
      DO 71 I=1,NMUFF
      RR=R(I)
71      Z(I)=-2.D+0*Z(I)/RR+VCONST+VMDLG
      DO 72 I=NMUFF,NMESH
72      Z(I)=0.D+0
C
C
      EE=EEMIN
      WRITE(3,120)
      DO 90 INDEX=1,NEND
      DO 80 LL=1,NPHS
      L=LL-1
      E=EE/13.6D+0+VCONST
C
C      COMPUTE RADIAL WAVE FUNCTION P(I). STORE THE RADIAL
C      WAVE FUNCTION FOR THE FIRST ENERGY POINT
C      IN WAVE.
      CALL INTOUT(E,VCONST,L,Z0,Z1,ALPHA,BETA,
1DH,NMESH,NMUFF,NF,NDV,DEL)
      IF(INDEX>1) GO TO 80
      DO 79 I=1,NDV
      WAVE(LL,I)=P(I)
79      CONTINUE
      WRITE(3,122) Z0,Z1,ALPHA,BETA
      WRITE(3,123) NF,NMUFF,NDV
80      PHS(LL)=DEL
      WRITE(3,121) EE,(PHS(L),L=1,NPHS)
      WRITE(21,111) EE,(PHS(L),L=1,NPHS)
90      EE=EE+EEINC
      DO 115 I=1,NDV
      WRITE(22,111) R(I),(WAVE(J,I),J=1,NPHS)
115      CONTINUE
      CLOSE(UNIT=20)
      CLOSE(UNIT=21)
      CLOSE(UNIT=22)
      STOP

```

END

C
C
CSUBROUTINE INTOUT(E,VCONST,L,Z0,Z1,ALPHA,BETA,
1DH,NMESH,NMUFF,NF,NBV,DEL)C
C

```

IMPLICIT REAL*8 (A-H,O-Z)
COMMON R(200),P(200),Z(200),V(200),HF(200)
FL=DFLOAT(L)
FLLP1=DFLOAT(L*(L+1))
DO 1 INDX=1,NMESH
  RR=R(INDX)
  V(INDX)=Z(INDX)+FLLP1/(RR*RR)

```

1
C
C

PWR SERIES EXPANSION OF P(R)

```

ALPHA=(2.D+0*Z0*Z0-(FL+1.D+0)*(2.D+0*Z1-E))/
1(2.D+0*(2.D+0*FL+3.D+0)*(FL+1.D+0))
BETA=Z0*((2.D+0*Z0*Z0-(3.D+0*FL+4.D+0)*(2.D+0*Z1-E))/
1(6.D+0*(FL+1.D+0)*(FL+2.D+0)*(2.D+0*FL+3.D+0)))
DO 2 I=1,2
  RR=R(I)

```

2

```

  F(I)=RR**((L+1)*(1.D+0-Z0*RR/(FL+1.D+0)+ALPHA*RR*RR-
1BETA*RR*RR*RR)

```

H=1H

H212=H*H/12.D+0

AAA=H212*(V(1)-E)

BBB=H212*(V(2)-E)

AA=1.D+0-AAA

MHI=1

3

MLOW=MHI+2

MHI=MLOW+8

11

DO 4 I=MLOW,MHI

CCC=H212*(V(I)-E)

BB=2.D+0+10.D+0*BBB

CC=1.D+0-CCC

F(I)=(F(I-1)*BB-F(I-2)*AA)/CC

AA=1.D+0-BBB

4

BBB=CCC

IF (MHI-NMUFF) 5,5,7

5

IF (MHI-NF) 6,10,10

10

MLOW=MHI+1

MHI=NMUFF+3

GO TO 11

6

H=H+H

C

CHANGE MESH WIDTH

H212=H212*4.D+0

AA=1.D+0-H212*(V(MHI-2)-E)

AAA=H212*(V(MHI)-E)

BBB=H212*(V(MHI+1)-E)

F(MHI+1)=(F(MHI)*(2.D+0+10.D+0*AAA)

```

1-P(MHI-2)*AA)/(1.D+0-BBB)
AA=1.D+0-AAA
GO TO 3
7 CONTINUE
300 FORMAT(8F10.5)
NDV=MHI-1
DERLN=((1.D+0-H212*(V(NDV+1)-E))*P(NDV+1)-(1.D+0-H212
1*(V(NDV-1)-E))*P(NDV-1))/(2.D+0*H*P(NDV))
ESQT=DSQRT(E)
BFARG=R(NDV)*ESQT
CALL CALCBF(BFARG,FL,BFJ1,BFN1)
FLP1=FL+1.D+0
CALL CALCBF(BFARG,FLP1,BFJ2,BFN2)
A1=(FLP1/R(NDV)-DERLN)*BFJ1-ESQT*BFJ2
A2=(FLP1/R(NDV)-DERLN)*BFN1-ESQT*BFN2
DEL=3.14159265D+0/2.D+0
IF (DABS(A2)-1.D-5) 9,9,8
8 ARG=A1/A2
DEL=DATAN(ARG)
RETURN
9 WRITE(3,12)
12 FORMAT(38H WARNING POSSIBLE SCATTERING RESONANCE )
RETURN
END

C
C
C
C

SUBROUTINE TEST(ZNUC,VMDLG,NMUFF,RMUFF,EEMIN,NMESH,NEND)
IMPLICIT REAL*8 (A-H,Q-Z)
COMMON R(200),P(200),Z(200),V(200),HF(200)
DIMENSION ARG(2),BJ(2),BN(2),BDJ(2),BDN(2)
7 FORMAT(1X,'SEE TEST NUMBER',I4)
PI=3.14159D+0
RYD=13.6D+0
NEND=-NEND
WRITE(3,7) NEND
GO TO (10,20,30,40) NEND
10 NMUFF=100
COMMENT THOMAS-FERMI POTL V(R)=Z(R)/R WITH Z(R)=ZNUC*DEXP(-ALPHA*R)
C TO USE, CALL TEST WITH NEND=-1. NOTE THERE MAY
C BE SLIGHT ERROR IN THE PWR SERIES AT THE ORIGIN.
C SHOULD HAVE Z1=-ALPHA
C
RMUFF=R(NMUFF)
VMDLG=0.D+0
ALPHA=1.12905D+0
EEMIN=.579D+0*.579D+0*RYD
ZNUC=3.D+0
DO 1 I=1,NMESH
1 Z(I)= ZNUC*DEXP(-ALPHA*R(I))
NEND=1

```



```

WRITE(3,11)
11  FORMAT(1X,'T-F PHASE SHIFTS-ASIK THESIS-.0994,.434,.035')
RETURN
20  NMUFF=100
    RMUFF=R(NMUFF)
    NM1=NMUFF-1
    A=(R(NM1)+RMUFF)/2.D+0
    X=EEMIN
    DUM=(PI/A)**2
    E=X*X*DUM
    V0=(2.D+0*X+1.D+0)*DUM
    EEMIN=RYD*E
    ZNUC=0.D+0
    NEND=1
    DO 2 I=1,NM1
2    Z(I)=V0*R(I)/2.D+0
    DO 5 I=NMUFF,NMESH
5    Z(I)=0.D+0
    ARG(1)=X*PI
    ARG(2)=(X+1.D+0)*PI
    DO 8 I=1,2
    BJ(I)=DSIN(ARG(I))/ARG(I)
    BN(I)=-DCOS(ARG(I))/ARG(I)
    BDJ(I)=(ARG(I)*DCOS(ARG(I))-DSIN(ARG(I)))/(ARG(I)*ARG(I))
    BDN(I)=(ARG(I)*DSIN(ARG(I))+DCOS(ARG(I)))/(ARG(I)*ARG(I))
8    CONTINUE
    GAM=ARG(2)*BDJ(2)/BJ(2)
    TAND=(ARG(1)*BDJ(1)-GAM*BJ(1))/(ARG(1)*
1    BDN(1)-GAM*BN(1))
    PHS=DATAN(TAND)
    WRITE(3,9) EEMIN,V0,RMUFF,PHS
9    FORMAT(7H FOR E=,E12.5,5H V0=,E12.5,9H RADIUS=,
1    E12.5,20H THE PHASE SHIFT IS,E12.5)
4    RETURN
30  NFIT=50
    ALPHA=ALOG(ZNUC/Z(NFIT))/R(NFIT)
    DO 31 I=1,NMESH
31  Z(I)=ZNUC*DEXP(-ALPHA*R(I))
    NEND=51
    WRITE(3,32) ALPHA
32  FORMAT(1X,'T-F APPROX TO V(R),ALPHA=,E12.5)
    RETURN
40  ZNUC=.5D+0
    XK=1.D+0
    ALPHA=XK
    DO 41 I=1,NMESH
41  Z(I)=ZNUC*R(I)/(DEXP(ALPHA*R(I))-1.D+0)
    EEMIN=XK*XK*RYD
    NEND=1
    WRITE(3,42)
42  FORMAT(1X,'HULTHEN POTL L=0, E=V0=ALPHA PS=.73293')
    RETURN

```

END

C

C

C

COMMENT SPHERICAL BESSEL FUNCTIONS 'J' AND 'N'

C FENDRY CAVENDISH JUNE 1970

SUBROUTINE CALCBF(Z,CL,BJ,BN)

IMPLICIT REAL*8 (A-H,O-Z)

L=IDINT(CL)

IF (CL-0.5D+0) 10,10,4

10 BJ=1.0D+0

IF (1.0D-6-DABS(Z)) 11,11,8

11 BJ=DSIN(Z)/Z

GO TO 8

4 IF (1.1D+0*CL-DABS(Z)) 12,12,6

12 BJ=0.0D+0

IF (1.0D-6-DABS(Z)) 13,13,8

13 BF2=DSIN(Z)/Z

BF1=DSIN(Z)/(Z*Z)-DCOS(Z)/Z

BFJ=2.0D+0

IF (L-1) 23,23,22

22 DO 14 J=2,L

BFS=BF1

BF1=(2.0D+0*BFJ-1.0D+0)*BF1/Z-BF2

BF2=BFS

14 BFJ=BFJ+1.0D+0

23 BJ=BF1

GO TO 8

6 BFP=1.0D+0

BF=0.0D+0

BFLL=2.0D+0*CL+3.0D+0

BFSR=1.0D+0

BFSX=0.5*Z*Z

7 BF=BF+BFP

BFP=-BFP*BFSX/(BFSR*BFLL)

BFSR=BFSR+1.0D+0

BFLL=BFLL+2.0D+0

IF (DABS(BFP)-DABS(BF)*1.0D-6) 15,15,7

15 BFLX=1.0D+0

BFNM=1.0D+0

DO 16 J=1,L

BFLX=Z*BFLX

16 BFNM=BFNM+1.0D+0

BFZ=1.0D+0

BFY=2.0D+0*CL+1.0D+0

LL=IDINT(BFY)+1

DO 17 JRB=1,LL,2

BFZ=BFZ*BFY

17 BFY=BFY-2.0D+0

BJ=BFLX*BF/BFZ

8 IF (CL-0.5D+0) 18,18,9

18 BN=-DCOS(Z)/Z

```
GO TO 5
9  BF2=-DCOS(Z)/Z
   BF1=-DCOS(Z)/(Z*Z)-DSIN(Z)/Z
   BFJ=2.0D+0
   IF (L-1) 21,21,20
20  DO 19 J=2,L
   BFS=BF1
   BF1=(2.0D+0*BFJ-1.0D+0)*BF1/Z-BF2
   BF2=BFS
19  BFJ=BFJ+1.0D+0
21  BN=BF1
5   RETURN
   END
@
```

```

C ROUTINE LEED
C MAIN PROGRAM FOR LEED INTENSITY CALCULATION.
C DEVELOPED BY H. HJALMARSON AT URBANA FROM ROUTINE IN
C "LOW ENERGY ELECTRON DIFFRACTION" BY J. B. PENDRY.
C THIS ROUTINE COMPUTES LAYER T MATRICES FOR A MC2
C MATERIAL (METAL DICHALOGENIDE). EITHER RFS OR A VARIANT
C OF LAYER DOUBLING CAN BE USED BETWEEN LAYERS.
C INPUT CONSISTS OF STRUCTURAL AND FORM FACTOR INFORMATION.
C
C COMPUTATIONAL
C EMACH MACHINE ACCURACY.
C CRTOUT AND CRTIN CONVERGENCE CRITERIA FOR RFS.
C HARTRE AND BOHR ATOMIC UNITS.
C MULT 0 MEANS KINEMATICAL SCATTERING.
C 1 MULTIPLE SCATTERING
C NCDW 0 NO CHARGE DENSITY WAVES
C 1 CDW SPECIFIED BY INPUT FROM CDW.DAT.
C NOT WELL TESTED.
C NDCNG SEE SAND.FOR
C N1 NUMBER OF NEAREST NDERS USED IN THE GREEN'S FUNCTION
C CALCULATION IN MAT.FOR.
C N NUMBER OF BEAMS.
C NLM NUMBER OF CLEBSCH-GORDON COEFFICIENTS USED.
C DEPENDS ON LMAX.
C INCMN NUMBER OF ENERGY POINTS SKIPPED.
C GRID SUPPLIED BY PHASE SHIFT INPUT.
C INCNUM NUMBER OF ENERGY POINTS FOR WHICH INTENSITY
C IS COMPUTED.
C
C STRUCTURAL
C A,C LATTICE CONSTANTS.
C SURF,ASM1,AND ASM2 3-D VECTORS WHICH SET UP CARTESIAN
C COORDINATE SYSTEM.
C AR1 AND AR2 2-D SURFACE LATTICE VECTORS.
C RAR1 AND RAR2 2-D RECIPROCAL SURFACE LATTICE VECTORS.
C AREA UNIT CELL SURFACE AREA.
C THETA AND FI ANGLE OF INCIDENT BEAM WRT THE SAMPLE.
C IDEG SYMMETRY IN EACH PLANE OF ATOMS.
C
C FORM FACTOR
C E ENERGY
C PHASEC AND PHASEM TEMPERATURE CORRECTED CHALCOGENIDE
C AND METAL PHASE SHIFTS AT ENERGY E.
C SELF ENERGY IS USELFR+I*VSELF1.
C USELFR CONSTANT PORTION OF XTAL POTL.
C VSELF1=SQRT(2E)/2XMFP.
C XMFP ENERGY DEPENDENT MEAN FREE PATH SPECIFIED BY
C XMFP0 AND XMFP1.
C DIMENSION D(4,3),SURF(3)
C DIMENSION AR1(2),AR2(2),RAR1(2),RAR2(2)
C DIMENSION PHS(8),PHSC(8),PHSM(8),DPHS(8)

```

```

DIMENSION AS(3),ASM1(3),ASM2(3)
DIMENSION CDWC(2),CDWM(2),CDWR(3)
COMPLEX AF,RC,TC,BM,CM,RM
COMPLEX PHS,PHSC,PHSM,DPHS
COMPLEX RCC,TCC,RCM,TCM
COMPLEX XODDC,XEVENC,XODDM,XEVENM
COMPLEX CEXP,CMPLX,CI
COMPLEX CZERO
COMPLEX AFC,AFM
COMMON AFC(8),AFM(8)
COMMON RCC(55,55),TCC(55,55),RCM(55,55),TCM(55,55)
COMMON PQF(2,55),PQ(2,55)
COMMON E,A,THETA,FI,VSELF,CLM(1925)
COMMON /X1/D
COMMON /X2/AR1,AR2
COMMON /X3/CDWC,CDWM
COMMON /X4/AREA
DATA SURF(1),SURF(2),SURF(3)/1.,0.,0./
DATA ASM1(1),ASM1(2),ASM1(3)/0.,1.,0./
DATA ASM2(1),ASM2(2),ASM2(3)/0.,0.,1./
7  FORMAT(7F10.5)
9  FORMAT(10I4)
10 FORMAT(2E12.5)
C
C  INITIALIZE CONSTANTS
222 HARTRE=27.2
    ECENT=100./HARTRE
    BOHR=.529
    PI=3.14159265
    CZERO=CMPLX(0.0,0.0)
    CI=CMPLX(0.0,1.0)
    DO 215 I1=1,55
    DO 215 I2=1,55
    RCC(I1,I2)=CZERO
    TCC(I1,I2)=CZERO
    RCM(I1,I2)=CZERO
215  TCM(I1,I2)=CZERO
    DO 14 I1=1,8
    AFM(I1)=CZERO
    PHS(I1)=CZERO
    PHSC(I1)=CZERO
    PHSM(I1)=CZERO
14  AFC(I1)=CZERO
C
    OPEN(UNIT=20,FILE='CLM.DAT',DIALOG)
    OPEN(UNIT=21,FILE='BEM6.DAT',DIALOG)
    OPEN(UNIT=22,FILE='LDTISE.DAT',DIALOG)
    OPEN(UNIT=25,DEVICE='DSK',FILE='CDW.DAT',DIALOG)
    OPEN(UNIT=23,FILE='PTSE40.DAT',DIALOG)
    OPEN(UNIT=24,FILE='PTTI40.DAT',DIALOG)
    OPEN(UNIT=30,MODE='BINARY',FILE='LEED.DAT',
1DIIRECTORY='4,270',DIALOG)

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```

OPEN(UNIT=61,DEVICE='DSK',FILE='SFAC.DAT',DIALOG)
OPEN(UNIT=62,DEVICE='DSK',FILE='UCAMP.DAT',DIALOG)
OPEN(UNIT=63,FILE='INTOUT.DAT',DIALOG)

C
C READ INPUT
READ(22,9) MULT,NCDW,NDCNG,IDEG,N1,N,LMAX,INCMN,INCNUM,NLM
READ(22,7) A,C,THETA,FI,EMACH,VSELF,VSSELF
READ(22,10) CRTOUT,CRTIN
READ(22,10) XMFP0,XMFP1
WRITE(5,300) MULT,NCDW,NDCNG,INCMN,INCNUM
300 FORMAT(1X,'MULT,NCDW,NDCNG,INCMN,INCNUM...',/,5I5)
WRITE(5,301) N,N1,NLM,LMAX,EMACH,CRTIN,CRTOUT
301 FORMAT(1X,'N,N1,NLM,LMAX,EMACH,CRTIN,CRTOUT...',/,4I5,3E12.5)
WRITE(5,302) A,C,THETA,FI,IDEG
302 FORMAT(1X,'A,C,THETA,FI,IDEG...',/,4F12.5,I5)
WRITE(5,303) VSELF,XMFP0,XMFP1
303 FORMAT(1X,'VSELF,XMFP0,XMFP1...',/,3E12.5)
XMFP0=XMFP0/BOHR
XMFP1=XMFP1/BOHR
EMACH=EMACH*1.E-5
READ(20,43) (CLM(J),J=1,NLM)
43 FORMAT (5E14.5)
2 FORMAT(3F7.1)
C
C STRUCTURAL INFORMATION
READ(22,3) AS
AS(2)=SQRT(3.)/2.
3 FORMAT (3F12.5)
WRITE(5,1)
1 FORMAT (///,15H SURF ASM1 ASM2)
WRITE(5,2) SURF,ASM1,ASM2
AA=0.0
BB=AA
CC=AA
DD=AA
DO 44 J=1,3
AA=AA+ASM1(J)**2
BB=BB+ASM2(J)**2
CC=CC+AS(J)*ASM1(J)*A
44 DD=DD+AS(J)*ASM2(J)*A
AR1(1)=CC/SQRT(AA)
AR1(2)=DD/SQRT(BB)
CC=0.0
DD=CC
WRITE(5,46) AS
46 FORMAT (13H SURFACE VECs,/,3F12.5)
READ(22,3) AS
DO 45 J=1,3
CC=CC+AS(J)*ASM1(J)*A
45 DD=DD+AS(J)*ASM2(J)*A
AR2(1)=CC/SQRT(AA)
AR2(2)=DD/SQRT(BB)

```

```

WRITE(5,3) AS
48  FORMAT(3F15.10)
DO 31 I=1,4
READ(22,3) (D(I,J),J=1,3)
D(I,2)=SQRT(3.)/3.
DO 30 J=2,3
30  D(I,J)=D(I,J)*A
D(I,1)=D(I,1)*C
WRITE(5,22) (D(I,J),J=1,3)
31  CONTINUE
22  FORMAT(19H LAYER DISPLACEMENT,/,3F12.5)
AREA=ABS(AR1(1)*AR2(2)-AR1(2)*AR2(1))
WRITE(5,35) AREA
35  FORMAT(1X,'UNIT CELL AREA',E12.5)
5   FORMAT(3I5)
C
C   CDW DATA
READ(25,10) CDWC
READ(25,10) CDWM
DO 32 I=1,2
CDWC(I)=CDWC(I)*A
32  CDWM(I)=CDWM(I)*A
NC=N
READ(21,6) (PQF(1,J),PQF(2,J),J=1,N)
N=N+NCDW
6   FORMAT (2F7.1)
IF(NCDW,EQ.0) GO TO 11
READ(25,6) (PQF(1,J),PQF(2,J),J=NC+1,N)
11  RAR1(1)=AR2(2)*2.0*PI/AREA
RAR1(2)=-AR2(1)*2.0*PI/AREA
RAR2(1)=AR1(2)*2.0*PI/AREA
RAR2(2)=-AR1(1)*2.0*PI/AREA
DO 12 J=1,N
PQ(1,J)=PQF(1,J)*RAR1(1)+PQF(2,J)*RAR2(1)
PQ(2,J)=PQF(1,J)*RAR1(2)+PQF(2,J)*RAR2(2)
12  CONTINUE
WRITE(5,41)
WRITE(5,6) (PQF(1,J),PQF(2,J),J=1,N)
41  FORMAT(15H BEAMS INCLUDED,/,14H PQF1 PQF2)
LIM=LMAX+1
COMMENT REFLECTION,RC,AND TRANSMISSION,TC,
C   COEFFICIENTS FOR A SINGLE LAYER ARE FOUND
READ(23,108) NUM,NPHASE,FMAX
READ(24,108) NUM,NPHASE,FMAX
108  FORMAT (2I4,F8.5)
INC=1
NSUM=INCMN+INCNUM
C
C
107 IF(INC-NSUM) 205,205,19
205 READ(23,111) EE,(PHS(L),L=1,NPHASE)
WRITE(5,16)

```

```

16  FORMAT(20X,13H PHASE SHIFTS)
    WRITE(5,111) EE,(PHS(L),L=1,NPHASE)
    E=EE/27.2
    E=E+VSELEFR
    IF(XMFP0.LE.0.0) GO TO 15
    XMFP=XMFP0*(ALOG(E/ECENT))**2+XMFP1
    VSELEFI=-SQRT(2.*E)/(XMFP*2.)
    XMFP=XMFP*BOHR
15  CONTINUE
    DO 203 L=1,LIM
203  AFC(L)=CSIN(PHS(L))*CEXP(CI*PHS(L))
    READ(24,111) EE,(PHS(L),L=1,NPHASE)
    WRITE(5,111) E,(PHS(L),L=1,NPHASE)
    WRITE(5,8) XMFP,VSELEFI,E
8    FORMAT(1X,'MEAN FREE PATH,VSELEFI,AND ENERGY E...',/,3E12.5)
    DO 204 L=1,LIM
204  AFM(L)=CSIN(PHS(L))*CEXP(CI*PHS(L))
    READ(30) EE,((RCC(I,J),TCC(I,J),RCM(I,J),TCM(I,J),
    1I=1,N),J=1,N)
    IF (INC=INCMN) 109,109,201
C201  CALL MSMAT(N,LMAX,N1,IDEG,NC,MULT,EMACH)
201  CONTINUE
999  FORMAT(8F9.4)
C    WRITE(30) EE,((RCC(I,J),TCC(I,J),RCM(I,J),TCM(I,J),I=1,N),
C    1,J=1,N)
    CALL PERTA(N,NDCNG,CRTOUT,CRTIN,EMACH)
211  FORMAT(5E12.5)
109  INC=INC+1
    GO TO 107
111  FORMAT(7E12.5,/,6E12.5)
19  CONTINUE
    CLOSE(UNIT=20)
    CLOSE(UNIT=21)
    CLOSE(UNIT=22)
    CLOSE(UNIT=23)
    CLOSE(UNIT=24)
    CLOSE(UNIT=25)
    CLOSE(UNIT=30)
    CLOSE(UNIT=61)
    CLOSE(UNIT=62)
    CLOSE(UNIT=63)
    STOP
    END

```



```

C      ROUTINE SREF
C      THIS ROUTINE CALCULATES REFLECTED INTENSITY AT(G) VERSUS
C      ENERGY E GIVEN RC (REFLECTION COEFFICIENTS) FOR METAL
C      DICHALCOGENIDES IN RCM AND RCC.  SIMILARLY FOR TCM AND TCC
C      N NUMBER OF BEAMS
C      NDCNG SETS SURFACE RELAXATION MODEL.
C      NDCNG=0  ALL UNIT CELLS IDENTICAL GIVEN BY D(1,I)
C              (M-C DISTANCE) AND D(2,I) (M-M DISTANCE)
C              WITH I=1 PERPENDICULAR AND I=2,3 PARALLEL
C              TO THE SURFACE.
C
C      NDCNG=1  ALL UNIT CELLS AS ABOVE EXCEPT OUTERMOST WHICH
C              HAS M-C DISTANCE IN D(3,I).
C      NDCNG=2  SAME AS ABOVE BUT ALSO HAS M-M DISTANCE IN
C              D(3,I).
C
C      SUBROUTINE PERTA(N,NDCNG,CRTOUT,CRTIN,EMACH)
C      DIMENSION REF1(55),REF2(55),PK(2,4,55)
C      DIMENSION D(4,3),DD(4,3),AT(55),STRFAC(55)
C      DIMENSION UCA(55)
C      COMMON AFC(8),AFM(8)
C      COMMON RCC(55,55),TCC(55,55),RCM(55,55),TCM(55,55)
C      COMMON PQF(2,55),PQ(2,55)
C      COMMON E,SPA,THETA,FI,VSELF,CLM(1925)
C      COMMON /X1/DD
C      COMPLEX CONE,CI,CZERO
C      COMPLEX EK,EK1,EK2
C      COMPLEX RCC,TCC,RCM,TCM
C      COMPLEX PHI
C      COMPLEX REF1,REF2,PK
C      COMPLEX S1,S2,DUM,R
C      COMPLEX AFC,AFM
C      CZERO=CMPLX(0.0,0.0)
C      CI=CMPLX(0.0,1.0)
C      CONE=CMPLX(1.,0.)
C      PHI=CEXP(CI*3.14159/2.)
C      AK=SQRT(2.0*E)*SIN(THETA)
C      AKK=SQRT(2.0*E)
C      BK2=AK*COS(FI)
C      BK3=AK*SIN(FI)
C      DO 1 I=1,3
C      D(1,I)=DD(1,I)
C      D(2,I)=DD(1,I)+DD(2,I)+DD(1,I)
C      D(3,I)=DD(3,I)
C      D(4,I)=DD(3,I)+DD(4,I)+DD(3,I)
C      DO 2 J=1,N
C      AK2=BK2+PQ(1,J)
C      AK3=BK3+PQ(2,J)
C      AT(J)=0.0
C      QRED=0.0
C      A=2.0*E-AK2*AK2-AK3*AK3
C      IF (A) 43,43,42

```

```

42  QRED=SQRT(A)
    AT(J)=QRED/(AKK*COS(THETA))
43  EK=CMPLX(A,-2.0*VSELF1+0.000001)
    DO 2 I=1,3,2
      EK1=CSQRT(EK)*D(I,1)
      EK2=CSQRT(EK)*D(I+1,1)
      EK1=CEXP(0.5*CI*EK1)
      EK2=CEXP(1.0*CI*EK2)
      EKM1=AK2*D(I,2)+AK3*D(I,3)
      EKM2=AK2*D(I+1,2)+AK3*D(I+1,3)
      PK(1,I,J)=CEXP(0.5*CI*EKM1)*EK1
      PK(1,I+1,J)=CEXP(1.0*CI*EKM2)*EK2
      PK(2,I,J)=CEXP(-0.5*CI*EKM1)*EK1
      PK(2,I+1,J)=CEXP(-1.0*CI*EKM2)*EK2
2   CONTINUE
    DO 22 J=1,N
      DUM=PK(2,1,J)*PK(2,1,J)*PK(1,1,1)*PK(1,1,1)
      REF2(J)=RCM(J,1)+RCC(J,1)*(DUM+CONE/DUM)
      DUM=PK(2,3,J)*PK(2,3,J)*PK(1,3,1)*PK(1,3,1)
      REF1(J)=RCM(J,1)+RCC(J,1)*(DUM+CONE/DUM)
      DUM=PK(2,3,J)*DUM*PK(1,3,1)
      S1=PK(2,4,J)*PK(1,4,1)
      S2=PK(2,2,J)*PK(1,2,1)
      S2=CONE/(CONE-S2)
      REF1(J)=DUM*REF1(J)
      REF2(J)=DUM*REF2(J)
      R=REF1(J)+S1*REF2(J)*S2
      S1=CONE/(CONE-S1)
      STRFAC(J)=CABS(S1)*CABS(S1)
      UCA(J)=AT(J)*CABS(REF1(J))*CABS(REF1(J))
      AT(J)=AT(J)*CABS(R)*CABS(R)
22  CONTINUE
    WRITE(5,45)
45  FORMAT(29H      BEAM      INTENSITY )
    WRITE(5,46) (PQF(1,J),PQF(2,J),AT(J),J=1,N)
46  FORMAT (2F7.1,1E15.5)
    WRITE(5,47)
47  FORMAT(////)
    WRITE(63,49) E,AT(1),AT(2),AT(3),AT(8),AT(14),AT(15)
    WRITE(62,49) E,UCA(1),UCA(2),UCA(3),UCA(8),UCA(14),UCA(15)
    WRITE(61,49) E,STRFAC(1),STRFAC(2),STRFAC(3),STRFAC(8)
    1,STRFAC(14),STRFAC(15)
49  FORMAT(7E12.5)
    WRITE(5,50)
50  FORMAT(1X,'REFLECTIVITY FROM FIRST SANDWICH,SECOND
1SANDWICH AND STRUCTURE FACTOR')
    CALL OUTPUT(REF1,E,N)
    CALL OUTPUT(REF2,E,N)
    CALL OUTPUT(STRFAC,E,N)
    RETURN
    END

```

```
      SUBROUTINE OUTPUT(A,E,N)
C      FOR COMPLEX ARRAY A THIS ROUTINE
C      PRINTS THE MAGNITUDE B AND PHASE C.
      DIMENSION A(55),B(55),C(55)
      COMPLEX A
      DO 1 I=1,N
      B(I)=CABS(A(I))
      C(I)=ATAN2(AIMAG(A(I)),REAL(A(I)))
1      CONTINUE
      WRITE(5,10) E,B(1),B(2),B(3),B(8)
      WRITE(5,10) E,C(1),C(2),C(3),C(8)
10     FORMAT(5E12.5)
      RETURN
      END
```

@

C ROUTINE PERTA IN FILE SAND.FOR
 C THIS ROUTINE USES RFS TO COMPUTE THE REFLECTIVITY OF
 C A CRYSTAL COMPOSED OF SANDWICHES WHOSE SHEETS OF
 C ATOMS HAVE REFLECTION AMPLITUDES RCM AND TCM. THE
 C SANDWICH REFLECTION AMPLITUDES ARE CALCULATED BY
 C LRPT USING LAYER DOUBLING. THE STRUCTURAL INFORMATION
 C IS CONTAINED IN ARRAY D.
 C

```

SUBROUTINE PERTA(N,NDCNG,CRTOUT,CRTIN,EMACH)
  DIMENSION PHI(2,4,55),BC(2,55)
  DIMENSION ANEW(31,36),AW(31,3)
  DIMENSION AS(3),D(4,3),DD(4,3)
  DIMENSION WV(55),AT(55)
  DIMENSION RDM1(55,55),TDM1(55,55),RDM2(55,55),TDM2(55,55)
  COMMON AFC(8),AFM(8)
  COMMON RCC(55,55),TCC(55,55),RCM(55,55),TCM(55,55)
  COMMON PQF(2,55),PQ(2,55)
  COMMON E,SPA,THETA,FI,VSELF1,CLM(1925)
  COMMON /X1/DD
  COMPLEX EK,EKM,CZERO,CI
  COMPLEX XMON
  COMPLEX AK,RK
  COMPLEX RCC,TCC,RCM,TCM
  COMPLEX PHI,RDM1,TDM1,RDM2,TDM2,BC
  COMPLEX EK1,EK2,EKM1,EKM2,EKBC
  COMPLEX WV,AW,ANEW
  COMPLEX BBB
  COMPLEX AFC,AFM
  COMPLEX XX,RR,TT,CONE,AA,BB
  ALPHA=1.0
  I1=1
  I2=2
  CZERO=CMPLX(0.0,0.0)
  CI=CMPLX(0.0,1.0)
  CONE=CMPLX(1.0,0.0)
  DO 1 I=1,3
    D(1,I)=DD(1,I)
    D(2,I)=DD(2,I)
    D(2,I)=D(1,I)+D(2,I)+D(1,I)
    D(3,I)=DD(3,I)
    D(4,I)=DD(4,I)
1    D(4,I)=D(3,I)+D(4,I)+D(3,I)
    AKX=SQRT(2.0*E)*SIN(THETA)
    AKK=SQRT(2.0*E)
    BK2=AKX*COS(FI)
    BK3=AKX*SIN(FI)
    DO 2 J=1,N
      AK2=BK2+PQ(1,J)
      AK3=BK3+PQ(2,J)
      AT(J)=0.0
      A=2.0*E-AK2*AK2-AK3*AK3
  
```

```

      IF (A) 43,43,42
42    AT(J)=SQRT(A)/(AKK* $\cos$ (THETA))
43    EK=CMPLX(A,-2.0*VSELF1+0.000001)
      DO 3 I=1,3,2
      EK1=CSQRT(EK)*D(I,1)
      EK2=CSQRT(EK)*D(I+1,1)
      EKBC=CEXP(0.5*CI*EK1)
      EK1=EKBC*EKBC
      EK2=CEXP(0.5*CI*EK2)
      EKM1=AK2*D(I,2)+AK3*D(I,3)
      EKM2=AK2*D(I+1,2)+AK3*D(I+1,3)
      PHI(1,I,J)=CEXP(-1.0*CI*EKM1)*EK1
      PHI(1,I+1,J)=CEXP(-0.5*CI*EKM2)*EK2
      PHI(2,I,J)=CEXP(1.0*CI*EKM1)*EK1
      PHI(2,I+1,J)=CEXP(0.5*CI*EKM2)*EK2
3    CONTINUE
      BC(1,J)=CEXP(-0.5*CI*EKM2)*EKBC
      BC(2,J)=CEXP(0.5*CI*EKM2)*EKBC
2    CONTINUE
      IF(NDCNG<1) GO TO 100
      DO 99 I=1,N
      DO 99 J=1,N
      RDM1(I,J)=RCC(I,J)
      TDM1(I,J)=TCC(I,J)
      RDM2(I,J)=RCM(I,J)
99    TDM2(I,J)=TCM(I,J)
      CALL LRPT(PHI,RDM1,TDM1,RDM2,TDM2,3,N,EMACH)
100   CALL LRPT(PHI,RCC,TCC,RCM,TCM,1,N,EMACH)
      COMMENT ANEW(J,I) IS THE CONTRIBUTION OF THE CURRENT
      C      ORDER OF RFS PERTURBATION THEORY TO THE
      C      AMPLITUDE OF THE J TH BEAM BETWEEN THE (I-1) THE
      C      AND I TH LAYERS.
      C      IO IS THE NUMBER OF THE PASS BEING EXECUTED.
102   CONTINUE
      DO 5 I=1,N
      WV(I)=CZERO
      DO 5 J=1,36
5     ANEW(I,J)=CZERO
      COMMENT INWARD PASS STARTS HERE
      ANEW(1,1)=CMPLX(1.0,0.0)
      IO=0
      IFAIL=0
      ANORM1=1.0E-6
6     ANORM2=0.0
      I1=1
      I2=2
      ALPHI=1.0
      IO=IO+1
      COMMENT OLD AMPLITUDES AT THE (I-1) TH LAYER
      I=1
7     BNORM=0.0
      NRECON=2

```

```

I=I+1
IF(I.EQ.2 .AND. NDCNG>1.5) NRECON=4
DO 30 K=1,N
AW(K,2)=PHI(I2,NRECON,K)*ANEW(K,I-1)
AW(K,3)=PHI(I1,NRECON,K)*ANEW(K,I)
30 CONTINUE
IF(I.EQ.2.AND.NDCNG>.5) GO TO 201
DO 31 IG=1,N
AW(IG,1)=CZERO
DO 31 K=1,N
31 AW(IG,1)=AW(IG,1)+TCM(IG,K)*AW(K,2)+RCM(IG,K)
1*AW(K,3)
GO TO 202
201 CONTINUE
DO 231 IG=1,N
AW(IG,1)=CZERO
DO 231 K=1,N
231 AW(IG,1)=AW(IG,1)+TDM2(IG,K)*AW(K,2)+
1RDM2(IG,K)*AW(K,3)
202 CONTINUE
DO 39 IG=1,N
ANEW(IG,I)=PHI(I2,NRECON,IG)*AW(IG,1)
AAA=CABS(ANEW(IG,I))
39 BNORM=BNORM+AAA*AAA
NRECON=2
COMMENT TESTS AND CHECKS ON THE DEPTH OF PENETRATION INTO THE
C CRYSTAL.FOR INCREASED PENETRATION INCREASE THE SECOND
C DIMENSION OF ANEW AND CHANGE IF STATEMENT 11
C IDUM=I1
C I1=I2
C I2=IDUM
IF(I0-1)40,40,41
40 IF(BNORM-CRTIN )14,14,11
41 ALPHI=ALPHI*ALPHA
IF(SQRT(ALPHI*BNORM)-CRTIN )14,14,11
11 IF(I-32)7,12,12
12 WRITE(5,13)
13 FORMAT(23H0**FIRST ORDER TOO DEEP,/)
IFAIL=1
GO TO 16
14 CONTINUE
WRITE(5,15) I,I0,CRTIN
15 FORMAT(7H LAYERS,I3,5X,7H ORDER ,I3,5X,8H CRTIN =,E10.5)
16 IMAX=I-1
17 FORMAT(8H IMAX = ,I2,5X,8HBNORM = ,E12.4,/,
1 4X,3HWVR,9X,3HWVI)
IMAX=IMAX+1
COMMENT IT IS ASSUMED THAT THE REAM IS NOW SO STRONGLY
C ATTENUATED THAT IT HAS EFFECTIVELY ZERO AMPLITUDE
DO 18 IG=1,N
18 ANEW(IG,IMAX+1)=CZERO
COMMENT OUTWARD PASS STARTS HERE

```

```

DO 20 I=1,IMAX
  II=IMAX-I+1
  IF(II.EQ.1.AND.NDCNG>1.5) NRECON=4
  DO 60 K=1,N
    AW(K,2)=PHI(I1,NRECON,K)*ANEW(K,II+1)
    AW(K,3)=PHI(I2,NRECON,K)*ANEW(K,II)
60  CONTINUE
    IF(II.EQ.1.AND.NDCNG>.5) GO TO 301
    DO 61 IG=1,N
      AW(IG,1)=CZERO
    DO 61 K=1,N
61  AW(IG,1)=AW(IG,1)+TCM(IG,K)*AW(K,2)+RCM(IG,K)
    1*AW(K,3)
    GO TO 302
301  CONTINUE
    DO 361 IG=1,N
      AW(IG,1)=CZERO
    DO 361 K=1,N
361  AW(IG,1)=AW(IG,1)+TDM2(IG,K)*AW(K,2)+
    1RDM2(IG,K)*AW(K,3)
302  CONTINUE
    DO 19 IG=1,N
19  ANEW(IG,II)=PHI(I1,NRECON,IG)*AW(IG,1)
C    IDUM=I1
C    I1=I2
C    I2=IDUM
    NRECON=2
20  CONTINUE
COMMENT CONTRIBUTION OF THE CURRENT PASS TO AMPLITUDES AT THE
C    SURFACE (ASSUMED HALF WAY BETWEEN TWO LAYERS)
    DO 21 IG=1,N
      AAA=CABS(ANEW(IG,1))
      ANORM2=ANORM2+AAA*AAA
      WV(IG)=WV(IG)+ANEW(IG,1)
21  ANEW(IG,1)=CZERO
COMMENT CHECKS ON CONVERGENCE OVER PASSES
    ANORM1=ANORM1+ANORM2
    WRITE(5,24) ANORM1
24  FORMAT(9H ANORM = ,E12.4,/)
    IF(IFAIL-1)25,26,25
25  IF(ANORM2/ANORM1-CRTOUT)26,26,50
50  IF(IO-1)51,51,52
51  ALPHA=EXP(ALOG(BNORM)/FLOAT(IMAX-1))
    GOTO 6
52  IF (IO-6) 6,53,53
53  WRITE(5,54) IO
54  FORMAT(/,24H ***NO CONVERGENCE AFTER,
11I4,11H ITERATIONS)
26  CONTINUE
    DO 44 J=1,N
C    WV(J)=AK(1,J)*DELTA(J)*DELTA(J)*DELTA(J)*RCM(J,1)
    BBB=WV(J)

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      BBB=BC(1,J)*PHI(1,3,J)*BBB*BC(2,1)*PHI(2,3,1)
      1/(PHI(1,4,J)*PHI(2,4,1))
      BB1=CABS(BBB)*CABS(BBB)
44      AT(J)=BB1*AT(J)
      WRITE(5,45)
45      FORMAT(29H      BEAM      INTENSITY )
      WRITE(5,46) (PQF(1,J),PQF(2,J),AT(J),J=1,N)
46      FORMAT(2F7.1,1E15.5)
      WRITE(5,47)
47      FORMAT(////)
      WRITE(63,49) E,AT(1),AT(2),AT(3),AT(8),AT(14),AT(15)
49      FORMAT(7E12.5)
      RETURN
      END
C
      SUBROUTINE LRPT(PHI,RCC,TCC,RCM,TCM,NRN,N,EMACH)
      DIMENSION PHI(2,4,55)
      DIMENSION RR(31,31),TT(31,31),BB(31)
      DIMENSION XX(31,31),AA(31),IP(31)
      DIMENSION RCC(55,55),TCC(55,55),RCM(55,55),TCM(55,55)
      COMPLEX PHI
      COMPLEX XX,RR,TT,IP,CONE,AA,BB
      COMPLEX CI
      COMPLEX RCC,TCC,RCM,TCM,CZERO
      CZERO=CMPLX(0.0,0.0)
      CI=CMPLX(0.0,1.0)
      CONE=CMPLX(1.0,0.0)
C      WRITE(6,111) ((RCC(I1,I2),I1=1,25),I2=1,25)
C      WRITE(6,111) ((RCM(I1,I2),I1=1,25),I2=1,25)
      DO 1 I=1,N
      DO1 J=1,N
      RCC(I,J)=RCC(I,J)*PHI(1,NRN,I)*PHI(2,NRN,J)
1      TCC(I,J)=TCC(I,J)*PHI(2,NRN,J)/PHI(2,NRN,I)
      DO 200 I=1,N
      DO 10 J=1,N
      XX(I,J)=CZERO
      RR(I,J)=CZERO
      TT(I,J)=CZERO
      DO 10 K=1,N
10      XX(I,J)=XX(I,J)-RCM(I,K)*RCC(K,J)
200      XX(I,I)=XX(I,I)+CONE
      CALL ZGE(XX,IP,N,N,EMACH)
      DO 500K=1,N
      DO 300J=1,N
300      AA(J)=TCM(J,K)
      CALL ZSU(XX,IP,AA,N,N,EMACH)
      DO 400J=1,N
      BB(J)=CZERO
      DO 400L=1,N
      TT(J,K)=TT(J,K)+TCC(J,L)*AA(L)
400      BB(J)=BB(J)+RCC(J,L)*AA(L)
      DO 500J=1,N

```



```

RR(J,K)=RCM(J,K)
DO 500 L=1,N
500 RR(J,K)=RR(J,K)+TCM(J,L)*BB(L)
C   WRITE(6,111) ((RR(I1,I2),I1=1,13),I2=1,13)
DO 2 I=1,N
DO 2 J=1,N
RCC(I,J)=RCC(I,J)*PHI(2,NRN,I)*PHI(1,NRN,J)
1/(PHI(1,NRN,I)*PHI(2,NRN,J))
2   TCC(I,J)=TCC(I,J)*PHI(2,NRN,I)*PHI(2,NRN,I)
1/(PHI(2,NRN,J)*PHI(2,NRN,J))
DO 70 I=1,N
DO 600 J=1,N
XX(I,J)=CZERO
RCM(I,J)=CZERO
TCM(I,J)=CZERO
DO 600 K=1,N
600 XX(I,J)=XX(I,J)-RCC(I,K)*RR(K,J)
70   XX(I,I)=XX(I,I)+CONE
CALL ZGE(XX,IP,N,N,EMACH)
DO 100 K=1,N
DO 80 J=1,N
80   AA(J)=TCC(J,K)
CALL ZSU(XX,IP,AA,N,N,EMACH)
DO 90 J=1,N
BB(J)=CZERO
DO 90 L=1,N
TCM(J,K)=TCM(J,K)+TT(J,L)*AA(L)
90   BB(J)=BB(J)+RR(J,L)*AA(L)
DO 100 J=1,N
RCM(J,K)=RCC(J,K)/(PHI(2,NRN,J)*PHI(1,NRN,J)
1*PHI(1,NRN,K)*PHI(2,NRN,K))
DO 100 L=1,N
100 RCM(J,K)=RCM(J,K)+TCC(J,L)*PHI(2,NRN,L)*PHI(1,NRN,L)*BB(L)
1/(PHI(2,NRN,J)*PHI(1,NRN,J))
111  FORMAT(8E11.5)
RETURN
END

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C      ROUTINE FIT
C      THIS ROUTINE COMPARES LEED DATA FROM FILE DTAMN.DAT
C      WITH THEORY FROM FILE ITHRY.DAT.  EACH OF THE
C      EXPERIMENTAL CURVES ARE NORMALIZED TO THE
C      CORRESPONDING THEORETICAL CURVE.  BY SPECIFYING ESHIFT
C      ONE CAN VARY THE ENERGY OF THE ENERGY GRID OF THE
C      THEORETICAL CURVE TO MINIMIZE THE CHI-SQUARE.
C      THE CHI-SQUARE FIT IS PERFORMED FOR A SURFACE DISTANCE
C      XS; THE SMOOTHED DATA CURVE IS STORED IN IEFTD.DAT.
C      AND THE SMOOTHED THEORETICAL CURVE IS STORED IN
C      IEFTT.DAT.  BOTH ARE STORED AS A FUNCTION OF MOMENTUM
C      TRANSFER Q IN IFTQ.DAT.
C      PERFORM CHI-SQUARE OF YFIT(I) TO NPTS OF DATA IN Y(I)
C      AT POINTS X(I).
      DIMENSION X(200),XX(200),Y(200,6),YTHRY(200,6),YFIT(200,6)
      DIMENSION SCALE(6),SCALE1(6),BKGND(6),BKGND1(6)
      DIMENSION SIGM2(6),SIGM21(6)
      DIMENSION IFST(6),ILST(6)
      DIMENSION DQ(129,6),AT(129,6),AD(129,6),BT(129,6),BD(129,6)
      DIMENSION FMAG1(21,6),FMAG2(21,6),TDIFF(6),TPROD(6)
      DIMENSION PDIFF(21,6)
      DIMENSION YDIFF(200,6)
      DIMENSION QCONST(6)
      COMMON/QSHIFT/QCONST
      DATA RYD2,HZERO/27.2,0.0/
      DATA MPTS/20/
      DATA NULCUV/2/
      DATA ESHFTE/0./
      DATA SCALE/1.,1.,1.,1.,1.,1./
      DATA BKGND/0.,0.,0.,0.,0.,0./
      DATA SIGM2/1.,1.,1.,1.,1.,1./
C      TISE2
C      DATA QCONST/0.0,1.178,1.178,3.535,4.713,4.713/
C
C      TIS2
      DATA QCONST/0.0,1.271,1.271,3.812,5.083,5.083/
      OPEN(UNIT=20,FILE='DTAMN.DAT',DIALOG)
      OPEN(UNIT=21,FILE='ITHRY.DAT',DIALOG)
      OPEN(UNIT=22,FILE='IEFTD.DAT',DIALOG)
      OPEN(UNIT=23,FILE='IEFTT.DAT',DIALOG)
      OPEN(UNIT=24,FILE='IFTQ.DAT',DIALOG)
1      FORMAT(2I4,F8.5)
2      FORMAT(E12.5)
3      FORMAT(7E12.5)
14     FORMAT(1X,'WARNING NOT ENOUGH THEORY')
40     CONTINUE
      REWIND 20
      REWIND 21
      WRITE(5,30)
30     FORMAT(1X,'ENERGY SHIFT,SCALE,BKGND,STND DEV'
1//,'6//,6G//,6G//,6G')

```

```

ACCEPT 31, ESHFT1, SCALE1, BKGND1, SIGM21
31  FORMAT(G,/,6G,/,6G,/,6G)
    IF(SCALE1(1).LT.0.) GO TO 50
    DO 20 J=1,6
    IF(ESHFT1.EQ.0.) GOTO 15
    ESHFTE=ESHFT1
15  IF(SCALE1(J).EQ.0.) GOTO 16
    SCALE(J)=SCALE1(J)
16  IF(BKGND1(J).EQ.0.) GOTO 17
    BKGND(J)=BKGND1(J)
17  IF(SIGM21(J).EQ.0.) GOTO 20
    SIGM2(J)=SIGM21(J)
20  CONTINUE
    WRITE(5,19) ESHFTE,SCALE,BKGND,SIGM2
19  FORMAT(1X,'ESHIFT,SCALE,BKGND,SIGM2',/,
11X,F12.5,/,6E12.5,/,6E12.5,/,6E12.5)
    READ(20,1) NPTS,NCURV,DUM
    READ(20,3) (X(I),(Y(I,J),J=1,6),I=1,NPTS)
    READ(21,1) NTHRY,NCURVT,DUM
    IF(NCURVT.LT.NCURV) WRITE(5,14)
    DO 13 I=1,NTHRY
C   READ(21,3) (XX(I),YTHRY(I,4),YTHRY(I,1),YTHRY(I,2),YTHRY(I,3))
    READ(21,3) XX(I),(YTHRY(I,J),J=1,6)
13  CONTINUE
33  FORMAT(6E12.5)
    ESHFT=ESHFTE/RXD2
    DO 11 I=1,NTHRY
11  XX(I)=XX(I)+ESHFT
    DO 4 J=2,NCURV
    SIGM2(J)=SIGM2(J)**2
C
C   SUBTRACT BACKGROUND, DO NOT MODIFY
C   POINTS WITH ZERO INTENSITY.
    DO 4 I=1,NPTS
    IF(Y(I,J)<.0001) GOTO 4
    Y(I,J)=(Y(I,J)-BKGND(J))
    IF(Y(I,J).LE.HZERO) Y(I,J)=HZERO
4   CONTINUE
    DO 5 J=1,NPTS
    NFST=J
    IF(X(J).GT.XX(1)) GO TO 6
5   CONTINUE
6   DO 7 J=1,NPTS
    NLST=J-1
    IF(X(J).GT.XX(NTHRY)) GO TO 8
7   CONTINUE
8   CALL INTRP(NFST,NLST,NCURVT,NTHRY,YTHRY,YFIT,XX,X)
    WRITE(5,1) NFST,NLST,ESHFT
    WRITE(5,3) X(NFST),(YFIT(NFST,J),J=1,6)
    WRITE(5,3) X(NLST),(YFIT(NLST,J),J=1,6)
    DO 10 J=2,NCURV
    ICNT=0

```

```

DO 75 I=NFST,NLST
IF(Y(I,J).LE.HZERO) GOTO 75
QQ=X(I)-ESHFT-QCONST(J)
IF(QQ.LE.0.0) GOTO 75
ICNT=ICNT+1
ILST(J)=I
75 CONTINUE
IFST(J)=ILST(J)+1-ICNT
C
SUMD=0.0
SUMT=0.0
I1=IFST(J)
I2=ILST(J)
DO 200 I=I1,I2
SUMD=SUMD+Y(I,J)
200 SUMT=SUMT+YFIT(I,J)
IF(SUMD<1.E-7) SUMD=1.0
SCALE(J)=SUMT/SUMD
TOTPT=FLOAT(I2+1-I1)
IF(TOTPT.LE. 1.0) GOTO 10
DO 201 I=1,NPTS
201 Y(I,J)=Y(I,J)*SCALE(J)
YEAVE=SUMD*SCALE(J)/TOTPT
CHI=HZERO
VARD=HZERO
VART=HZERO
ICNT=0
DO 9 I=I1,I2
YE=Y(I,J)
IF(YE.LE.HZERO) GO TO 35
SCHI=YFIT(I,J)-YE
SVARD=YE-YEAVE
SVART=YFIT(I,J)-YEAVE
YDIFF(I,J)=SCHI
ICNT=ICNT+1
GO TO 45
35 SCHI=HZERO
SVARD=HZERO
SVART=HZERO
45 VARD=VARD+SVARD*SVARD
VART=VART+SVART*SVART
9 CHI=CHI+SCHI*SCHI
VAR=AMAX1(VARD,VART)
CHI=CHI/(VAR*SIGM2(J))
VARD=SQRT(VARD/TOTPT)/SCALE(J)
YEAVE=YEAVE/SCALE(J)
WRITE(5,100) J,CHI,YEAVE,VARD,ICNT,ESHFTE,
1SCALE(J),BKOND(J),SIGM2(J)
100 FORMAT(1X,'FOR THE',I4,'TH CURVE'3X,'CHI SQ=',E12.5,/,
11X,'EXPERIMENTAL AVE=',E12.5,1X,'STND DEV=',E12.5,/,
21X,'NUMBER OF POINTS=',I5,5X,'FOR ESHIFT,SCALE,BKOND,SIGM2...',
3,/,5X,4E12.5)

```

```

10  CONTINUE
C
    WRITE(5,150)
150  FORMAT(1X,'FOURIER ANALYSIS---SURFACE DISTANCE(1G)?')
    ACCEPT 151, XS
151  FORMAT(1G)
C
    CALL FTRAN(Y,X,IFST,ILST,NPTS,NCURV,DQ,AD,BD,ESHFT)
    CALL FTRAN(YFIT,X,IFST,ILST,NPTS,NCURV,DQ,AT,BT,ESHFT)
    RTEST=0.0
    DO 400 J=2,NCURV
    DIFF=0.0
    PROD=0.0
    FNORM1=0.0
    FNORM2=0.0
    FMAG1(1,J)=AD(1,J)
    FMAG2(1,J)=AT(1,J)
    FAVE2=AD(1,J)*AD(1,J)
    DO 300 I=2,20
    ARG=DQ(I,J)/XS
    BROAD=SIN(ARG)/ARG
    IF(XS>50.0) BROAD=1.0
    AA1=AD(I,J)*BROAD
    AA2=AT(I,J)*BROAD
    BB1=BD(I,J)*BROAD
    BB2=BT(I,J)*BROAD
    PROD=PROD+AA1*AA2+BB1*BB2
    PDIFF(I,J)=(AA1-AA2)**2+(BB1-BB2)**2
    DIFF=DIFF+PDIFF(I,J)
    SUMSQ1=AA1*AA1+BB1*BB1
    SUMSQ2=AA2*AA2+BB2*BB2
    FMAG1(I,J)=SUMSQ1
    FMAG2(I,J)=SUMSQ2
    FNORM1=FNORM1+SUMSQ1
    FNORM2=FNORM2+SUMSQ2
300  CONTINUE
    FNORM=AMAX1(FNORM1,FNORM2)
    DO 305 IJ=1,MPTS
    PDIFF(IJ,J)=PDIFF(IJ,J)/FNORM
305  CONTINUE
    TPROD(J)=PROD/(SQRT(FNORM1*FNORM2))
    TDIFF(J)=DIFF/FNORM
    RTEST=RTEST+TDIFF(J)
400  CONTINUE
    WRITE(5,405) (TPROD(JJ),JJ=2,NCURV)
    WRITE(5,401) (JJ,TDIFF(JJ),JJ=2,NCURV)
    DO 402 I=1,3
402  WRITE(5,405) (DQ(I,J),PDIFF(I,J),J=2,NCURV)
401  FORMAT(1X,'X(M) AND SURFACE CHI-SQUARE FOR EACH BEAM',/,
11X,6(I2,'-TH BEAM ',E11.4))
405  FORMAT(1X,12E11.4)
    WRITE(5,406) RTEST

```

```

406  FORMAT(1X,'SUM OF CHI-SQUARES',E11.4)
      GO TO 40
50   CONTINUE
      CALL FTINV(AD,BD,DQ,XS,DUM,MPTS,NPTS,NCURV)
      CALL FTINV(AT,BT,DQ,XS,DUM,MPTS,NPTS,NCURV)
      WRITE(22,1) NPTS,NCURV,DUM
      WRITE(22,3) (X(I),(Y(I,J),J=1,6),I=1,NPTS)
      WRITE(23,1) NTHRY,NCURVT,DUM
      WRITE(23,3) (XX(I),YTHRY(I,1),YTHRY(I,2),
1 YTHRY(I,3),YTHRY(I,4),I=1,NTHRY)
      CLOSE(UNIT=20)
      CLOSE(UNIT=21)
      CLOSE(UNIT=22)
      CLOSE(UNIT=23)
      CLOSE(UNIT=24)
      STOP
      END
      SUBROUTINE INTERP(NFST,NLST,NCURVT,NTHRY,Y,YFIT,XX,X)
      DIMENSION X(200),XX(200),Y(200,6),YFIT(200,6)
      DATA HONE,H1B2,HTWO/1.0,0.5,2.0/
      DX=X(2)-X(1)
      DO 1 I=NFST,NLST
      DO 2 J=1,NTHRY
      JJ=J
      DDX=ABS(XX(J)-X(I))
      IF(DDX.LE.DX) GO TO 3
2     CONTINUE
      WRITE(5,4)
3     DEL=DDX/DX
      DO 1 K=1,NCURVT
      A=Y(JJ,K)
      B=Y(JJ+1,K)-Y(JJ,K)
      C=H1B2*(Y(JJ+2,K)-HTWO*Y(JJ+1,K)+Y(JJ,K))
1     YFIT(I,K)=A+B*DEL+C*DEL*(DEL-HONE)
4     FORMAT(23H WARNING  INTERP FAILED )
      RETURN
      END

C
C
      SUBROUTINE INTRP(NFST,NLST,NCURVT,NTHRY,Y,YFIT,X,XFIT)
      DIMENSION V(6,200),X(200),XFIT(200),Y(200,6),YFIT(200,6)
      DIMENSION YY(200)
      DATA EPS/.001/
      DO 30 J=2,NCURVT
      DO 10 I=1,NTHRY
10     YY(I)=Y(I,J)
      CALL SP3A(NTHRY,EPS,X,YY,PROXI,V)
      DO 30 I=NFST,NLST
      XF=XFIT(I)
      CALL SP3B(NTHRY,X,YY,XF,YF,V,SS1,SS2)
30     YFIT(I,J)=YF
      RETURN

```

```

END
SUBROUTINE FTRAN(YE,XE,IFST,ILST,NNPTS,NCURV,DQ,FCOS,FSIN,ESHFT)
  DIMENSION V(6,129)
  DIMENSION YE(200,6),XE(200),YY(200),XQ(200)
  DIMENSION DQ(129,6),FCOS(129,6),FSIN(129,6)
  DIMENSION FNT(129),A(129),B(129)
  DIMENSION QCONST(6),IFST(6),ILST(6)
  DIMENSION QFST(6),QLST(6)
  COMMON/QGRD/QFST,QLST
  COMMON/QSHFT/QCONST
  PI=3.14159265
  M=20
  NUMF=64
  N=2*NUMF+1
  EPS=.001
  DO 10 J=2,NCURV
    NFST=IFST(J)
    NLST=ILST(J)
    NPTS=NLST+1-NFST
    DO 20 I=1,NPTS
      K=I+NFST-1
      YY(I)=YE(K,J)
20    XQ(I)=SQRT(2.*(XE(K)-ESHFT)-QCONST(J))+SQRT(2.*(XE(K)-ESHFT))
      QFST(J)=XQ(1)
      QLST(J)=XQ(NPTS)
      QLNGTH=XQ(NPTS)-XQ(1)
      DELQ=QLNGTH/FLOAT(N-1)
      CALL SP3A(NPTS,EPS,XQ,YY,PROXI,V)
      DO 30 I=2,N-1
        QF=XQ(1)+FLOAT(I-1)*DELQ
        CALL SP3B(NPTS,XQ,YY,QF,YQ,V,SS1,SS2)
        FNT(I)=YQ
        DQ(I,J)=2.0*PI*FLOAT(I-1)/QLNGTH
30    CONTINUE
      FNT(1)=YY(1)
      FNT(N)=YY(NPTS)
      DQ(1,J)=0.0
      DQ(N,J)=2.0*PI*FLOAT(N-1)/QLNGTH
      CALL FORIT(FNT,NUMF,M,A,B,IER)
      DO 40 II=1,M
        FCOS(II,J)=A(II)
40    FSIN(II,J)=B(II)
10    CONTINUE
  RETURN
END

C
SUBROUTINE FORIT(FNT,N,M,A,B,IER)
C  FROM SSP---EXPLICIT AND SLOW VERSION
  DIMENSION A(129),B(129),FNT(129)
  PI=3.14159265
  TWPI=2.0*PI
  NUM=2*N+1

```

```

FNUM=1.0/FLOAT(NUM)
COFF=2.0*FNUM
MP1=M+1
A(1)=0.
B(1)=0.
DO 50 I=1,NUM
50  A(1)=A(1)+FNT(I)
    A(1)=A(1)*FNUM
C
DO 100 J=2,MP1
A(J)=0.0
B(J)=0.0
DO 90 I=1,NUM
ARG=TWPI*FLOAT(I-1)*FLOAT(J-1)*FNUM
A(J)=A(J)+FNT(I)*COS(ARG)
B(J)=B(J)+FNT(I)*SIN(ARG)
90  CONTINUE
    A(J)=A(J)*COFF
    B(J)=B(J)*COFF
100 CONTINUE
RETURN
END
SUBROUTINE FTINV(A,B,DQ,XS,SCALE,MPTS,NPTS,NCURV)
DIMENSION A(129,6),B(129,6),DQ(129,6)
DIMENSION X(200),Y(200)
DIMENSION QFST(6),QLST(6)
COMMON/QGRD/QFST,QLST
PI=3.14159265
GRID=2.0*PI/FLOAT(NPTS-1)
DO 700 J=2,NCURV
QGRID=(QLST(J)-QFST(J))/FLOAT(NPTS-1)
DO 600 IQ=1,NPTS
Q=GRID*FLOAT(IQ-1)
X(IQ)=QFST(J)+QGRID*FLOAT(IQ-1)
Y(IQ)=A(1,J)
DO 600 M=2,MPTS
ARG=DQ(M,J)/XS
BROAD=SIN(ARG)/ARG
FM=FLOAT(M-1)
600 Y(IQ)=Y(IQ)+(A(M,J)*COS(FM*Q)+B(M,J)*SIN(FM*Q))*BROAD
WRITE(24,50) NPTS,NCURV,SCALE
WRITE(24,55) (X(I),Y(I),I=1,NPTS)
50  FORMAT(2I4,F8.5)
55  FORMAT(2E12.5)
700 CONTINUE
RETURN
END
@

```


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CHAPTER TWO

Theory of Deep Traps

I. INTRODUCTION

Why does O produce a deep electron trap in GaAs although S produces a shallow trap? This question, until now unanswered, illustrates the problem of understanding and predicting the properties of deep traps in semiconductors. Although traps, which are unoccupied impurity energy states in the critical bandgap, control the technologically important properties of semiconductors, existing theories have not successfully predicted which impurities form deep traps.^{1-4/} The discussion presented here outlines the basic physics of a deep trap and shows how to make gross predictions of deep trap energies using essentially only a table of impurity atomic orbital energies.

In the following section, in which we focus on the prediction of electronic properties of impurities in semiconductors, we shall illustrate the microscopic physics of deep traps in the bandgap of semiconductors in order to predict which atoms are likely to form such deep traps. These predictions can be made by using tables of atomic orbital energies. Furthermore, application of formal scattered wave theory to the problem of the impurity interacting with a perfect crystal leads to semiquantitative predictions of all impurity electronic and vibrational properties.

Throughout the discussion of these properties, the focus is on predictions based on the chemical trends of electronic properties. In all stages of the solution of the impurity problem the inessential details are ignored and only the features which mainly control the impurity properties are retained. The resulting procedure retains enough physics and simplicity to allow predictions for most of the commonly known semiconductors--a total of 14 from column II through VI of the Periodic Table--for a total of 300 different host: impurity predictions.

To illustrate the relation between deep trap energies and atomic energies before doing a calculation, we plot the best known experimentally determined trap energies for Si as a function of the atomic energy of the impurity which creates the trap. At this point we have not yet concentrated on simple point defects but instead consider the energy level data, gathered into Table I, for all impurity associated traps in Si. For simplicity we plot all traps, both shallow and deep, as a function of

$$V_0 = \epsilon_{\text{imp}}^h - \epsilon_{\text{Si}}^h$$

where $\epsilon^h = \frac{1}{4}E^s + \frac{3}{4}E^p$ is the average valence orbital energy of each atom (see Table II). In this plot, we include both shallow and deep traps distinguished by their binding energy to the band edges. Thus a trap located in the bandgap within about 0.025 eV (the room temperature thermal energy) from the conduction or valence bands is conventionally labelled a shallow trap while one more deeply bound is called a deep trap.

Thus, first inspection of Fig. 1 indicates that atomic energies and the trap energies, such as V_0 , have no relation because, although atomic energies range from -25 to +10 eV, the traps are confined within the bandgap of width $\Delta = 1.15$ eV. Workers searching for chemical trends, i.e. a relationship to the periodic chemical properties within rows or columns of the Periodic Table, between impurity atoms and trap energies, have been unsuccessful.^{10/} One naturally attempts to find a linear relationship $E \propto V_0$ but exceptions to any such relationship have frustrated most attempts.

However, if we fit the trap energies E and the atomic energies V_0 with

$$\frac{1}{V_0} = \frac{\alpha}{E} + \frac{\alpha}{E-\Delta} \quad (1)$$

Table I Silicon Data^{5,6,7/}

Impurity	Energy (eV)	Type (a=acceptor, d=donor s=substitutional)
Al	0.057	a,s
As	1.101	d,s
B	0.045	a,s
Bi	1.08	d,s
Cd	0.70	a
	0.95	d
	0.55	a
	0.30	a
Ga	0.065	a,s
Ge	0.88	d
	0.50	a
Hg	0.84	a
	0.79	a
	0.33	a
	0.25	d
	0.82	d
	0.80	a
	0.36	a
	0.39	d
In	0.16	a
O	0.99	d
	0.64	d
	0.41	a
	0.03	a
	0.77	a
N	1.01	d
P	1.11	s
Pb	0.98	a
	0.78	a
S	0.97	d
	0.89	d
	0.78	d
	0.48	d
	0.63	d,s
Sb	1.11	d,s
Se	0.90	d
	0.75	d
Sn	0.98	d
Te	1.01	d
Tl	0.26	a,s
Zn	0.31	a

TABLE II Atomic Energies^{8,9/}

Atom	Energy (eV)			
	E^S	E^P	$\bar{E}^S$	$\bar{E}^P$
B	-13.46	- 8.43		
C	-19.19	-11.79	-4.26	
N	-25.71	-15.44	-4.99	
O	-33.85	-17.19	-7.94	
F	-42.77	-19.87	-7.04	
Al	-10.70	- 5.71	-2.57	
Si	-14.68	- 8.08	-3.11	
P	-18.94	-10.65	-3.27	
S	-23.92	-11.90	-5.27	
Cl	-29.18	-13.77		
Zn	-17.96	- 3.48		
Ga	-11.55	- 5.67	-2.60	
Ge	-15.05	- 7.82	-3.04	
As	-18.66	-10.05	-3.55	
Se	-22.78	-10.96	-4.89	
Br	-27.00	-12.43		
Cd	- 7.20	- 2.99		
In	-10.14	- 5.37	-2.34	
Sn	-12.96	- 7.21	-2.64	
Sb	-15.83	- 9.10	-3.33	
Te	-19.06	- 9.79	4.19	
I	-22.33	-10.97		
Hg	- 7.10	- 1.50		
Tl	- 9.82	- 5.23		
Pb	-12.41	- 6.95		
Bi	-15.01	- 8.70		
Po	-17.90	- 9.28		
At	-20.82	-10.33		

Fig. 1 An empirical fit to all well-known traps in Si; the fit does not distinguish between electron ($\circ$) and hole ($\bigcirc$) traps. Atoms with lowest energy are associated with conduction band electron traps while atoms with highest energy are associated with valence band derived hole traps.

and $\alpha = 0.1$ eV, we obtain the two-branched curve shown in Fig. 1. This empirical fit does remarkably well for most of the traps with its most glaring failures confined to O and Zn. One must bear in mind the scatter in the data, indicated in the figure, arises partially from experimental uncertainty and also the charge state of the trap. The empirical relation characterized by only one parameter, α , not determined by the data is similar to but not the final relation which we develop; rather it shows us how to organize the data to see the close connection between trap energies and atomic energies.

II. BACKGROUND

A. Defining the Problem

To appreciate this exploration of the connection between deep trap energies and atomic energies we will establish the following points:

(i) traps are technologically very important, (ii) shallow traps are well understood; deep traps are not, (iii) the energy position of a trap within the bandgap is important knowledge, (iv) experimenters have data about energies of unidentified deep traps, (v) theorists have not produced a predictive theory. Therefore, a simple predictive theory of deep trap energies is needed. After the above points are discussed, we will begin discussion of a simple theory which predicts trap energies via a simple relation similar to Eq. (1).

Traps are associated with defects in the host crystal; we shall focus on those arising from point defects, either substitutional impurities or vacancies, with the main emphasis on impurities. The defect potential caused by substitution of an impurity atom for a host atom has three possible distinct contributions schematically indicated in Fig. 2: (i) a short-range central cell potential, (ii) a long-range Coulomb potential, and (iii) an electron-lattice interaction caused by distortion of the lattice around the impurity. The central-cell potential is essentially the difference between the atomic potential of an impurity atom with Z protons and electrons and the host atom with Z_0 electrons and protons. Defined by $V = H - H^0$ where H^0 is the Hamiltonian of the host crystal and H is the Hamiltonian of the host with one impurity, this potential becomes essentially a difference of the atomic energies of atoms near the defect when we write the matrix elements of the Hamiltonian in a localized, atomic basis. The Coulomb potential, screened because of the solid-state environment, is the limit of $H - H^0$ at large r

Fig. 2 Schematic of the three contributions to the potential caused by a point defect: (i) Coulomb potential, (ii) central cell potential, and (iii) lattice relaxation and polarization.

$$\frac{N-N_o}{\epsilon r}$$

(2)

when N_o valence electrons are replaced by N electrons in a crystal with dielectric constant ϵ . Most difficult to understand and quantify is the effect within a few inter-atomic distances of the defect; electronic polarization and lattice distortion, both very difficult to model, must be taken into account. In the next section we outline the progress made in understanding the control of trap energy by the defect potential.

Technologically important shallow traps have captured the attention of both experimenters and theorists since the time the transistor was invented.^{11/} Localized and controlled concentrations of shallow traps which ionize at room temperatures control the unique, directional conductivity responsible for the operation of the transistor. An added impurity either produced a donor which when ionized, donates excess valence electrons to the conduction band, or an acceptor which can accept electrons ionized from the valence band thus creating a hole.

By 1957, the basic theory of shallow traps was worked out by Kohn and Luttinger.^{12/} They focused on the long-range, screened Coulomb potential set up by an impurity with either an excess or deficiency of electrons. Because of the small effective mass and screening of the Coulomb potential the problem reduces to a hydrogen atom calculation with an attendant Rydberg series with an effective Rydberg ≈ 0.1 eV. The large orbital radii of the localized electrons with such small energy justify neglect of the short-range central cell potential.

The hydrogenic effective mass theory was worked out by a method developed by Koster and Slater which is equivalent to formal scattering theory applied to the solid-state.^{13/} They and most other workers have concentrated on the interaction of the defect electron with the nearest host energy band. Spin-orbit effects produce complexity in both the theory and the experiments

because spectroscopic multiplets must be considered;^{14/} also recently coupling between nearly degenerate critical points in the bandstructure has been found to be important in the calculation for donors in Si and Ge. Later we shall understand the enormous impact that the effective mass theory has had on the intellectual framework used to tackle the deep trap problem.

Deep traps, discovered in 1952,^{15/} are important because they control the lifetimes of carriers in luminescent devices. They are used to enhance the probability of radiative electron-hole recombination in Light Emitting Diodes enough that the intensity of the emitted light is sufficient to make these devices commercially competitive as light sources.^{16/} Deep traps, usually of unknown origin and thus uncontrollable, degrade the performance of lasers by quenching build-up of electron-hole pairs before coherent emission can be achieved.^{17/} In either case, the defect which causes a deep trap must be identified before measures can be devised to control their concentration in the solid.

Deep traps are characterized mainly by their energy referred to a band edge rather than by, for instance, their energy multiplet separation as a function of magnetic field. Experiments which measure emission or absorption usually reveal little information other than the energy of the defect state. In addition much data about energy position in the bandgap of unknown traps has been gathered by use of Deep Level Transient Spectroscopy (DLTS).^{18/} A useful theory of deep traps would provide a way of identifying the impurities which cause the complicated spectra gathered by DLTS.

Recognizing the importance of the short-ranged central cell potential associated with a deep trap, early workers tried to simulate it and the surrounding crystal with a small cluster of atoms; then the Schrödinger equation was directly solved for this small crystal. Coulson and Kearsley

applied this method to the vacancy in diamond with little quantitative success.^{19/} Messmer and Watkins used a large cluster, 70 atoms, to tackle the same problem with the Huckel approximation for the Hamiltonian; both of these calculations suffered from lack of quantitative success in relating the defect energies to the perfect crystal bandgap.^{20/}

Contemporary to these cluster calculations, workers have extended Koster-Slater techniques to progressively deeper traps. These calculations assumed a one-band model for the host bandstructure and calculated the defect potential in either a momentum representation or a localized Wannier function basis.^{21/} In one such calculation the phenomenological defect potential used was much smaller than the difference of pseudopotentials expected to model the impurity;^{22/} in another, the phenomenological potential for a calculation of the energy states of an impurity in an alloy was found to be composition dependent.^{23/}

Recently, Jaros has performed Koster-Slater calculations using a localized basis for a vacancy and 0 in Si using a pseudopotential representation for the defect potential.^{24/} His results were not very helpful in producing insight about what makes 0 deep; in fact, he found that the results were insensitive to the choice of impurity potential. Recently, two different groups have produced results for the vacancy in Si; their methods seem to be a tour de force but results for other systems will not be available for some time.^{25,26/}

Assessing the work in the field, we think it will be very worthwhile to perform a semi-empirical calculation in an atomic basis in order to obtain insight and extract trends in trap energies. Such a calculation was first done by Lannoo and Lengler but they evidently made so many approximations in the calculation of the host-crystal bandstructure that they

abandoned the effort before doing any systematic calculations.^{27/} However, before doing the actual calculation let us direct our attention to a defect molecule model of point defects.

B. The Qualitative Solution Via the Defect Molecule

The qualitative features of the deep trap problem can be obtained by concentrating on only the defect wavefunction, rather than the host crystal wavefunction, by expanding it in terms of a few molecular orbitals surrounding the defect.^{19/} First we calculate the energy and wavefunction of the central atom and then observe their behavior as we convert this atom into a defect, either a substitutional impurity or a vacancy, by varying its atomic energy.

The essential physics can be understood by considering only the central atom and its four nearest neighbors to which it bonds. We focus on the interaction of the two symmetric molecular wavefunctions composed of the hybrid orbitals pointing along the bonds between the atoms. We shall assume the orbital energy ϵ_c of the central atom lower than the orbital energy ϵ_o of the other atoms. Now, if we turn on the transfer energy, t , interaction between the atoms, the two states will repel each other as shown in Fig. 3. The lowest state, called a bonding state because it is occupied by the two bonding electrons, is analogous to the valence band, and the unoccupied upper state, called an anti-bonding, is analogous to the conduction band. When we decrease the central atom's orbital energy by V_o to simulate an electron-attractive substitutional impurity, the two states become energetically further apart and thus repel each other less. The net result is creation of two impurity states--one is an occupied bonding state, energetically much lowered and thus of no technological interest; the other

Fig. 3 Defect Molecule A_1 (symmetric) states repel each other less when an attractive impurity potential V_0 is created. The deep trap state is the anti-bonding impurity state. The two defect molecule states (left side) repel each other less when an attractive (lower energy) impurity replaces the central atom (right side). The higher energy state associated with the impurity is only slightly reduced in energy compared with the impurity potential V_0 .

is an unoccupied anti-bonding state which is slightly lowered from the original value, enough that it may trap electrons injected into the anti-bonding, or conduction, states.

Focusing on the anti-bonding state, which we refer to as the trap, we see from the figure that for $\lim V_o \rightarrow \infty$ the trap state becomes "pinned" to the orbital energy ϵ_o of the other atoms. When interactions with the rest of the host crystal are turned on, the energy of the other atoms is modified but the behavior of the system with change in "atomic" energy is the same. Furthermore, because the prototype conduction and valence bands broaden, the defect potential V_o must exceed a threshold V_t before a state can be pulled from the conduction band. Thus, unless the potential exceeds a threshold which depends on the host crystal, the short-range central-cell defect potential can neither create nor control an electron trap.

The trap energy in the 2-state system becomes "pinned" in the limit of a very attractive defect potential V_o . This can be seen by examination of the solution

$$V_o = \frac{(E - E_v)(E - E_c)}{(E - \epsilon_o)} \quad (3)$$

with $\left(\frac{E_c}{E_v}\right) = \frac{(\epsilon_o + \epsilon_c)}{2} \pm \left[\left(\frac{\epsilon_o - \epsilon_c}{2}\right)^2 + t^2\right]^{1/2}$; in the limit of $V_o \rightarrow \pm\infty$, $E \rightarrow \epsilon_o$. Furthermore, the plot of E versus V_o has a characteristic shape which corresponds to that for the rigorous solution. For this we use units of t and set $\epsilon_o = 0$ and $\epsilon_c = 2$. Then E versus v_o displayed in Fig. 4 has a characteristic behavior; as v_o becomes attractive (negative) E decreases rapidly at first, then more slowly and finally becomes pinned to $\epsilon_c = 1$. For the same parameters ϵ_c and ϵ_o we show the behavior of the defect molecule wavefunction as a function of impurity potential v_o in Fig. 5. Note that the potential on the central site produces an unoccupied

Fig. 4 — Shows how the characteristic E versus V curve becomes pinned for $\lim V_0 \rightarrow \pm \infty$. This characteristic curve of E versus V has two branches representing the two states, bonding and anti-bonding, controlled by the impurity potential V . The higher energy anti-bonding state represents the unoccupied state, caused by an impurity, which can trap an electron. Note that for very attractive V the deep trap becomes pinned to an energy determined by the atoms surrounding the impurity.

Fig. 5 Schematic diagram showing that as the impurity potential strength increases the wavefunction becomes less like the impurity atom and more characteristic of the "other" atoms in the crystal. The anti-bonding wavefunction becomes more characteristic of the atom surrounding the impurity as the potential V_0 becomes more attractive. Here we plot $A(E)^2$ where $A(E)$ is the impurity S-orbital amplitude in the anti-bonding wavefunction.

state which predominantly sits on the nearest neighbor sites--in the limit of a very deep potential the impurity and trap wavefunction become completely separated. In this limit the wavefunction has associated energy characteristic of the nearest neighbor orbitals.

The characteristic E versus V curve obtained in the defect molecule problem is a universal feature of the deep trap problem. This feature appeared in the data shown in Fig. 1; without doing any calculation one can make predictions of which impurities will form deep traps by using plots of impurity data for the SP^3 bonded impurities. This characteristic curve will also appear in the rigorous crystal calculation which we begin to develop in the next section.

III. THEORY

In this section we develop the formalism needed to calculate the properties of the localized defect in a semiconductor by use of scattering theory applied to the solid-state^{1/} We solve for the energy E and wavefunction Ψ of the defect state in terms of the perfect-crystal Hamiltonian H^0 and the defect potential V . By exploiting the crystal symmetry about the point defect the equations to be solved can be simplified and the resulting defect state energies and wavefunctions can be uniquely labelled by symmetry. Finally, useful energy-moment properties of the electronic density of states are developed; one gives the number of states and another gives the electronic energy.

The goal is to solve the Schrödinger equation $H\Psi = E\Psi$ for the energies E and wavefunctions Ψ of a Hamiltonian H which describes the electronic properties of a semiconductor containing a localized defect. For the defect-free, translationally invariant perfect crystal with a Hamiltonian H^0 , the Schrödinger equation $H^0\psi_{nk} = E_{nk}\psi_{nk}$ produces an energy bandstructure E_{nk} with associated eigenvectors ψ_{nk} . The two systems are related by the Lippman-Schwinger equation

$$\Psi = \lim_{\epsilon \rightarrow 0} \{\Psi + G(E+i\epsilon)V\Psi\} \quad (4)$$

We thus formally allow the defect potential to scatter the state ψ into an interacting defect-crystal state Ψ . Here

$$G(E) = (E - H^0)^{-1} \quad (5)$$

is the perfect crystal Green's function or resolvent operator and

$$V = H - H^0 \quad (6)$$

is the defect potential. The boundary conditions of Ψ are determined by the sign of ϵ , to make the impurity states decay in time we must choose $\epsilon \geq 0$.

The bound states have real energies E_b which are solutions to the determinantal equation

$$D(E) = \text{Det} || 1 - G(E)V || = 0 \quad (7)$$

The origin of this equation can be understood by noting that the large amplitude scattering states are associated with the poles of $(1-G(E)V)^{-1}$ in the solutions of Eq. (4):

$$\Psi = (1 - G(E)V)^{-1} \psi. \quad (8)$$

Furthermore, the states uniquely identified with the impurity must be orthogonal to the perfect crystal states. This requirement, together with Eq. (8), gives

$$0 \equiv \langle \psi | \Psi \rangle = \langle \psi | 1 - G(E)V | \psi \rangle \quad (9)$$

which has a non-trivial solution if $D(E) = 0$. In general the solutions, of form $E = E_b + i\Gamma$, correspond to a state of energy E_b with lifetime $\hbar/\Gamma$. In the discussion to follow we explicitly consider the bound state energies, which are real, and implicitly consider the resonance states with complex energy.

Given the bound state energies E_b , the defect states $|\psi(E_b)\rangle$ are determined by the operator equation

$$\psi(E_b) = G(E_b) V \psi(E_b) \quad (10)$$

which is solved in the basis used in the determinantal equation. The eigenstates at all other energies correspond to slightly perturbed perfect crystal states $|\Psi(E)\rangle$ given by

$$|\Psi(E)\rangle = (1 - G(E)V)^{-1} |\psi(E)\rangle. \quad (11)$$

Note that in both Eq. (10) and (11) E is the physical energy which is always real. Thus resonance states, which mix with the perfect crystal continuum states, are produced by Eq. (11) when $E = E_b$, the real part of the energy pole, $E_b + i\Gamma$, responsible for a resonance state.

The electronic properties of the host crystal required to solve the defect problem are contained in the spectral density operator which depends on the eigenvalues and eigenvectors of the Hamiltonian H^0 . Using the identity,

$$\frac{1}{X+i\epsilon} = p \frac{1}{X} - i\pi\delta(X) \quad (12)$$

with p meaning Cauchy principle value, the resolvent operator can be written as

$$G^0(E) = p \int \frac{\delta(E' - H^0)}{E - E'} dE' - i\pi \delta(E - H^0) \quad (13)$$

The spectral density operator, $\delta(E - H^0)$ with δ meaning the Dirac delta function, written as

$$\delta(E - H^0) = \sum_{\vec{n}\vec{K}} |\vec{n}\vec{K}\rangle \delta(E - E_{\vec{n}\vec{K}}) \langle \vec{n}\vec{K}| \quad (14)$$

depends only on the eigenvalues $E_{\vec{n}\vec{K}}$ and eigenvectors $|\vec{n}\vec{K}\rangle$ of the host crystal.

The range, in coordinate space, of the defect potential dictates the representation used to define its matrix elements and thus also the matrix elements of $G^0(E)$. The representation is always chosen to minimize the matrix elements needed to define V ; designating matrix elements inside the range of V by I and those outside by 0 , one can schematically write

$$V = \begin{pmatrix} V_{II} & 0 \\ 0 & 0 \end{pmatrix} \quad (15)$$

and

$$G^0(E) = \begin{pmatrix} G_{II}^0 & G_{IO}^0 \\ G_{OI}^0 & G_{OO}^0 \end{pmatrix} \quad (16)$$

Then $D(E)$ becomes

$$D(E) = \text{Det} ||1 - G_{II}^0(E)V_{II}|| \quad (17)$$

a matrix equation whose size is determined by the range of the potential. Even though the wavefunction of the defect may extend throughout the host crystal all its electronic properties depend on a finite-sized matrix if the representation is chosen properly.

The representation used to define the defect potential usually is not adapted to the symmetry of the point defect. Suppose we define the matrix in terms of the representation $|a_i\rangle$ used to define the Hamiltonians. Then using the point-group symmetry of the defect, we can define a symmetry-adapted representation $|s_i^{(r)}\rangle$ which block-diagonalizes the defect potential into R irreducible representations $v_{i,j}^{(r)}$. Thus

$$v_{ij}^{(r)} = \begin{pmatrix} v_{ij}^{(1)} & & 0 \\ & v_{ij}^{(2)} & \\ 0 & & v_{ij}^{(R)} \end{pmatrix} \quad (18)$$

or

$$v = \sum_r \sum_{ij} |s_i^{(r)}\rangle v_{ij}^{(r)} \langle s_j^{(r)}| \quad (19)$$

Because $G^0(E)$ has the same or higher symmetry it too can be block-diagonalized into irreducible representations^{26/}

$$G^0(E) = \sum_r \sum_{i,j} |s_i^{(r)}\rangle G_{i,j}^{or}(E) \langle s_j^{(r)}| \quad (20)$$

Now the determinantal equation $D(E)$ factors into a product of determinantal equations labelled by symmetry. The determinant of a block diagonal matrix is a product of determinants of the blocks so we have

$$D(E) = \prod_{r=1}^{\text{reps}} D^{(r)}(E) \quad (21)$$

with

$$D^{(r)}(E) = \text{Det} ||1 - G^{(r)}(E) v^{(r)}|| \quad (22)$$

which has bound state solutions $E_b^{(r)}$ labelled by the representation. For instance, we will later obtain one s-state and three degenerate p-state energies for a substitutional impurity.

Having chosen the symmetry-adapted basis for our problem we turn again to the spectral density of states whose first two energy moments can be related to the total number of states and the total electronic energy. The density of states for any representation r can be generated by taking the trace of the spectral density of states,

$$N^{(r)}(E) = \text{Tr } \delta(E - H^0) = \sum_{n\vec{K}} \delta(E - E_{n\vec{K}}), \quad (23)$$

and the usual density of states is

$$N(E) = \sum_{r=1}^{\text{reps}} N^{(r)}(E) \quad (24)$$

The 0th moment of the density of states,

$$N = \int N(E) dE = \sum_{n\vec{K}} (1) \quad (25)$$

is the total number of states N and the 1st energy moment,

$$E_T = \int E N(E) dE = \sum_{n\vec{K}} E_{n\vec{K}}, \quad (26)$$

is the total electronic energy, E_T , of the host crystal. Similar moments, defined for each representation, can be computed during a calculation to verify the accuracy of the calculation.

In a similar way one could define and compute related quantities for the electronic properties of an imperfect crystal with an impurity; but a more practical approach is to concentrate on changes in these properties. First we relate $\Delta N(E)$, the change in the density of states, to $D(E)$ defined

in Eq. (17). The new density of states appears in the imaginary portion of the new resolvent operator $G(E)$ defined by

$$G(E) = (E-H)^{-1} \quad (27)$$

which can be related to $G^0(E)$ by

$$G(E) = G^0(E) + G^0(E) V G(E) \quad (28)$$

or

$$G(E) = (1 - G^0(E)V)^{-1} G^0(E) \quad (29)$$

Then the change in the density of states is

$$\Delta N(E) = -\frac{1}{\pi} \text{Im Tr } [G(E) - G^0(E)] ,$$

obtained by using Eqs. (13), (27) and (28). By using (29) and doing some algebra one obtains

$$\Delta N(E) = -\frac{1}{\pi} \frac{d}{dE} \phi(E) \quad (30)$$

with the phase shift $\phi(E)$ defined by

$$\phi(E) = \text{Tan}^{-1} \frac{\text{Im}D(E)}{\text{Re}D(E)} \quad (31)$$

In a similar way one can define and compute the change in density of states for each representation in terms of the phase shifts for that representation; for instance, phase shifts labelled by S, P, D... in the angular momentum representation.

The moment relationships for the change in occupied states and total energy follow from $\Delta N(E)$. The change in occupied states, useful for verifying which states are occupied, is the number of bound states, N_b , given by

$$N_b = \int_{-\infty}^{E_F} \Delta N(E) dE = -\frac{\phi(E_f)}{\pi} \quad (32)$$

with E_F , the Fermi energy, defined as the maximum energy of the occupied states. The change in electronic energy,

$$\Delta E = -\frac{1}{\pi} \int_{-\infty}^{E_F} E \frac{d\phi(E)}{dE} dE \quad (33)$$

can be used to calculate the change in the total electronic energy as a function of lattice relaxation around the impurity.

Later we shall realize that these energy moments are very important when approximating the resolvent operator $G^0(E)$ for empirical fits to deep trap energies. Thus at this point we note that at energies E which correspond to bound states and thus are not equal to bandstructure energies $E_{n\vec{k}}$ we can rewrite Eq. (13) as

$$G^0(E) = \sum_{n=0}^{\infty} \frac{M^{(M)}}{(\bar{E}-E)^{n+1}} \quad (34)$$

$$M^{(M)} = \int_{-\infty}^{\infty} (\bar{E}-E')^n \delta(E'-H^0) dE' = (\bar{E}-H^0)^n \quad (35)$$

where $\bar{E}$ is arbitrary but can be chosen so that the 1st moment always vanishes.

Later we shall approximate the solution for deep trap energies in terms of symmetry-adapted matrix elements of the moment operator. First we continue the pursuit of a quantitative solution by specifying the model for the electronic properties of the host crystal.

IV. THE HOST CRYSTAL HAMILTONIAN

A. The LCAO Method

In the following section we define the host crystal properties in terms of matrix elements of the Hamiltonian which are empirically obtained from experimentally determined energy bandstructure. The fitting procedure is first defined for all possible matrix elements which result if we allow interaction only between SP^3 atomic orbitals centered on nearest neighbor atoms. The resulting energy bandstructures agree very well with experimental bandstructure except for the conduction bands. Mainly to place the minimum energy of the lowest conduction bands at the correct symmetry point, we introduce an additional, higher energy S state on each atom. The resulting bandstructure agrees very well with experimental bandstructure for all compounds considered. The matrix elements contain chemical trends; those which couple orbitals on the same atom are atom-like while those which couple nearest neighbors scale like inverse bond length squared.

The host crystal energy eigenvalues and eigenvectors were obtained from a wavefunction defined as a Linear Combination of Atomic Orbitals (the LCAO or tight-binding method). Schematically, one writes the crystal wavefunction $\psi(\vec{r})$ as a linear combination of Bloch functions $\phi_j(\vec{r})$ each of which depends on only one type of orbital. Using the variational principle, the energy

$$E = \frac{\langle \psi | H^0 | \psi \rangle}{\langle \psi | \psi \rangle} \quad (36)$$

is minimized by varying the coefficients C_i ; this produces the equation

$$(H_{ij}^0 - E \delta_{ij}) C_j = 0 \quad (37)$$

which has non-trivial solutions only if

$$\text{Det } ||H_{ij}^0 - E \delta_{ij}|| = 0 \quad (38)$$

where

$$H_{ij} = \langle \phi_i | H | \phi_j \rangle \quad (39)$$

From the eigenvalues, E_i , one can obtain the coefficients C_{ij} now labelled by their eigenvalue.

Each Bloch wavefunction, composed of a linear combination of atomic orbitals of one type, depends on the structure of the host crystal. The primitive vectors of the zincblende (fcc) lattice,

$$\begin{aligned} \vec{A}_1 &= \frac{a}{2} (\hat{X} + \hat{Y}) \\ \vec{A}_2 &= \frac{a}{2} (\hat{Y} + \hat{Z}) \\ \vec{A}_3 &= \frac{a}{2} (\hat{X} + \hat{Z}) \end{aligned} \quad (40)$$

with a the lattice constant, produce a bcc reciprocal space $\vec{k}$ with primitive vectors

$$\begin{aligned} \vec{a}_1 &= \frac{2\pi}{a} (\hat{X} + \hat{Y} - \hat{Z}) \\ \vec{a}_2 &= \frac{2\pi}{a} (-\hat{X} + \hat{Y} + \hat{Z}) \\ \vec{a}_3 &= \frac{2\pi}{a} (\hat{X} + \hat{Y} + \hat{Z}) \end{aligned} \quad (41)$$

Most important for our purposes, application of the Bloch theorem shows that the amplitude of each atomic orbital's contribution to the Bloch wavefunction is $e^{i\vec{k} \cdot \mathbf{R}_j}$ where $\vec{k}$ ranges within the first Brillouin zone, essentially the unit cell in K -space. These K -vectors are defined by

$$\vec{k} = \frac{2\pi}{a} (M_1, M_2, M_3) \quad (42)$$

with

$$M_1 + M_2 + M_3 \leq 3/2 \quad (43)$$

Furthermore, the positions of the four atoms nearest to a central anion are given by

$$\begin{aligned}\tau_1 &= \frac{a}{4} (111) \\ \tau_2 &= \frac{a}{4} (\bar{1}\bar{1}\bar{1}) \\ \tau_3 &= \frac{a}{4} (\bar{1}\bar{1}1) \\ \tau_4 &= \frac{a}{4} (1\bar{1}\bar{1})\end{aligned}\quad (44)$$

and the positions of the anions in the twelve nearest unit cells are given by the non-zero combinations of $\tau_i - \tau_j$, $i, j = 1, 4$.

The Bloch wavefunction for SP^3 orbitals in a zincblende lattice can be written as

$$\begin{aligned}\phi_{i\beta, \vec{k}}(\vec{r}) &= \langle \vec{r} | \phi_{i\beta, \vec{k}} \rangle \\ &= N^{-1/2} \sum_{\ell} e^{i\vec{k} \cdot (\vec{R}_{\ell} + \beta \vec{\tau}_i)} a_{i\beta}(\vec{r} - \vec{R}_{\ell} - \beta \vec{\tau}_i)\end{aligned}\quad (45)$$

The atomic orbitals $a_{i\beta}(\vec{r} - \vec{R}_{\ell} - \beta \vec{\tau}_i)$ are centered on anion sites if $\beta=0$; for $\beta=1$ the orbitals are centered on the cation site displaced by $\vec{\tau}_1$ from the anion at $\vec{R}_{\ell}$. The labels $i=0, 3$ correspond to S, P_X , P_Y , and P_Z in that order. The eigenvectors (C's) of the wavefunction

$$\psi_{n\alpha, \vec{k}}(\vec{r}) = \sum_{i\beta} C(\vec{k})_{n\alpha, i\beta} \phi_{i\beta, \vec{k}}(\vec{r})\quad (46)$$

will be determined entirely by matrix elements of the Hamiltonian in terms of the orthonormal atomic orbitals.

Before explicitly solving the Schrödinger equation for the perfect crystal, we consider the wavefunction expected for the tetrahedrally bonded semiconductors. These semiconductors, all with zincblende structure (for diamond structure we simply put two identical atoms in the zincblende

unit cell), consist of nearly neutral atoms; four slightly positively charged ($+Q, Q \sim +1e$) cations surround each negatively, charged ($-Q$) anion. The crystal consists of N translationally invariant unit cells, each containing an anion and a cation, sitting at positions R_j ($j=1, N$) that define a zincblende lattice. Because the atoms interact, and thus bond together, mainly via the outermost s and p electrons, only atomic orbitals for these electrons need be considered in a calculation of the electronic properties unique to a crystal. We use one s -orbital and three p -orbitals per atom to get most of the physics; later to adjust the conduction band structure we, in addition, include the next energetically higher s -state on each atom.

The normalization of the atomic orbitals $a(r)$ must be handled correctly -- mainly in one of two ways. The overlap matrix $S_{ij}(l,m) = \langle a_i(r-R_l) | a_j(r-R_m) \rangle$ either appears directly in the secular equation $\text{Det}|H-ES| = 0$ or indirectly in a transformation to an orthonormal basis,

$$\tilde{a}_i(\vec{r}-\vec{R}_j) = S_{i,m}^{-1/2}(j,n) a_m(\vec{r}-\vec{R}_n) \quad (47)$$

called Löwdin orbitals.

These orbitals serve our conceptual purposes quite well because we will consider matrix elements of the Hamiltonian, rather than do actual calculations involving the orthonormal orbitals. Thus the atomic and hybrid orbitals are assumed orthonormal; furthermore, because overlaps between orbitals are small, our intuition about atomic orbitals still applies to these new "pseudoatomic" orbitals.

The Hamiltonian can now be defined in terms of undetermined atomic-like energies, in terms of orbitals on the same atom and bond energies, determined in terms of orbitals on adjacent atoms. The Hamiltonian matrix, which

includes the excited S state as well, is written out in Table III in terms of the four intra-atomic matrix elements:

$$\epsilon_a^S = \langle a_{00}(\vec{r}) | H^0 | a_{00}(\vec{r}) \rangle, \quad \epsilon_c^S = \langle a_{01}(\vec{r}-\vec{\tau}_1) | H^0 | a_{01}(\vec{r}-\vec{\tau}_1) \rangle \quad (48)$$

$$\epsilon_a^P = \langle a_{10}(\vec{r}) | H^0 | a_{10}(\vec{r}) \rangle, \quad \epsilon_c^P = \langle a_{11}(\vec{r}-\vec{\tau}_1) | H^0 | a_{11}(\vec{r}-\vec{\tau}_1) \rangle \quad (49)$$

and five inter-atomic matrix elements:

$$V_{SS} = 4 \langle a_{00}(\vec{r}) | H^0 | a_{01}(\vec{r}-\vec{\tau}_1) \rangle \quad (50)$$

$$V_{XX} = 4 \langle a_{10}(\vec{r}) | H^0 | a_{11}(\vec{r}-\vec{\tau}_1) \rangle \quad (51)$$

$$V_{XY} = 4 \langle a_{10}(\vec{r}) | H^0 | a_{21}(\vec{r}-\vec{\tau}_1) \rangle \quad (52)$$

$$V_{S_0P_1} = 4 \langle a_{00}(\vec{r}) | H^0 | a_{11}(\vec{r}-\vec{\tau}_1) \rangle \quad \text{and} \quad (53)$$

$$V_{S_1P_0} = 4 \langle a_{10}(\vec{r}) | H^0 | a_{01}(\vec{r}-\vec{\tau}_1) \rangle \quad (54)$$

In addition we later will consider the interaction of a higher energy S-state on each atom with the nearest neighbor P-states. Thus we also define the S-state energies:

$$\epsilon_a^{\bar{S}} = \langle a_{50}(\vec{r}) | H^0 | a_{50}(\vec{r}) \rangle \quad (55)$$

and

$$\epsilon_c^{\bar{S}} = \langle a_{51}(\vec{r}) | H^0 | a_{51}(\vec{r}-\vec{\tau}_1) \rangle \quad (56)$$

and their coupling to P-states:

$$V_{\bar{S}_0P_1} = 4 \langle a_{50}(\vec{r}) | H^0 | a_{11}(\vec{r}-\vec{\tau}_1) \rangle \quad (57)$$

and

$$V_{\bar{S}_1P_0} = 4 \langle a_{10}(\vec{r}) | H^0 | a_{51}(\vec{r}-\vec{\tau}_1) \rangle \quad (58)$$

TABLE III
The Ten-state Hamiltonian

	$\bar{s}_0$	$\bar{s}_1$	s_0	s_1	x_0	y_0	z_0	x_1	y_1	z_1
$\bar{s}_0$	$E_{\bar{s}_0}$	$V_{\bar{s}s}g_0$	0	0	0	0	0	$V_{\bar{s}_0p}g_1$	$V_{\bar{s}_0p}g_2$	$V_{\bar{s}_0p}g_3$
$\bar{s}_1$	$V_{\bar{s}s}g_0^*$	$E_{\bar{s}_1}$	0	0	$-V_{\bar{s}_1p}g_1^*$	$-V_{\bar{s}_1p}g_2^*$	$-V_{\bar{s}_1p}g_3^*$	0	0	0
s_0	0	0	E_{s_0}	$V_{ss}g_0$	0	0	0	$V_{s_0p}g_1$	$V_{s_0p}g_2$	$V_{s_0p}g_3$
s_1	0	0	$V_{ss}g_0$	E_{s_1}	$-V_{s_1p}g_1^*$	$-V_{s_1p}g_2^*$	$-V_{s_1p}g_3^*$	0	0	0
x_0	0	$-V_{\bar{s}_1p}g_1$	0	$-V_{s_1p}g_1$	E_{p_0}	0	0	$V_{xx}g_0$	$V_{xy}g_3$	$V_{xy}g_2$
y_0	0	$-V_{\bar{s}_1p}g_2$	0	$-V_{s_1p}g_2$	0	E_{p_0}	0	$V_{xy}g_3$	$V_{xx}g_0$	$V_{xy}g_1$
z_0	0	$-V_{\bar{s}_1p}g_3$	0	$-V_{s_1p}g_3$	0	0	E_{p_0}	$V_{xy}g_2$	$V_{xy}g_1$	$V_{xx}g_0$
x_1	$V_{\bar{s}_0p}g_1$	0	$V_{s_0p}g_1^*$	0	$V_{xx}g_0^*$	$V_{xy}g_3^*$	$V_{xy}g_2^*$	E_{p_1}	0	0
y_1	$V_{\bar{s}_0p}g_2$	0	$V_{s_0p}g_2^*$	0	$V_{xy}g_3^*$	$V_{xx}g_0^*$	$V_{xy}g_1^*$	0	E_{p_1}	0
z_1	$V_{\bar{s}_0p}g_3$	0	$V_{s_0p}g_3^*$	0	$V_{xy}g_3^*$	$V_{xy}g_1^*$	$V_{xx}g_0^*$	0	0	E_{p_1}

$$g_0(\vec{k}) = \cos \pi \frac{k_1}{2} \cos \pi \frac{k_2}{2} \cos \pi \frac{k_3}{2} - i \sin \pi \frac{k_1}{2} \sin \pi \frac{k_2}{2} \sin \pi \frac{k_3}{2},$$

$$g_1(\vec{k}) = -\cos \pi \frac{k_1}{2} \sin \pi \frac{k_2}{2} \sin \pi \frac{k_3}{2} + i \sin \pi \frac{k_1}{2} \cos \pi \frac{k_2}{2} \cos \pi \frac{k_3}{2},$$

$$g_2(\vec{k}) = -\sin \pi \frac{k_1}{2} \cos \pi \frac{k_2}{2} \sin \pi \frac{k_3}{2} + i \cos \pi \frac{k_1}{2} \sin \pi \frac{k_2}{2} \cos \pi \frac{k_3}{2},$$

$$g_3(\vec{k}) = -\sin \pi \frac{k_1}{2} \sin \pi \frac{k_2}{2} \cos \pi \frac{k_3}{2} + i \cos \pi \frac{k_1}{2} \cos \pi \frac{k_2}{2} \sin \pi \frac{k_3}{2}$$

This completes the specification of the properties of the host crystal in terms of matrix elements of the Hamiltonian which are to be determined empirically.

B. Determination of the Hamiltonian Matrix

The matrix elements of the Hamiltonian are fit to the bandstructure of the crystal, mainly the valence bands. The valence bands are important because, being the lowest energy states formed from the bonding orbitals, they depend almost entirely on the bonds between nearest neighbor atoms. These energy states are surprisingly atomic-like compared to the conduction band states whose wavefunctions are very delocalized. Furthermore, the data for valence bands is more reliable than for conduction band states because experiments can directly measure the valence density of electron states at a given energy in $\vec{k}$ -space; equivalent experiments do not exist for the unoccupied conduction bands.

The many schemes for fitting irreducible tight-binding matrix elements to bandstructure differ in physical insight and effort required to make the fit. If too few matrix elements are used, the fit is very poor, even for the valence bands, but the fitting procedure is straightforward. If too many parameters are used the equations are overdetermined; one such fit used 13 interatomic matrix elements for Si, required a numerical least-squares minimization and produced mediocre quality conduction and valence bands.^{29/} Between these extremes, a computerized least squares fit to Si with 7 parameters, including second nearest neighbor interactions, has successfully modeled the valence and lowest conduction bands.^{30/}

The method developed by Harrison concentrates on only the valence bands in order to extract matrix elements which reflect chemical trends associated with the relative positions of atoms in the Periodic Table;^{31/} for instance,

he finds that inter-atomic matrix elements scale as inverse bond-length squared, a relationship that can be used to estimate the effect of lattice distortion about the defect on the electronic properties of the defect.^{32/}

Our approach has been to preserve these relationships between matrix elements, the chemical trends, but at the same time fit the conduction bands, in particular the lowest energy band which defines the bandgap.

Our method, developed by trial and error, produces Hamiltonian matrix elements which are determined by atomic energies shown in Table II and the bandstructure at symmetry points Γ and X as shown in Fig. 6, a plot of the Si bandstructure generated by our method. First, the atomic energies E^S and E^P , listed in Table III, are used to define energy differences between S and P orbitals on the two atoms in each unit cell by

$$\epsilon_c^S - \epsilon_a^S = \beta_S (E_c^S - E_a^S) \quad , \quad (59)$$

and

$$\epsilon_c^P - \epsilon_a^P = \beta_P (E_c^P - E_a^P) \quad . \quad (60)$$

The coefficients β_S and β_P , which are discussed later, were obtained empirically by comparing orbital energy differences in the solid, determined by their relationship to spin-orbit splitting, with orbital energies of free atoms. Finally, the remaining matrix elements, whose relationship to symmetry points in the bandstructure can be seen in Fig. 7, are defined by

$$\epsilon_c^S + \epsilon_a^S = E_{\Gamma_1^V} + E_{\Gamma_1^C} \quad (61)$$

and

$$\epsilon_c^P + \epsilon_a^P = E_{\Gamma_{15}^C} \quad (62)$$

Fig. 6 The bandstructure of Si obtained by fitting the Hamiltonian matrix elements to experimentally determined bandstructure at Γ and X.

Fig. 7 The anion and cation S and P orbital energies, ϵ_a^s , ϵ_a^p , ϵ_c^s and ϵ_c^p , and their interactions, V_{ss} , V_{xx} , V_{xy} , $V_{s_0p_1}$, are fit to bandstructure energies at symmetry points Γ_{1v} , Γ_{15v} , Γ_{1c} , Γ_{15} , X_{1v} , X_{3v} , X_{5v} , X_{1c} , and X_{3c} .

which set the zero of energy at the top of the valence band and

$$V_{SS} = \frac{1}{2} \left[(E_{\Gamma_1^C} - E_{\Gamma_1^V})^2 - (\epsilon_c^S - \epsilon_a^S)^2 \right]^{1/2} \quad (63)$$

$$V_{XX} = \frac{1}{2} \left[E_{\Gamma_{15}^C}^2 - (\epsilon_c^P - \epsilon_a^P)^2 \right]^{1/2} \quad (64)$$

$$V_{XY} = \left[\left(\frac{1}{2} (E_{\Gamma_{15}^C} - E_{X_5^V}) \right)^2 - \frac{1}{4} (\epsilon_c^P - \epsilon_a^P)^2 \right]^{1/2} \quad (65)$$

$$V_{S_0P_1} = \left[\left(\frac{1}{2} (\epsilon_a^S + \epsilon_c^P) - E_{X_1^V} \right)^2 - \frac{1}{4} (\epsilon_a^S - \epsilon_c^P)^2 \right]^{1/2} \quad (66)$$

and

$$V_{S_1P_0} = \left[\left(\frac{1}{2} (\epsilon_c^S + \epsilon_a^P) - E_{X_3^V} \right)^2 - \frac{1}{4} (\epsilon_c^S - \epsilon_a^P)^2 \right]^{1/2} \quad (67)$$

which define the inter-atomic matrix elements. This procedure produces (i) orbital energy differences directly from orbital energies of free atoms, (ii) inter-atomic matrix elements which scale like inverse bond length squared, and (iii) good overall bandstructure for all the compounds investigated.

Justification for the proportionality of the diagonal matrix elements to atomic energies comes from an alternative procedure which uses a relationship^{33/} between p-orbital energy in the solid and the spin-orbit splitting, Δ_0 , of the two highest energy valence bands to determine the matrix elements. Defining the spin-orbit splitting of P-orbitals centered on anions as Δ_a and those on cations as Δ_c ,^{33/} we can use

$$\epsilon_c^P - \epsilon_a^P = \frac{[\Delta_0 - (\Delta_a + \Delta_c)/2]}{(\Delta_a - \Delta_c)/2} E_{\Gamma_{15}^C} \quad (68)$$

to determine the P-orbital energy difference from the bandstructure energy $E_{\Gamma_{15}^C}$ of the lowest conduction band; then we use

$$\epsilon_c^S - \epsilon_a^S = \epsilon_c^P - \epsilon_a^P + (E_{X_3^V} - E_{X_1^V}) + (E_{X_3^C} - E_{X_1^C}) \quad (69)$$

to determine the S-orbital splitting. The linear relation between the orbital energy differences of atoms in the solid compared with free atoms can be seen in Figs. 8 and 9. From this figure we find the coefficients β_S and β_P , used in Eqns. (59) and (60) to be roughly $\beta_S=0.8$ and $\beta_P=0.6$. With this knowledge of the chemical trend of orbital energy differences we simply use Eqns. (59) and (60), rather than the spin-orbit relationship, to determine the orbital energy differences in the solid.

An important chemical trend, useful for extension of the model to include effects of lattice relaxation around the impurity atom, is the scaling of inter-atomic matrix elements with bond length. Figure 10 shows that the matrix element V_{SS} , defined in Eqn. (63), scales as approximately inverse bond length squared. The other matrix elements exhibit similar scaling with bond length.

The fitting procedure produced bandstructures and density of states which agree excellently with published bandstructure. In particular we compare our GaP bandstructure, with and without inclusion of the additional S-state, with published GaP bandstructure calculated by an empirical pseudopotential method.^{34/} Comparing our GaP bandstructure in Fig. 11 with the published GaP bandstructure in Fig. 12 shows that our result agrees very well for the valence bands but does not reproduce the indirect gap of the lowest conduction band. In general, our method works reasonably well for even the lowest conduction band of the direct gap materials such as GaAs but for the indirect gap materials, such as GaP and Si the lowest conduction band has too much dispersion; thus its energies become too high at all points other than the Γ point (which was fitted).

Fig. 8 The energy difference between S-orbitals of the two different atoms in the unit cell (anion and cation) is proportional to the energy difference between the two isolated atoms. The shape of a linear fit to these points is about 0.8.

Fig. 9 Similar to Fig. 8, the energy difference of anion and cation P-orbitals is proportional to the energy difference of isolated atoms. The slope of a linear fit to these points is about 0.6.

Fig. 10 The inter-atomic interaction V_{ss} scales as d^{-2} , where d is the length of the band between adjacent atoms. The remaining interatomic matrix elements exhibit similar scaling which can be used to estimate effects of lattice distortion.

Fig. 11 The bandstructure of GaP obtained by an LCAO calculation which uses SP^3 orbitals on each atom. This bandstructure reproduces the valence bands very well but the method does not have sufficient flexibility to reproduce the indirect bandgap of GaP.

Fig. 12 Bandstructure of GaP determined by a non-local empirical pseudopotential method. Both the valence and conduction bands faithfully represent the best available experimental data.

Inclusion of an additional S-state produces a GaP bandstructure, shown in Fig. 13, which agrees very well with the published bandstructure shown in Fig. 12. Similarly, the bandstructures for the other semiconductors considered, shown in Appendix A, agree very well with the valence bands and the first conduction bands of published bandstructures for these materials.

This completes the discussion of the Hamiltonian of the perfect crystal except for remarks about modification of the lowest conduction band made by assuming interactions with an additional S-orbital on each atom. The bandstructure tabulated in Table IV generated the Hamiltonian matrix elements listed in Table V. These matrix elements completely define the electronic properties of both the perfect crystal and the impurity atom; at this point we can turn to Section V for the detailed discussion of the defect potential.

Recognizing that positioning the density of states of the lowest conduction band was essential to correct positioning of trap energies within the bandgap, we considered orbital interactions other than nearest-neighbor coupled SP^3 orbitals. These conduction bands could be made to agree better with experiment by several means; for instance, by (i) inclusion of D-orbitals, very difficult because the simplicity of the model and uniqueness of the parameters would both be destroyed, (ii) inclusion of next-nearest neighbor interactions, again very difficult especially because all probably would have similar value and thus all would, in principle, need to be included, and finally (iii) inclusion of additional states to simulate the non-ground, excited states of the individual atomic orbitals required to simulate non-groundstate conduction bands.

We have chosen to include an excited S-state on each atom because its coupling to the nearest neighbor P-states affects mainly the density

Fig. 13 Bandstructure of GaP determined by an LCAO method which uses an SP^3 basis together with an additional S-state on each atom. Both the valence bands and the lowest conduction band agree very well with the bandstructure shown in Fig. 12.

Table IV Bandstructure

Energy at Symmetry Points (Zincblende notation)

Name	Γ_1^V	Γ_1^C	Γ_{15}^C	X_1^V	X_3^V	X_5^V	X_1^C	X_3^C	References
C	-27.27	18.18	7.68	-16.14	-16.14	-7.83	5.48	5.48	a,b
Si	-12.50	4.10	3.43	- 7.69	- 7.69	-2.86	1.13	1.13	b,c
Ge	-12.66	0.90	3.22	- 8.65	- 8.65	-3.29	0.76	0.76	b,c
α -Sn	-11.34	0.00	2.66	- 7.88	- 7.88	-2.75	-0.42	-0.42	c
AlAs	-11.73	3.04	4.57	- 9.52	- 5.69	-2.20	2.30	2.68	d,e
AlP	-12.70	3.60	5.60	- 9.80	- 5.40	-2.26	2.50	3.00	f,g
GaAs	-12.55	1.55	4.71	- 9.83	- 6.88	-2.89	2.03	2.38	b,c
GaP	-13.19	2.88	5.24	- 9.46	- 7.07	-2.73	2.35	2.90	c,h
GaSb	-12.00	0.78	3.77	- 9.33	- 6.76	-2.37	1.72	1.79	c,d
InAs	-12.69	0.43	4.63	-10.20	- 6.64	-2.37	2.28	2.66	c,d
InP	-11.42	1.41	4.92	- 8.91	- 6.01	-2.06	2.44	2.97	c,d
InSb	-11.71	0.23	3.59	- 9.20	- 6.43	-2.24	1.71	1.83	c,d
ZnSe	-14.50	2.68	7.50	-12.50	- 5.60		4.54	5.17	b,i
ZnTe	-13.31	2.56	6.75	-11.90	- 5.67		5.97	6.94	b,i

a Reference^{35/}b Reference^{36/}c Reference^{37/}d Reference^{38/}e Reference^{39/}f Reference^{40/}g Reference^{41/}h Reference^{42/}i Reference^{43/}

Table V Hamiltonian Matrix Elements

Compound	ϵ_a^S	ϵ_a^P	ϵ_c^S	ϵ_c^P	V_{SS}	V_{XX}	V_{XY}	$V_{S_0P_1}$	$V_{S_1P_0}$	$V_{\bar{S}_0P_1}$	$V_{\bar{S}_1P_0}$	$\bar{\epsilon}_a^S$	$\bar{\epsilon}_c^S$
C	- 4.55	3.84	-4.54	3.84	-22.73	3.84	11.67	15.22	15.22	11.37	11.37	8.21	8.21
Si	- 4.20	1.72	-4.20	1.72	- 8.30	1.72	4.58	5.73	5.73	6.69	6.69	5.37	5.37
Ge	- 5.88	1.61	-5.88	1.61	- 6.78	1.61	4.40	5.47	5.46	6.39	6.39	5.22	5.22
Sn	- 5.67	1.33	-5.67	1.33	- 5.67	1.33	4.08	4.51	4.51	5.90	5.90	5.89	5.89
AlAs	- 8.34	1.04	-2.66	3.67	- 6.45	1.95	5.08	4.48	5.78	8.59	6.74	4.84	4.81
AlP	- 7.85	1.32	-1.25	4.28	- 7.45	2.37	4.84	5.25	5.28	8.71	7.42	5.25	4.64
GaAs	-11.84	1.51	0.02	5.99	- 6.21	3.01	5.99	3.50	6.32	7.59	8.99	2.59	3.95
GaP	- 8.11	1.13	-2.20	4.12	- 7.47	2.15	5.14	4.28	6.32	8.52	7.19	4.65	5.10
GaSb	- 7.32	0.86	-3.90	2.91	- 6.16	1.58	4.13	4.96	4.67	6.64	5.98	4.39	3.48
InAs	- 8.02	0.67	-3.46	2.91	- 5.52	1.40	3.88	3.79	4.59	6.45	5.94	3.57	3.41
InP	- 8.53	0.87	-1.48	4.05	- 5.36	1.88	4.23	2.23	5.58	8.26	7.07	3.46	4.48
InSb	- 9.54	0.91	-2.72	3.72	- 5.61	1.84	4.47	3.04	5.44	7.41	6.74	3.37	3.91
ZnSe	- 7.53	0.98	-1.16	3.59	- 6.66	1.88	4.29	5.11	5.50	7.48	6.73	4.52	5.00
ZnTe	- 9.82	1.48	-0.94	5.27	- 6.58	2.80	5.47	5.98	5.82	7.08	8.27	1.32	1.24

of states at the X and L points of the lowest conduction band. Clearly, without such an energetically higher state, the SP^3 states on the atom, which repel each other to form the valence and conduction bands, produce conduction band eigenvalues which are not, but should be, repelled downward in energy by energetically higher states in the eigenvalue spectrum of the atomic basis. The excited S-states help remedy this deficiency in the conventional SP^3 tight-binding basis.

The excited S state for all the II-VI column atoms lies within a very narrow range of energies with respect to the vacuum reference energy. Thus in the solid the excited S-states all lie at about the same energy--about 6 to 8 eV--because the solid state environment shifts all energies by about a constant amount. This means that substitution of an impurity atom for a host atom causes little change in either the excited S-state, which is located high in the conduction band, or the unoccupied nearest-neighbor-like impurity state.

In other words, the defect potential will be determined by the S and P impurity energies, not by the S^* impurity energy. This is not only because the S^* state does not couple strongly to the lower energy states, but most importantly because the S^* (and P^*) states are about the same energies for all atoms.

The excited state energies were derived from a table of spectroscopic energy levels by averaging over multiplets of angular momentum.^{9/} For atoms the interactions of orbital angular momentum $\vec{L}$ with the electron spin $\vec{S}$ produces coupling proportional to $\vec{L} \cdot \vec{S}$ which splits the states into multiplets with energies differing by an increment ~ 0.2 eV of energy. For heavier atoms, an analogous coupling proportional to the total angular momentum splits these orbital degeneracies. In the SP^3 coupled systems the coupling between

atoms is much stronger than angular momentum coupling effects and then the relevant states are the unperturbed orbitals energies.

Just as we ignored spin-orbit effects in determination of SP^3 atomic energies shown in Table II we also ignore spin-orbit effects in the excited S-state energies also shown in Table II.

The excited S state can be viewed mainly as an ad hoc adjustment to the lowest conduction band, in particular the spectral density of states. Unfortunately, it is very difficult to make a strong argument for inclusion of an additional S state and exclusion of the effects of D-orbitals and distant neighbor matrix elements. Its main utility is that once its orbital energy is chosen all other parameters can be chosen in a unique way (by equations similar to Eqns. (66) and (67), essentially only the important lowest conduction band is modified and finally, the chemical trends in the Hamiltonian matrix elements are unchanged.

V. THE DEFECT POTENTIAL

The defect potential V describes the many-body interaction of an electron (or hole) with the host crystal and the impurity atom which, because of its size, slightly distorts its lattice environment and because of its charge, slightly polarizes neighboring atoms. By writing the potential

$$V = H - H^0 \quad (70)$$

as difference of Hamiltonian operators one could in principle calculate the defect properties to the same degree of accuracy as the original Hamiltonian. For instance, one could in principle construct a self consistent potential which depends on lattice relaxation around the defect and the change in the local charge-density near the impurity atom. However, these small effects on the impurity properties cannot be calculated very accurately with an empirical tight-binding model of electronic and lattice properties. Thus at this point we ignore them in order to understand the dominating features of the problem by using the simplest possible approximation for the impurity potential.

At this point we adapt an operational definition of a deep trap--a trap is deep if its properties are controlled by the central cell potential. We ignore the screened Coulomb potential, responsible for binding energies of about 0.1 eV, and concentrate on whether the short range potential, just a difference of atomic energies, can bind an electron or hole.

Now we construct the simplest realistic model for the defect potential--a one-site potential with no lattice relaxation--which will reduce to a difference of atomic energies. The potential, just as the one used in the defect molecule, is defined by directed hybrid orbitals pointing along bonds between the impurity atom and its four nearest neighbors. The four hybrid orbitals centered on each atom are defined by

$$h_{\alpha i}(\vec{r}) = U_{ij} a_{\alpha j}(\vec{r}) \quad (71)$$

with

$$U = \frac{1}{2} \begin{pmatrix} 1 & 1 & 1 & 1 \\ 1 & 1 & -1 & -1 \\ 1 & -1 & 1 & -1 \\ 1 & -1 & -1 & 1 \end{pmatrix} \quad (72)$$

In this basis the defect potential is an 8×8 matrix; by using group theory for this T_d symmetry defect, we can produce symmetry-adapted wavefunctions S_α^r

$$S_\alpha^r = U_{rj} h_{\alpha j} \quad (73)$$

which can be labelled by symmetry; $r=0$ corresponds to an A_1 state which we will refer to as an S-state and $r=1,3$ correspond to T_2 states which we will call P-states.

Now the defect potential matrix becomes block-diagonal (See Eqs. (19) and (20)); it contains one two-by-two S-symmetry matrix and three two-by-two P-symmetry matrices. The symmetry dependent defect potential matrices are

$$V_{i,j}^r = \begin{pmatrix} \epsilon_{c,imp}^r - \epsilon_{c,host}^r & V_{imp}^r - V_{host}^r \\ V_{imp}^r - V_{host}^r & \epsilon_{o,imp}^h - \epsilon_{o,host}^h \end{pmatrix} \quad (74)$$

where $i,j=c$ or o for central atom or other atom interactions. Using the chemical trends in the matrix elements we immediately can make two simplifications.

To a good approximation, the atomic energy difference between two atoms in a solid is similar to the difference between two free atoms. Also, using the scaling with inverse bond length squared, the difference of interatomic matrix elements must be very small. Putting these two approximations together we reduce each two-by-two defect potential to a scalar

$$V_{ij}^r = \begin{pmatrix} \epsilon_{imp}^r - \epsilon_{host}^r & 0 \\ 0 & 0 \end{pmatrix} \quad (75)$$

in which we drop the label for the central atom.

Writing the matrix element between symmetry adapted orbitals on the central atom for the resolvent operator as

$$G_{cc}^{(r)}(E) = P \int_{-\infty}^{\infty} \frac{\langle c^r | \delta(E' - H_0) | c^r \rangle}{E - E'} dE' \quad (76)$$

where $\langle c^r | \delta(E' - H_0) | c^r \rangle$ is the matrix element for the spectral density operator, ($r=S, P_X, P_Y, P_Z$), we can reduce the defect problem to the solution of one equation:

$$\frac{1}{V^r} = P \int_{-\infty}^{\infty} \frac{\langle c^r | \delta(E' - H_0) | c^r \rangle}{E_b - E'} dE' \quad (77)$$

which is valid when E_b corresponds to a bound state within the bandgap.

VI. COMPARISON WITH DATA

We begin comparison of our theory with data by examining the traps thought to be associated with anion sites in GaP, whose impurities tend to be substitutional rather than interstitial, as for Si. Figure 14 shows a plot of trap energy E , in the bandgap, as a function of impurity potential V_o^S for both the S (or A_1) and P (or T_2) states; this figure is actually a graphical solution to Eq. (77). The solution, E versus V , has two branches for each state; the upper one describes traps associated with the conduction band and the lower one describes traps associated with valence band. A plot of the upper branch for the A_1 donor state shows that when the potential becomes increasingly attractive, a bound state does not form until V_o^S equals a threshold potential V_o^S . Then a bound state is pulled out of the conduction band; rapidly at first but more slowly as it becomes more bound until finally, when $V_o^S \rightarrow -\infty$, it becomes pinned to E_p^S , the S-state pinning energy. Although not shown in this figure because of the unphysically large potential required, the hole trap pulled upward from the valence band has similar behavior; its threshold potential, V_v^S , is different but it becomes pinned to the same energy E_p^S as $V_o^S \rightarrow \infty$. The T_2 state exhibits similar behavior except the physical branch of its characteristic curve corresponds to an acceptor state pulled up in energy from the valence band.

The pinning energy E_p^S is the energy of an ideal vacancy; ideal because the vacancy has not moved the atoms surrounding it. An atom in the solid can be operationally converted into a vacancy by removing its S and P-orbital energies to infinite energy; thus it corresponds to a vacancy because it no longer couples to the rest of the semiconductor. Similar to the defect molecule, the pinning energy is to a large extent controlled by the nearest neighbor to the defect. For instance, the A_1 state pinning energy of an

Fig. 14 Comparison of predicted binding energies of electron and hole traps in GaP with data for substitutional anion-site impurities. Impurities causing electron traps are in order of increasing S-orbital energy; the impurities causing hole traps are in order of increasing P-orbital energy.

anion site is mainly determined by the S-orbital energy of the cations in the semiconductor. Because anion states are lower in energy than cation states, all anion site pinning energies (both A_1 and T_2) are lower in energy than their corresponding cation site pinning energies.

Using Fig. 14 we can predict that the SP^3 bonded anion-site impurities F, O, Cl, Br, N; S, Se, and I are likely to form deep electron traps. For the A_1 states, the chemical symbol of each of these atoms labels the point, along the conduction band edge, which represents the potential, V_O^S , created by each of these atoms when it substitutes for P. Each of these points lies lower in energy than the threshold potential, T_C^S , required to remove an S-state from the conduction; this threshold is the potential at which the characteristic curve merges into the conduction band.

The predictions of this theory exhibit remarkable agreement with the existing reliable data (see Table VI) for electron and hole traps shown in Fig. 14. Each data point, labelled by chemical symbol, is at the potential determined by the atomic energy of the impurity; each predicted energy E is defined by the intersection of a vertical line from the data point and the curve E versus V_O . Experiments show that O is genuinely deep, its predicted energy agrees with experiment to within 0.1 eV.^{46/} Experiments show that N in GaP forms a trap which is energetically shallow but conceptually deep because, being isoelectronic and thus without a long-range Coulomb potential, the short-range central-cell potential controls the trap energy.^{47/} We predict N to be a deep trap, too deep by about 0.2 eV.

Experiments show that S and Se are energetically not deep; these traps are controlled by both a short and a long range impurity potential. Our theory indicates that S, Se and I, which are near the threshold of deep trap behavior, should be borderline deep traps which exhibit both deep and shallow trap properties.

TABLE VI GaP Data

P-site Impurities

Name	Binding Energy (eV)	Type
O	0.896	donor
N	0.008	isoelectronic
S	0.104	donor
Se	0.102	donor
Te	0.0895	donor
Si	0.082	acceptor
Ge	0.300	acceptor
Si	0.203	acceptor
C	0.048	acceptor

We have made predictions of the impurity atoms responsible for deep electron and hole traps for all fourteen semiconductors studied. These predictions are displayed in Figs. 15, 16, 17, and 18 which show the predicted energy of deep traps caused by any one of the SP^3 bonded substitutional impurity atoms. Just as for GaP, for each type of trap there is an associated threshold potential T ; in general: (i) properties of impurities whose impurity potential V_o satisfies $|V_o| > |T|$ are controlled by the central cell potential; usually these traps are energetically deep and (ii) properties of impurities whose impurity potential satisfies $|V_o| < |T|$ are controlled by the screened Coulomb potential; these traps will be shallow.

For example, Fig. 15 shows that the impurities S, N, Br, Cl, O, or F cause successively deeper electron traps when substituted for an anion (such as P in GaP). Figure 16 shows that the impurities Cd, Zn, or Hg cause successively deeper hole traps when substituted for an anion. Figures 17 and 18 give corresponding information about substitutional cation-site impurities.

Next we discuss the traps in the alloy $GaAs_{1-x}P_x$; by doing so we will understand the claim that the theory predicts chemical trends. Figure 19 shows the predicted energy in the bandgap of the deep traps caused by F, O, Cl, Br, N, S, Se and I as the composition varies from GaAs to GaP; points indicate the existing data for O and N. The virtual crystal approximation was used to compute the matrix elements which produced the bandstructure; the direct-to-indirect crossover occurs at about $X = 0.5$ which agrees well with the experimental value, $X = 0.44$.^{47/}

The primary feature of the theory is the excellent agreement between the slope of the theory and data as a function of composition; this means

Fig. 15 The predicted energies of A_1 states caused by substitutional anion-site impurities. The impurity atoms are ordered in increasing S-orbital energy which corresponds to decreasing probability of causing a deep trap. This figure together with the following three figures depict the predictions for both anion and cation substitutional impurities.

A_1 States - Anion Site Impurities Electron Traps

Fig. 16 The predicted energies for T_2 states caused by anion-site impurities in various SP^3 bonded semiconductors.

T₂ States - Anion Site Impurities P-Orbital Energy (eV)

Fig. 17 The A_1 states associated with substitutional impurities on cation sites lie closer to the valence band than A_1 states caused by anion site impurities.

A_1 States - Cation Site Impurities Electron Traps

Fig. 18 The T_2 states associated with substitutional impurities on cation sites originate from conduction band states and lie at energies higher than the A_1 states shown in Fig. 17.

Fig. 19 Shows predictions for O, N, S, and Se as a function of alloy composition for $\text{GaAs}_{1-x}\text{P}_x$. Data for O (o) and N (---) are shown. The deep traps in $\text{GaAs}_{1-x}\text{P}_x$ are predicted to follow the compositional dependence of the pinning energy rather than the Γ or X point of the bandedge. The data for O and N exhibit this detachment from the bandedge.

that we have succeeded in predicting the overall chemical trend of these traps as one progresses from GaAs to GaP. Secondly, the absolute energy prediction of the trap energy for both O and N is correct to within 0.2 eV at all points measured. Note that N merges into the conduction band at about $X = 0.2$ which agrees very well with the experimental value, $X = 0.22$.^{47/}

Figure 19 illustrates that experimentally N in $\text{GaAs}_{1-x}\text{P}_x$ is a deep trap even though it is not energetically deep for either GaAs or GaP. In the composition region $x = 0.3$ to $x = 0.9$, N is truly energetically deep; at $x = 0.5$, it is bound by 0.5 eV. This detachment from the bandedge is a characteristic signature of deep traps in alloys. In contrast, traps which are not deep, such as Te, follow the bandedge by remaining bound by a relatively constant energy as the composition varies.

Finally, we focus on using existing data for substitutional impurities to make more refined predictions based on a phenomenological model. By inspection of Fig. 15 we see the pinning energy of Si will be about -1.0 eV which is in reasonable agreement with a calculation of the energy of a Si vacancy using a slightly different tight-binding scheme.^{48/} Rather than concentrate on comparison of our theory with the Si data, we turn to phenomenological method which is based on our knowledge of the control of deep trap energies by both the valence and conduction bands together with the atomic energy of the impurity.

VII. PHENOMENOLOGICAL METHODS

For many predictive purposes the Green's function can be fit to empirical data for known deep traps and then used to predict which other impurity atoms can also form deep traps. The real part of the Green's function can be simulated quite well--in the band gap--by essentially any density of states which is normalized to the right number of states, because outside the density of states the real portion of the Green's function is insensitive to differing electron energy distribution. This can be made intuitive by drawing an analogy between the density of states and a one-dimensional charge distribution.

Outside the region of the charge distribution, the potential created is insensitive to the details within the charge distribution. In an analogous way, outside of the region of perfect crystal energy states, the real part of the crystal essentially depends only on the number of states. The error made by approximating the density of states by a normalized delta function, corresponding to a point charge, depends on the higher order moments of the density of states which are analogous to higher order multipoles of a charge distribution.

Applying this knowledge to the A_1 density of states shown in Fig. 20 we see that there are essentially two contributions: one, with a lot of structure, from the lower two valence bands and the other from the lowest conduction band. Clearly, we should regard the valence and conduction band densities of states separately and take moments of each of them. Thus, similar to the moment formalism developed in Eqs. (34) and (35) except now computing moment matrix elements and the average energy separately for the valence and conduction bands, we can define

$$N_V^{(s)} = \int_{-\infty}^0 \langle c^s | \delta(E' - H_0) | c^s \rangle dE' \quad (78)$$

Fig. 20 The A_1 density-of-states for Si splits into a pair of well defined contributions; one at about -10.0 eV and another at about 2.3 eV.

and

$$N_c^{(S)} = \int_0^\infty \langle c^S | \delta(E' - H_0) | c^S \rangle dE' \quad (79)$$

which satisfy $N_v^{(S)} + N_c^{(S)} = 1$ because one S-orbital is associated with the anion symmetry adapted S-orbital $(A_1) |c^S\rangle$.

The average energies for both the valence and conduction density of states are

$$E_v^S = \bar{E}_v^S / N_v^S \quad (80)$$

and

$$E_c^S = \bar{E}_c^S / N_c^S \quad (81)$$

where

$$\bar{E}_v^S = \int_{-\infty}^0 \langle c^S | \delta(E' - H_0) | c^S \rangle E' dE' \quad (82)$$

and

$$\bar{E}_c^S = \int_0^\infty \langle c^S | \delta(E' - H_0) | c^S \rangle E' dE' \quad (83)$$

Then we can write the approximation to the energy resolvent as

$$\bar{G}^S(E) = \frac{N_v^S}{E - E_v^S} + \frac{N_c^S}{E - E_c^S} \quad (84)$$

which is very similar to the empirical rule in Eq. (1).

Rather than use our computed values for N_v and N_c let us empirically fit to the data for Si. We can rewrite $\bar{G}^S(E)$ and use $\bar{G}^S(E) = 1/V_0^S$ to obtain

$$V_0^S = \frac{(E - E_v^S)(E - E_c^S)}{(E - E_p^S)} \quad (85)$$

where we have used $N_v^S + N_c^S = 1$ and defined the pinning energy as

$$E_p^S = N_{cV}^S E_V^S + N_{vC}^S E_C^S. \quad (86)$$

Similarly we define analogous quantities for the P (T_2) states. To fit the data, we plot it as in Fig. 1, determine pinning energies from the data, and energy centers for the densities of states from either the bandstructure or density of states.

We empirically fit the data for substitutional impurities in Si to produce predictions, shown in Fig. 21, of the binding energy of deep traps caused by other substitutional impurities. This empirical fit has the following parameters: $E_V^S = -10.0$ eV, $E_V^P = -2.0$ eV, $E_C^S = 1.3$ eV, $E_C^P = 2.0$ eV, $E_p^S = 0.0$ eV, and $E_p^P = 1.5$ eV. By inspection of Fig. 20, we see that by using the data for S we predict the deep trap energies of other substitutional impurities such as O, N, and the halogens. Furthermore, if we relax the restriction of the model to simple substitutional impurities we would obtain a plot, similar to Fig. 1, showing the characteristic dependence of the trap energy on the atomic energy of the impurity. By analogy to the defect molecule model, the energy of non-substitutional deep traps will be determined by the energies of the nearest neighbors of the impurity atom.

Fig. 21 The predictions of the phenomenological model depend on:

- (i) a pinning energy obtained from the data (see also Fig. 1),
- (ii) the orbital energies of the impurity, and (iii) the energy centers of the valence and conduction band density-of-states.

VIII. CONCLUSIONS

Our simple theory of deep traps enables one to use a table of atomic energies to predict which impurities will form deep traps in semiconductors. We argue qualitatively, using the defect molecule, and quantitatively, using a semi-empirical Koster-Slater calculation, that deep trap energies, of order 0.1 to 1.0 eV, are controlled by atomic energies, of order 1.0 to 10.0 eV.

Turning to the introductory question about the binding energy of O compared with S in GaAs, we now understand that binding energies are determined by the difference between the atomic energy of the impurity atom and the atom which it replaces. Thus O is deep in GaAs because its impurity potential (-12 eV) is much more attractive than sulfur's potential (-5 eV). However, experimentally S is deep in Si and we predict O also to be deep because both produce a very attractive impurity potential in Si; the potential of O is -16 eV and for S it is -7 eV.

Using a simple model we have produced quantitative predictions for substitutional anion and cation impurities in fourteen different covalently bonded materials. These predictions, valid when an impurity potential is strong enough to control the binding energy, were shown to be in quantitative agreement with the data for GaP and the alloy $\text{GaAs}_{1-x}\text{P}_x$. To enable predictions independent of the actual Koster-Slater calculation, we developed a phenomenological fit (Eqn. (85)) which empirically incorporates the important features of both the valence and conduction band density of states. This fit, which has a form similar to the result of the defect molecule model (Eqn. (3)), relates deep trap energies to: (i) atomic energies, (ii) the pinning energy and (iii) the energy centers of the valence and conduction band density of states. This phenomenological model was then used to predict which substitutional impurities in Si form deep traps.

APPENDIX A

Bandstructure Figures

Figures for C, Ge, α -Sn, AlAs, AlP, GaAs, GaSb, InAs, InP, InSb, ZnSe, and ZnTe, showing the bandstructure used in the Koster-Slater calculations of deep trap energies, are gathered together on the following pages.

Fig. 22 Bandstructure for C.

Fig. 23 Bandstructure for Ge.

Fig. 24 Bandstructure for α -Sn.

Fig. 25 Bandstructure for AlAs.

Fig. 26 Bandstructure for AlP.

Fig. 27 Bandstructure for GaAs.

Fig. 28 Bandstructure for GaSb.

Fig. 29 Bandstructure for InAs.

Fig. 30 Bandstructure for InP.

Fig. 31 Bandstructure for InSb.

Fig. 32 Bandstructure for ZnSe.

Fig. 33 Bandstructure for ZnTe.

APPENDIX B

Computer Routines

The main calculation involves solution of Eqn. (77) using the spectral density of states, $\langle C^r | \delta(E - H_0) | C^r \rangle$, obtained from the experimentally determined bandstructure of the perfect crystal. The routine HFIT generates the matrix elements of the Hamiltonian of the perfect crystal which are then used as input to DEN4, the routine which computes the spectral density of states. Given the imaginary part of the perfect crystal Green's function, defined by the spectral density of states, the routine GREEN solves Eqn. (77) by computing the Hilbert transform for energies E defined on an energy grid.

```

C      ROUTINE HFIT
C      THIS ROUTINE USES EIGENVALUES FROM EKEXP.DAT AND
C      ORBITAL ENERGY DIFFERENCES, ESA AND EPA, TO COMPUTE
C      HAMILTONIAN MATRIX ELEMENTS. ESA AND EPA EITHER ARE
C      COMPUTED FROM ATOMIC ENERGIES IN ION.DAT OR SPIN-ORBIT
C      ENERGIES IN HFIT.DAT (USING THE RELATION IN CHADI'S
C      PAPER).
C      ROUTINE TO FIT SLATER-KOSTER HAMILTONIAN MATRIX ELEMENTS
C      TO BANDSTRUCTURE AT SYMMETRY POINTS.
C      INPUT BANDSTRUCTURE AT GAMMA=(000) AND X=(001)
C      TOGETHER WITH SPIN-ORBIT COUPLING. SEE PHYS. STAT. SOL. B ,
C      68,405(1975).
C      GAM15V=0; FOR DIAMOND X1=X3.
      DIMENSION VS(100),VP(100)
      DIMENSION P(21),VK(3)
      DIMENSION EIVR(10,10),EIVI(10,10),EN(10)
      COMMON/FLAG/ NSTATE,IEGVC,KPTGAP
      DATA Q0,QP5,QP25/0.0,0.5,0.25/
      DATA Q3/3.0/
      DATA ALPHA,BETAS,BETAP,RYD/1.0,0.8,0.6,13.6/
      DATA NSTATE,NCMPD/10,14/
      OPEN(UNIT=20,FILE='ION.DAT',DIALOG)
      OPEN(UNIT=21,FILE='EKEXP.DAT',DIALOG)
      OPEN(UNIT=22,FILE='HFIT.DAT',DIALOG)
      OPEN(UNIT=23,FILE='TBPRM.DAT',DIALOG)
      READ(20,5) (VS(I),VP(I),I=1,54)
5      FORMAT(2F10.6)
      DO 999 N=1,NCMPD
      WRITE(5,1)
      READ(21,10) GAM1V,GAM1C,GAM15C,X1V,X3V,X5V,X1C,X3C,X5C
      READ(22,11) DO,DA,DC,ES3INC,ES4INC,NA,NC,BOND
      WRITE(5,12) GAM1V,GAM1C,GAM15C,X1V,X3V,X5V,X1C,X3C,X5C
      WRITE(5,14) DO,DA,DC
11      FORMAT(5F8.4,2I3,F8.3)
12      FORMAT(1X,'BAND ENERGIES  GAM1V,GAM1C,GAM15C,X1V,X3V,X5V
1,X1C,X3C,X5C ...',/,1X,9F8.4)
14      FORMAT(1X,'SPIN-ORBIT SPLITTING  DO,DA,DC ...',/,1X,3F8.4)
10      FORMAT(21F8.4)
      EPA=Q0
      IWARN=0
      NLOOP=0
C      EXCITED STATE
      IF(ES3INC.LE.0.0) ES3INC=90.0
      IF(ES4INC.LE.0.0) ES4INC=90.0
      ES3INC=90.0
      ES4INC=90.0
      EGAP=X1C
2      CONTINUE
      IF(X1V.EQ.X3V) GOTO 20
      EPAC=ALPHA*(DO-QP5*(DA+DC))*GAM15C/(QP5*(DA-DC))
      ESAC=EPAC+X3C-X1C+X3V-X1V

```

```

C      USE ATOMIC S AND P ENERGIES.
      EPA=-BETAP*RYD*(VP(NC)-VP(NA))
      ESA=-BETAS*RYD*(VS(NC)-VS(NA))
      EPA=EPAC
      ESA=ESAC

C
20     EPS=GAM15C
      EP1=-QP5*EPA+QP5*EPS
      EP2=QP5*EPA+QP5*EPS
      ESS=GAM1V+GAM1C
      ES1=-QP5*ESA+QP5*ESS
      ES2=QP5*ESA+QP5*ESS
      VSS=((GAM1C-GAM1V)**2-ESA**2)
      IF(VSS.LE.0.0) VSS=0.0
      VSS=-QP5*SQRT(ABS(VSS))
      VXX=(GAM15C**2-EPA**2)
      IF(VXX.LE.0.0) VXX=0.0
      VXX=QP5*SQRT(ABS(VXX))
      VS2P=((QP5*(ES2+EP1)-X3V)**2-QP25*(ES2-EP1)**2)
      IF(VS2P.LE.0.0) VS2P=0.0
      VS2P=SQRT(ABS(VS2P))
      VS1P=((QP5*(ES1+EP2)-X1V)**2-QP25*(ES1-EP2)**2)
      VS1P=(ES1-X1V)*(EP2-X1V)
      IF(VS1P.LE.0.0) VS1P=0.0
      VS1P=SQRT(ABS(VS1P))
      VXY=((QP5*GAM15C-X5V)**2-QP25*((EP2-EP1))**2)
      IF(VXY.LE.0.0) VXY=0.0
      VXY=SQRT(ABS(VXY))

C
C
C      EXCITED S STATES
      EHA=QP25*(ES1+Q3*EP1)
      EHC=QP25*(ES2+Q3*EP2)
      ES3=ES3INC+EP1
      ES4=ES4INC+EP2
      VS3P=Q0
      VS4P=Q0
      IF(ES4.LE.0.0.OR.ES4.GE.50.0) GOTO 25
      V=VS2P*VS2P
      CALL SSTATE(V,VS,X3V,X3C,ES4,ES2,EP1)
      VS2P=SQRT(V)
      VS4P=SQRT(VS)
25     IF(ES3.LE.0.0.OR.ES3.GE.50.0) GOTO 30
      V=VS1P*VS1P
      CALL SSTATE(V,VS,X1V,X1C,ES3,ES1,EP2)
      VS1P=SQRT(V)
      VS3P=SQRT(VS)
30     CONTINUE

C
C
      F(1)=ES1
      F(2)=EP1

```

```

P(3)=ES2
P(4)=EP2
P(5)=VSS
P(6)=VXX
P(7)=VXY
P(8)=VS1P
P(9)=VS2P
P(10)=ES3
P(11)=ES4
P(12)=VS3P
P(13)=VS4P
C   MODIFICATION FOR CATION SITE IMPURITIES
C
C   P(1)=ES2
C   P(2)=EP2
C   P(3)=ES1
C   P(4)=EP1
C   P(8)=VS2P
C   P(9)=VS1P
C   P(10)=ES4
C   P(11)=ES3
C   P(12)=VS4P
C   P(13)=VS3P
C
C   FOR INDIRECT GAP MATERIALS
C   THIS ROUTINE ADJUSTS THE BANDGAP TO INPUTTED X1C=EGAP
C   BY ADJUSTING VS3P AND VS4P  THUS INPUT CONDUCTION BAND
C   MINIMUM VIA X1C;  THE ROUTINE MAKES SURE EGAP IS
C   AT K=(1,0,0),(.5,.5,.5), OR (.7,0,0).
39  FORMAT(1X,'LOOP IN BANDGAP ADJUSTMENT')
   IF(ES3.GT.50.0.OR.ES4.GT.50.0) GOTO 45
   IF(GAM1C<EGAP) GOTO 45
   IF(NLOOP>50) WRITE(5,39)
   VK(1)=.7
   VK(2)=Q0
   VK(3)=Q0
   CALL HHYBR(VK,P,EN,EIVR,EIVI,IDUM)
   EI=EN(5)
   IF(EI<EGAP) GOTO 40
   VK(1)=.5
   VK(2)=.5
   VK(3)=.5
   CALL HHYBR(VK,P,EN,EIVR,EIVI,IDUM)
   EL=EN(5)
   IF(EL<EGAP) GOTO 40
   GOTO 45
40  EINC=.05
   X1C=X1C+EINC
   X3C=X3C+EINC
   NLOOP=NLOOP+1
   GOTO 2
45  CONTINUE

```

```

C      WRITE(23,10) (P(I),I=1,13)
      WRITE(5,75) (P(I),I=1,13)
75     FORMAT(1X,'S-P PARAMETERS  ES1,EP1,ES2,EP2,VSS,VXX,VXY,
      1VS1F,VS2F,ES3,ES4,VS3F,VS4F  ',/,1X,13F8.4)
C
      DO 60 I=1,3
60     VK(I)=0.
      CALL HHYBR(VK,P,EN,EIVR,EIVI,IDUM)
      VALGAM=EN(4)
      DO 61 I=1,NSTATE
61     EN(I)=EN(I)-VALGAM
      WRITE(5,200) VK,(EN(IND),IND=1,NSTATE)
      VK(1)=1.
      CALL HHYBR(VK,P,EN,EIVR,EIVI,IDUM)
      DO 62 I=1,NSTATE
62     EN(I)=EN(I)-VALGAM
      WRITE(5,200) VK,(EN(IND),IND=1,NSTATE)
      DO 63 I=1,3
63     VK(I)=.5
      CALL HHYBR(VK,P,EN,EIVR,EIVI,IDUM)
      DO 64 I=1,NSTATE
64     EN(I)=EN(I)-VALGAM
      WRITE(5,200) VK,(EN(IND),IND=1,NSTATE)
      VK(1)=.7
      VK(2)=0.0
      VK(3)=0.0
      CALL HHYBR(VK,P,EN,EIVR,EIVI,IDUM)
      DO 65 I=1,NSTATE
65     EN(I)=EN(I)-VALGAM
      WRITE(5,200) VK,(EN(IND),IND=1,NSTATE)
C      VK(1)=.75
C      VK(2)=.75
C      VK(3)=0.
C      CALL HHYBR(VK,P,EN,EIVR,EIVI,IDUM)
C      DO 66 I=1,NSTATE
C66     EN(I)=EN(I)-VALGAM
C      WRITE(5,200) VK,(EN(IND),IND=1,NSTATE)
C      CALL CHARGE(P)
      DO 85 I=1,13
85     P(I)=P(I)*BOND*BOND
      WRITE(5,86) ESAC,ESA,EPAC,EPA,P(5),P(6),P(7),P(8),P(9)
86     FORMAT(1X,'CHEMICAL TRENDS',/,
      11X,'S ENERGY DIFF.  SOLID ',F10.4,' ATOMIC',F10.4,/,
      21X,'P ENERGY DIFF.  SOLID ',F10.4,' ATOMIC',F10.4,/,
      31X,'INTERATOMIC  VSS,VXX,VXY,VS1F,VS2F  ',5F10.4)
999    CONTINUE
      CLOSE(UNIT=20)
      CLOSE(UNIT=21)
      CLOSE(UNIT=22)
      CLOSE(UNIT=23)
      STOP

```

```

1      FORMAT(16(/),1H0,5X,'TIGHT-BINDING-PARAMETERS FOR'//)
100     FORMAT(1H0,5X,'RESULTING PARAMETERS'//
1         5X,'IN ORDER ES1,EP1,ES2,EP2,VSS,VXX,VXY,VS1P,VS2P'
2         //5X,11F12.4//5X,'IN ORDER EHA,EHC,V2,V1S,V1A,V1XS,'
3         ',V1XA,V4,V5'//5X,11F12.4////)
200     FORMAT(5X,'RESULTING BANDS AT K-VECTOR...',3F10.3/
15X,10F12.4)
      END
      SUBROUTINE SSTATE(V,VS,E1,E2,A0,B0,C0)
      A1=A0-E1
      B1=B0-E1
      C1=C0-E1
      A2=A0-E2
      B2=B0-E2
      C2=C0-E2
C      V=B1*B2*(A2*C2-A1*C1)/(A2*B1-A1*B2)
      VS=A2*(C2-V/B2)
      RETURN
      END

```

@

```

C      ROUTINE HHYBER IN FILE HJOANH.FOR
C      THIS ROUTINE COMPUTES THE EIGENVALUES ,EN, AND
C      EIGENVECTORS, VR AND VI, AT K-POINT VK GIVEN
C      LCAO MATRIX ELEMENTS IN PAR.
      SUBROUTINE HHYBR(VK,PAR,EN,VR,VI,IERR)
      DIMENSION HR(10,10),HI(10,10),EN(10),FV1(10),FV2(10),FM1(2,10)
      DIMENSION PAR(21),C(3),S(3),VK(3)
      DIMENSION VR(10,10),VI(10,10)
      COMPLEX H(10,10),G0,G1,G2,G3
      COMPLEX CG0,CG1,CG2,CG3
      COMPLEX CQ1,CGI,CQ0
      CQ1=CMPLX(1.0,0.0)
      CGI=CMPLX(0.0,1.0)
      CQ0=CMPLX(0.0,0.0)
      PI=3.1415927
      NSTATE=10
      P2=PI/2.
      DO 10 J=1,3
      C(J)=COS(VK(J)*P2)
      S(J)=SIN(VK(J)*P2)
      G0=CMPLX(C(1)*C(2)*C(3),-S(1)*S(2)*S(3))
      G1=CMPLX(-C(1)*S(2)*S(3),S(1)*C(2)*C(3))
      G2=CMPLX(-S(1)*C(2)*S(3),C(1)*S(2)*C(3))
      G3=CMPLX(-S(1)*S(2)*C(3),C(1)*C(2)*S(3))
      CG0=CONJG(G0)
      CG1=CONJG(G1)
      CG2=CONJG(G2)
      CG3=CONJG(G3)
      DO 20 I=1,NSTATE
      DO 20 J=1,I
      H(I,J)=CQ0
      DIAGONAL TERMS
      H(1,1)=CQ1*PAR(1)
      H(2,2)=CQ1*PAR(3)
      H(3,3)=CQ1*PAR(2)
      H(4,4)=CQ1*PAR(2)
      H(5,5)=CQ1*PAR(2)
      H(6,6)=CQ1*PAR(4)
      H(7,7)=CQ1*PAR(4)
      H(8,8)=CQ1*PAR(4)
      OFF-DIAGONAL TERMS
      H(2,1)=PAR(5)*CG0
      H(3,2)=-PAR(9)*G1
      H(4,2)=-PAR(9)*G2
      H(5,2)=-PAR(9)*G3
      H(6,1)=PAR(8)*CG1
      H(7,1)=PAR(8)*CG2
      H(8,1)=PAR(8)*CG3
      H(6,3)=PAR(6)*CG0
      H(7,4)=PAR(6)*CG0

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H(8,5)=PAR(6)*CG0
H(6,4)=PAR(7)*CG3
H(6,5)=PAR(7)*CG2
H(7,5)=PAR(7)*CG1
H(7,3)=PAR(7)*CG3
H(8,3)=PAR(7)*CG2
H(8,4)=PAR(7)*CG1
C   EXCITED S STATES
H(9,9)=PAR(10)
H(10,10)=PAR(11)
H(9,6)=PAR(12)*G1
H(9,7)=PAR(12)*G2
H(9,8)=PAR(12)*G3
H(10,3)=-PAR(13)*CG1
H(10,4)=-PAR(13)*CG2
H(10,5)=-PAR(13)*CG3
      DO 30 I=1,NSTATE
      DO 30 J=1,I
        HR(I,J)=REAL(H(I,J))
        HI(I,J)=AIMAG(H(I,J))
30    CONTINUE
C   CALL MATOUT(HR,10,10)
      CALL HTRIDI(NSTATE,NSTATE,HR,HI,EN,FV1,FV2,FM1)
      DO 40 I=1,NSTATE
      DO 39 J=1,NSTATE
39    VR(I,J)=0.
40    VR(I,I)=1.
      CALL IMTQL2(NSTATE,NSTATE,EN,FV1,VR,IERR)
      IF(IERR.NE.0) STOP 1234
      CALL HTRIBK(NSTATE,NSTATE,HR,HI,FM1,NSTATE,VR,VI)
      RETURN
      END

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C      ROUTINE DEN4
C      THIS ROUTINE COMPUTES THE SPECTRAL DENSITY OF STATES,
C      DENSR AND DENSI, ON AN ENERGY GRID X GIVEN EIGENVALUES
C      EN AND EIGENVECTORS ANR AND ANI. THE ROUTINE ALSO CAN
C      CAN COMPUTE THE DENSITY OF STATES DER AND DEI.
C      THIS ROUTINE LOOKS UP LCAO MATRIX ELEMENTS USED AS INPUT
C      TO ROUTINE HHYBR.
C      IMPLICIT REAL*8 (A-H,O-Z)
C      LOGICAL ITRUE,IFLS
C      DIMENSION DENSR(600),DENSI(600),X(600)
C      DIMENSION DER(600,10),DEI(600,10),ANR(10,6),ANI(10,6)
C      DIMENSION EN(10),PARAM(21)
C      COMMON/EANDA/ E(10,900),AR(10,6,900),AI(10,6,900)
C      COMMON /AKTEST/ITRUE,IFLS
C      COMMON/LATSYM/IPLANE
C      COMMON/PARAMS/PARAM
C      DATA KPTS,MPTS,MXC,MXIJC/900,600,1,1/
C      DATA IPLANE/1000/
C      DATA FO,VALGAM/0.E+0,0.E+0/
C      LOOK UP PARAMETERS IN TABLE; FOR ALLOYS MAKE THE
C      VIRTUAL CRYSTAL APPROXIMATION.
C
C      ACCEPT 701,NROW1,NROW2,COMP
701  FORMAT(3G)
C
C      OPEN(UNIT=20,FILE='EKINPT.DAT',DIALOG)
C      OPEN(UNIT=21,FILE='GBAND.DAT',DIALOG)
C      OPEN(UNIT=22,FILE='DNSE.DAT',DIALOG)
C      OPEN(UNIT=23,FILE='GRN.DAT',DIRECTORY='4,66',DIALOG)
C      OPEN(UNIT=23,FILE='GRN.DAT',DIALOG)
C      OPEN(UNIT=24,FILE='TBPRM.DAT',DIALOG)
C      WRITE(5,1)
1    FORMAT(1X,'WRITTEN BY H. HJALMARSON; LAST MODIFICATION
1    ON 5-JULY-79')
C
C      READ(20,900) NKGAMX,NBAND1,NBAND2,NINCR,IITRU,EI,EF,EGRID
900  FORMAT(5I4,3F11.5)
C      READ THE PARAMS USED IN LCAO CALC IN EKDEN.FOR
C      NRMAX=AMAX0(NROW1,NROW2)
C      IPRM=13
C      USE DENSR FOR TEMPORARY STORAGE.
C      DO 702 I=1,NRMAX
C      INDX=(I-1)*IPRM
702  READ(24,904) (DENSR(INDX+II),II=1,13)
C
C      DO 703 II=1,13
C      INDX1=(NROW1-1)*IPRM+II
C      INDX2=(NROW2-1)*IPRM+II
703  PARAM(II)=(1.0-COMP)*DENSR(INDX1)+COMP*DENS(INDX2)
C      WRITE(23,904) (PARAM(II),II=1,13)
904  FORMAT(13F8.4)

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WRITE(23,908) EGRID,EI,EF,EI,EF
908  FORMAT(5F11.5)
WRITE(5,906) (PARAM(II),II=1,13)
906  FORMAT(1X,'ES1,EP1,ES2,EP2,VSS,VXX,VXY,VSP1,VSP2',
1,'ES3,ES4,VSP3,VSP4=',/,1X,13F8.4)
WRITE(5,901) NKGAMX,NBAND1,NBAND2,NINCR,IITRU,EI,EF,EGRID
901  FORMAT(1X,'NKGAMX,NBAND1,NBAND2,NINCR',3X,4I4,/,
110X,'IITRU,EI,EF,EGRID',3X,I4,3F11.5)
C
C  SET IITRU=0 FOR DENSITY OF STATES
C  SET IITRU=1 FOR SPECTRAL DENSITY OF STATES
ITRUE=.FALSE.
IFLS=.TRUE.
IF(IITRU.GT..5) ITRUE=.TRUE.
IF(IITRU.GT..5) IFLS=.FALSE.
IF(ITRUE) MXC=3
C  IF FCC SET IPLANE WITH NEXT LINE
IPLANE=3*(NKGAMX/2)
NPTS=INT((EF-EI)/EGRID+.5)+1
IF (NPTS.LE.MPTS) GO TO 2
WRITE(5,905) NPTS,MPTS
905  FORMAT(' ', 'NPTS =',I5,' .GT. MPTS =',I5)
CALL EXIT
2  WRITE(5,902) NPTS
902  FORMAT(1X,'NPTS',I4)
DO 230 I=1,NPTS
X(I)=(FLOAT(I-1)*EGRID+EI)
230  CONTINUE
N1=NKGAMX+1
XN1=FLOAT(NKGAMX)
KMAX=(N1*(N1+1)*(N1+2))/6
WRITE(5,903) KMAX,KPTS
IF(KMAX>KPTS) CALL EXIT
903  FORMAT(1X,'NUMBER OF POINTS IN SC IRRED WEDGE',I4,
1/,1X,'MUST BE LESS THAN',I4)
DO 10 IIX=1,N1
DO 10 IIY=1,IIX
DO 10 IIZ=1,IIY
IF (IIX+IIY+IIZ-3.GT.IPLANE) GO TO 10
XK=FLOAT(IIX-1)/XN1
YK=FLOAT(IIY-1)/XN1
ZK=FLOAT(IIZ-1)/XN1
ICNT=((IIX**2-1)*IIX)/6+((IIY-1)*IIY)/2+IIZ
ICNT0=ICNT
CALL EK(EN,ANR,ANI,XK,YK,ZK,NBAND1)
IF(ICNT0.EQ.1) VALGAM=EN(4)
DO 10 N=NBAND1,NBAND2,NINCR
E(N,ICNT)=EN(N)-VALGAM
IF(IFLS) GO TO 10
IJC=0
DO 6 IC=1,MXC
DO 6 JC=IC,MXC

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      IJC=IJC+1
      MXIJC=IJC
      AR(N,IJC,ICNT)=ANR(N,IJC)
6      AI(N,IJC,ICNT)=ANI(N,IJC)
10     CONTINUE
      WRITE(5,340) VALGAM
340    FORMAT(1X,'ZERO OF ENERGY AT',E11.4)
      WRITE(21,931) (X(I),I=1,NPTS)
      DO 300 IJC=1,MXIJC
      DO 350 I=1,NPTS
350    DENSR(I)=F0
      DENSI(I)=F0
      IDUM=IJC
      CALL DENSE(DER,DEI,EI,EF,EGRID,NKGAMX,NPTS,
1NBAND1,NBAND2,NINCR,IDUM)
      DO 360 N=NBAND1,NBAND2,NINCR
      DO 360 I=1,NPTS
360    DENSR(I)=DENSR(I)+DER(I,N)
      DENSI(I)=DENSI(I)+DEI(I,N)
      WRITE(21,931) (DENSR(I),DENSI(I),I=1,NPTS)
      IF(IJC>1) GO TO 300
931    FORMAT(10E11.4)
      WRITE(22,931) (X(I),I=1,NPTS)
      WRITE(22,931) ((DER(I,N),I=1,NPTS),N=NBAND1,NBAND2,NINCR)
C      PRINT 930, (((X(I),DER(I,N)),I=1,NPTS),N=NBAND1,
C      1NBAND2,NINCR)
930    FORMAT(1X,10E11.4)
300    CONTINUE
      CLOSE(UNIT=20)
      CLOSE(UNIT=21)
      CLOSE(UNIT=22)
      CLOSE(UNIT=23)
      STOP
      END
      SUBROUTINE DENSE(DER,DEI,EI,EF,EGRID,NKGAMX,NPTS,
1NBAND1,NBAND2,NINCR,IJC)
C      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION ETET(4),ECOR(4)
      DIMENSION ATETR(4),ATETI(4),ACORR(4),ACORI(4)
      DIMENSION DER(600,10),DEI(600,10)
      COMMON/EANDA/ E(10,900),AR(10,6,900),AI(10,6,900)
      DIMENSION ITETC(3,4,5)
      DIMENSION VOLTET(5)
      COMMON/AKTEST/ITRUE,IPLS
      COMMON /LATSYM/IPLANE
      LOGICAL ITRUE,IPLS
      DATA F0,F1B4,EMACH/0.E+00,.25E+00,1.E-7/
      DATA F2,F6/2.E+00,6.E+00/
      DATA ITETC/ 0,0,0, 1,0,1, 1,1,0, 0,1,1,
1          0,0,0, 1,0,0, 1,1,0, 1,0,1,
2          0,0,0, 0,1,0, 1,1,0, 0,1,1,
3          0,0,0, 0,0,1, 1,0,1, 0,1,1,

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4          1,1,1, 1,0,1, 1,1,0, 0,1,1/
VOL=1.0D+0/FLOAT(NKGAMX**3)
XN1=FLOAT(NKGAMX)
ITST=3*(NKGAMX/2)
IF(ITST.EQ.IPLANE) VOL=2.E+0*VOL
IWARN=0
VOLTET(1)=VOL/3.
DO 10 I=2,5
10  VOLTET(I)=VOL/6.
DO 100 N=NBAND1,NBAND2,NINCR
DO 100 I=1,NPTS
DER(I,N)=F0
100  DEI(I,N)=F0
15  FORMAT(1X,'CUBE INDEX',3I4)
16  FORMAT(1X,'TET #',I4,'ICNT',I4,/,
1,1X,'ECOR',E11.4,'KPNT',3F8.3)
DO 700 N=NBAND1,NBAND2,NINCR
DO 600 IIX=1,NKGAMX
DO 600 IIY=1,NKGAMX
DO 600 IIZ=1,NKGAMX
C  WRITE(5,15) IIX,IIY,IIZ
C  TEST TO SEE IF IN IRRED. WEDGE. FCC.
IFCC=IIX+IIY+IIZ-IPLANE
IF(IFCC>2) GOTO 600
DO 400 ITET=1,5
DO 200 IVTEX=1,4
IKX=IIX+ITETC(1,IVTEX,ITET)-1
IKY=IIY+ITETC(2,IVTEX,ITET)-1
IKZ=IIZ+ITETC(3,IVTEX,ITET)-1
C  TEST TO SEE IF IN IRRED. WEDGE. FCC.
C  IFCC=IKX+IKY+IKZ-IPLANE
C  IF(IFCC>0) GO TO 400
IF(IFCC-1) 20,19,18
18  IF(ITET<5) GOTO 400
IKX=IKX+1-2*ITETC(1,IVTEX,ITET)
IKY=IKY+1-2*ITETC(2,IVTEX,ITET)
IKZ=IKZ+1-2*ITETC(3,IVTEX,ITET)
GOTO 20
19  IF(ITET.EQ.5) GOTO 400
20  CONTINUE
XK=FLOAT(IKX)/XN1
YK=FLOAT(IKY)/XN1
ZK=FLOAT(IKZ)/XN1
IF (IKZ.LE.IKY) GO TO 30
C  IF NOT, FOLD IN TO WEDGE.
ITEMP=IKZ
IKZ=IKY
IKY=ITEMP
30  IF (IKZ.LE.IKX) GO TO 40
ITEMP=IKZ
IKZ=IKX
IKX=ITEMP

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40 IF (IKY.LE.IKX) GO TO 50
   ITEMF=IKY
   IKY=IKX
   IKX=ITEMF
50 IKX=IKX+1
   IKY=IKY+1
   IKZ=IKZ+1
   ICNT=((IKX**2-1)*IKX)/6+((IKY-1)*IKY)/2+IKZ
   ECOR(IVTEX)=E(N,ICNT)
   ACORR(IVTEX)=AR(N,IJC,ICNT)
   ACORI(IVTEX)=AI(N,IJC,ICNT)
C   WRITE(5,16) ITET,ICNT,ECOR(IVTEX),XK,YK,ZK
200 CONTINUE
C   ORDER ENERGIES ON TET. CORNERS. E(1)<E(2)<E(3)<E(4).
   DO 120 K=1,4
   ATETR(K)=ACORR(K)
   ATETI(K)=ACORI(K)
120 ETET(K)=ECOR(K)
   DO 150 K=1,3
   EMIN=ETET(K)
   K1=K+1
   DO 150 L=K1,4
   IF (ETET(L).GT.EMIN) GO TO 150
   EMIN=ETET(L)
   ETET(L)=ETET(K)
   ETET(K)=EMIN
   ATEMPR=ATETR(L)
   ATEMPI=ATETI(L)
   ATETR(L)=ATETR(K)
   ATETI(L)=ATETI(K)
   ATEPR=ATEMPR
   ATETI(K)=ATEMPI
150 CONTINUE
C   TEST TO MAKE SURE TET IS WITHIN ENERGY RANGE.
   IF(ETET(1).GT.EI.AND.ETET(4).LT.EF) GOTO 160
   WRITE(5,155) ETET(1),ETET(4)
155 FORMAT(1X,'ENERGY RANGE EXCEEDED AT ETET(1)= ',
1,E11.4,'OR ETET(4)= ',E11.4)
   GOTO 400
160 CONTINUE
C   CHECK FOR GRADIENT OF E(K) EQUAL TO ZERO.
   IF((ETET(4)-ETET(1)).LT.EGRID) GO TO 350
C   DEFINE ENERGY DIFFERENCES.
   E21=ETET(2)-ETET(1)
   E31=ETET(3)-ETET(1)
   E41=ETET(4)-ETET(1)
   E32=ETET(3)-ETET(2)
   E42=ETET(4)-ETET(2)
   E43=ETET(4)-ETET(3)
C   DEFINE DENOMINATORS OF F (USED IN LEHMAN AND TAUT)
   DENOM1=E21*E31*E41
   DENOM2=E21*E32*E42

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DENOM3=E31*E32*E43
DENOM4=E41*E42*E43
DO 300 IVTEX=1,3
E1=ETET(IVTEX)
E2=ETET(IVTEX+1)
IF(E1.GT.EF.OR.E2.LT.EI) GO TO 300
C ENERGY GRID DEFINED
EMIN=AMAX1(EI,E1)
EMAX=AMIN1(EF,E2)
MMIN=INT((EMIN-EI)/EGRID)+2
MMAX=INT((EMAX-EI)/EGRID)+1
IF(MMAX.LT.MMIN) GO TO 300
170 DO 290 M=MMIN,MMAX
EE=EI+EGRID*FLOAT(M-1)
EE1=EE-ETET(1)
EE2=EE-ETET(2)
EE3=EE-ETET(3)
EE4=EE-ETET(4)
GO TO (210,220,230)IVTEX
210 TEMP=EE1**2/DENOM1
GO TO 280
220 IF(E21.LT.EMACH) GO TO 225
TEMP=(DENOM2*EE1**2-DENOM1*EE2**2)/(DENOM1*DENOM2)
C TEMP=EE1**2/DENOM1-EE2**2/DENOM2
III=21
IF(TEMP.LT.EMACH) WRITE(5,900) TEMP,III,EE,M
1,IIX,IIY,IIZ,ITET,(ETET(JJ),JJ=1,4)
GO TO 280
225 IF(E43.LT.EMACH) GO TO 300
TEMP=(DENOM3*EE4**2-DENOM4*EE3**2)/(DENOM3*DENOM4)
C TEMP=EE4**2/DENOM4-EE3**2/DENOM3
III=43
IF(TEMP.LT.EMACH) WRITE(5,900) TEMP,III,EE,M
1,IIX,IIY,IIZ,ITET,(ETET(JJ),JJ=1,4)
GO TO 280
900 FORMAT(1X,'TEMP=',E11.4,4X,'AT E',I2,'=',E11.4,/,
11X,'M=',I4,'ILATPT =',3I4,3X,'ITET =',I4,/,
21X,'ETET(1),...=',4E11.4)
230 TEMP=EE4**2/DENOM4
280 DADDR=TEMP*VOLTET(ITET)*F6
DADDI=F0
IF(IFLS) GOTO 290
AAVER=(ATETR(1)+ATETR(2)+ATETR(3)+ATETR(4))*F1B4
AAVEI=(ATETI(1)+ATETI(2)+ATETI(3)+ATETI(4))*F1B4
DADDR=DADDR*AAVER
DADDI=DADDR*AAVEI
290 DER(M,N)=DER(M,N)+DADDR
DEI(M,N)=DEI(M,N)+DADDI
300 CONTINUE
GO TO 400
350 EMIN=AMAX1(EI,ETET(1))
MM=INT((EMIN-EI)/EGRID)+1

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```
DADDI=F0
DADDR=F2*VOLTET(ITET)/EGRID
IWARN=IWARN+1
IF(IWARN.LE.100.AND.IJC.EQ.1) PRINT 370, IWARN,MM
1,IIX,IIY,IIZ,ITET,(ETET(JJ),JJ=1,4)
IF(IFLS) GOTO 360
DADDR=DADDR*ATETR(1)
DADDI=DADDR*ATETI(1)
360 DER(MM,N)=DER(MM,N)+DADDR
DEI(MM,N)=DEI(MM,N)+DADDI
400 CONTINUE
600 CONTINUE
PRINT 371, IWARN,N
DEI(NPTS,N)=DEI(NPTS-1,N)
700 DER(NPTS,N)=DER(NPTS-1,N)
370 FORMAT(1X,'WARNING,MM...',2I4,'LAT PT',3I4,'ITET',I4,
1'ETET',4E12.4)
371 FORMAT(1X,I5,'WARNINGS AT BAND',I5)
RETURN
END
```

e

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C      ROUTINE EK IN FILE EKDEND.FOR
C      SUBROUTINE EK(E,ANR,ANI,XK,YK,ZK,NBAND1)
C      THIS ROUTINE PRODUCES ENERGY EIGENVALUES AND EIGENVECTORS
C      TO BE THE INPUT TO A SPECTRAL DENSITY ROUTINE. IT
C      ALSO CONVERTS FROM AN SP3 BASIS TO A HYBRID BASIS.
C      IMPLICIT REAL*8 (A-H,O-Z)
      DIMENSION ANR(10,6),ANI(10,6),E(10)
      DIMENSION X(21),VK(3)
      DIMENSION AR(10,10),AI(10,10)
      DIMENSION FR(10,10),FI(10,10)
      DIMENSION U(4,4),V(4,4)
      DIMENSION A(10,10),F(10,10)
      DIMENSION DR(10,10),DI(10,10)
      DIMENSION A1R(2,2),T2R(2,2),CHGA(10),CHGC(10),C(10),CC(10)
      DIMENSION PHS(4)
      COMMON /FLAG/NN,II,KK
      COMMON/PARAMS/X
      COMPLEX A1,CZERO
      COMPLEX A,F
      COMPLEX PX,PY,PZ,PHS,CONST,S1,S2,CI
      COMPLEX DCC,DCA,DAA,SCC,SCA,SAA,C,CC
      CZERO=CMPLX(.0E+0,.0E+0)
      DATA U/.5,.5,.5,.5,.5,-.5,.5,-.5
1,.5,-.5,-.5,.5,.5,.5,-.5,-.5/
      DATA V/.5,-.5,-.5,-.5,.5,.5,-.5,.5
1,.5,.5,.5,-.5,.5,-.5,.5,.5/
      PI=3.14159265
      CI=CMPLX(0.E+0,1.E+0)
      F0=0.0
      F1B4=.25E+0
      F1B12=1.0/12.0
      F1B8=.125E+0
      CONST=PI*CI*F1B4
      PX=CEXP(CONST*XK)
      PY=CEXP(CONST*YK)
      PZ=CEXP(CONST*ZK)
      PHS(1)=PX*PY*PZ
      PHS(2)=PY/(PX*PZ)
      PHS(3)=PZ/(PX*PY)
      PHS(4)=PX/(PY*PZ)
      NN=10
      VK(1)=XK
      VK(2)=YK
      VK(3)=ZK
      CALL HHYBR(VK,X,E,DR,DI,IEIVC)
C      CALL MATOUT(DR,NN,NN)
C      CALL MATOUT(DI,NN,NN)
      DO 3 I=1,10
      DO 3 J=1,10
      A(I,J)=CZERO
3      CONTINUE

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C      SP3 TO HYBRID CONVERSION.  SP3 BASIS IN ORDER X,X,Y,Z
C      ON THE ANION, THEN THE CATION ORBITALS AND FINALLY S-ANION
C      AND S-CATION ORBITALS.  HYBRID BASIS HAS CATION CENTER; THEREFORE
C      THE ANION HAS AN ADDITIONAL PHASE FACTOR AND ITS P-ORBITALS
C      INVERTED.
      DO 4 N=1,10
        F(1,N)=CMPLX(DR(1,N),DI(1,N))
        F(2,N)=CMPLX(DR(3,N),DI(3,N))
        F(3,N)=CMPLX(DR(4,N),DI(4,N))
        F(4,N)=CMPLX(DR(5,N),DI(5,N))
        F(5,N)=CMPLX(DR(2,N),DI(2,N))
        F(6,N)=CMPLX(DR(6,N),DI(6,N))
        F(7,N)=CMPLX(DR(7,N),DI(7,N))
        F(8,N)=CMPLX(DR(8,N),DI(8,N))
      DO 4 I=1,4
      DO 4 J=1,4
        A(I+4,N)=A(I+4,N)+U(J,I)*F(J,N)*CONJG(PHS(I))
        A(I,N)=A(I,N)+V(J,I)*F(J+4,N)*PHS(I)
4      CONTINUE
      DO 50 N=1,NN
        DCC=CZERO
        DCA=CZERO
        DAA=CZERO
        SCC=CZERO
        SCA=CZERO
        SAA=CZERO
      DO 30 I=1,4
        C(I)=A(I,N)*PHS(I)
        C(I+4)=A(I+4,N)*PHS(I)
        CC(I)=CONJG(C(I))
        CC(I+4)=CONJG(C(I+4))
30      CONTINUE
      DO 40 I=1,4
      DO 40 J=1,4
        IF(I.EQ.J) GOTO 35
        SCC=SCC+C(I)*CC(J)
        SCA=SCA+C(I)*CC(J+4)
        SAA=SAA+C(I+4)*CC(J+4)
        GOTO 40
35      DCC=DCC+C(I)*CC(I)
        DCA=DCA+C(I)*CC(I+4)
        DAA=DAA+C(I+4)*CC(I+4)
40      CONTINUE
        A1R(1,1)=F1B4*REAL(DCC+SCC)
        T2R(1,1)=F1B4*REAL(DCC)-F1B12*REAL(SCC)
        A1R(1,2)=F1B4*REAL(DCA+SCA)
        T2R(1,2)=F1B4*REAL(DCA)-F1B12*REAL(SCA)
        A1R(2,2)=F1B4*REAL(DAA+SAA)
        T2R(2,2)=F1B4*REAL(DAA)-F1B12*REAL(SAA)
        CHGA(N)=REAL(DAA)
        CHGC(N)=REAL(DCC)
        IJC=0

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DO 50 I=1,2
DO 50 J=1,2
IJC=IJC+1
ANR(N,IJC)=A1R(I,J)
ANR(N,IJC+3)=T2R(I,J)
ANI(N,IJC)=F0
ANI(N,IJC+3)=F0
50 CONTINUE
C E(NBAND1)=XK**2+YK**2+ZK**2
C E(NBAND1)=-COS(XK*PI)-COS(YK*PI)-COS(ZK*PI)
C E(NBAND1)=2.
C PRINT 100, VK,E
100 FORMAT(1H0,5X,'VK=',3F10.4/6X,'E=',12F10.4)
C PRINT 125
125 FORMAT(15X,'A1 CC      A1 CA      A1 AA'
1,6X,'T2 CC      T2 CA      T2 AA')
DO 150 N=1,9
C PRINT 200, N,(ANR(N,II),II=1,6)
150 CONTINUE
200 FORMAT(1X,'AN(',I2,')=',5X,6E11.4)
C PRINT 300, (NCNT,CHGA(NCNT),NCNT,CHGC(NCNT),NCNT=1,NN)
300 FORMAT(1X,'CHGA(',I2,')=',E11.4,10X,'CHGC(',I2,')=',E11.4)
RETURN
END

```

@

```

C      ROUTINE GREEN
C      USING THE SPECTRAL DENSITY OF STATES, DENR, THIS
C      ROUTINE COMPUTES THE REAL PART ,GRNR, AND IMAGINARY
C      PART, GRNI, OF THE GREEN'S FUNCTION.
C      COMPUTE THE GREEN'S FUNCTION G(E;I,J) FOR THE PERFECT
C      CRYSTAL.
      DIMENSION PARAM(21)
      DIMENSION EE(600),DR(3,600),DI(3,600),CFIT(6,600)
      DIMENSION DENR(600),DENI(600)
      DIMENSION GRNR(3,600),GRNI(3,600)
      COMMON/MISC/NGRID,NDIM,NDIM2,EMIN,EMAX,EDUM,EPSS,EPSC
      COMMON/INTGRD/DENR,EE,CFIT

C
C      DIMENSION FIXED BY NDIM
      DATA NDIM,NDIM2/2,4/
      DATA F1B2,F0/.5,0./
      DATA PI/3.14159265/
      DATA EPSS,EPSC/.5E-03,.5E-03/

C
      OPEN(UNIT=20,FILE='GBAND.DAT',DIALOG)
      OPEN(UNIT=23,FILE='GRN.DAT',DIALOG)
      WRITE(5,1) EPSS,EPSC
1      FORMAT(1X,'CONVERGENCE CRITERIA: SPLINE AND CAUCHY',
12X,2E11.4,/,1X,'WRITTEN BY H. HJALMARSON; LAST MODIFICATION ON
2 14-NOV-78. SIMPSON RULE USED.')
```

```

      READ(23,8) (PARAM(II),II=1,13)
8      FORMAT(13F8.4)
      WRITE(5,9) (PARAM(II),II=1,13)
9      FORMAT(1X,'EHA,EHC,V2,V1S,V1A,V1XS,V1XA,V4,V5=',/,
11X,13F8.4)
      READ(23,4) GRID,EMIN,EMAX,EL,ER
4      FORMAT(5F11.5)
      NGRID=INT((EMAX-EMIN)/GRID)+1
      READ(20,5) (EE(I),I=1,NGRID)

C
C
C      READ DENS OF STATES AND VDFCT FOR A1 AND T2.
      DO 2000 IGROUP=1,2
C      1 FOR A1; 2 FOR T2
      DO 10 IJC=1,3
      READ(20,5) (DR(IJC,I),DI(IJC,I),I=1,NGRID)
      DO 10 I=1,NGRID
      DR(IJC,I)=F1B2*DR(IJC,I)
      DI(IJC,I)=F1B2*DI(IJC,I)
10     CONTINUE
5     FORMAT(10E11.4)
C
C
C      IJC=0
      DO 900 IC=1,NDIM

```

```

DO 900 JC=IC,NDIM
IJC=IJC+1
C   DEFINE DENSITY OF STATES ON THE NEW GRID
C   ASSUME DI=0
DO 100 I=1,NGRID
100  DENR(I)=DR(IJC,I)
C
C   COMPUTE THE HILBERT TRANSFORM:
C   I(E)=P SUM (DNEW(E')/(E-E'))
C   OMIT FIRST TWO AND LAST TWO POINTS.  THE GREEN
C   FUNCTION IS NOT CALCULATED FOR THESE POINTS.
C
NGM2=NGRID-2
IGRID=0
C
C   CALL GOUT(FER,GRID,IDUM,IGRID)
C   GOUT FOR GAUSSIAN QUADRATURE; GREEN FOR SIMPSON'S RULE.
C
WRITE(5,250) IJC
250  FORMAT(1X,'IJC=',I4,2X,'AND ALL IS WELL')
DO 300 ISING=3,NGM2,2
IDUM=ISING
CALL GREEN(FER,DENR,EE,GRID,NGRID,IDUM)
C   CALL GOUT(FER,GRID,IDUM,IGRID)
GRNR(IJC,ISING)=FER
GRNI(IJC,ISING)=-PI*DENR(ISING)
300  CONTINUE
IJCMX=IJC
900  CONTINUE
DO 400 I=3,NGRID,2
C   PRINT 302, (GRNR(IJ,I),GRNI(IJ,I),IJ=1,IJCMX),EE(I)
400  WRITE(23,301) (GRNR(IJ,I),GRNI(IJ,I),IJ=1,IJCMX),EE(I)
301  FORMAT(7E11.4)
302  FORMAT(1X,7E11.4)
2000 CONTINUE
CLOSE(UNIT=20)
CLOSE(UNIT=23)
20  STOP
END
C
C
C
SUBROUTINE GREEN(FER,DE,E,GRID,NGRID,ISING)
C   THIS ROUTINE COMPUTES THE HILBERT TRANSFORM WITH
C   SIMPSON'S RULE.
DIMENSION DE(600),E(600)
DATA F0,F1B2,F4,F16/0.0,0.5,4.0,16.0/
F1B9=1./9.
GRIDB3=GRID/3.
ES=E(ISING)
FER=F0
IL=ISING-1

```

```

IR=NGRID-ISING
IMAX=MAX0(IL,IR)
DO 300 INC=2,IMAX,2
ADD1=F0
ADD2=F0
ADD3=F0
INCL=ISING-INC
INCR=ISING+INC
IF(INC>2) GOTO 100
DL1=DE(INCL)
DL2=DE(INCL+1)
DR1=DE(INCR)
DR2=DE(INCR-1)
ADD1=F1B9*(DL1-DR1+F16*(DL2-DR2))
GOTO 250
100 CONTINUE
IF(INCL<1) GOTO 200
DL1=DE(INCL)/(ES-E(INCL))
DL2=DE(INCL+1)/(ES-E(INCL+1))
DL3=DE(INCL+2)/(ES-E(INCL+2))
ADD2=GRIDB3*(DL1+F4*DL2+DL3)
200 IF(INCR>NGRID) GOTO 250
DR1=DE(INCR)/(ES-E(INCR))
DR2=DE(INCR-1)/(ES-E(INCR-1))
DR3=DE(INCR-2)/(ES-E(INCR-2))
ADD3=GRIDB3*(DR1+F4*DR2+DR3)
250 FER=FER+ADD1+ADD2+ADD3
300 CONTINUE
RETURN
END

```

C
C

```

SUBROUTINE GOUT(HLBRT,GRID,ISING,IGRID)
EXTERNAL F
COMMON/INTGRD/FF,EE,CFIT
COMMON/MISC/NGRID,NDIM,NDIM2,E1,E2,ESING,EPSS,EPSSG
DIMENSION FF(600),EE(600),CFIT(6,600)
IF(IGRID>0) GO TO 500
CALL SP3A(NGRID,EPSS,EE,FF,PROXI,CFIT)
IGRID=1
RETURN
500 CONTINUE
ESING=EE(ISING)
EMIN=EE(1)
EMAX=EE(NGRID)
HLBRT=CAUCH(F,EMIN,EMAX,ESING,EPSSG)
RETURN
END

```

C
C

```

FUNCTION F(E)
COMMON/INTGRD/FF,EE,CFIT

```

```
COMMON/MISC/NGRID,NDIM,NDIM2,EMIN,EMAX,ESING,EPSS,EPSSG  
DIMENSION FF(600),EE(600),CFIT(6,600)  
CALL SP3B(NGRID,EE,FF,E,FDUM,CFIT,SS1,SS2)  
F=FDUM/(ESING-E)  
RETURN  
END
```

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