$$(-\tfrac{1}{2}\nabla^2 + V)\Psi_{E+\Delta E} = (E+\Delta E)\Psi_{E+\Delta E}\,. \tag{A9}$$

Now cross multiply by $R^*_{E,l'}Y^*_{l'm'}$ and $R^*_{l',E+\Delta E}Y^*_{l'm'}$ and proceed as in the atomic problem. This gives

$$-\tfrac{1}{2}r^2R^2_{lE}\frac{d}{dE}\left(\frac{\partial R_{lE}/\partial r}{R_{lE}}\right)_{r=r_c} = \int_0^{r_c} R^*_{lE}R_{lE}\,r^2\,dr \tag{A10}$$

for every l. Thus in order that the charge density of the solid be properly represented between cores it is necessary to fit the ground and excited states of all symmetries.

It should be noted that this theorem is only valid if V is independent of the energy E, for then $[d/dE, V]=0$ and the potential terms in (A3) cancel.

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Forward-Scattering Approximation for Disordered Systems*

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Changes in the Fermi surface with disorder can be defined for only two cases: (a) when ordinary perturbation theory is applicable and (b) when the forward-scattering approximation is applicable. In the forward-scattering approximation (FSA) the perturbation is large in the vicinity of the forward direction or diagonal elements, but the average off-diagonal element is small, in contrast to the ordinary perturbation approximation where all perturbing matrix elements are small. The multiple scattering problem is solved for the FSA, and its close relation to ordinary perturbation theory is discussed. All the results of ordinary perturbation theory can be carried over to the FSA if proper account is taken of the self-energies of the states and interband mixing. The self-consistent condition on the potential imposed by shielding is given. The fact that the FSA can satisfy this self-consistency makes it a physically realistic approximation. All systems with a large concentration of disorder whose properties still can be approximated by the concepts of ordered systems, such as a Fermi surface, must be describable by either the FSA or ordinary perturbation theory.

I. INTRODUCTION

In the development of our understanding of a given subject, it is helpful to have models which are simple yet good approximations to physical reality. The field of disordered systems is such a developing subject, but its progress is being hampered by a scarcity of such simple models. One simple approximation that has proven to be successful is perturbation theory.[1] Both disordered alloys[2] and liquid metals[3] have examples which have been successfully described by perturbation theory. However, especially for disordered alloys, the most interesting and most numerous cases cannot be described in terms of perturbation theory.

Much effort has been expended on developing other approximations which can supplement perturbation theory. Perhaps the best known and most widely pursued one has been the coherent-potential approximation (CPA).[4–6] The CPA has the advantage that it is relatively simple if applied to the highly localized perturbation model where the random perturbations are localized to a single site and enter into only the diagonal elements of a

Wannier-function representation. This highly localized perturbation model has been used extensively, not only in the CPA, but also in studying other approaches[7] which attempt to include the correlation effects between neighboring scatterers which are neglected in the CPA. However, recently it has been shown[8] that when the self-consistency requirement on the potential is taken into account, the highly localized perturbation model cannot be applied to any real physical system. Although one may hope that qualitatively the highly localized perturbation model will give still reasonable results, this can only be a hope because of the unphysical nature of the model.

In a recent paper[9] a new simple approximation was presented which can satisfy the self-consistency condition on the potential; thus it is physical and is applicable to a class of real disordered systems, namely, those for whom changes in their Fermi surfaces can be defined. The properties of this new approximation were described semiquantitatively, but the explicit multiple scattering solution was not then given. This paper presents such a solution for this approximation which is called the "forward-scattering approximation" (FSA) for reasons to be given in Sec. II. As will be discussed in Sec. IV, the FSA is closely related to perturbation theory and is as simple.

In Sec. II the FSA is characterized in terms of the energy shift or self-energy introduced by alloying. The essence of the material in Sec. II was presented previously, [9] but is summarized here in a form more appropriate for the subsequent development. The relation between the T and V matrices is given in Sec. III, which gives the solution to the multiple scattering problem encountered in disordered systems. In Sec. IV a discussion is given of the self-consistency condition on the potential in the FSA and of the relationship between the FSA and ordinary perturbation theory. Section V consists of a summary and conclusion.

II. ENERGY SHIFTS AND SCATTERING THEORY

When a pure crystalline solid is disordered in some manner, such as by alloying or by being made amorphous, its energy spectrum is, of course, modified. One way to describe this modification is in terms of the self-energy or energy shift of the energies of the Bloch states $E_0(\vec{k})$. If I denote the Bloch states by $|\vec{k}\rangle$, then they satisfy the relation

$$H_0|\vec{k}\rangle = E_0(\vec{k})|\vec{k}\rangle , \tag{1}$$

where H_0 is the Hamiltonian describing the crystalline solid. The disordering process will modify this Hamiltonian to H, where

$$H = H_0 + V , \tag{2}$$

and V is the appropriate random perturbation introduced by the disorder.

The self-energy or energy shift $\Sigma(\vec{k})$ of $|\vec{k}\rangle$ introduced by disordering is defined as the complex change in its energy as V is adiabatically turned on. Writing

$$\Sigma(\vec{k}) = \Sigma_1(\vec{k}) + i\Sigma_2(\vec{k}) , \tag{3}$$

where Σ_1 and Σ_2 are the real and imaginary parts of $\Sigma(\vec{k})$, $\hbar[2\Sigma_2(\vec{k})]^{-1}$ is a measure of the lifetime of $|\vec{k}\rangle$ in the disordered system; i.e., if an electron were created in the state $|\vec{k}\rangle$, it would decay in a time of order $\hbar/2\Sigma_2(\vec{k})$ in the disordered system. The usefulness and correctness of interpreting

$$\mathrm{Re}E(\vec{K}) = E_0(\vec{k}) + \Sigma_1(\vec{k}) \tag{4}$$

as accurately indicating the energy change of $|\vec{k}\rangle$ in the disordered system depends on the relative sizes of $\Sigma_2(\vec{k})$ and $\Sigma_1(\vec{k})$. $2\Sigma_2(\vec{k})$ is a measure of the half-width of the uncertainty in the energy introduced by the decay. If

$$\delta(\vec{k}) \equiv \Sigma_2(\vec{k})/\Sigma_1(\vec{k}) \gtrsim 1 , \tag{5}$$

then the uncertainty in the energy shift is as great or larger than the energy shift, and one *cannot* interpret (4) as the energy of $|\vec{k}\rangle$ in the disordered system having increased by $\Sigma_1(\vec{k})$. However, if

$$\delta(\vec{k}) \ll 1 , \tag{6}$$

then (4) can be so interpreted. As shown in Ref. 9, $\delta(k) \ll 1$ is the necessary and sufficient condition that when disorder is introduced, both (a) changes in the Fermi surfaces can be defined and (b) the concept of the Fermi surface maintains validity for all amounts of disorder. Thus $\delta(k) \ll 1$ includes a very important class of disordered systems.

It is important to note that it is not sufficient that

$$\frac{\Sigma_2(k)}{\mathrm{Re}E(k)} \ll 1 \tag{5$'$}$$

for (a) and (b) above to be valid. Relation (5′) does indicate that both the energy $E(k)$ and the Fermi surface are well defined, but unless (6) is also valid, then *changes* in $\mathrm{Re}E(k)$ are not well defined, because the uncertainty in $\mathrm{Re}E(k)$ is as large as its change. For dilute impurities, both $\Sigma_1(k)$ and $\Sigma_2(k)$ are proportional to the concentration c, and it is clear that (5′) can always be satisfied, and thus the Fermi surface is well defined when c is small enough. This is, of course, the motivation for purifying materials when experimental measurements on the Fermi surface are made. However, when defining *changes* in the Fermi surface, one is not helped by decreasing c, since $\delta(k)$ is independent of c in the dilute limit. It is true that the uncertainty decreases with c, but so does the change. Conversely, when the concentration c is large, only (6) guarantees that relation (5′) remains true.

I next analyze the condition (6) in terms of the scattering caused by V. For simplicity, I consider V to consist of a small number of discrete scatters which can be analyzed individually, and interband matrix elements are neglected. In Sec. III the more general case is considered. The energy shift is given by[10]

$$\Sigma(\vec{k}) = \frac{(\vec{k}\,|V|\,\vec{k}\rangle}{(\vec{k}\,|\,\vec{k}\rangle} \;, \tag{7}$$

where $|\vec{k})$ is the state in the disordered system which is adiabatically related to $|\vec{k}\rangle$. From my simplifying assumption on V, Eq. (7) becomes

$$\Sigma(\vec{k}) = \frac{N_2(\vec{k}\,|\,v\,|\,\vec{k}\rangle}{(\vec{k}\,|\,\vec{k}\rangle} \;, \tag{8}$$

where v is that part of V that comes from a single scatterer, and N_2 is the total number of scatters. I am assuming that N_2 is a small enough number that I need expand $\Sigma(\vec{k})$ to only first order in N_2. Since (8) is already of order N_2, the denominator need only be calculated to zero order where it equals 1. Thus,

$$\Sigma(\vec{k}) = N_2(\vec{k}\,|\,v\,|\,\vec{k}\rangle = N_2 t_{kk} \;, \tag{8$'$}$$

and t_{kk} is the diagonal matrix element of the t matrix for $|\vec{k}\rangle$. The t matrix is defined by

$$t\,|\,\vec{k}\rangle = v\,|\,\vec{k}) \;. \tag{9}$$

Condition (6) on $\Sigma(\vec{k})$ gives, by (8′), the condition on $t_{kk'}$

$$\mathrm{Re}\,t_{kk} \gg \mathrm{Im}\,t_{kk} \;. \tag{6$'$}$$

By the optical theorem,

$$\mathrm{Im}\,t_{kk} = 2\pi \sum_{k' \neq k} |\,t_{kk'}|^2\,\delta(E_0(\vec{k}) - E_0(\vec{k}')) \;. \tag{10}$$

Choosing the appropriate average value $|\,t_{kk'}|^2_{\mathrm{av}}$, $\mathrm{Im}\,t_{kk}$ can be obtained from (10) to be

$$\mathrm{Im}\,t_{kk} = 2\pi\,|\,t_{kk'}|^2_{\mathrm{av}}\,\rho(E(\vec{k})) \;. \tag{10$'$}$$

Using the order-of-magnitude estimate that $\rho(E(\vec{k})) \sim N/W$, where W is the width of the band and N is the total number of atoms in the system, I have

$$\mathrm{Im}\,t_{kk} \sim |\,t_{kk'}|^2_{\mathrm{av}}\,N/W \;. \tag{11}$$

If $|\,t_{kk}| \ll W/N$, then perturbation theory is valid and we know the result in that case. I am interested in the case where perturbation theory is no longer valid so that $|\mathrm{Re}\,t_{kk}| \sim |\,t_{kk}| \sim W/N$ or larger. Using this plus (11), conditions (6) and (6′) become

$$\frac{|\,t_{kk'}|^2_{\mathrm{av}}}{|\,t_{kk}|^2} \ll 1 \;. \tag{6$''$}$$

We expect that $|\,t_{kk'}|$ be normally a continuous function of $\vec{k}'$.[11] Continuity implies that for $\vec{k}'$ near $\vec{k}$, $|\,t_{kk'}| \simeq |\,t_{kk}|$, but for (6″) to be true, $|\,t_{kk'}|^2 \ll |\,t_{kk}|^2$ for most of the remaining $\vec{k}'$. Thus $|\,t_{kk'}|^2$ is peaked in the forward direction. Since $|\,t_{kk'}|^2$ is proportional to the scattering probability, equivalent conditions (6), (6′), and (6″) are designated as the "forward-scattering approximation."

III. MULTIPLE SCATTERING PROBLEM

In disordered systems the main mathematical difficulty to overcome is the multiple scattering problem. In this section I solve the multiple scattering problem for the FSA.

To do so, I introduce the Green's function G_E for the alloy, defined as

$$G_E = (E - H)^{-1} \;. \tag{12}$$

Such a Green's function has both diagonal and off-diagonal matrix elements. If I desire to calculate the density of states of the alloy, I need know only the diagonal elements. Let me define G_{AE} by requiring it to be diagonal in a Bloch-state representation to be specified, and equal to the diagonal elements of G_E. Since G_{AE} is diagonal, it must correspond to some periodic Hamiltonian H_A (not necessarily Hermitian) defined by

$$G_{AE} = (E - H_A)^{-1} \;, \tag{13}$$

where

$$\begin{aligned} H_A &= H_0 + A = H - V + A \;, \\ A &= \sum_{n,n',\vec{K}} A(nn'\vec{K})\,|\,n\vec{K}\rangle\,\langle n'\vec{K}| \;. \end{aligned} \tag{14}$$

The states $|\,n\vec{K}\rangle$ are defined to be those Bloch states which diagonalize H_A. The reduced-zone scheme is used, and n represents the band index, while $\vec{K}$ represents the wave vector. As shown in the Appendix, the states $|\,n\vec{K}\rangle$ comprise an orthonormal set, even though H_A is not Hermitian.

In what follows I will drop the E subscript and the n index whenever convenient to simplify notation. G_A and G are related to one another by

$$G = G_A + G_A(V - A)G \;. \tag{15}$$

Defining the multiple scattering T matrix by

$$TG_A = (V - A)G \;, \tag{16}$$

I obtain for (15)

$$G = G_A + G_A T G_A \;. \tag{17}$$

In order that the diagonal elements of G equal those of G_A, I require[12]

$$T_{KK}(nn') = 0 \;, \tag{18}$$

where $T_{KK}(nn')$ are the matrix elements of T between the states $|\,n\vec{K}\rangle$ and $|\,n'\vec{K}\rangle$.

The self-energy $\Sigma(\vec{k})$ is closely related to $A(nn\vec{K}) \equiv A(n\vec{K})$. By definition, $\Sigma(\vec{k})$ represents the difference between the complex-alloy energy corresponding to an initial state $|\,n_0\vec{k}\rangle$ and its initial energy $E_0(\vec{k})$. To understand the relationship between $\Sigma(\vec{k})$ and $A(n\vec{K})$, I must determine the relationship between $|n\vec{\mathrm{k}}\rangle$, our eigenstates of H_0, and $|n\vec{\mathrm{K}}\rangle$, the eigenstates of H_A. To do so, I note that both H_0 and H_A have the same periodicity. Thus $|n\vec{\mathrm{K}}\rangle$ and $|n\vec{\mathrm{k}}\rangle$ span exactly the same Brillouin-zone space. We have defined the state $|n_0\vec{\mathrm{K}}\rangle$ which corresponds to $|n_0\vec{\mathrm{k}}\rangle$ by requiring that both states have the same wave vector. The difference between $|n_0\vec{\mathrm{k}}\rangle$ and $|n_0\vec{\mathrm{K}}\rangle$ is in their periodic parts. In the spacial representation I can write

$$|n_0\vec{\mathrm{k}}\rangle = N^{-1/2}e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}}\,U_{n_0k}(\vec{\mathrm{r}})\ , \tag{19}$$

$$|n_0\vec{\mathrm{K}}\rangle = N^{-1/2}e^{i\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}}\,\phi_{n_0k}(\vec{\mathrm{r}})\ , \tag{20}$$

where N is the total number of atoms, and both $U_{n_0k}(\vec{\mathrm{r}})$ and $\phi_{n_0k}(\vec{\mathrm{r}})$ are periodic with the same periodicity as H_0 and H_A, and differ from one another because of interband matrix elements of A.

The set of equations that relate U_{n_0k} to ϕ_{n_0k} are

$$\phi_{mk} = \sum_n a(mn\vec{\mathrm{k}})U_{nk}\ , \tag{21}$$

where

$$\sum_n |a(mn\vec{\mathrm{k}})|^2 = 1 \tag{22}$$

and

$$a(mn_0\vec{\mathrm{k}})E(m\vec{\mathrm{K}}) = \sum_n a(mn\vec{\mathrm{k}})\,\langle n_0\vec{\mathrm{k}}|H_A|n\vec{\mathrm{k}}\rangle\ . \tag{23}$$

Here

$$E(m\vec{\mathrm{K}}) \equiv \langle m\vec{\mathrm{K}}|H_A|m\vec{\mathrm{K}}\rangle\ . \tag{24}$$

To obtain the above relationships for the $a(mn\vec{\mathrm{k}})$, I used the requirement that $|m\vec{\mathrm{K}}\rangle$ diagonalize H_A.

From (13), (14), (17), and (18) I have

$$G_{KK}(n_0) = G_{AKK}(n_0) = [E - E_0(n_0\vec{\mathrm{K}}) - A(n_0\vec{\mathrm{K}})]^{-1}\ , \tag{25}$$

where

$$E_0(n_0\vec{\mathrm{K}}) = \langle\vec{\mathrm{K}}n_0|H_0|n_0\vec{\mathrm{K}}\rangle\ ,$$

and the matrix elements of G and G_A are denoted by the same notation as used in (18) for T. By the definition of $\Sigma(\vec{\mathrm{k}})$, I have

$$\Sigma(n_0\vec{\mathrm{k}}) = E(n_0\vec{\mathrm{K}}) - E_0(n_0\vec{\mathrm{k}})\ ,$$

where $E(n_0\vec{\mathrm{K}})$ is given by (24) and also has the relationship

$$E(n_0\vec{\mathrm{K}}) = E_0(n_0\vec{\mathrm{K}}) + A(n_0\vec{\mathrm{K}})\ , \tag{26}$$

and

$$H_0|n_0\vec{\mathrm{k}}\rangle = E_0(n_0\vec{\mathrm{k}})|n_0\vec{\mathrm{k}}\rangle\ . \tag{1$'$}$$

Thus, if I can solve for $A(\vec{\mathrm{K}})$, I can determine Σ and the diagonal elements of G.

To solve for $A(\vec{\mathrm{K}})$, I first find a relation for T by using (17) in (16) to obtain

$$T = (V - A) + (V - A)G_A T\ . \tag{27}$$

Using (18) and (25), I calculate the diagonal elements of (27) to obtain

$$A(n'n\vec{\mathrm{K}}) = V_{KK}(n'n) + \sum_{n'',\vec{\mathrm{K}}''\neq\vec{\mathrm{K}}} \frac{V_{KK''}(n'n'')T_{K''K}(n''n)}{E - E(n''\vec{\mathrm{K}}'')}\ . \tag{28}$$

The off-diagonal elements of (27) become, using (28),

$$T_{K'K}(n'n) = \left(V_{K'K}(n'n) + \sum_{n'',\vec{\mathrm{K}}''\neq(\vec{\mathrm{K}},\vec{\mathrm{K}}')} \frac{V_{K'K''}(n'n'')T_{K''K}(n''n)}{E - E(n''\vec{\mathrm{K}}'')}\right) \times\left(1 + \sum_{n'',\vec{\mathrm{K}}''\neq\vec{\mathrm{K}}'} \frac{V_{K'K''}(n'n'')T_{K''K'}(n''n')}{E - E(n''\vec{\mathrm{K}}'')}\,G_A(n'\vec{\mathrm{K}}')\right)^{-1}\ . \tag{29}$$

In the FSA we expect that

$$\frac{\mathrm{Im}A(n\vec{\mathrm{K}})}{\mathrm{Re}A(n\vec{\mathrm{K}})} \equiv x^2 \ll 1\ . \tag{6$'''$}$$

This follows immediately from (6) and (26) if interband effects are negligible, because then $\Sigma(\vec{\mathrm{k}}) = A(\vec{\mathrm{K}})$. It is reasonable to expect (6$'''$) to be true in general, because, except for special cases, interband mixing does not change the magnitude of $A(\vec{\mathrm{K}})$. From (28) and (29), the only way for (6$'''$) to be valid and still maintain $\mathrm{Re}A(n\vec{\mathrm{K}})$ large is for

$$\frac{|V_{K'K}(n'n)|^2_{\mathrm{av}}}{|V_{KK}(n)|^2} \sim O(x^2)\ ; \tag{30}$$

the magnitude squared of $V_{K'K}$ is on the average of order x^2 times that of $|V_{KK}|^2$. In obtaining (30) I made use of the fact that $G_A(\vec{\mathrm{K}}') \sim 1/W$ and $V_{KK} \sim cW$ or larger, where W is the magnitude of the spread of the important values of $E(K)$, $c = N_2/N$, and N_2 is the total number of scattering sites in a system of N total number of atoms. We are interested in the case where perturbation theory does not apply, and thus are considering the case where $V_{KK} \sim cW$ or larger. It is important to note that (30) does not say that all matrix elements of $V_{K'K}$ are small. On the contrary, by continuity we expect that $V_{K'K} \sim V_{KK}$ when $\vec{\mathrm{K}}' \simeq \vec{\mathrm{K}}$. Just as in (6$''$), Eq. (30) indicates that in some sense V is strongly peaked in the forward direction.

Relation (6$'''$) can also lead to ordinary perturbation theory if we assume that $\mathrm{Re}A(n\vec{\mathrm{K}})$ is small, and thus that all elements of V are small. In that case, (6$'''$) is satisfied because the $\mathrm{Im}A$ is second order in V, while $\mathrm{Re}A$ is first order. Ordinary perturbation theory and FSA exhaust the possibilities to satisfy (6'''), because either $\mathrm{Re}A(n\vec{K})$ is small or it is not. If it is small, then perturbation theory applies, while if it is not, then FSA applies.

Using x as the expansion parameter, it is easy to find from (28) and (29) that

$$A(n'n\vec{K}) = V_{KK}(n'n) + \sum_{n'',\vec{K}''\neq\vec{K}} \frac{V_{KK''}(n'n'')V_{K''K}(n''n)}{E - E(n''\vec{K}'')} + O(x^3) , \tag{28'}$$

$$T_{K'K}(n'n) = V_{K'K}(n'n) + \sum_{n'',\vec{K}''\neq\vec{K},\vec{K}'} \frac{V_{K'K''}(n'n'')V_{K''K}(n''n)}{E - E(n''\vec{K}'')} + O(x^3) . \tag{29'}$$

Note from (29') and (30) that the average off-diagonal element of T is of order x, and thus scattering effects in FSA disordered systems can be calculated by expansions in x.

I conclude this section by deriving a Friedel-type sum rule imposed by the requirement of shielded potentials. When the perturbing potentials are shielded, the Fermi level remains fixed, say, at μ, regardless of the concentration of scattering centers.[13] As mentioned in Sec. II, the FSA permits the definition of a Fermi surface. The Fermi surface in the band n is defined by[9]

$$\mathrm{Re}E(n\vec{K}) = \mu . \tag{31}$$

Say that I have some parameter Ω with which I can describe the disorder in our system. This could be the concentration c of a second component in a disordered alloy or a measure of the disorder in an amorphous or liquid system. If I change Ω a small amount but maintain shielding of the potentials, then the new Fermi surface can be defined by differentiating (31) to find

$$\hbar\vec{v}(\vec{K}) \cdot \Delta\vec{k} + \frac{\partial E(n\vec{K})}{\partial\Omega}\Delta\Omega = 0 ,$$

where

$$\vec{v}(\vec{K}) = \hbar^{-1}\nabla_k E(n\vec{K}) . \tag{32}$$

The additional electron charge ΔQ enclosed by the Fermi surface is

$$\Delta Q = \frac{2}{(2\pi)^3}\oint_\mu d\vec{S}\cdot\Delta\vec{k} ;$$
$$q = -(4\pi^3\hbar)^{-1}\,\mathrm{Re}\oint_\mu \frac{dS}{|\vec{v}(\vec{K})|}\,\frac{\partial E(n\vec{K})}{\partial\Omega} , \tag{33}$$

where

$$q = \frac{\partial Q}{\partial\Omega} .$$

Here $d\vec{S}$ is an element of area on the Fermi surface, and the integration is on the Fermi surface. Equation (33) is a generalized form of the Friedel sum rule in the FSA valid to order x^2 for all concentrations of disorder. The usual form of the Friedel sum rule[9,14] is applicable only in cases of dilute disorder.

For example, consider the case of a binary disordered alloy consisting of type-1 and type-2 atoms, where $\Omega = c$, the concentration of type-2 atoms. Each type-2 atom increases the number of electrons in the system by Z. Then, as shown in the Appendix, (33) becomes, in this case,

$$Z = -(4\pi^3\hbar)^{-1}\oint_\mu v_{21KK}(n)\, d\vec{S}\, |\vec{v}(\vec{K})|^{-1} , \tag{34}$$

where v_{21} is the potential change introduced when a type-1 atom at a given site is replaced by a type-2 atom. If I now replace $v_{21KK}(n)$ by its value $\langle v_{21KK}(n)\rangle$ averaged over the Fermi surface (*not* averaged over configurations), (34) becomes

$$\rho(\mu) = -Z/\langle v_{21KK}(n)\rangle , \tag{34'}$$

where $\rho(\mu)$ is the alloy density of states at the Fermi energy. Equation (34') gives a direct relation between $\rho(\mu)$ and the alloy potential. It is important to note that this relation comes directly from the self-consistency requirement on the potential. It is a special case of the general theorem[15] that the alloy density of states is intimately related to the self-consistency requirement on the potential.

The total number of states in our band n is equal to mN, where m is usually some integer; e.g., for an s band, $m = 2$, while for a d band, $m = 10$. If Z is of the order of m, then the band becomes filled when the number of type-2 atoms becomes of the order of N. If the band is initially near empty, then the states from near the bottom of the band to near the top sweep through the Fermi level as $N_2 \to N$. This means that $\Sigma_1(\vec{k}) \simeq V_{kk} \sim cW$, as was assumed, and ordinary perturbation theory is not valid.

IV. DISCUSSION

It is instructive to note the relationship between Eqs. (28), (28'), (29), and (29') and ordinary perturbation theory. If in (15) I had considered $V - A$ small in the sense of ordinary perturbation theory, I would have ended up with the same formulas as (28') and (29'). Yet $V - A$ does not satisfy the requirement for ordinary perturbation theory, namely, that *all* matrix elements of $V - A$ be small. We know that off-diagonal elements of $V - A$ are given by V alone, since A has only diagonal elements. If $Z \sim m$, we expect $V_{KK'}$ to be large for $\vec{K} \sim \vec{K}'$, as discussed previously. What is small is $|V_{KK'}|_{\mathrm{av}}$, because V is highly peaked in the forward direction. A discussion of the matrix elements of V, where there are many random scatterers, is complicated somewhat by the fact that the magnitude of the off-diagonal elements are of the order of $(N_2)^{-1/2}$ times those of the diagonal elements. When appropriate sums are taken as in (28′), the $(N_2)^{-1/2}$ sorts itself out so that all terms are the same order in N_2. In the FSA the additional parameter x remains and gives us our expansion parameter.

It is important to note that V could not be treated by ordinary perturbation theory directly because of the large value of V_{KK}. Ordinary perturbation theory with H_0 as the basis would have used $|\vec{k}\rangle$ in place of $|\vec{K}\rangle$ to calculate the matrix elements and $E_0(k)$ in place of $E(\vec{K})$. The difference between these energies is $A(K) \sim cW$, and is not negligible. However, the inverse is true. Ordinary perturbation theory becomes a special case of the FSA when V_{KK} and $V_{KK'}$ are small.

Returning to our self-consistency condition on the potential given in (33) and (34), note that if Z is small compared to m, then V_{KK} will also be small compared to cW. In that case it might be possible to treat V by ordinary perturbation theory. In this view it is possible to understand why liquid metals have so successfully been treated by perturbation theory.[3] In the disordering process that leads to the liquid from the periodic solid, q or $Z=0$.

Besides the self-consistency condition of (33), the potential must also be self-consistent with respect to the potential produced by the electron charges in its vicinity. For example, in a disordered alloy, if one constituent at a given site is replaced by another, the potential perturbation is the sum of both the perturbation introduced by the changing ion-core potentials and the perturbation introduced by the changing distribution of the shielding electrons. The change in the distribution of the shielding electrons can be estimated by comparing the V and T matrices. From (9) note that any changes from $|\vec{K}\rangle$ are reflected in the difference between T and V. Since the difference between V and T in (29′) is of order x^2, the change in the wave function is of order x, because V itself contributes one order of x. The change in potential is proportional to the square of the change in the wave function and thus is proportional to x^2; i.e., both the change in shielding cloud and the change in the potential are of order x^2 in the FSA. If this were the whole story, then $A(K)$ would be equal to V_{KK} *produced by the ion cores alone* to order x^2. However, as I shall discuss in the next paragraph, one does not expect the FSA to be valid for all occupied states in the "band." Since the shielding charge comes from all occupied electron states, those states that cannot be described by the FSA could give a large shielding contribution to V_{KK}, and one *cannot* conclude that the V_{KK} comes from only the ion cores. It is interesting to note that in ordinary perturbation theory, the shielding contribution to V could be of second order in the perturbation, since it is possible for all states in the band to be described by perturbation theory.

If we consider the dilute limit as discussed in Sec. II, we note that (8′), when compared with (28′), implies that $t_{kk}=v_{kk}$ to order x^2. The forward-peaked character of V_{KK} and v_{kk} can come about because v has a spatial extent large compared to the wavelength corresponding to $\vec{k}$. Clearly, when one considers states lower down in the band, there must come a region where the electron wavelength is of the order of or greater than v. When that occurs, the scattering will be s-like with a more or less spherical distribution about the scattering center. For those states, the FSA does not apply. From this type of reasoning we see that the FSA is expected to be appropriate only for metallic-type alloys where the Fermi level is not near the bottom of the band.

By comparing with appropriate experimental data, it is possible to calculate x^2 for some dilute alloys. We can obtain Σ_1 and Σ_2 in the dilute case from the forward-scattering amplitude as per (8′). Analysis of experimental data[16] has determined the phase shifts introduced by various impurities in Ag. From these phase shifts, the forward-scattering amplitude can be calculated by standard formulas leading to the values of x^2 listed in Table I. Note, from Table I, that the α phase of AgCd alloys can be well approximated by the FSA, while AgSn and AgSb alloys cannot be so approximated. The alloy AgIn is an intermediate case. The last row in Table I corresponds to a positive point-charge impurity of one charge unit screened by a free-electron gas of the density of silver. If screening in Ag can be approximated by the free-electron model, then the last row in Table I should approximate the AgCd case. Such is clearly not the case, and we note that the $Z=1$ model cannot be approximated by the FSA.

The presentation in this paper has omitted a step which is common to most all discussions of disordered systems, namely, averaging over possible configurations of the alloy. It is usually found necessary to perform such an average in order to obtain expressions which can be managed. The

TABLE I. Calculated values of x for some dilute alloys. The $Z=1$ row refers to a free-electron gas with the density of Ag and dilute impurities of a positive point charge of unit charge.

	x	x^2
AgCd	0.470	0.221
AgIn	0.669	0.448
AgSn	0.855	0.731
AgSb	1.037	1.074
$Z=1$	0.879	0.773

argument for this is that, because of the large number N of atoms involved, the average is a good representation of any given alloy, because the fractional fluctuations about the average are of the order of $N^{-1/2}$. The technique employed in this paper requiring use of (18) instead of $\langle T \rangle = 0$, as is standard,[5] sidesteps the need for an average and presents the result for a *given* configuration. If desired, an average over configuration can be performed later, but, by not averaging, no information is lost. Thus the expressions (28), (28′), (29), and (29′) have all the information in them after insertion into (17) to calculate all other properties of the alloy, such as transport properties. Because of its formal similarity to ordinary perturbation theory, the transport properties of the FSA alloys can be calculated from a Boltzmann equation, but with the reference states $|n\vec{K}\rangle$ and reference energies $\mathrm{Re}E(n\vec{K})$. In fact, FSA alloys are closely analogous to pure materials with a small amount of scattering. All the formulas derived for the case of pure materials with a small amount of scattering apply to FSA alloys if the unperturbed reference states $|n\vec{K}\rangle$ and energies $\mathrm{Re}E(n\vec{K})$ are used in place of $|n\vec{k}\rangle$ and $E_0(n\vec{k})$.

V. SUMMARY AND CONCLUSION

Changes in the Fermi surface with disorder can be defined in just two different cases: (a) when ordinary perturbation theory is applicable and (b) when the FSA is valid. The FSA differs from ordinary perturbation theory in that the diagonal matrix elements of the disordering perturbation and others in its vicinity are large. The perturbation is highly peaked in the forward direction, so that the average off-diagonal matrix element of the disordering perturbation is small, giving the expansion parameter for the FSA. The band character with its gaps is not greatly perturbed in the FSA, because the matrix elements of the perturbing potential at the large wave vectors corresponding to the gaps are small. If the FSA is applicable, it is expected to be so for metalliclike systems with the Fermi level far from the bottom of the band, and where the valence difference between the constituents is of the order of the number of states per atom in the band.

The fact that the FSA has the same solution as ordinary perturbation theory when $E(\vec{K})$ and the $|\vec{K}\rangle$ are used in place of $E_0(\vec{k})$ and the $|\vec{k}\rangle$ basis means physically that *all* the properties of pure materials also apply to those systems that satisfy the FSA, except that the energies $E(\vec{K})$ and the states $|\vec{K}\rangle$ depend on the disorder. As discussed previously,[9] the Fermi surfaces of FSA systems change their dimensions in $\vec{k}$ space qualitatively as predicted by the rigid-band model, expanding as the electron-per-atom ratio increases, and the de Haas–van Alphen effect measures the shape of the Fermi surface of the disordered system. The results of this paper show that all the transport properties of FSA systems about *their* Fermi surfaces have exactly the same dependence on V as given by ordinary perturbation theory. Since in ordinary perturbation theory the Boltzmann equation is applicable, it is also applicable for the FSA, though account must be taken of the change in the Fermi surface with disorder. The optical properties of FSA systems are also the same as those predicted by ordinary perturbation theory, at least around the Fermi surface. For energies where states near the bottom of the conduction band contribute appreciably to the optical properties, deviation from perturbation-theory behavior will occur because, as discussed in Sec. IV, these states are not described by the FSA. Recent optical data[17–19] on the FSA alloy systems AgCd, AgZn, AgMg, AgSn, and CuZn are in agreement with this analysis.

The complete solution for the FSA is given in this paper. By "complete solution" is meant in the usual sense where the perturbing potentials are assumed known, and the multiple scattering effects are calculated. However, in actual practice the perturbing potentials have to be determined self-consistently,[8, 15] and this part of the problem has not been solved. The FSA has the important feature that it can satisfy the restriction imposed by shielding and is thus a physical approximation as opposed to the highly localized approximation.[8] In giving the solution to the FSA summarized by Eqs. (17), (28′), and (29′), no averaging over disorder whatsoever was performed. Thus these equations have all the information necessary to calculate all properties of the disordered system, including transport properties.

APPENDIX

In this appendix I calculate $\partial E(n\vec{K})/\partial c$ for an alloy in the FSA that satisfies the assumptions that lead to (34). By definition,

$$H_A|n\vec{K}\rangle = E(n\vec{K})|n\vec{K}\rangle \ . \tag{A1}$$

I change c by replacing a type-1 atom at a given site with a type-2 atom. This corresponds to a change in c of

$$\Delta c = N^{-1} \ . \tag{A2}$$

With this change, and using (14) and (28′), the new Hamiltonian that defines $|\vec{K}\rangle$ is, to order x^2,

$$H'_A = H_A + \sum_{n,n',\vec{K}} v_{21KK}(n,n')|n\vec{K}\rangle\langle n'\vec{K}| \ , \tag{A3}$$

where v_{21} is the perturbation introduced by the substitution of a type-1 atom by a type-2 atom at a given site. In general, v_{21} may vary from site to site. We have an expansion parameter in (A3) because $v_{21KK}(nn')$ is of order N^{-1}, and we need to consider any quantity only to order N^{-1}. Expanding in terms of the states $|n\vec{K}\rangle$, the new eigenstates of (A3) will be

$$\psi_n'(\vec{K}) = |n\vec{K}\rangle + \sum_{n'} a(n'K)\,|n'\vec{K}\rangle \ , \tag{A4}$$

where the $a(n'\vec{K})$ are of order N^{-1}.

The $\psi_n'(\vec{K})$ satisfy the equation

$$H_A'\psi_n'(\vec{K}) = [E(n\vec{K}) + \Delta E(n\vec{K})]\,\psi_n'(\vec{K}) \ , \tag{A5}$$

where $\Delta E(n\vec{K})$ is of order N^{-1}. One can calculate the desired $\Delta E(n\vec{K})$ by finding the overlap of (A5) with $|n\vec{K}\rangle$ and keeping terms to order N^{-1}. One then finds

$$v_{21KK}(n) = \Delta E(n\vec{K}) . \tag{A6}$$

Using (A2) in (A6), one obtains

$$\frac{\partial E(n\vec{K})}{\partial c} = N v_{21KK}(n) \ , \tag{A7}$$

which, inserted in (33), leads to (34).

In this appendix and also in the text it was implicitly assumed that the eigenstates $|n\vec{K}\rangle$ form an orthonormal set. Off-hand, this is not obvious, because H_A is not Hermitian. That states of different $\vec{K}$ are orthogonal to one another follows immediately from Fourier analysis. The states with different $\vec{K}$ have no Fourier components in common. What does not follow immediately is that $|n'\vec{K}\rangle$ and $|n\vec{K}\rangle$ are orthogonal. To see that they are orthogonal, note that the ImA does not have any interband matrix elements because of its small value that produces a requirement of approximate energy conservation in (28). Therefore, the interband matrix elements of H_A between $|n'\vec{K}\rangle$ and $|n\vec{K}\rangle$ are Hermitian because they have no contribution from ImA, and the usual proof[20] follows that the states are orthogonal to one another. It should be noted that though ImA has no interband matrix elements, the ReA will have, in general, interband matrix elements. In summary, the states with different $\vec{K}$ are orthogonal to one another because they contain no common Fourier components, while the states with the same $\vec{K}$ but in different bands are orthogonal to one another because the ImA has no interband matrix elements.

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[1] By perturbation theory we include all modifications such as pseudopotential theory where the psuedopotential is weak. In general, we define perturbation theory as the case where a potential or pseudopotential can be defined such that *all* its matrix elements are small compared to the appropriate energies of the system.

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[11] There is some ambiguity in this statement since t_{kk} depends on choice of the zero of energy but $t_{kk'}$ does not. For example, it is possible to introduce a perturbation such as $V = v(\vec{r}-\vec{R}_n) + B$ where $\vec{R}_n$ is, say, the location of a lattice point, B is a constant independent of space, and $v(\vec{r}-\vec{R}_n)$ is some continuously varying potential localized about the point $\vec{R}_n$. The matrix elements of v, namely $v_{kk'}$, then will be a continuous function of $\vec{k}'$ while $V_{kk'}$ will not be continuous at $\vec{k}'=\vec{k}$. The discontinuous nature at $\vec{k}'=\vec{k}$ is trivial and occurs because of a shift of the zero of energy. We will not concern ourselves with this case but will limit ourselves to the case where $v_{kk'}$ is continuous at $\vec{k}'=\vec{k}$. Physically this requires that $v(\vec{r}-\vec{R}_n)$ be localized about $\vec{R}_n$. As shown at the end of Sec. IV, the FSA is physically realizable only for metallic disordered systems where shielding would localize the perturbations. As shown in this paper, the fact the $t_{kk'}$ is peaked about the forward direction occurs because $v(\vec{r}-\vec{R}_n)$ is spread over dimensions large compared to the Fermi wavelength. E. J. Moore [Phys. Rev. 160, 607 (1967)] discussed the FSA up to fourth-order in the scattering potential and showed, in agreement with this paper, that the Boltzmann equation can be used if the real part of the energy shift is added to the energy of a state.

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Free Energy of an Inhomogeneous Binary Solid Solution in the Yang–Li Approximation. I. Inhomogeneity due to Concentration Fluctuation

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The free energy of a binary fcc metallic solid solution is calculated using the statistical approximation of Yang and Li. The analytic expression permits one to separate, in the free-energy contribution, the homogeneous part from any inhomogeneity due to an arbitrary one-dimensional concentration fluctuation. The extra free energy introduced by a nonuniform solid solution is shown to be completely equivalent to the gradient free-energy term introduced phenomenologically by Landau and Lifshitz. By comparison with the Bragg–Williams approximation, the gradient coefficient is no longer constant, but concentration dependent at low temperature in a solution with miscibility gap as well as in a system exhibiting ordering. The free energy obtained is consistent with the discontinuous order-disorder transition in a fcc structure of the CuAu type.

I. INTRODUCTION

A supercooled solid solution tends to evolve towards its equilibrium state, either by infinitesimally small fluctuations that are extended in space, or by intense fluctuations that are localized, as noted by Gibbs.[1] In either way, spatial variation of concentration in the solid solution is produced, and this introduces an excess free energy into the system, generally called the "gradient free energy." The repercussion of the inhomogeneity of an internal parameter on the free energy was first taken into account phenomenologically by Landau and Lifshitz[2] for the density $n(r)$ of a one-component fluid. Considered as a function of n and of its spatial derivatives, and restricting the development to quadratic terms, the free energy is written as

$$F=\int [f(n)+K(\nabla n)^2+\cdots]\,dV , \tag{1}$$

$f(n)$ being the free energy per unit volume of a homogeneous fluid of density n, and K a coefficient generally listed as the "gradient coefficient." Such an expression, widely used afterwards for numerous internal parameters, was apparently introduced in the treatment of binary solid solutions by Hillert,[3] who found for a one-dimensional variation of concentration

$$F=\sum_n \{ f(C_n)+\tfrac{1}{2}K[(C_{n+1}-C_n)^2+(C_{n-1}-C_n)^2]\} , \tag{2}$$

C_n being the concentration in a plane indexed n,

$$K=-zv , \tag{3}$$

z being the number of nearest neighbors that an atom has in one of the adjacent planes, and $v=\frac{1}{2}(v_{AA}+v_{BB})-v_{AB}$ is the interaction energy between nearest neighbors.

The free energy F was calculated from statistical thermodynamics assuming the Bragg–Williams approximation of a "regular" or "lattice" model. In the regular model of solid solutions the atoms are supposed to occupy a regular rigid lattice, so that all volume effects are thus omitted (this may be a good approximation for atoms of nearly equal size); the interaction energies between atoms of two species A and B—$v_{AA}(r)$, $v_{BB}(r)$, and $v_{AB}(r)$—are supposed to be a function of the distance between them but not of concentration or of local arrangement. Generally interactions are limited to nearest neighbors, although interaction between more distant atoms might be included if necessary. In the Bragg–Williams approximation, the atoms are assumed to be distributed among the sites in a random manner, exactly as if the well-known interaction energy $v=\frac{1}{2}(v_{AA}+v_{BB})-v_{AB}$ were zero.[4]

For negative interaction energy v, the phenome-