THE ELECTRONIC STRUCTURE AND THE STATE OF COMPOSITIONAL ORDER IN METALLIC ALLOYS

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MASTER

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1. INTRODUCTION

1.1. The nature of compositional order

Many two-component (A,B) systems crystallize into a random solid solution (1). In such a state the atoms occupy a more or less regular array of lattice sites but each site can be A or B in a random fashion. Then, on lowering the temperature, the system will either phase separate or order, starting at some transition temperature T_c . The aim of these lectures is to present a microscopic approach to the understanding of these scientifically interesting and technologically important processes.

To have a clear idea of the basic physics we have in mind, let us recall the salient features of both kinds of phase transformations.

In Fig. 1, we display one of the simplest phase diagrams in the book of Hansen (1). It shows a single coexistence curve along which regions of fcc solid solution of Pd and Rh with concentration on c_1 coexist with macroscopically large regions of concentration c_2 . Except at the critical point,

FIGURE 1. Crystal structure of substitutional solid solution Rh_cPd_{1-c} alloys (left). Phase diagram of fcc Rh_cPd_{1-c} alloys (right).

$c = 0.5$, the phase-separation phase-transition is first order. At $c = 0.5$ the transition is continuous and the full range of the associated critical phenomena (2) should occur.

In Fig. 2, we show two well-known examples of compositional ordering. In the case of $\text{Cu}_{0.5}\text{Zn}_{0.5}$, the ordering takes place on a bcc lattice which naturally breaks up into two sublattices: the corners (I) and the body centers (II).

Above the transition temperature T_c both sublattices are equally likely to be occupied by both kinds of atoms. At T_c the concentration of the copper atoms on sublattice I, c_I , suddenly becomes different from that on sublattice II, c_{II} . Evidently, when this happens the translational invariance on the lattice, i.e., a symmetry of the high-temperature phase, is broken. The order parameter of the phase transition is

$$\eta(T) = c_I - c_{II} \quad (1)$$

It is zero above T_c and increases from 0 to 1 as T decreases to $T = 0$ following the trajectory depicted in Fig. 2a. Thus, in this instance, the ordering transition is continuous.

FIGURE 2. The crystal structure and the order parameter $\eta(T)$ for (a) $\text{Cu}_{0.5}\text{Zn}_{0.5}$ and (b) $\text{Cu}_{0.75}\text{Au}_{0.25}$ alloys.

Another famous ordering process takes place in the $\text{Cu}_c\text{Au}_{1-c}$ system (1), near $c = 0.75$, on an fcc lattice. This can be thought of as four interpenetrating simple cubic sublattices starting at the points labeled by 1, 2, 3, and 4, respectively. At the transition temperature the concentration of copper on the sublattice forming the corners of the picture shown, c_I , becomes less than that on the other three sublattices $c_{II} = c_{III} = c_{IV}$. The order parameter, η , is again $c_I - c_{II}$. However, as shown in Fig. 2b, η drops to zero at T_c discontinuously. Namely, the phase transition is first order.

To increase the precision of our discussion let us introduce the occupation variable

$$\xi_i = \begin{cases} 1 & \text{if there is an A atom at } \vec{R}_i \\ 0 & \text{if there is a B atom at } \vec{R}_i \end{cases}, \quad (2)$$

where $\vec{R}_i$ is the position vector of the i^{th} site. The thermal average of ξ_i is the local concentration

$$c_i = \langle \xi_i \rangle. \quad (3)$$

In a homogeneous random solid solution c_i is the same, $\bar{c}$, for all sites. Symmetry is broken if some subset of $\{c_i\}$ is different from the others. This situation is conveniently described in the language of concentration waves (3). In short, one writes the deviation of c_i from the average concentration $\bar{c}$ as a linear superposition of static concentration waves

$$c_i = \bar{c} + \frac{1}{2} \sum_{\vec{v}} (c_v e^{i\vec{k}_v \cdot \vec{R}_i} + c_v^* e^{-i\vec{k}_v \cdot \vec{R}_i}), \quad (4)$$

with wave vectors $\vec{k}_v$ and amplitudes c_v . Usually only a few wave vectors are needed. For instance, the Cu_3Au ($L1_2$) structure is described by

$$c_i = \bar{c} + \frac{1}{4} \eta (e^{i\vec{k}_1 \cdot \vec{R}_i} + e^{i\vec{k}_2 \cdot \vec{R}_i} + e^{i\vec{k}_3 \cdot \vec{R}_i}), \quad (5)$$

where the wave vectors are $\vec{k}_1 = 2\pi/a(1,0,0)$, $\vec{k}_2 = 2\pi/a(0,1,0)$, $\vec{k}_3 = 2\pi/a(0,0,1)$ and a is the lattice parameter. It can be easily ascertained that Eq. (5) gives $c_I = \bar{c} - \eta$ and $c_{II} = c_{III} = c_{IV} = \bar{c} + \eta$.

A fact that makes the above description particularly attractive is that the concentration waves can be directly observed in X-ray, electron, and neutron diffraction experiments (4). If we denote $\{\vec{R}_i\}$, the reciprocal lattice vectors of the underlying lattice then, in the solid solution, one observes Bragg peaks at $\{\vec{R}_i\}$. These are called the fundamentals. When the symmetry is broken and one or more concentration waves acquire a finite amplitude, there will be some extra, superlattice spots in the diffraction pattern at $\{\vec{R}_i + \vec{k}_v\}$. The intensity of the superlattice peaks measure the amplitudes $\{c_v\}$.

In addition to the Bragg peaks, diffraction experiments can also measure the diffuse scattering intensity distributed all through the Brillouin zone (BZ). From the point-of-view of our present concern, this is interesting for it contains useful information about the occupational, two-point, correlation function

$$q(i,j) = \langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle , \quad (6)$$

in other words, short-range order.

In the disordered translational invariant, state $q(i,j)$ depends only on the coordinate difference $\vec{R}_i - \vec{R}_j$ and hence may be written as

$$q(i,j) = \int_{\text{BZ}} d^3k \, q(\vec{k}) e^{i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)} . \quad (7)$$

It turns out that the measured diffuse scattering intensity $I(\vec{k})$, where $\hbar\vec{k}$ is the momentum transfer in the scattering process, is proportional to $q(\vec{k})$ (Ref. 4).

Interestingly, for alloys with a tendency for the like elements to cluster $q(\vec{k})$ peaks around the fundamentals. For ordering, alloys $q(\vec{k})$ show peaks where the superlattice Bragg peak will be in the ordered state.

To summarize, the state of compositional order is well-described by the wave vectors $\{\vec{k}_v\}$ and amplitudes $\{c_v\}$ of the concentration waves, which spontaneously break the translational symmetry of the random solid solution, and the correlation function $q(i,j)$. Moreover, these quantities can be directly measured.

The fundamental question these lectures aim to answer is:

1.2 What drives these phase transformations?

This question may be answered on three different levels. The first is the frankly phenomenological approach of Landau (5). The second is more microscopic and is based on effective pair-potential models. The third is the fully microscopic theory which describes the energies of various compositional configurations in electronic terms. We shall now outline all three approaches to the problem.

1.2.1 The Landau theory. Landau formulated his celebrated theory of second order (continuous) phase transition with the specific example of ordering in metallic alloys in mind (5). His basic ideas were elaborated at length by Lifschitz (6), Lyubarskii (7), and more recently by de Fontaine (8), Birman (9), and Khachaturyan (3). They consist of two quite separate sets of notions (9). The first set of these comprise a group theoretic analysis of the ways the symmetry of the random solid solution may be broken and the energy cost of the symmetry breaking modulation of the concentration (8). Explicitly, denoting the deviation of the local concentration c_i from the average c by δc_i the free energy associated with a concentration fluctuation defined by the set $\{\delta c_i\}$ is assumed to be given by

$$\begin{aligned} \delta F(\{\delta c_i\}) = & \frac{1}{2T} \sum_{ij} Y_{ij}^{(2)} \delta c_i \delta c_j + \frac{1}{3T} \sum_{ijk} Y_{ijk}^{(3)} \delta c_i \delta c_j \delta c_k \\ & + \frac{1}{4T} \sum_{ijkl} Y_{ijkl}^{(4)} \delta c_i \delta c_j \delta c_k \delta c_l . \end{aligned} \quad (8)$$

Then the algebra of symmetries, namely group theory, is used to classify the symmetry allowed values of the coefficients, $Y_{ij}^{(2)}$, $Y_{ijk}^{(3)}$, etc. They are assumed to be functions of the state variables such as temperature and pressure and are properties of the high-temperature symmetric phase.

The second set of notions refer to the use the above expression for δF can be put to. For example, in the original formulation the equilibrium state was given by the minimum of $\delta F(\{\delta c_i\})$. Namely, the equilibrium distribution of concentration given by $\{\delta c_i\}$ is a solution of the Euler-Lagrange equation

$$\left. \frac{\partial(\delta F)}{\partial(\delta c_i)} \right|_{\{\delta c_i\}} = 0 . \quad (9)$$

Following this line of reasoning a second-order phase transition will occur when the high-temperature homogeneous state, $\delta c_i = 0$ for all i , becomes unstable to some specific distortion $\{\delta c_i^v\}$. The relevant modes of distortions $\{\delta c_i^v\}$ are eigen "vectors" of the matrix $Y_{ij}^{(2)}$:

$$\sum_{ij} Y_{ij}^{(2)} \delta c_i^v = \lambda_v \delta c_i^v . \quad (10)$$

Evidently, the free-energy associated with a small amplitude concentration fluctuation, described by $\{\delta c_i^v\}$, is given by $\delta F_v = \lambda_v \sum_i (\delta c_i^v)^2$. Thus

a fluctuation $\{\delta c_i\}$ for which the eigenvalue $\lambda_v < 0$ lowers the free energy. In short, the homogeneous state becomes unstable when the lowest eigenvalue λ_0 becomes zero and therefore the transition temperature T_c is given by $\lambda_0(T_c) = 0$.

The basis of the concentration wave approach of Khachaturyan (3) to compositional fluctuations is the observation that for $Y_{ij}^{(2)}$ which depends only on the coordinate difference $\vec{R}_i - \vec{R}_j$ between the positions of the i th

and the j th site the eigenvectors are lattice waves: $\delta c_i^{\vec{k}} \sim e^{i\vec{k} \cdot \vec{R}_i}$. Then, the ordered state is described by finite amplitude concentration waves as in Eq. (4). It also follows that the eigenvalues which can be labeled by wave vectors, $\vec{k}$, in the first Brillouin zone of the disordered state, are the lattice Fourier transforms of $Y_{ij}^{(2)}$. Namely,

$$\lambda_{\vec{k}} = \gamma^{(2)}(\vec{k}) = \frac{1}{N} \sum_i e^{i\vec{k} \cdot (\vec{R}_i - \vec{R}_j)} \gamma_{ij}^{(2)}. \quad (11)$$

Since the instability occurs when the lowest eigenvalue goes through zero, the ordering wave vectors $\{\vec{k}_v\}$ are given by a set of degenerate minima of $\gamma^{(2)}(\vec{k})$. In other words they are the solutions of the equation

$$\vec{\nabla}_{\vec{k}} \gamma^{(2)}(\vec{k}) \Big|_{\vec{k}_v} = 0. \quad (12)$$

A surprising feature of the above theory is that although nothing specific is assumed about the physical forces which give rise to the coefficients $\gamma_{ij}^{(2)}$, some discrete set of characteristic wave vectors emerge as generic solutions of Eq. (12). In fact, as was shown in a remarkable analysis by Lifshitz (6), the interplay of the point group and space group of the disordered phase yields a set of Special Points, at which $\gamma^{(2)}(\vec{k})$ is a minimum, that are determined by symmetry alone.

For example, the Special Points of the fcc lattice are the

$$\begin{aligned} &(1 \ 0 \ 0), (0 \ 1 \ 0), (0 \ 0 \ 1) \\ &(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), (\frac{\sqrt{2}}{2} \ \frac{1}{2} \ \frac{1}{2}), (\frac{1}{2} \ \frac{\sqrt{2}}{2} \ \frac{1}{2}), (\frac{1}{2} \ \frac{1}{2} \ \frac{\sqrt{2}}{2}) \\ &(\frac{1}{2} \ 1 \ 0), (1 \ 0 \ \frac{1}{2}), (0 \ \frac{1}{2} \ 1), (\frac{\sqrt{2}}{2} \ \bar{1} \ 0), (\bar{1} \ 0 \ \frac{\sqrt{2}}{2}), (0 \ \frac{\sqrt{2}}{2} \ \bar{1}), \end{aligned} \quad (13)$$

The $L1_2$ structure described by Eq. (5) is generated by the Special Points (100), (010), and (001). As a further example, we note that the Special Points of the bcc lattice are

$$\begin{aligned} &(1 \ 1 \ 1) \\ &(\frac{1}{2} \ \frac{1}{2} \ 0), (0 \ \frac{1}{2} \ \frac{1}{2}), (\frac{1}{2} \ 0 \ \frac{1}{2}), (\frac{1}{2} \ \frac{\sqrt{2}}{2} \ 0), (0 \ \frac{1}{2} \ \frac{\sqrt{2}}{2}), (\frac{1}{2} \ 0 \ \frac{\sqrt{2}}{2}) \\ &(\frac{1}{2} \ \frac{1}{2} \ \frac{1}{2}), (\frac{\sqrt{2}}{2} \ \frac{\sqrt{2}}{2} \ \frac{\sqrt{2}}{2}) \end{aligned} \quad (14)$$

and the ordered $\text{Cu}_{0.5}\text{Zn}_{0.5}$ superstructure is generated by the Special Point $2\pi/a(1,1,1)$ where a is the lattice parameter.

In a way the above theory is spectacularly successful: the Special Points generate most of the observed ordered phases and there are representative systems corresponding to most Special Points (3,8). Even where it seems to fail, as in the case of incommensurate ordering, the failure is more apparent than real. Since these processes will be of interest later, we shall now comment on them, briefly, to stress their significance.

Landau's group theoretic arguments do not preclude the possibility that $\gamma^{(2)}(\vec{k})$ have minima other than those forced by symmetry. However, it is asserted that if there were some ordering wave vectors $\vec{Q}$, other than the Special Points, they would depend on the accidental, special features of the microscopic interactions and therefore would be extremely rare. Moreover, the periodicities corresponding to such wave vectors would most likely be incommensurate with the underlying lattice. Since at the time when the theory was developed (6) no incommensurate alloy phases were observed, the corresponding sector of the theory was not developed.

However, during the past two decades or so a variety of incommensurate phases have been discovered and the subject of their theoretical description has attracted considerable attention. Our current general understanding of incommensurate phases have been well reviewed by Levanyuk (10). In short, they are natural outcomes of the phenomenological Landau theory with many unexpected features (11,12).

What such phenomenological considerations cannot give are suggestions as to where the new periodicities, incommensurate with that of the disordered state, might come from. For insight in this matter we must turn to more microscopic theories. As we shall try to show in these lectures a very general mechanism which naturally drives incommensurate order has to do with the size and geometry of the Fermi Surface.

1.2.2. Pair potential models. This is a semi-microscopic approach which provides a more satisfactory answer to the question: "What drives the transition?" than the otherwise very powerful symmetry arguments above. Nevertheless, it is based on an effective, classical Hamiltonian and bypasses the essentially quantum mechanical nature of the electronic binding of solids.

The basic assumption of the model is that the configurational part of the energy of a two-component crystalline solid may be written as a sum over pairwise contributions:

$$H_{\text{eff}} = -\frac{1}{2} \sum_{ij} [v_{ij}^{AA}\xi_i\xi_j + v_{ij}^{AB}\xi_i(1-\xi_j) + v_{ij}^{BA}(1-\xi_i)\xi_j + v_{ij}^{BB}(1-\xi_i)(1-\xi_j)] , \quad (15)$$

where $v_{ij}^{\alpha\beta}$ is the interaction energy of an $\alpha(=A,B)$ atom at the site i with $\beta(=A,B)$ atom at the site j and the ξ_i 's are the occupation variables defined previously. Although a great deal of physics has been neglected in writing down Eq. (15) (Ref. 8), the above Hamiltonian provides a very direct and plausible answer to our question. To see this we rearrange the terms according to the powers of the occupation variables as

$$H_{\text{eff}} = -\frac{1}{2} \sum_{ij} v_{ij}^{(2)}\xi_i\xi_j - \sum_i v_i^{(1)}\xi_i - v^{(0)} , \quad (16)$$

where

$$v_{ij}^{(2)} = v_{ij}^{AA} + v_{ij}^{BB} - 2v_{ij}^{AB} ,$$

$$v_i^{(1)} = \sum_j (v_{ij}^{AB} - v_{ij}^{BB}) ,$$

$$v^{(0)} = \frac{1}{2} \sum_{ij} v_{ij}^{BB}. \quad (17)$$

Evidently, if $v_{ij}^{(2)} > 0$ two A atoms at sites i and j ($\xi_i = 1, \xi_j = 1$) have lower energy than a pair of AB atoms ($\xi_i = 1, \xi_j = 0$) then like atoms cluster together leading to a lower energy and hence, at low enough

temperature, to phase separation. On the other hand, for $v_{ij}^{(2)} < 0$ unlike pairs are energetically more favourable than like pairs. Clearly, this gives rise to an ordering tendency. Thus, $-v_{ij}^{AB}$ being more negative than $-v_{ij}^{AA}$ and $-v_{ij}^{BB}$ means $v_{ij}^{(2)} < 0$ and hence drives ordering processes.

The opposite case, i.e., $-v_{ij}^{AA}$ and $-v_{ij}^{BB}$ being more negative than $-v_{ij}^{AB}$, implies $v_{ij}^{(2)} > 0$ and hence clustering.

From a technical point-of-view the problem defined by the above Hamiltonian is to find the grand partition function

$$Z(T, V, v) = \sum_{\{\xi_i\}} e^{-\beta[H_{\text{eff}}(\{\xi_i\}) - v \sum_i (\xi_i - \frac{1}{2})]}, \quad (18)$$

where V is the volume, v is the chemical potential difference $\mu^A - \mu^B$ and hence the grand potential

$$\Omega = -\frac{1}{\beta} \ln Z. \quad (19)$$

Although we shall not make use of this formalism directly in these lectures, we mentioned the above details because there is one result we shall need. Allow, formally, the chemical potential difference v_i to vary from site to site in Eq. (18). Namely, replace $v \sum_i \xi_i$ by $\sum_i v_i \xi_i$. Then it is straightforward to show that Ω becomes the generator of the correlation functions

$$\langle \xi_i \rangle = c_i = -\left(\frac{\partial \Omega}{\partial v_i}\right)_v \quad (20)$$

$$\langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle = q(i, j) = \frac{1}{\beta} \left(\frac{\partial c_i}{\partial v_j}\right)_v = -\frac{1}{\beta} \left(\frac{\partial^2 \Omega}{\partial v_i \partial v_j}\right)_v. \quad (21)$$

As usual, after the various derivatives have been taken, v_i is set equal to the thermodynamic value of v at all sites. In what follows we shall make use of the above device repeatedly for generating the correlation functions of the occupation variables.

1.2.3. The electronic theory of compositional order. In the real world the positively charged atomic nuclei of solids are held together by the electron "glue" between them. This "glue" is a strongly interacting degenerate Fermi-liquid with deeply quantum mechanical properties.

Although it is tempting to attempt to apportion the electrons among the nuclei in such a way that the resulting roughly neutral, atomic-like, objects are only weakly, and therefore only pairwise, interacting; this cannot, in general, be done with impunity. The resulting attractively simple picture, which we have described in Sect. 1.2.2. will continue to break down in unpredictable fashion. Thus, there is a strong case for developing a theory of compositional fluctuations as well as that of crystal structures on the basis of an electronic description of the configurational energies. Obviously, this style of reasoning will provide an explanation of ordering and clustering in terms of the corresponding, presumably favorable, changes in the electronic structure in the spirit of the celebrated paragraph of Peierls' book (13). Closer to our specific concern, an example of how useful such an approach can be is provided by the work of da Silva, et al. (14).

Of course, the charged Fermi-liquid of electrons in an external potential, in the present case resulting from the atomic nuclei, is not fully understood by any means. Consequently, the following discussion will involve many approximations.

However, the burden of the above remarks is that even a very approximate treatment of the electrons may contain qualitative features which are central to the physics of the phenomena in question but have no counterpart in the essentially classical and local description by effective pair potential models.

The first step towards a sensible formulation of the problem is to make the adiabatic approximation. This can be safely done since the mechanism by which an *A* atom can be interchanged with a *B* atom is diffusion, and it is observed to be a very slow process compared with the fast motion of the electrons $v_{\text{fermi}} \sim 10^8 \text{ cm/sec} < v_{\text{diffusion}} \sim 10^6 \text{ cm/sec}$. Thus, the energy associated with a compositional configuration, specified by a set of occupation variables $\{\xi_i\}$ is the electronic grand potential $\Omega_e(T, \mu, \{\xi_i\})$. It depends on the temperature *T*, because it includes the entropy associated with thermal fluctuations of electron hole pairs, and the electronic chemical potential μ which determines the average number of electrons $\bar{N}$. This latter quantity has to be carefully related to the total number of *A* and *B* atoms, N^A and N^B , respectively, in such a way that the whole system is neutral. Clearly, $\Omega_e(\{\xi_i\})$, where to simplify the notation we suppressed the dependence on *T* and μ , should be regarded as an effective Hamiltonian for the occupational degrees of freedoms. Hence, the problem at hand is to study the statistical mechanics summarized by the partition function

$$Z = \sum_{\{\xi_i\}} e^{-\beta[\Omega_e(\{\xi_i\}) - \sum_i v_i(\xi_i - \frac{1}{2})]} , \quad (22)$$

and the free energy

$$\Omega = - \frac{1}{\beta} \ln Z . \quad (23)$$

Although we have arrived at a formulation which is very close to that encapsulated by Eqs. (18) and (19), it is important to note the difference. $H_{\text{eff}}(\{\xi_i\})$ in Eq. (18) is a simple polynomial in the occupation variables while $\Omega_e(\{\xi_i\})$ in Eq. (22) is decidedly not. This difference reflects the long-ranged and nonlocal nature of the interactions between site

occupations communicated by the electrons. Of the three different modes of analysis described above we shall follow the last in these lectures.

Although the problems have been simplified by the adiabatic approximation, it is still too difficult to be usefully tackled head on. Note that according to Eqs. (22) and (23) we have to solve the full many-electron problem for each compositional configuration $\{\xi_i\}$ and then the summation over each configuration has to be carried out. To render the problem tractable we shall make three closely related approximations, each in the spirit of mean field theory. Therefore, we shall call the collective results of these a *first principles mean field theory*. The logic of the whole scheme will be described in the next section. The way it can be implemented will be the subject of the third section. In the final section we shall make contact with the phenomenological Landau theory and derive a first principles version of the Cahn-Hilliard theories which are particularly useful for describing alloys with macroscopic inhomogeneities.

2. A FIRST PRINCIPLES MEAN-FIELD THEORY OF COMPOSITIONAL ORDER

2.1. A mean-field theory for the statistical mechanics of the concentration fluctuations

In this subsection we assume that $\Omega_e(\{\xi_i\})$ is known and investigate how it determines such physical quantities as c_i and $q(i,j)$ defined in Eqs. (3) and (6). Ways of calculating the relevant features of $\Omega_e(\{\xi_i\})$ by solving the quantum mechanical problem of the many electron system in the presence of the atomic nuclei will be dealt with in the next subsection.

The three most well-tried methods for solving classical statistical mechanical problems like the one defined in Eqs. (22) and (23) are the mean field approximation (2,3,8), the cluster variational method (15), and Monte Carlo simulations (16). In its general aim the first of these is the most modest and we shall follow this. We do this for three slightly different reasons. The first is the technical one that only for the mean field theory can we devise a tractable scheme for a consistent treatment of the electronic structure. The second, obviously less relevant, consideration is that of the three, only the mean field theory can be equally reliably implemented for short- and long-range interactions. Thirdly, we note that, by now, the mean field theory has a very special and well-understood status in statistical mechanics as the reference from which fluctuations are reckoned. Indeed, it is at this level that a microscopic theory can make contact with the Landau theory mentioned earlier. Also, even if the mean field theory phase diagrams have the wrong shape, as they invariably do, they represent a first systematic step toward understanding the forces which determine them. Hence, the mean field theory provides a useful level at which to compare different systems. In fact such comparisons are quite central to our material specific, nonuniversal concern which is to answer the question, "What drives the transitions?"

If the electronic grand potential $\Omega_e(\{\xi_i\})$ consisted of pairwise contributions, like H_{eff} in Eq. (16), the approximation procedure of the mean field theory would be entirely straightforward. One would merely replace products like $\xi_i \xi_j$ by $\langle \xi_i \rangle \xi_j$ and carry out the sums over all configurations in Eq. (22) without further difficulty. However, because $\Omega_e(\{\xi_i\})$ is not even a polynomial in the occupation variables, a more complicated argument has to be deployed. One way to proceed is the concentration functional approach of Gyorffy and Stocks (17). Here we follow an alternative root to the mean field theory for a general interaction function $\Omega_e(\{\xi_i\})$. The elegant formal device we shall use was invented by Peirls (18), Bogulubov (19), Feynman (20), and probably others, independently. It consists of taking a trial Hamiltonian H_0 , which is a function

of the occupation variables and depends on a number of parameters to be determined later, and expanding Ω in Eq. (23) in powers of $\Omega_e - H_0$. To first order we find

$$\Omega \approx \Omega(1) = \Omega_0 + \langle \Omega_e - H_0 \rangle, \quad (24)$$

where $\Omega_0 = (1/\beta) \ln Z_0$, with $Z_0 = \sum_{\{\xi_i\}} e^{-\beta[H_0(\{\xi_i\}) - \sum_i v_i(\xi_i - 1/2)]}$ and $\langle \rangle_0$ means averaging with respect to the probability distribution

$$P(\{\xi_i\}) = \frac{1}{Z_0} e^{-\beta[H_0(\{\xi_i\}) - \sum_i v_i(\xi_i - 1/2)]}. \quad (25)$$

The key to the method is the proof, given in Feynman's book (20), that $\Omega(1)$ is a variational upperbound for an arbitrary H_0 , i.e.,

$$\Omega \leq \Omega(1). \quad (26)$$

The procedure to follow is now quite clear. We have to pick some reasonable trial Hamiltonian and then minimize $\Omega(1)$ with respect to the parameters contained in H_0 . For the minimal values of the parameters $\Omega(1)$ is a variational approximate to Ω .

As it turns out the mean field theory corresponds to taking H_0 to be of the form

$$H_0 = \sum_i v_i \xi_i, \quad (27)$$

where the set $\{v_i\}$ are the variational coefficients. They are determined by the Euler-Lagrange equations

$$\frac{\partial \Omega(1)}{\partial v_i} = 0. \quad (28)$$

To put the above theory into a convenient form we note that in view of Eq. 27 $P(\{\xi_i\})$ factorizes into a product of local probabilities

$$P(\{\xi_i\}) = \prod_i P_i(\xi_i), \quad (29)$$

where $P_i(\xi_i) = e^{-\beta(v_i - v_i)\xi_i} / [e^{-\beta(v_i - v_i)} + 1]$. Furthermore, the average of ξ_i is given by $\langle \xi_i \rangle = c_i = [e^{\beta(v_i - v_i)} + 1]^{-1}$. Let us now reparametrize $P_i(\xi_i)$ in terms of the local concentration c_i in place of v_i . It is easy to show that

$$P_i(\xi_i) = c_i \xi_i + (1 - c_i)(1 - \xi_i) . \quad (30)$$

Since the relation between V_i and c_i is monotonic we may change variables in $\Omega^{(1)}$ from V_i to c_i and minimize with respect to c_i . To find $\Omega^{(1)}$ in terms of $\{c_i\}$ we recall that $\Omega_0 - \langle H_0 \rangle_0 = -TS_0$ where S_0 is the entropy of the trial ensemble corresponding to $P_0\{\xi_i\} = \prod_i P_i(\{\xi_i\})$. It then follows that

$$\begin{aligned} \Omega^{(1)}(\{c_i\}) = k_B T \sum_i [c_i \ln c_i + (1 - c_i) \ln(1 - c_i)] \\ + \langle \Omega_e \rangle_0 - \sum_i v_i (c_i - \frac{1}{2}) . \end{aligned} \quad (31)$$

Thus, our new Euler-Lagrange equations are $\partial \Omega^{(1)} / \partial c_i = 0$ and hence the equation of state is given by

$$k_B T \ln \frac{\bar{c}_i}{1 - \bar{c}_i} + S_i^{(1)}(\{c_i\}) - v_i = 0 , \quad (32)$$

where $\bar{c}_i$ is our approximation to the equilibrium concentration and

$$S_i^{(1)} = \left(\frac{\partial \langle \Omega_e \rangle_0}{\partial c_i} \right) \{\bar{c}_i\} . \quad (33)$$

As we have mentioned in the introduction, a theory of compositional order must be, at least, a theory of c_i and the correlation function $q(i,j)$. To find the latter, within the above framework, we take the derivative of Eq. (32) with respect to c_j . This gives

$$\frac{k_B T}{\bar{c}_i (1 - \bar{c}_i)} \delta_{ij} + S_{ij}^{(2)} - \frac{\partial v_i}{\partial c_j} = 0 , \quad (34)$$

where

$$S_{ij}^{(2)} = \left(\frac{\partial S_i^{(1)}}{\partial c_j} \right) \{\bar{c}_i\} = \left(\frac{\partial^2 \langle \Omega_e \rangle_0}{\partial c_j \partial c_i} \right) \{\bar{c}_i\} . \quad (35)$$

Then, recalling Eq. (21), we note that $\partial v_i / \partial c_j = k_B T q^{-1}(i,j)$ and hence Eq. (34) can be rearranged to read

$$q(i,j) = \beta \bar{c}_i (1 - \bar{c}_i) \delta_{ij} - \beta \bar{c}_i (1 - \bar{c}_i) \sum_l S_{il}^{(2)} q(l,j) . \quad (36)$$

This is a rather general equation for $q(i,j)$ useful for studying fluctuations in a variety of states of long-ranged order. However, the most

frequently studied problem is that of correlations in the disordered state. Then $\bar{c}_i = \bar{c}$ for all i and $q(i,j)$ depends only on the coordinate difference $\vec{R}_i - \vec{R}_j$. Under these circumstances we can take the lattice Fourier transform of Eq. (36) and solve the resulting algebraic equation for $q(\vec{k})$ to obtain

$$q(\vec{k}) = \frac{\beta \bar{c}(1 - \bar{c})}{1 - \beta \bar{c}(1 - \bar{c})S^{(2)}(\vec{k})}. \quad (37)$$

There are many versions of this formula in the literature. The oldest one is due to Krivogolaz (4) and Clapp and Moss (21). These authors were working with a pair-potential model, like the one described by Eq. (16), and used the random-phase approximation. They arrived at Eq. (37) with $S^{(2)}(\vec{k})$ replaced by the lattice Fourier transform of the interchange potential $v_{ij}^{(2)}$ namely, $v^{(2)}(\vec{k})$. However, as was stressed by Gyorffy and Stocks (17), Eq. (37) is an exact formula if $S_{ij}^{(2)}$ is the exact direct correlation function (22). In the present derivation $S_{ij}^{(2)}$ is the mean field theory approximation (equivalent to the random-phase approximation) to the direct correlation function. However, it is for an electronic description of the interchange energy rather than an effective pair-potential model. The first electronic theory of $q(\vec{k})$ in the form of Eq. (37) was proposed by Ducastelle et al. (23,24). Apart from minor technical details their work differs from those described in these lectures only in the technique of handling the electronic structure. Theirs are non-self-consistent tight-binding calculations while we shall make use of the local-density approximation within the context of density functional theory. Also there is a slight difference in the interpretation given to $S^{(2)}(\vec{k})$. They regard it as an effective pair potential to be used in a full statistical mechanical calculation while we prefer to view it as the mean field theory approximation to the direct correlation function. The reasons for this interpretation will be elaborated on in the next section. A recent discussion of these various views has been given by Turchi et al. (25).

To summarize this section, our principal results are the equation of state given in Eq. (32), the formula for the correlation function $q(k)$ given in Eq. (37), and the definitions of the direct correlation functions $S_i^{(1)}$ and $S_{ij}^{(2)}$ given in Eqs. (33) and (35). The main point is that all this has been achieved on the basis of a fully electronic description of the free energy associated with thermal fluctuations of the composition. Evidently, this information is contained in the averaged electronic grand potential $\langle \Omega_e \rangle_0$ which is by construction, a function of the local concentrations $\{c_i\}$. The task for the rest of the theory is to evaluate the relevant derivatives of $\langle \Omega_e \rangle_0$.

2.2. The mean field theory for the crystal potential

We shall base our discussion of the electrons on the density functional theory of Hohenberg and Kohn (26). In particular we shall describe the states of the electron system using the local density approximation (LDA) (27). Clearly, given the success of the corresponding self-consistent

band theory in accounting for cohesive and structural energies of ordered solids (28-30), a study of ordering energies on the same basis is called for. As we have stressed already, our aim here is to provide the foundation of just such analysis.

It would take us too far from the main line of our argument to recall the formal structure of the density functional theory or to derive the LDA. Let it suffice to summarize its implications for the problem at hand. These are that for a fixed configuration $\{\xi_i\}$ the equilibrium charge density $n(\vec{r};\{\xi_i\})$ is given by

$$n(\vec{r};\{\xi_i\}) = \sum_n |\psi_n(\vec{r};\{\xi_i\})|^2 f[\epsilon_n(\{\xi_i\})] , \quad (38)$$

where $f(\epsilon)$ is the usual Fermi function: $1/[e^{\beta(\epsilon-\mu)} + 1]$ for the inverse temperature β and electron chemical potential μ , and the Kohn-Sham wave functions $\psi_n(\vec{r};\{\xi_i\})$ are solutions of the self-consistent Schrödinger equation

$$\{-\nabla^2 + \sum_i v_i(\vec{r};[n])\} \psi_n(\vec{r}) = \epsilon_n \psi_n(\vec{r}) . \quad (39)$$

Unlike in the usual applications of the theory for ordered systems, here the potential function in each unit cell $v_i(\vec{r};[n])$ is different from that in all the others. Nevertheless, this is only a consequence of the configuration dependence of $n(\vec{r};\{\xi_i\})$ and $v_i(\vec{r};[n])$ is the same LDA functional of $n(\vec{r};\{\xi_i\})$ as it is in the ordered case.

The above two equations, Eqs. (38) and (39), are a complete statement of the theory for the ground state charge density $n(\vec{r};\{\xi_i\})$. Moreover, since the electronic grand potential Ω_e is a unique functional of the charge density $n(\vec{r};\{\xi_i\})$, it is also the LDA theory of the sought-after quantity: $\Omega_e(\{\xi_i\})$. To find an explicit expression for $\Omega_e(\{\xi_i\})$ one merely has to integrate the Maxwell relation

$$\bar{N}(\mu, \{\xi_i\}) = - \left(\frac{\partial \Omega_e}{\partial \mu} \right) , \quad (40)$$

where the average number of electrons is given by

$$\bar{N}(\mu, \{\xi_i\}) = \int d^3r \, n(\vec{r};\{\xi_i\}) . \quad (41)$$

Thus, to find $\langle \Omega_e \rangle_0$ of Eqs. (33) and (34), we must solve Eq. (39) self-consistently, using the LDA for the crystal potential, for each configuration $\{\xi_i\}$, evaluate the corresponding grand potential $\Omega_e(\{\xi_i\})$ and average the result with respect to the product distribution given in Eq. (29). Clearly, this is an impossible task which must be simplified if

the theory is to be of practical use. The purpose of this section is to introduce such a simplification in the spirit of the mean field theory.

The way to make progress is not very difficult to see: when considering the site at $\vec{R}_i$ we should neglect the fluctuations at the other sites. Namely, in evaluating $u_i(\vec{r};[n(\vec{r};\{\xi_i\})])$ we should replace all ξ_j $j \neq i$ by their thermal averages c_j :

$$u_i(\vec{r};n) \equiv u_i(\vec{r};\{\xi_i\}) \approx \bar{u}_i(\vec{r};\xi_i;\{c_j\}) . \quad (42)$$

More explicitly,

$$\bar{u}_i(\vec{r};\xi_i;\{c_j\}) = \xi_i \bar{u}^A(\vec{r} - \vec{R}_i;\{c_j\}) + (1 - \xi_i) \bar{u}^B(\vec{r} - \vec{R}_i;\{c_j\}) . \quad (43)$$

To highlight the physical meaning of this approximation, we note that in the disordered state, where most calculations to date have been carried out, $c_i = \bar{c}$ for all i and hence all the potential wells on the A or B sites are described by the same potential functions $\bar{u}^A(\vec{r})$ or $\bar{u}^B(\vec{r})$, respectively. In other words the fluctuations in the environment have been neglected. This is fully consistent with our guiding spirit of the mean field approximation.

When Eq. (43) is used in Eq. (39) the problem of self-consistent solution is still intractable. However, the mean-field-like approximation in the previous paragraph suggests another. In short, we may interchange the process of self-consistency and averaging and demand self-consistency only on the average.

This very fruitful idea was first proposed and implemented by Stocks and Winter (31). To put it into explicit form consider the equation for the Greens function of Eq. (39)

$$[\epsilon + \nabla^2 + \sum_i u_i(\vec{r} - \vec{R}_i)] G(\vec{r}, \vec{r}'; \epsilon) = \delta(\vec{r} - \vec{r}') , \quad (44)$$

where

$$u_i(\vec{r} - \vec{R}_i) = \xi_i \bar{u}_i^A(\vec{r} - \vec{R}_i) + (1 - \xi_i) \bar{u}_i^B(\vec{r} - \vec{R}_i) , \quad (45)$$

and, for simplicity, we denoted the full dependence of u^A and u^B defined in Eq. (43), on $\{c_i\}$ by the suffixes i .

Let us now assume that for a fixed set of potential wells we can solve for various averages of the solution to Eq. (44), $G(\vec{r}, \vec{r}'; \epsilon; \{\xi_i\})$, with respect to the distribution defined in Eq. (29). Clearly, if there is an α (A or B) type of atom at the site i the configurationally average charge density is given by

$$\bar{n}_i^{\alpha}(\vec{r} - \vec{R}_i) = -\frac{1}{\pi} \int d\epsilon f(\epsilon) \text{Im} \langle G(\vec{r}, \vec{r}'; \epsilon; \{\xi_i\}) \rangle_{i,\alpha} , \quad (46)$$

where $\alpha = A$ or B and the partial average $\langle G \rangle_{i,\alpha}$ denotes the average of G over all members of the compositional ensemble which have an α -type atom at $\vec{R}_i$. It should be stressed that these partially averaged charge densities are defined in such a way that the fully averaged charge density is

$$\bar{n}_i(\vec{r} - \vec{R}_i) = c_i \bar{n}_i^A(\vec{r} - \vec{R}_i) + (1 - c_i) \bar{n}_i^B(\vec{r} - \vec{R}_i). \quad (47)$$

It is now fairly straightforward to say what is meant by a theory which is self-consistent on the average. Since $\bar{v}_i^\alpha(\vec{r} - \vec{R}_i)$ depends only on the charge density in the unit cell centered on $\vec{R}_i$ and the average charge density elsewhere, at the end of the above calculations we can use $\bar{n}_i^A(\vec{r} - \vec{R}_i)$, $\bar{n}_i^B(\vec{r} - \vec{R}_i)$, and $\bar{n}_i(\vec{r} - \vec{R}_i)$ to recalculate $\bar{v}_i^A(\vec{r} - \vec{R}_i)$ and $\bar{v}_i^B(\vec{r} - \vec{R}_i)$. With these new values of $\bar{v}_i^A$ and $\bar{v}_i^B$ one can, at least in principle, return to Eq. (44) and start the whole process over again. This iteration procedure must be continued until the output potentials are the same as the input potentials within some preset limit, i.e., until convergence in the charge density is obtained. This scheme is depicted in Fig. 3.

FIGURE 3. The density-functional scheme for self-consistency on the average as implemented in SCF-KKR-CPA calculations.

To summarize, Eq. (43), together with the above self-consistency procedure, constitute our mean field theory for the crystal potential. Of course, the theory is incomplete until a method for calculating the partial averages $\langle G \rangle_{i,A}$ and $\langle G \rangle_{i,B}$ are given. We shall provide the appropriate recipes in the next section.

2.3. The mean field theory for the disorder scattering of electrons - the KKR-CPA

Finally, in this section we complete the theory of $\langle \Omega_e \rangle_0$ by specifying an approximation scheme for calculating $\langle G(\vec{r}, \vec{r}'; \epsilon; \{\xi_i\}) \rangle_0$ starting with Eqs. (44) and (45). The method is based on a multiple scattering version of the Korringa (32), Kohn, and Rostoker (33) (KKR) method of band theory and the coherent-potential approximation (CPA) idea (34,35). The combination of these two techniques is the only reliable first principles method for dealing with the electronic structure of disordered systems. It is

called the KKR-CPA. Over the past decade or so it has been reviewed several times at length (31,36-38), and therefore we shall give only the bare outline of the argument here.

Nevertheless, before entering into a technical description of the KKR-CPA, a general remark concerning the CPA is in order. As is emphasized in Ref. 33, it is a very general idea for describing elementary excitations in disordered solids, and it has proved to be remarkably reliable in a variety of circumstances. Significantly, from the point of view of our present concern, it is sometimes referred to as the mean-field theory of disorder. Although it might sound strange to talk about a mean-field approximation in the present context, which is so different from statistical mechanics where the term originates, it is, nevertheless, a legitimate use of the phrase because for many models the CPA can be shown to be exact in the limit where the number of nearest-neighbors go to infinity (39). It is this mean-field-like feature which makes the CPA ideally suited as an approximation scheme for calculating $\langle \Omega_e \rangle_0$. In fact, we believe that this is the only approach which is consistent with the rest of the theory.

As we have already indicated, the KKR-CPA consist of two main parts. Firstly, it is a multiple scattering theory. It is this feature which enables the method to treat the crystal potential from first principles. Secondly, it is a way of accounting for the effects of disorderly arrangement of sites. We begin our discussion by focusing on the first part.

The multiple scattering approach to solving Schrödinger equations, like that in Eq. (44), is most powerful when the scattering centers are described by nonoverlapping potential wells separated by regions, however small, of a constant, interstitial, potential. Band theory calculations based on the density functional theory and LDA often assume that the crystal potential is of this form and maintain this constraint during the self-consistency iterations. For metals this procedure appears to work very well, and in what follows we shall adopt it without further ado. Moreover, we shall assume that each potential well is spherically sym-

metric. Thus, $v_i(\vec{r} - \vec{R}_i)$ in Eq. (44) depends only on the magnitude $|\vec{r} - \vec{R}_i|$ and only out to the radius of the inscribed sphere of the i^{th} unit cell, i.e., the muffin-tin radius, r_{MT} . Between the cell boundary and the muffin-tin sphere, the potential is taken to be a constant, V_{MTZ} , which is assumed to be the same over the whole crystal.

The essence of multiple scattering theory is that one solves all the relevant single scattering problems first and then combines the results to find the energy eigenstates in the presence of many scatterers. When the scattering centers are not overlapping, as in the present case, it is sufficient to know the partial wave scattering amplitudes $f_{i,l}(\epsilon)$, where l is the azimuthal quantum number and polar quantum number m does not appear because of spherical symmetry. As shown in Ref. 36, for example, the scattering amplitudes $f_{i,l}$ may be written in terms of the corresponding scattering phase shifts

$$f_{i,l}(\epsilon) = \frac{1}{2i} [e^{i2\delta_l^i(\epsilon)} - 1] . \quad (48)$$

For technical reasons we shall not make use of these scattering amplitudes directly but develop the theory in terms of the closely related t-matrix on the energy shell

$$t_{i,L}(\epsilon) = - \frac{1}{\sqrt{\epsilon}} f_{i,l}(\epsilon) . \quad (49)$$

where L stands for both ℓ and m .

The t -matrix $t_{i,L}(\epsilon)$ is the amplitude of the out-going spherical wave with angular momentum L due to an incident wave to i^{th} site of unit amplitude in the same angular momentum channel. The multiple scattering generalization of $t_{i,L}(\epsilon)$ is the scattering-path t -matrix $\tau_{LL'}^{ij}(\epsilon)$ which is the amplitude of the outgoing wave emanating from the site i in the angular momentum channel L if there was a unit amplitude scattering wave incident to the site j in the angular momentum channel L' . As is also shown in Ref. 36, this quantity is determined by the individual scattering matrices, $\{t_{i,L}(\epsilon)\}$, and the geometrical arrangement of the scattering centers according to the matrix equation

$$\sum_{L'} [\tau_{i,L}^{-1}(\epsilon) \delta_{iL} \delta_{LL'} - G_{LL'}(\vec{R}_i - \vec{R}_j; \epsilon)] \tau_{LL'}^{ij}(\epsilon) = \delta_{ij} \delta_{LL'}, \quad (50)$$

where the real space KKR structure constant $G_{LL'}(\vec{R}_i - \vec{R}_j; \epsilon)$ is given by

$$G_{LL'}(\vec{R}_i - \vec{R}_j; \epsilon) = 4\pi \sum_{L''} i^{2-L''} C_{LL''}^{L'} h_{L''}^+(\sqrt{\epsilon} |\vec{R}_i - \vec{R}_j|) Y_{L''}(\hat{R}_{ij}) \quad (51)$$

for $i \neq j$. The quantities $C_{LL'}^{L''}$, $h_{L''}^+$ and $Y_{L''}$ are the Clebsch-Gordon coefficient-like Gaunt numbers, outgoing wave spherical Hankel functions and the real spherical harmonics, respectively.

Evidently, the matrix $\tau^{-1} - G$, where τ^{-1} stands for $\tau_{i,L}^{-1} \delta_{iL} \delta_{LL'}$ and G for $G_{LL'}(\vec{R}_i - \vec{R}_j; \epsilon)$ is an infinite by infinite matrix in both the site, $i, j, \dots$, etc. and angular momentum labels, $L, L', \dots$, etc. Because the relevant energy bands are all within a Ry or so of V_{MTZ} it is customary to make the low energy approximation of neglecting angular momentum labels beyond a certain ℓ_{max} . In our discussions ℓ_{max} will be mostly two, but occasionally the theory will have been implemented with $\ell_{\text{max}} = 3$.

There are two more general remarks about the matrix $\tau^{-1} - G$ which, as can be seen in Eq. (50), is the inverse of $\tau = \tau_{LL'}^{ij}$, that are in order.

The first is the observation that the dependence on the potential functions is limited to the diagonal elements, and the off-diagonal elements are purely concerned with the propagation of free particle spherical waves between the sites, namely the geometrical arrangement of the sites. This separation of potential dependence and geometry of scattering centers is a unique feature of the multiple scattering approach to solving the Schrödinger equation for arrays of potential wells and is the main reason for the fact that the CPA idea can be readily implemented in this framework. The second point which may serve to orient the reader is that if, in addition to the sites forming a regular lattice, all the potential wells and, therefore, all the single-site t -matrices are the same, the matrix $\tau^{-1} - G$

can be diagonalized with respect to the site indices by taking its

lattice Fourier transform. Indeed, by taking the lattice Fourier transform of Eq. (50), we find, using an obvious notation, that

$$\tau_{LL}^{-1}(\vec{k};\epsilon) = [t_L^{-1}(\epsilon)\delta_{LL} - G_{LL}(\vec{k};\epsilon)]^{-1}. \quad (52)$$

A brief scrutiny of the meaning of $\tau_{LL}^{-1}(\vec{k};\epsilon)$ reveals that for the $\vec{k}$ and ϵ where it diverges there is a scattered wave even if there is no incident wave. This means that there is an energy eigenstate for the system of scatterers at that $\vec{k}$ and ϵ . Thus to find the spectrum of eigenvalues we must find for each $\vec{k}$ the ϵ 's for which the determinant $||t^{-1} - G||$ vanishes. Since we have neglected $\epsilon > \epsilon_{\max}$, $|t^{-1} - G(\vec{k};\epsilon)|$ is a finite matrix and hence its determinant can be evaluated with relative ease. In fact, this is the well-known KKR method. Because of that we shall refer to $t^{-1} - G$, whether in real space or in Fourier transform space, as the KKR matrix. Evidently, the scattering path t-matrix τ_{LL}^{ij} and its lattice Fourier transform $\tau_{LL}^{-1}(\vec{k};\epsilon)$ are the inverses of the corresponding KKR matrices.

Assuming that the multiple scattering theory has been solved for $\tau_{LL}^{ij}(\epsilon)$, one can calculate the Greens function $G(\vec{r}, \vec{r}'; \epsilon)$. For $\vec{r}$ within the i th muffin-tin sphere and $\vec{r}'$ is the j th muffin-tin sphere, as shown in Fig. 4,

$$G(\vec{r}, \vec{r}'; \epsilon) = \sum_{LL'} [Z_L^i(\vec{r}_i; \epsilon) \tau_{LL'}^{ij}(\epsilon) Z_{L'}^j(\vec{r}_j; \epsilon) - Z_L^i(\vec{r}_i; \epsilon) J_{L'}^j(\vec{r}_j; \epsilon) \delta_{ij} \delta_{LL'}], \quad (53)$$

where the functions $Z_L^i(\vec{r}_i; \epsilon)$ are the regular solutions of the Schrödinger equation in the i th muffin-tin sphere matching smoothly to $t_{i,L}^{-1} j_L + h_L^+ Y_L$ where j_L and h_L^+ are the spherical Bessel and Hankel functions, respectively, $J_L^j(\vec{r}_j; \epsilon)$ is a solution which is irregular at the origin and matches smoothly to $j_L Y_L$ and, as before, $Y_L(\hat{r})$ is a real spherical harmonic.

The two main uses for the above Greens function are the calculations of the local density of states

FIGURE 4. Schematic diagram of nonoverlapping spherically symmetric potential wells. In the interstitial region the potential is constant.

$$n_i(\epsilon) = -\frac{1}{\pi} \int_{V_i} d^3r \operatorname{Im} G(\vec{r}, \vec{r}; \epsilon), \quad (54)$$

where the integral is over the i^{th} unit cell and the local charge densities

$$n_i(\vec{r}) = -\frac{1}{\pi} \int d\epsilon f(\epsilon) \operatorname{Im} G(\vec{r}, \vec{r}; \epsilon). \quad (55)$$

Clearly, Eq. (53) is the relevant expression to be used in Eq. (46). In particular

$$\begin{aligned} \bar{n}_i^{\alpha}(\vec{r}_i) = & -\frac{1}{\pi} \operatorname{Im} \sum_{LL'} \int d\epsilon f(\epsilon) [Z_L^{1,\alpha}(\vec{r}_i; \epsilon) Z_{L'}^{1,\alpha}(\vec{r}_i; \epsilon) \langle \tau_{LL'}^{11}(\epsilon) \rangle_{1\alpha} \\ & - Z_L^{1,\alpha}(\vec{r}_i; \epsilon) J_{L'}^{1,\alpha}(\vec{r}_i; \epsilon)], \end{aligned} \quad (56)$$

where $\alpha = A$ or B . Thus the purpose of our theory must be to calculate $\langle \tau_{LL'}^{11}(\epsilon) \rangle_{1,\alpha}$.

Consider now the relatively simple, homogeneous case: $c_i = \bar{c}$ for all i . Then the CPA argument runs as follows: We assume that the average lattice is described by the effective scattering amplitude $t_{c,L}(\epsilon)$ in the sense that

$$\langle \tau_{LL'}^{11}(\epsilon) \rangle = \tau_{LL'}^{c,11}(\epsilon), \quad (57)$$

where $\tau_{LL'}^{c,11}$ is the solution to Eq. (50) for $t_{1,L} = t_{c,L}$ for all i . More explicitly, using Eq. (52), we find

$$\tau_{LL'}^{c,11}(\epsilon) = \int_{V_{BZ}} d^3k [t_{c,L}^{-1}(\epsilon) \delta_{LL'} - G_{LL'}(\vec{k}; \epsilon)]^{-1}. \quad (58)$$

We then study an α - (A or B) type impurity at i in this effective lattice. Such impurity is described by the solution of Eq. (50) for $t_{j,L}(\epsilon) = t_{j,c}(\epsilon)$ for all $j \neq i$ and $t_{i,L} = t_{\alpha,L}(\epsilon)$. Namely,

$$\tau_{LL'}^{\alpha,11}(\epsilon) = [\underline{1} + \tau_{LL'}^{c,11}(\underline{t}_A^{-1} - \underline{t}_c^{-1})]^{-1} \tau_{LL'}^{c,11}, \quad (59)$$

where, for simplicity of notation, we replaced the explicit angular momentum label by matrix notation. Up to now the effective t -matrix is not known. The CPA prescription for finding $t_{c,L}(\epsilon)$ is to require that the average of $\tau_{LL'}^{\alpha,11}$ is equal to $\tau_{LL'}^{c,11}$, i.e.,

$$\bar{c} \tau_{LL}^{A,ii}(\epsilon) + (1 - \bar{c}) \tau_{LL}^{B,ii}(\epsilon) = \tau_{LL}^{C,ii}(\epsilon) . \quad (60)$$

Together Eqs. (58), (59), and (60) are the fundamental equations of the KKR-CPA. Their solution gives $t_{c,L}(\epsilon)$ and, obviously, determines $\tau_{LL}^{C,ii}$ directly. Practical schemes for solving Eqs. (58), (59), and (60) are discussed at length in Refs. 30, 35, and 36.

Combining the theory presented in this section with the ideas of the previous one, we can formulate the following self-consistent scheme.

Starting with the charge densities $\bar{n}^A(\vec{r})$ and $\bar{n}^B(\vec{r})$, we can calculate the partially averaged potential functions $\bar{v}^A(\vec{r})$ and $\bar{v}^B(\vec{r})$ using the LDA. Then placing these randomly on a lattice, we can solve for the partially averaged Greens functions $\langle G(\vec{r}, \vec{r}'; \epsilon) \rangle_{i,\alpha}$ using the KKR-CPA. From such Greens functions we can calculate the partially averaged charge densities $\bar{n}^A(\vec{r})$, $\bar{n}^B(\vec{r})$ and compare them with their starting values. If they disagree at a preset level, repeat the process until convergence. The first such self-consistent KKR-CPA calculation was performed by Stocks and Winter (40). A variety of interesting applications of the method are described in their review article (31).

However, the above homogeneous self-consistent KKR-CPA is not sufficient to solve the problem of calculating the direct correlation

functions $S_{ij}^{(1)}$, and $S_{ij}^{(2)}$ defined in Eqs. (33) and (35). Fortunately, the formal structure of the theory generalizes to the case of the inhomogeneous randomness described by the distribution function given in Eqs. (29) and (30). Clearly, for such an ensemble one should search for an effective lattice with the CPA t -matrix varying from site to site $t_{c,i,L}(\epsilon)$. This implies an infinite set of CPA equations. One for each site:

$$c_i \tau_{LL}^{A,ii}(\epsilon) + (1 - c_i) \tau_{LL}^{B,ii}(\epsilon) = \tau_{LL}^{C,ii} . \quad (61)$$

These are coupled since $\tau_{LL}^{C,ii}$ depends on the $t_{c,i,L}(\epsilon)$ on every site. Nevertheless, if they are solved the $\tau_{LL}^{A,ii}$'s will lead, via Eq. (56) and the starting A and B potential functions, to different A and B charge densities $\bar{n}_i^A(\vec{r})$ on each site. These differences reflect the differences in the local probabilities c_i that the sites i is occupied by an atom of the A species. Although one might start with the same charge density $\bar{n}^A(\vec{r})$ on all A sites and the same $\bar{n}^B(\vec{r})$ on the B sites at the end of the first iteration all the $\bar{n}_i^A(\vec{r})$'s will be different and hence further iterations will converge to an inhomogeneous distribution of local charge densities.

The above self-consistent inhomogeneous KKR-CPA scheme is the foundation of our electronic theory of concentration fluctuations. However, as it stands, it is not fully complete. We still need an explicit expression for $\Omega_e^{CPA}(\{c_i\})$ which will be our approximation to $\langle \Omega_e \rangle_0$ in Eq. (31). To find such an expression we start with the appropriate version of Eq. (41). Namely,

$$\bar{N}^{\text{CPA}}(\mu; \{c_i\}) = \sum_i [c_i \int_{V_i} d^3r_i \bar{n}_i^A(\vec{r}_i) + (1 - c_i) \int_{V_i} d^3r_i \bar{n}_i^B(\vec{r}_i)] , \quad (62)$$

and integrate it with respect to the electron chemical potential:

$$\Omega_e^{\text{CPA}}(\mu; \{c_i\}) = - \int_0^\mu d\mu' \bar{N}^{\text{CPA}}(\mu'; \{c_i\}) . \quad (63)$$

As shown in Ref. 41, Eq. (IV-7), this leads to

$$\begin{aligned} \Omega_e^{\text{CPA}}(\mu; \{c_i\}) = & \mu Z - \int_{-\infty}^{\infty} d\epsilon \bar{N}^{\text{CPA}}(\epsilon; \{c_i\}) f(\epsilon) - e^2 \sum_{i \neq j} \int_{V_i} d^3r \int_{V_j} d^3r' \frac{\bar{n}_i(\vec{r}) \bar{n}_j(\vec{r}')}{|\vec{r} - \vec{r}'|} \\ & - e^2 \sum_{i\alpha} c_{i,\alpha} \int_{V_i} d^3r \int_{V_i} d^3r' \frac{\bar{n}_i^\alpha(\vec{r}) \bar{n}_i^\alpha(\vec{r}')}{|\vec{r} - \vec{r}'|} \\ & + \sum_{i\alpha} c_{i,\alpha} \int_{V_i} d^3r [\epsilon_{xc}^{\text{LDA}}(\bar{n}_i^\alpha) - v_{xc}^{\text{LDA}}(\bar{n}_i^\alpha)] \bar{n}_i^\alpha(\vec{r}) , \end{aligned} \quad (64)$$

where the first two terms are the single particle contributions, Ω_{sp}^{CPA} , and the rest are usually referred to as the double-counting corrections. The averaged integrated density of states $\bar{N}^{\text{CPA}}(\epsilon; \{c_i\})$ is given by

$$\begin{aligned} \bar{N}^{\text{CPA}}(\epsilon; \{c_i\}) = & N_0(\epsilon) - \frac{1}{\pi} \text{Im} \ln || \underline{\underline{t}}_{C,i}^{-1}(\epsilon) \delta_{ij} - \underline{\underline{G}}(\vec{R}_i - \vec{R}_j; \epsilon) || \\ & - \frac{1}{\pi} \sum_{i\alpha} c_{i,\alpha} \text{Im} \ln || \underline{\underline{1}} + (\underline{\underline{t}}_{i,\alpha}^{-1} - \underline{\underline{t}}_{i,C}^{-1}) \underline{\underline{t}}_{C,i}^{-1} || , \end{aligned} \quad (65)$$

where $N_0(\epsilon)$ is the free electron contribution.

Having arrived at the principal result of this section, Eq. (64), we pause to take note of its general features.

Clearly, the coupled equations of the inhomogeneous KKR-CPA, Eq. (61), cannot be solved in general. The cases where it has been solved or is conceivable that a numerical solution will be affordable are the homogeneous limit $c_i = \bar{c}$ for all i or circumstances where the c_i 's form a regular pattern. Examples of the latter cases are superlattices and modulated alloys. Recall that such patterns, as the examples also indicate, correspond to long-range order which breaks the underlying symmetry of the lattice. However, crucial as such solutions will be to practical applications of the first principle's mean-field theory, they are not the main function of the above self-consistent inhomogeneous KKR-CPA scheme. That role is purely formal. The point is that because the scheme allows, explicitly, all the

local concentrations to be different, it facilitates the formal evaluation of the derivatives $\partial \Omega^{\text{CPA}} / \partial c_i$, $\partial^2 \Omega^{\text{CPA}} / \partial c_i \partial c_j$ which determine the direct

correlation functions $S_i^{(1)}$ and $S_{ij}^{(2)}$. Thus, we have derived a method for generating explicit expressions for all the direct correlation functions $S_i^{(1)}$, $S_{ij}^{(2)}$, $S_{ijk}^{(3)}$, Moreover, once these expressions have been derived for an arbitrary concentration configuration $\{c_i\}$ they can be evaluated in all of the solvable arrangements discussed above. As will be seen presently this means that we have tractable theories for various states of long-range order, i.e., spontaneously formed concentration waves, and fluctuations about these states.

The second feature of the above general framework we wish to call attention to is its self-consistency in the density functional sense. The inhomogeneous CPA idea was first used by Gautier et al. (24) for more or less the same purpose as we have done here. However, they worked with a tight-binding model Hamiltonian description of the electrons and hence, their scope for charge self-consistency was limited to ad hoc procedures. The present theory is a synthesis of advances in band theory (KKR), density functional theory (LDA), and theory of disordered systems (CPA) at a level where all these elements fit together in a consistent fashion. It is this consistency which makes the present approach a fully first-principles one in the sense that the calculations are free of parameters. We shall return to a general discussion of the full significance of this fact toward the end of these lectures.

To summarize Sect. II and Subsects. 1, 2, and 3, we have developed the three principal steps which together constitute a general first principles mean-field theory of concentration fluctuations. This theory is general in the sense that it is applicable, for a fixed lattice, to arbitrary states of long-range order. We hasten to add that the full implication of this formal structure remains largely unexplored. In fact, all calculations to date are studies of the disordered state only. Thus, rather than developing the theory further in general terms, in the next chapter we explore some of its explicit consequences in the disordered state.

3. CONCENTRATION FLUCTUATIONS IN THE DISORDERED STATES

3.1 The averaged ground state energy

The simplest example where the rather elaborate framework of the previous section can be applied is that of a homogeneous random alloy, $c_i = \bar{c}$ for all i at zero temperature $T=0$. Of course, in accordance with the third law of thermodynamics, at $T=0$ such a state would not be an equilibrium state. Nevertheless, its configurationally averaged energy, $\bar{E}$, is of general interest as a reference energy for a variety of considerations. In this subsection, we report on the first ab initio total energy calculation of $\bar{E}$ for a random alloy. The particular system to be studied is $\text{Cu}_c\text{Zn}_{1-c}$.

Because it is much easier to work at a fixed chemical potential μ than with a fixed number of electrons, we shall study the $T \rightarrow 0$ limit of the averaged grand potential Ω_e , namely, $\bar{E} - \mu N$.

It follows from Eq. (64) and the CPA equations given in Eq. (61), as was first shown by Johnson et al. (42), that

$$\bar{E} = \sum_{\alpha} c_{\alpha} E^J[\bar{n}_{\alpha}, \bar{n}_0] , \quad (66)$$

where E^J is an expression of the same form as that obtained by Janak (43)

[see Eq. (25) in Ref. 43] for pure metal muffin-tin and interstitial charge densities, $n(\vec{r})$ and n_0 , respectively. Thus, having iterated the self-consistent KKR-CPA to convergence in the partially averaged charge densities $\bar{n}^\alpha(\vec{r})$ ($\alpha = A, B$) and the average interstitial charge density $\bar{n}_0$, the configurationally average total energy can be calculated with relatively modest further effort.

The first such calculation was carried out by Johnson et al. (42) using the exchange correlation potential of Hedin and Lundqvist. They calculated $\bar{E}$ for $\text{Cu}_c\text{Zn}_{1-c}$ in the α -phase at a number of lattice parameters for each concentration c . They then determined the equilibrium lattice parameter 'a' for which $\bar{E}$ is minimum. Their results for 'a' are shown in Fig. 5 as a function of concentration. Evidently, they find an almost linear relationship between 'a' and c , in good agreement with Vegard's rule (44) and experiments. Given the ab initio nature of the calculation, this agreement may be taken as strong evidence that the self-consistent KKR-CPA is a sound basis on which to build a theory of compositional order.

An important feature of the above calculation is the consistency between the mean-field-like approximation of the crystal potential, namely, the neglecting of fluctuations in the environment when calculating the potential function at a specified site, and the single-site nature of the CPA way of averaging over all configurations. It is due to this consistency

FIGURE 5. The calculated (solid circles) and experimentally observed (open circles) lattice parameter as a function of the concentration c for the fcc $\text{Cu}_c\text{Zn}_{1-c}$ alloys.

that the self-consistent KKR-CPA can be considered a proper, albeit approximate, density-functional theory for disordered systems. There are two formal consequences of Eq. (66) which are particularly significant from this point of view (45). The first is the fact that $\bar{E}$ is stationary with respect to variations in $\bar{n}_\alpha(\vec{r})$ for $\alpha = A$ or B , i.e.,

$$\frac{\delta}{\delta \bar{n}^\alpha(\vec{r})} \bar{E}[\bar{n}^A, \bar{n}^B, \bar{n}_0] = 0. \quad (67)$$

The second is that $\bar{E}$ may be uniquely broken up into a kinetic energy T and potential energy, U , contributions and, as shown in Ref. 45

$$\frac{\delta}{\delta \bar{n}^\alpha(\vec{r})} \bar{U}[\bar{n}^A, \bar{n}^B, \bar{n}_0] = \bar{v}^\alpha(\vec{r}). \quad (68)$$

It should be stressed that even though the order of charge self-consistency and averaging have been interchanged, the theory preserved these relations of the density functional theory because of the variational character of the CPA and the choice of the partially averaged local potentials.

3.2. Equation of state

It follows from Eqs. (32), (33), and the discussion in Sect. 2.1. that in the disordered state the equation of state is given by

$$k_B T \ln \frac{\bar{c}}{1 - \bar{c}} + S(1)(\bar{c}) - v = 0, \quad (69)$$

where the local molecular field contribution to the chemical potential is given by

$$S(1)(\bar{c}) = S_1^{(1)} \Big|_{c_1 = \bar{c}\psi_1}. \quad (70)$$

Evidently, the finite temperature version of the homogeneous CPA in the previous section would not provide sufficient information to calculate the derivative with respect to c_1 in Eq. (70). For this we must return to the inhomogeneous KKR-CPA of Sect. 2. Thus we proceed by taking the derivative of Eq. (64):

$$\frac{\partial \Omega_e^{\text{CPA}}}{\partial c_1} = - \int_{-\infty}^{\infty} d\epsilon \frac{\partial}{\partial c_1} \bar{n}^{\text{CPA}}(\epsilon; \{c_1\}) + \frac{\partial}{\partial c_1} (\delta \Omega_e^{\text{CPA}}), \quad (71)$$

where we collected all the double-counting corrections to Ω_e^{CPA} into the

symbol $\delta\Omega_e^{\text{CPA}}$. While it is fairly straightforward to continue our discussion retaining $\delta\Omega_e^{\text{CPA}}$, and it is frequently necessary in the interest of a more straightforward presentation, we shall drop this term in what follows.

The next step is to take the derivative of N^{CPA} in Eq. (65) with respect to c_i . This will have two contributions: the first is the result of taking the derivative with respect to c_i for fixed values of the effective t -matrices $\{t_{i,c,L}(\epsilon)\}$, and the second involves the derivatives of N^{CPA} with respect to the $t_{i,c,L}(\epsilon)$'s resulting from the chain rule. One of the striking properties of the KKR-CPA is that the averaged integrated density of states $\bar{N}^{\text{CPA}}$ is stationary with respect to variations in all the scattering amplitudes $t_{i,c,L}(\epsilon)$. Thus the second contributions to $\partial/\partial c_i N^{\text{CPA}}(\epsilon)$ will vanish identically and we obtain

$$S_{sp}^{(1)}(\bar{c}) = \int d\epsilon f(\epsilon) [\bar{N}^A(\epsilon) - \bar{N}^B(\epsilon)] , \quad (72)$$

where for $\alpha = A$ or B

$$\bar{N}^\alpha(\epsilon) = \frac{1}{\pi} \text{Im} \ln || \underline{1} + (\underline{t}_\alpha^{-1} - \underline{t}_c^{-1}) \underline{\tau}^{c,11} || , \quad (73)$$

and we have taken $c_i = \bar{c}$ for all i after differentiating with respect to c_i . Consequently, all the quantities are to be evaluated in the same homogeneous self-consistent KKR-CPA we have studied in Subsect. 3.1. The subscript sp on $S_{sp}^{(1)}$ indicates that we have included only the single particle (sp) contributions, and we have neglected those coming from the double-counting corrections.

The notation $\bar{N}^\alpha(\epsilon)$ for the right-hand side of Eq. (73) is designed to suggest that the corresponding expression is closely related to the integrated density of states on an α -type site. This would be strictly true if $\underline{t}_c(\epsilon)$ corresponded to an energy independent potential. However,

the effective scattering matrix $\underline{t}_{c,L}(\epsilon)$ corresponds to a potential function which is energy dependent, and therefore, the energy derivative of $N^A(\epsilon)$ and $N^B(\epsilon)$ defined in Eq. (73) is not the densities of states $n^A(\epsilon)$ and $n^B(\epsilon)$ defined by

$$\bar{n}_i^\alpha(\epsilon) = - \frac{1}{\pi} \int \frac{d^3r}{V_i} \text{Im} \langle G(\vec{r}, \vec{r}; \epsilon) \rangle_{i,\alpha}^{\text{CPA}} . \quad (74)$$

In spite of this ambiguity it is useful to regard $N^A(\epsilon)$ and $N^B(\epsilon)$ as integrated densities of states on A and B sites because then we can interpret the "molecular field" contribution to the local chemical potential $S_{sp}^{(1)}(c)$ in Eq. (72) as the difference between the local grand potential on an A site, $\delta\Omega^A$, and on a B site, $\delta\Omega^B$. This is a simple and physically very appealing consequence of our theory.

To summarize, we may determine the equilibrium concentration at a given temperature and chemical potential by solving Eq. (69) using $S^{(1)}(c)$

calculated at a sequence of concentrations using the homogeneous, self-consistent KKR-CPA. A schematic construction of the graphical solution is shown in Fig. 6. Clearly when $S^{(1)}(c)$ is a decreasing function of concentration a van der Waals loop can develop. It signals a phase separation transition for which the coexistence curve is given by the usual Maxwell construction.

Although, as yet, no system has been analysed using the above theory, the coexistence curve of the $\text{Pd}_{1-c}\text{Rh}_c$ system has been calculated by an equivalent procedure using self-consistent KKR-CPA calculations (46). The results are shown in Fig. 7. Further details about this calculation will be provided in the next section. Here we merely wish to note that for this simple system we appear to have an even quantitatively adequate theory.

Clearly, Eq. (69) can be formally integrated with respect to c and we obtain for the grand potential per unit cell

$$\frac{1}{N} \Omega(v) = k_B T [\bar{c} \ln \bar{c} + (1 - \bar{c}) \ln (1 - \bar{c})] + \Omega_e^{\text{CPA}}(\bar{c}) - v \bar{c}, \quad (75)$$

where Ω_e^{CPA} is to be calculated using a homogeneous self-consistent KKR-CPA. In fact, this latter computation would be just the finite temperature version of the average total energy calculation in the previous section. The temperature dependence of $\Omega_e^{\text{CPA}}(\bar{c})$ would come, principally, from the entropy associated with the production of electron-hole pairs by thermal fluctuations.

Note that Eq. (75) might be thought of as a sensible alternative to Eq. (69), and hence, as the starting point for studying the equilibrium state.

Before drawing this section to a close it should be noted

that the calculation of $S_i^{(1)}$ in various ordered states is a fairly straightforward generalization of those discussed above. As we have mentioned earlier such ordered states may be described by dividing up the basic lattice of all sites, fully invariant under lattice translations in the disordered state, into a finite set of sublattices with the concentration variable c_i being the same on all sites of a given sublattice but varying from sublattice to sublattice. Under these circumstances the basic CPA condition, Eq. (60), generalizes to a finite set of coupled equations, one for each crystallographically different site. The arguments leading to the charge self-consistency

FIGURE 6. The chemical potential difference $v = \mu^A - \mu^B$ (solid line) versus concentration c for a generic phase separating binary alloys. The dotted line gives the concentration from $S^{(1)}$ and the dashed line that from the entropy. The actual data is that for $\text{Rh}_{0.5}\text{Pd}_{0.5}$ at a temperature of 1200 K obtained during the phase diagram calculation of Fig. 7.

FIGURE 7. The phase boundary for $\text{Rh}_C\text{Pd}_{1-C}$ alloy as calculated by the first-principles KKR-CPA scheme (solid line), the calculated spinodal (triangles), and the experimentally determined coexistence line (dots with error bars). The experimental data is taken from J. E. Shield and R. K. Williams, *Scripta Met.* 21, 1475 (1987).

Since then a number of other workers (48) have also solved problems using that framework. Making these calculations self-consistent and pursuing them to the point where $S_i^{(1)}$, and therefore the order parameters are also calculated, is likely to be one of the more profitable fields in the first-principles studies of energetics in solids.

3.3. The direct correlation functions

Using Eqs. (35) and (71), we may write the single particle contribution to the direct correlation function as

$$S_{ij}^{(2)} = \left(\frac{\partial^2}{\partial c_i \partial c_j} \Omega_e^{\text{CPA}} \right) \Big|_{c_i = \bar{c}_i} = - \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \left[\frac{\partial^2}{\partial c_i \partial c_j} \bar{N}^{\text{CPA}}(\epsilon; \{c_i\}) \right] \Big|_{c_i = \bar{c}_i}. \quad (75)$$

The first of the two derivatives in the above relations can be taken in the same way as in the case of calculating $S_i^{(1)}$ in the previous subsection. This step leads to

$$S_{ij}^{(2)} = - \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \frac{\partial}{\partial c_j} [(\bar{N}_i^A(\epsilon) - \bar{N}_i^B(\epsilon))], \quad (76)$$

procedure and the formula for $S_i^{(1)}$, Eq. (70), also generalizes without any difficulty. Clearly, the equation of state will be a set of coupled equations for the sublattice concentrations c_I , each of the form given in Eq. (32). The solutions of these will then give the mean-field theory prediction for the order parameters, $c_I - c_I'$, of which there may be several. Unlike Landau theories which are designed to work near the transition temperature T_c , the above calculations would yield the order parameters all the way to $T=0$. Moreover, together with the prescription of the Maxwell construction, the theory is equally applicable to first- and second-order phase transitions.

Unfortunately, as yet, no such full-blooded calculation of compositional order parameters has been performed. However, the time is ripe. The first multiple sublattice KKR-CPA calculations were reported by Pindor et al. (47).

where the partially averaged "integrated density of states," $\bar{N}_i^a(\epsilon)$, are given by Eq. (73) with the suffix i and hence, the dependence on the whole inhomogeneous concentration field $\{c_i\}$ restored in a self-evident fashion.

When calculating $S_i^{(1)}$ in the disordered state, the $c_i = \bar{c}\psi_i$ limit was taken after a formal expression was derived for the first derivative $\partial/\partial c_i \bar{N}^{CPA}(\epsilon; \{c_i\})$. Here we retain the dependence of $\bar{N}_i^a(\epsilon)$ on $\{c_i\}$ and proceed to derive a formal expression for its derivative with respect to $c_j \psi_j$ before the limit $c_i = \bar{c}\psi_i$ is taken.

With the help of the fully inhomogeneous version of Eq. (73), we find

$$\frac{\partial}{\partial c_j} [\bar{N}_i^A(\epsilon) - \bar{N}_i^B(\epsilon)] = -\frac{1}{\pi} \text{Im} \sum_{l \neq i} \text{tr} \{ (D_{i,A} - D_{i,B}) (\underline{\tau}^{C,ii})^{-1} [\underline{\tau}^{C,il} (\frac{\partial \underline{t}_{l,c}^{-1}}{\partial c_j}) \underline{\tau}^{C,li}] \} \quad (77)$$

where "tr" denotes trace over the angular momentum indicies and

$$\underline{D}_{i,\alpha}(\epsilon) = [1 + (\underline{t}_{i,\alpha}^{-1} - \underline{t}_{i,c}^{-1}) \underline{\tau}^{C,ii}] . \quad (78)$$

Let us denote the new quantity $\frac{\partial}{\partial c_j} \underline{t}_{i,c}^{-1}(\epsilon)$ by

$$\Lambda_{LL'}^{ij}(\epsilon) = \frac{\partial}{\partial c_i} [\underline{t}_{i,c}^{-1}; LL'(\epsilon; \{c_i\})] . \quad (79)$$

Evidently, it is a response function which gives the change in $\underline{t}_{i,c}^{-1}$ at $\vec{R}_i$ due to a change in the concentration c_j at $\vec{R}_j$, i.e.,

$$\delta \underline{t}_{i,c}^{-1}; LL'(\epsilon) = \sum_j \Lambda_{LL'}^{ij}(\epsilon) \delta c_j . \quad (80)$$

One may derive a Bethe-Salpeter-like equation for this response function by taking derivatives of the basic inhomogeneous CPA equation given in Eq. (61). After some lengthy but straightforward algebra we find

$$\Lambda_{L_1 L_2}^{ij}(\epsilon) = \Lambda_{L_1 L_2}^{0;ij}(\epsilon) - \sum_{l \neq i} \sum_{L, L_0} I_{L_1 L_2; L, L_0}^{il}(\epsilon) \Lambda_{L, L_0}^{lj}(\epsilon) , \quad (81)$$

where

$$\Lambda_{L_1 L_2}^{0;ij}(\epsilon) = \frac{1}{2} [D_{iA}(\underline{t}_{i,A}^{-1} - \underline{t}_{i,B}^{-1}) D_{iB}]_{L_1 L_2} \delta_{ij} .$$

and the vertex part

$$I_{L_1 L_2; L_3 L_4}^{ij}(\epsilon) =$$

$$\sum_{L'} \{D_{1,A}(t_{1,A}^{-1} - t_{1,c}^{-1}) \gamma_{L_1 L'} (t_{1,B}^{-1} - t_{1,c}^{-1}) D_{1,B}\} L' L_2 X_{L' L''; L_3 L_4}^{ij}(\epsilon)$$

with

(82)

$$X_{L' L''; L_3 L_4}^{ij}(\epsilon) = \tau_{L' L_3}^{c, ij}(\epsilon) \tau_{L_4 L''}^{c, ji}(\epsilon) \quad i \neq j.$$

These equations describe the response function $\Lambda_{ij}^{ij}(\epsilon)$, and therefore, the direct correlation function $S_{ij}^{(2)}$ in an arbitrary inhomogeneous compositional state specified by $\{c_i\}$. As planned, we shall now focus on the disordered state $c_i = \bar{c}_i$ where actual calculations become feasible.

In the disordered state $\Lambda_{L_1 L_2}^{0; ij}$ becomes independent of i and j . Moreover, $\tau_{L_1 L_2}^{c, ij}$ and hence $X_{L_1 L_2; L_3 L_4}^{ij}$ depend only on the coordinate difference $R_1 - R_2$. Under these circumstances we may take the lattice Fourier transform of Eq. (81). The result is a finite matrix equation (because the angular momentum cut off at $l = l_{\max}$) at each k -point of the Brillouin zone and at each energy ϵ :

$$\Lambda_{L_1 L_2}(\vec{k}; \epsilon) = \Lambda_{L_1}^0(\epsilon) \delta_{L_1 L_2} - \sum_{L_3 L_4} I_{L_1 L_2; L_3 L_4}(\vec{k}; \epsilon) \Lambda_{L_3 L_4}(\vec{k}; \epsilon)$$

$$\Lambda_L^0(\epsilon) = \frac{1}{2} D_{A,LL}(\epsilon) [t_{A,L}^{-1}(\epsilon) - t_{B,L}^{-1}(\epsilon)] D_{B,LL}(\epsilon)$$

(83)

$$I_{L_1 L_2; L_3 L_4}(\vec{k}; \epsilon) = D_{A, L_1 L_1} (t_{A, L_1}^{-1} - t_{c, L_1}^{-1}) (t_{B, L_2}^{-1} - t_{c, L_2}^{-1}) D_{B, L_2 L_2} X_{L_1 L_2; L_3 L_4}(\vec{k}; \epsilon)$$

$$X_{L_1 L_2; L_3 L_4}(\vec{k}; \epsilon) = \frac{1}{\Omega_{BZ}} \int d^3 k' [\tau_{L_1 L_3}^c(\vec{k}' + \vec{k}; \epsilon) \tau_{L_4 L_2}^c(\vec{k}'; \epsilon)] - \tau_{L_1 L_3}^{c, ii} \tau_{L_4 L_2}^{c, ii}.$$

To solve these is now a matter of matrix algebra at each $\vec{k}$ and ϵ point.

With these results we may now return to Eq. (77). In the disordered state, $S_{ij}^{(2)}$ is diagonal in reciprocal space. Indeed we find

$$S_{sp}^{(2)}(\vec{k}) = \frac{1}{\pi} \text{Im} \int d\epsilon f(\epsilon) \sum_{LL'} D_{A,LL} (t_{A,L}^{-1} - t_{B,L}^{-1}) D_{B,LL} \Lambda_{L' L''}(\vec{k}; \epsilon)$$

$$\cdot X_{LL; L' L''}(\vec{k}; \epsilon),$$

(84)

which is the principle result of this section. Of course, as indicated by the subscript sp, this is only the single-particle contribution to $S^{(2)}(\vec{k})$. Contributions from the double-counting correction, $\partial/\partial c_i \partial/\partial c_j (\delta\Omega_e^{CP})$, can be important and will have similar form to $S^{(2)}(\vec{k})$ but will not be dealt with here.

What has been achieved may be summarized as follows. At the end of a full self-consistent KKR-CPA calculation, in possession of $t_{A,L}(\epsilon)$, $t_{B,L}(\epsilon)$, and $t_{C,L}(\epsilon)$, we may proceed to calculate the "susceptibility" $\chi_{L_1L_2L_3L_4}(\vec{k};\epsilon)$, see Eq. (83), and then solve Eq. (83) for the response function $\Lambda_{L,L'}(\vec{k};\epsilon)$. Furthermore, we may evaluate the formula for $S^{(2)}(\vec{k})$ given in Eq. (84). Finally, using the direct correlation function $S^{(2)}(\vec{k})$, so obtained, we determine the sought-after-correlation function $q(\vec{k})$ by evaluating the right-hand side of Eq. (37). By now a number of such calculations have been performed for various systems (49). In the next section we review the particularly interesting example of studies of ordering in the $\text{Cu}_c\text{Pd}_{1-c}$ system.

4. FERMI SURFACE DRIVEN INCOMMENSURATE ORDERING

As we have mentioned in the introduction, the diffuse scattering intensity $I(\vec{k})$ of X-rays or electrons from a random binary alloy is proportional to the correlation function $q(\vec{k})$. In fact

$$I(\vec{k}) = (f_A - f_B)^2 \bar{c}(1 - \bar{c})\alpha(\vec{k}), \quad (85)$$

where f_A and f_B are the scattering amplitudes of the A- and B-type of atoms, respectively, and $\alpha(k)$ is the well-known Warren-Cowley order

parameter (8) which is proportional to the correlation function: $q(\vec{k}) \equiv \bar{c}(1 - \bar{c})\alpha(\vec{k})$.

If a binary alloy, on an fcc lattice, near the AB_3 stoichiometric composition orders into the L1_2 (Cu_3Au) structure below a transition temperature T_c then, as a precursor to the transition, near, but above T_c the scattering intensity $I(\vec{k})$ show diffuse scattering peaks at the superlattice Bragg peaks of the ordered state. In the case of the L1_2 structure, these peaks are at the face centers and at the center of edges of the fcc reciprocal space unit cell as shown in Fig. 8. In Fig. 9 we show a sequence of diffuse scattering electron-diffraction pictures for the $\text{Cu}_c\text{Pd}_{1-c}$ system for $c = 0.126, 0.250$, and 0.332 , respectively taken from the work of Ohshima and Watanabe (50). Evidently, the precursor peak is not a single spot but four spots whose relative distance changes rapidly with concentration. There is a large class of alloys which behave in this interesting manner (11). They have attracted considerable attention for some thirty years. In particular, it was noted by Sato and Toth (11) that the distance of the four spots from the face center, where the peak would be in a normal L1_2 ordering process, is proportional to the electron per atom ratio e/a . In Fig. 10 we display their compilation of the relevant data. Furthermore, it was suggested by Moss (51) that e/a influences m through its effect on the geometry of the Fermi surface. However, the nature of the relevant Fermi surface and the precise mechanism by which it determined m remains obscure. In what follows we give a full microscopic

FIGURE 8. The large solid circles are the Bragg spots for the bcc reciprocal space corresponding to a fcc real-space lattice. The small open circles are the positions of the diffuse scattering maxima as the ordering transition into the $L1_2$ structure is approached from the high-temperature side.

(a)

(b)

(c)

FIGURE 9. Electron diffraction patterns from various $\text{Cu}_c\text{Pd}_{1-c}$ alloys taken from the work of Oshima and Watanabe.

account of this phenomena using the theory developed in these lectures. The results presented here will bring up to date the arguments first presented by Gyorffy and Stocks (17).

The $L1_2$ superlattice points are Lifshitz special points in the sense of our introduction. Conventionally, they correspond to ordering by spontaneous appearance of concentration waves with wave vectors $Q_1^0 = 100$, $Q_2^0 = 010$, and $Q_3^0 = 001$. From the point-of-view of our present concern, it is more useful to regard the same concentration wave pattern as due to the equivalent three waves of wave vectors $Q_1 = 110$, $Q_2 = 101$, and $Q_3 = 011$. The way these produce the same pattern of superlattice spots are illustrated in Fig. 8. Evidently, in view of Eq. (85), the relation

$c(1 - c)\alpha(\vec{k}) = q(\vec{k})$, and Eq. (37) to explain the experimental occurrence of

FIGURE 10. The deviation from the L_{12} commensurate wave of the modulation vectors of various incommensurately ordering systems. The data was compiled by Sato and Toth. The quantity $(1/2M)$ defined by Sato and Toth and used in this figure is the same as the quantity m defined in the text.

these diffuse scattering intensity peaks we must look for peaks in $S^{(2)}(\vec{k})$ along the wave vectors Q_1 , Q_2 and Q_3 .

To see how such structure might arise let us simplify Eq. (84) by setting D_A , $t_A^{-1} - t_B^{-1}$, D_B and Λ equal to 1 on the grounds that the principal $\vec{k}$ dependence in this formula comes from the factor

$\chi_{LL';L''}(\vec{k};\epsilon)$. Then, using Eq. (84) and a Krammers-Kronig relation for the scattering path matrices $\tau_{LL'}^C(\vec{k};\epsilon)$ we may write that

$$S^{(2)}(\vec{k}) \sim \sum_{L_1 L_2} \int d\epsilon \int d\epsilon' \frac{f(\epsilon) - f(\epsilon')}{\epsilon - \epsilon'} \text{Im} \tau_{L_1 L_2}(\vec{k}', \epsilon') \text{Im} \tau_{L_2 L_1}(\vec{k}' + \vec{k}; \epsilon) . \quad (86)$$

Next we note that the CPA approximation for the Bloch spectral function:

$$A(\vec{k};\epsilon) \equiv \sum_{ij} e^{i\vec{k}(\vec{R}_i - \vec{R}_j)} \int d^3r \text{Im} \langle G(\vec{r} + \vec{R}_i; \vec{r} + \vec{R}_j; \epsilon) \rangle ,$$

can be similarly simplified to give

$$A(\vec{k};\epsilon) \sim \text{Im} \tau_{LL}^C(\vec{k};\epsilon) . \quad (87)$$

Hence, at least, schematically,

$$S^{(2)}(\vec{k}) \sim \int d\epsilon \int d\epsilon' \frac{f(\epsilon) - f(\epsilon')}{\epsilon - \epsilon'} A(\vec{k};\epsilon') A(\vec{k}' + \vec{k};\epsilon) .$$

The interpretation of the Bloch spectral function $A(\vec{k};\epsilon)$ is that it is the density of states at a k -point. Therefore, for an ordered system

$$A_B(\vec{k};\epsilon) = \sum_{\nu} \delta(\epsilon - \epsilon_{\vec{k},\nu}) , \quad (88)$$

where $\epsilon_{\vec{k},\nu}$ is the energy eigenvalue of a Bloch wave with wave vector $\vec{k}$ and band index ν . Consequently, for an ordered system

$$S(2)(\vec{k}) \sim \sum_{\nu\nu'} \sum_{\vec{k}'} \frac{f(\epsilon_{\vec{k}',\nu'}) - f(\epsilon_{\vec{k}'+\vec{k},\nu})}{\epsilon_{\vec{k}',\nu'} - \epsilon_{\vec{k}'+\vec{k},\nu}} , \quad (89)$$

which is recognized as a generalized susceptibility factor.

As is well-known, the principle contributions to such factors comes from $\epsilon_{\vec{k},\nu}$'s close to the Fermi energy. Moreover, $S(2)(\vec{k})$ will be particularly large at the spanning vector $\vec{Q}$ of two parallel sheets of the Fermi surface. The reason for this is the vanishing of the denominator

$\epsilon_{\vec{k}',\nu'} - \epsilon_{\vec{k}'+\vec{k},\nu}$ at $\vec{k} = \vec{Q}$. Namely, $\epsilon_{\vec{k}',\nu'} - \epsilon_{\vec{k}'+\vec{k},\nu} = 0$ if $\vec{k}'$ is on one of the sheets of the Fermi surface and $\vec{k}' + \vec{k}$ is on another. Evidently, the larger the surface area of the parallel sheets the larger the intensity of the peak in $S(2)(\vec{k})$.

A large value of the response function at a particular $\vec{Q}$ implies large response to a small stimulus and therefore is an indication of an incipient instability. In physical terms, the above instability is due to the creation, by the stimulus (some external field), of a large number of electron-hole pairs with wave vector $\vec{Q}$ and essentially zero energy by exciting electrons from just below one of the Fermi surface sheets to previously empty states just above the other sheet.

This Fermi surface mechanism gives rise to a variety of celebrated instabilities of the metallic state. Usually, they are classified under the headings spin-density waves (SPD) (52) and charge-density waves (CDW) (53). We shall now add a third category to this list - concentration waves (CW).

The rough outline of the argument is now clear. Although the Bloch spectral function for an alloy describes smeared peaks in place of the delta-function peaks of the ordered systems, these may be quite

well-defined both in $\vec{k}$ and ϵ . In short, $A(\vec{k},\epsilon)$ may describe only slightly broadened Fermi surfaces. That this is indeed the case is illustrated in Fig. 11 where we plot $A(\vec{k};\epsilon_F)$ at the Fermi energy ϵ_F along various directions in the Brillouin zone for a $\text{Cu}_{0.75}\text{Pd}_{0.25}$ alloy. Evidently, the Fermi surface is quite well-defined on the scale set by its size. Under these conditions, it may be sensible to look for parallel sheets of Fermi surfaces described by $A(\vec{k},\epsilon)$. Indeed, our picture in Fig. 11 suggests that the Fermi surface is pretty flat perpendicular to the Γ - K (110) direction. The evolution of this flat piece of Fermi surface with concentration is

FIGURE 11. The Bloch spectral function $A_B(\vec{k}, \epsilon_F)$ at the Fermi energy ϵ_F along various directions emanating from the center of the Brillouin zone for $\text{Cu}_{0.75}\text{Pd}_{0.25}$ alloy. Note the existence of a fairly well-defined Fermi surface.

shown in Fig. 12. Clearly, it gets flatter and flatter as the Pd concentration increases from 0 to 0.4 without being smeared very much. Moreover, there is another similar flat piece of Fermi surface centered on the nearest-neighbour Γ -point along the (110) direction. As we shall argue presently, these are the pairs of parallel sheets of Fermi surfaces which drive the incommensurate ordering seen in the experiments referred to in Fig. 9. Taking the spanning vectors $\vec{\delta}$ from our calculations, we construct the expected diffuse scattering intensity maxima contours as shown in Fig. 13. Note that we expect peaks where the arcs from two different contributions cross.

Evidently, the arrangement of the predicted spots are in agreement with experiments. Moreover, they move with Pd concentration since the Fermi surface sheets move apart as the electron per atom ratio, e/a , decreases. This is also as found experimentally. Since the spanning vector $\vec{\delta}$ is

FIGURE 12. The evolution of the calculated Fermi surface of the $\text{Cu}_c\text{Pd}_{1-c}$ alloys with concentration. The focus of interest is the progressively flattened sheet perpendicular to the (110) (Γ -K) direction.

FIGURE 13. The loci of high-intensity diffuse scattering lines. The spots form where two such lines cross.

unlikely to be commensurate with the underlying lattice, the above mechanism provides a natural explanation of the four-way splitting of the $L1_2$ superlattice spots. Moreover, the changing size of the Fermi surface with changing c also furnishes a very natural cause for the relative movement of the spots. In fact, on the latter score, the agreement is even quantitative. To show this we plot the experimental and theoretical values of $m = 2[\sqrt{2} - 2k_F(011)]$ as a function of the Pd concentration in Fig. 14. Evidently, the agreement leaves little to be desired.

To summarize, random alloys with well-defined parallel sheets of Fermi surface will be unstable to formation of concentration waves whose wave vectors are the spanning vectors of the relevant Fermi surface sheets.

An appealing feature of the above mechanism is that it is quite robust in the sense that it does not depend on small delicate aspects of electronic structure. In fact, the Fermi surface of copper in the 110 direction is convex while that of palladium is concave. Thus, it is almost inevitable that, as the first changes into the second by alloying Pd into

FIGURE 14. The calculated and measured concentration variation in the diffuse scattering spots separation for the $\text{Cu}_c\text{Pd}_{1-c}$ alloys.

Cu, at some concentration the alloy Fermi surface will get very flat. The only delicate question may be whether or not the Fermi surface is well defined when it becomes flat. Indeed, as will be seen later, severe smearing may render the Fermi surface mechanism ineffective. Thus, we may conclude that this mechanism may be relevant to all the compounds of Sato and Toth (11) where the ordering wave vector varies with e/a .

Although it is tempting to regard the above arguments as conclusive, there are good reasons for following up the detailed predictions of the theory by actually calculating $q(\vec{k})$. One of these is the caution prompted by past experience with other would-be Fermi surface driven instabilities (54). In short, on various occasions appropriately oriented parallel sheets of Fermi surfaces were found to explain an instability, but when the corresponding susceptibility was calculated, it showed either no structure or only some very minor features at the spanning vectors. We shall presently report on our calculations of $q(\vec{k})$ which shows that the expected features at the spanning vectors of the Fermi surface sheets identified above indeed occur.

However, before doing that we wish to mention another reason for studying $q(\vec{k})$ all through the Brillouin zone. It has to do with the fact that modern diffuse scattering intensity measurement show a fair amount of highly reproducible detailed structure. If we are able to reproduce these on the basis of our first principles calculations, in which all such structures are the direct consequence of the intricate details of the electronic energy bands, not just states near the Fermi energy, then we would significantly strengthen the case for believing that the present theory captures the physical essence of the forces which drive the ordering processes.

Having solved the self-consistent KKR-CPA equations for various concentrations of the $\text{Cu}_{1-c}\text{Pd}_c$ system at $T = 0$, we have evaluated the formula for $S^{(2)}(\vec{k})$ given in Eq. (84) for a number of temperatures. The computationally most demanding part of this calculation was the evaluation of the response function $\chi_{LL;L'L''}(\vec{k};\epsilon)$. This was done by integrating the product $\tau_{LL}^C(\vec{k}',\epsilon)\tau_{L'L''}^C(\vec{k}' + \vec{k};\epsilon)$ effectively over the whole Brillouin zone along directions emanating from the Γ point. In our most careful calculations we have used 136 directions in one irreducible forty-eighth of the Brillouin zone. The energy integral was performed by working at the complex energy points corresponding to the Matsubara frequencies, and we have summed over them for various temperatures. Interestingly, at $T \gg T_C$ instead of the Fermi surface driven structure at Q , a peak at the X point, one of the Lifshitz special points, was dominant. However, near to (~ 1000 K) $T = T_C$ the peak at Q emerged as the major feature reassuringly fulfilling our expectations.

On calculating $q(\vec{k})$ we found that $q(\vec{Q},T)$ diverged at $T = T_{sp} = 950$ K. This is to be regarded as a spinodal temperature since the phase transition is expected to be first order. In fact, it is weakly first order experimentally. Unfortunately, we have not yet managed to do a sufficiently accurate $S^{(1)}(\vec{c})$ calculation to warrant solving the equation of state. Nevertheless, it is gratifying that this spinodal temperature is not too far from the experimentally observed $T_C = 927$ K.

In Fig. 15 we show $q(k,c)$, as calculated from Eq. (84) at $c = 0.07$, 0.25 , and 0.40 . Clearly, we find the split superlattice points as expected. Furthermore, they move with c in good agreement with the experiments. Thus, in this case, the Fermi surface mechanism dominates the

CALCULATED SHORT-RANGE ORDER DIFFUSE SCATTERING FROM $\text{Cu}_x\text{Pd}_{1-x}$ ALLOYS

FIGURE 15. The correlation function $q(\vec{k}, c)$, [proportional to the diffuse scattering intensity $I(\vec{k})$], in the plane containing the reciprocal lattice points 000, 020, 022, and 002 as calculated using the first-principles mean-field theory in the text for various $\text{Cu}_x\text{Pd}_{1-x}$ alloys.

symmetry-induced special points. As we remarked in the introduction this is allowed by the Landau argument. Indeed, in agreement with it, we found a material specific new length entering into the problem, Q^{-1} , which is not commensurate with the underlying lattice. The peak at $\vec{Q}$ dominating symmetry generated instabilities gives rise to an incommensurate modulation of the high-temperature symmetric phase at the temperature where it diverges.

In Fig. 16 we illustrate the temperature dependence of $q(\vec{k}, t)$. Unfortunately, there are only limited experimental data on the fading out of the above short-range-order structure with rising temperature. Clearly, such a study would be a useful contribution to establishing where the theory stands on the energy scales governing the thermal fluctuations.

In conclusion, it must be stressed that the above discussion is incomplete in two important respects. Firstly, we have neglected the contribution to the direct correlation function $S_{ij}^{(2)}$ coming from the double-counting corrections $\delta\Omega_e^{\text{CPA}}$ to the free energy Ω_e^{CPA} in Eq. (64). These will play a particularly interesting role in systems where charge transfer, e.g., electronegativity, is a significant effect. We shall return to a discussion of this feature of the theory in a future publication. Secondly, we have studied only a small part of the phase diagram of the $\text{Cu}_{1-x}\text{Pd}_x$ system. Indeed, we have investigated the instability of the disordered state only, leaving the nature of the incommensurate state and how it locks into commensurate phases at low temperatures unexamined. The appropriate region of the phase diagram appears to display a number of novel ordering phenomena and is currently under intensive experimental investigation (55). While it is hoped that, eventually, the above first-principles mean-field theory may make contact with these interesting experimental features, for now these issues may be best addressed in the semi-phenomenological manner introduced in the next section.

The above remarks notwithstanding, the single particle formula for $S_{ij}^{(2)}$, given in Eq. (84), on its own is a useful tool for investigating ordering and clustering tendencies in the random phases. We like to stress that this is so even when the Fermi surface does not play a dominant role.

As an example, we show our calculated $q(\vec{k})$ for the $\text{Pd}_{0.8}\text{Rh}_{0.2}$ alloy in Fig. 17. Clearly, the diffuse scattering intensity peaks are centered on

FIGURE 16. The evaluation of the correlation function $q(\vec{k}, T)$ with temperature for $\text{Cu}_{0.75}\text{Pd}_{0.25}$ in the plane defined by the reciprocal lattice vectors 000, 020, 022, and 002.

FIGURE 17. The correlation function $q(\vec{k})$ for $\text{Pd}_{0.25}\text{Rh}_{0.75}$ as calculated using the first-principles mean-field theory described in the text.

the fundamentals characteristic of the fully random alloys. Recall that this implies a clustering tendency and a phase-separation at low temperatures. It is gratifying to note that this is indeed what happens experimentally. The relevant phase separation curve is shown in Fig. 7. Given the parameter free nature of our calculation, the above qualitative success of the theory should be regarded as significant evidence that we have identified the electronic causes of the phase separation.

As a final example, we now comment on the possible origin of the spectacular sequences of long-period phases, discovered by van Tenderloo et al. in the $\text{Al}_{1-x}\text{Ti}_{1+x}$ system (56,57). As described in detail by Professors van Tenderloo and Selke in their contribution to this volume, these phases fit into a pattern usually associated with the axial next-nearest-neighbour Ising (ANNNI) model. Accordingly, it is argued that the sequences of

commensurate phases are due to competing short-range interactions (58). On the other hand, given our experience with long-period structures in the $\text{Cu}_{1-x}\text{Pd}_x$ system, one might suspect that, again, the Fermi surface mechanism, which can be thought of as long-range oscillatory interaction, is involved. To check this hypothesis we have performed a self-consistent KKR-CPA calculation for the random alloy $\text{Al}_{0.75}\text{Ti}_{0.25}$ on an fcc lattice. The spectral function at ϵ_F is shown in Fig. 18. Evidently, the shape of the Fermi surface is very much like that of pure aluminum and there are few hints of parallel sheets. Moreover, whatever Fermi surface there is, it is significantly broadened on the scale of the Brillouin zone. Thus, it appears highly unlikely that this Fermi surface plays a role in the ordering process.

As we have noted earlier, even when the Fermi surface mechanism is not operating, $S_{sp}^{(2)}(\vec{k})$ may be a good guide as to the causes of ordering. In the hope that we may discover the short-range competing interactions required by the ANNNI model, we have calculated the single-particle contributions to $S_{ij}^{(2)}$ and find no indication of the $(1 \frac{1}{2} 0)$ special point ordering of the DO_{22} structure. Moreover, calculations of the total energy of the L1_2 and DO_{22} ordered structure (59) on the same fcc lattice show that the L1_2 structure is favored.

As a means of investigating the matter further, Nicholson and Stocks have repeated the above calculation for a tetragonally distorted fcc lattice. Dramatically, it is found that the DO_{22} structure is favored over L1_2 for a c/a ratio close to that of experiment. This suggests that if we repeat our $S_{ij}^{(2)}$ calculation on a tetragonally distorted lattice we may find the relevant competing interactions. Thus, we appear to have discovered an example where lattice distortions and chemical ordering are critically coupled. Obviously, this calls for a theory where concentration and strain fluctuations are treated on an equal footing.

FIGURE 18. The Bloch spectral function at the Fermi energy $A_B(\vec{k}, \epsilon_F)$, along lines emanating from the Γ point in the $\Gamma\text{XWKWX}\Gamma$ (left) and $\Gamma\text{KLUX}\Gamma$ (right) planes, for a fcc TiAl , random alloy.

5. WAYS OF USING THE FIRST PRINCIPLES MEAN FIELD THEORY

In addition to making use of the scheme we have presented in the previous sections directly, we can extend its usefulness by forging a bridge

between it and various powerful phenomenological approaches to the problem of compositional variations in alloys. In what follows we shall discuss two such bridges.

5.1. First-principles coefficients for the Landau theory

Following Landau in his original paper, let us consider states for which the local concentration c_i deviates from the average $\bar{c}$ by a small amount δc_i . Then we may expand Eq. (64) about the homogeneous disordered state in powers of the deviations $\{\delta c_i\}$. This procedure is entirely analogous to the generalized perturbation theory of Ducastelle and Gautier (23). Comparing this expansion with the Landau theory given in Eq. (8), we find explicit microscopic expressions for the phenomenological coefficients as follows:

$$\begin{aligned} \gamma_{ij}^{(2)} &= \frac{k_B T}{\bar{c}(1 - \bar{c})} \delta_{ij} + S_{ij}^{(2)} \\ \gamma_{ijk}^{(3)} &= \frac{k_B T(2\bar{c} - 1)}{6\bar{c}^2(1 - \bar{c})^2} \delta_{ij}\delta_{ik} + S_{ijk}^{(3)} \\ \gamma_{ijkl}^{(4)} &= \frac{k_B T[1 - 3\bar{c}(1 - \bar{c})]}{12\bar{c}^3(1 - \bar{c})^3} \delta_{ij}\delta_{ik}\delta_{il} + S_{ijkl}^{(4)}, \end{aligned} \quad (90)$$

where the higher-order direct-correlation functions $S_{ij}^{(3)}$ and $S_{ijkl}^{(4)}$ are straightforward generalization of $S_{ij}^{(2)}$ and are given by

$$\begin{aligned} S_{ijk}^{(3)} &= \beta \left(\frac{\partial^3 \Omega_e}{\partial c_i \partial c_j \partial c_k} \right)_{c_i = \bar{c}}^{\text{CPA}} \\ S_{ijkl}^{(4)} &= \beta \left(\frac{\partial^4 \Omega_e}{\partial c_i \partial c_j \partial c_k \partial c_l} \right)_{c_i = \bar{c}}^{\text{CPA}}. \end{aligned} \quad (91)$$

Evidently, these microscopic coefficients $\gamma_{ij}^{(2)}$ and $\gamma_{ijk}^{(3)}$ depend on the temperature concentration and the volume as is usually assumed in the phenomenological theory. For $S_{ijk}^{(3)}$ and $S_{ijkl}^{(4)}$, we have not derived explicit KKR-CPA expressions. However, although laborious, it is a perfectly straightforward thing to do. As an indicator of the interesting results that can be obtained with such a powerful first-principles Landau theory, we mention the strong coupling charge density wave theory of Varma et al. (60). There important new features emerged when the analogies to the third- and fourth-order coefficients $S_{ijk}^{(3)}$ and $S_{ijkl}^{(4)}$ were calculated.

On the other hand, one may argue that $S(3)$ and $S(4)$ are small compared to $S(2)$. This is the line taken in the generalized perturbation method (GPM) of Ducastelle and Gautier (23). However, while within their tight-binding model Hamiltonian framework, there appears to be evidence that the direct correlation functions fall off rapidly with their order. Our self-consistent density functional description of the electrons does not allow such conclusions. Nevertheless, it may frequently be so, and it would be very helpful if this hypothesis was tested by explicit calculations.

Once the coefficients in Eq. (8) have been established, one may proceed to studying the Euler-Lagrange equation corresponding to minimizing $F(\{c_i\})$. In this way one may examine, for example, the domain structure of alloys, as was done by McMillan (61) for Cu,Au, on a first-principles basis. The theory may also be suitable for investigating anti-phase-boundary energies.

If for some reason the above mean-field theory proves insufficient, one may include the fluctuations by following the Ginzburg-Landau-Wilson prescription (62):

$$F = - \frac{1}{\beta} \ln Z$$

$$Z = \pi \int d(\delta c_i) e^{-\delta F(\{\delta c_i\})} . \quad (92)$$

Clearly, this is a sensible description only when most of the contribution to Z comes from small values of δc_i . For instance, this is the case near second-order phase transitions. When the delta-function contribution to all the γ_{ij} 's are summed up to all orders (neglecting all the direct correlation functions but that for $n = 2$), this prescription becomes equivalent to using S_{ij} as a pair potential in Eq. (18). Again, this is an uncontrolled approximation which nevertheless may be useful when $S(2)$ is a strong pair potential which gives rise to large concentration fluctuations, δc_i , but $S(n)$ is small by comparison.

5.2. A first-principle Cahn-Hilliard theory - the local concentration approximation (LCA)

In this final section we shall develop a theory which, in contrast to the Landau theory, is valid for large deviations from the average concentration $\bar{c}$. Such a Cahn-Hilliard (63) or van der Waals (64) theory will be useful for studying surface and interface concentration profiles, or critical droplets of a new phase embedded in the old near-first-order transformations, to mention but a few applications.

The key idea which allows us to make progress with the above project is that we restrict our attention to cases where, while c_i changes a lot, it changes slowly. Namely, the change from one site to the next will be required to be small, but it may mount up over many lattice sites. In fact, the theory will be good for (a) small changes, whether fast or slow, and (b) large changes, if they are slow. These two conditions are depicted pictorially for the concentration function $c(x)$, defined on a continuum, in Fig. 19. Obviously, this approximation is well-suited for taking the continuum limit.

We begin by breaking up the free energy $F(\{c_i\})$ into contributions from each site as follows

FIGURE 19. Schematic picture of compositional fluctuations for which the theory in the text is applicable.

$$\delta F(\{c_i\}) = \sum_i f_i(\{c_i\}) , \quad (93)$$

where f_i is a kind of internal Helmholtz free energy density which depends on the whole concentration configuration $\{c_i\}$. A completely local approximation would be if we assumed that f_i depends only on the local concentration c_i : $f_i(\{c_i\}) = f_i(c_i)$. Here we shall do better than that by expanding $f_i(\{c_i\})$ in the deviations $c_j - c_i$ for $j \neq i$. Note that we are expanding each free-energy contribution f_i about its own local concentration c_i .

$$\begin{aligned} f_i(\{c_i\}) = & f_i^0 + \sum_j f_{ij}^{(1)}(c_i)(c_j - c_i) \\ & + \frac{1}{2} \sum_{j\ell} f_{ij\ell}^{(2)}(c_i)(c_j - c_i)(c_\ell - c_i) + \dots \end{aligned} \quad (94)$$

This is like the gradient expansion in the Kohn-Sham theory of the electron-gas.

Since δF is a unique function of $\{c_i\}$, i.e., independent of the chemical potential, the above expansion must have the symmetry of the underlying lattice. Thus, as in the Landau theory, the coefficients obey symmetry rules. For instance, for cubic systems there can be no linear term in Eq. (94) and the quadratic term must have the form

$$\sum_j f_{ij}^{(2)}(c_i)(c_j - c_i)^2 . \quad (95)$$

It may be helpful if we recall that the above observation in the context of the gradient expansion of density functional theories for homogeneous systems corresponds to taking the quadratic term to have the form $|\vec{\nabla}n|^2$ where $n(\vec{r})$ is the charge density, on account of rotational invariance.

To continue, we note that in $\sum_i f_i$ there are two terms which are of the form of Eq. (95):

$$f_{ij}^{(2)}(c_i)(c_j - c_i)^2 \text{ and } f_{ji}^{(2)}(c_j)(c_i - c_j)^2. \quad (96)$$

We shall approximate these by $f_{ij}^{(2)}(\bar{c}_{ij})(c_j - c_i)^2$ where $\bar{c}_{ij} = \frac{1}{2}(c_i + c_j)$ and $f_{ij}^{(2)}(\bar{c}_{ij})$ depends only on $\vec{R}_i - \vec{R}_j$. Thus to quadratic order in the local deviations:

$$\delta F = \sum_i f_i^0(c_i) + \frac{1}{2} \sum_{ij} f_{ij}^{(2)}(\bar{c}_{ij})(c_i - c_j)^2. \quad (97)$$

Now, in the spirit of the previous section, we shall look for a microscopic theory for the coefficients $f_i^0(c_i)$ and $f_{ij}^{(2)}(\bar{c}_{ij})$. The way to proceed is to Taylor expand both δF in Eq. (37) and $\Omega_e^{\text{CPA}}(\{c_i\})$ and compare coefficients. Note that the expansion of Ω_e^{CPA} is in powers of δc_i , not $c_i - c_j$. That is why Eq. (97) also has to be expanded in powers of the deviations of c_i from a common mean. The calculations are straightforward and we find

$$\begin{aligned} f_i^0(\bar{c}) &= \Omega_e^{\text{CPA}}(\bar{c}) \\ f_{ij}^{(2)}(\bar{c}) &= -\frac{1}{2} S_{ij}^{(2)}. \end{aligned} \quad (98)$$

Consequently, according to the LCA

$$F(\{c_i\}) = \sum_i \Omega_e^{\text{CPA}}(c_i) - \frac{1}{4} \sum_{ij} S_{ij}^{(2)}(c_i - c_j)^2. \quad (99)$$

It is useful to remark that for pair-potential models the mean-field theory already has the LCA form with $\Omega_e^{\text{CPA}}(\bar{c})$ replaced by $Z\tilde{v}\bar{c}(1 - \bar{c})$ in case of nearest-neighbour interactions. However, in the approach we are advocating $\Omega_e^{\text{CPA}}(\bar{c})$ and $S_{ij}^{(2)}$ are calculated from first principles and both may be quite complicated functions of $\bar{c}$.

Since Eq. (99) is only valid for slowly varying concentrations, we might as well take its continuum limit. Taking $c_i = c(\vec{R}_i)$ and for a nearby R_j $c(R_j) = c(R_i) + (\vec{R}_j - \vec{R}_i) \cdot \vec{\nabla} c(R_i)$, it is easy to derive the following expression for the free energy

$$F[\{c(\vec{r})\}] = \int d^3r \{ \Omega_e^{\text{CPA}}[c(\vec{r})] + \vec{\nabla}[c(\vec{r}) \cdot \vec{S}^{(2)} \cdot \vec{\nabla} c(\vec{r})] \}, \quad (100)$$

where

$$S_{\alpha\beta}^{(2)} = \sum_j \vec{R}_{ij}^{\alpha} \vec{R}_{ij}^{\beta} S_{ij}^{(2)}. \quad (101)$$

This is the principal result of this section. Evidently, Eq. (100) is of the form of the much used concentration functional of Cahn and Hilliard (3,8,63). The only difference is the anisotropic form of the gradient term. Such anisotropy may often be useful in studying problems which involve interaction between compositional arrangements and the orientation of the lattice. However, when it can be neglected, Eq. (100) takes on the more usual form

$$F = F_0 \int d^3r [\bar{f}(\bar{c}) + \xi_0^2 |\vec{\nabla} \bar{c}|^2] ,$$

where

$$F_0 = -\frac{1}{2} \sum_i S_{ij}^{(2)} = \frac{k_B T}{\bar{c}(1-\bar{c})} \quad (102)$$

$$\bar{f}(c) = \Omega_e^{\text{CPA}}(c)/F_0$$

$$\xi_0^2 = \sum_j S_{ij}^{(2)} |\vec{R}_{1j}|^2 / \sum_j S_{ij}^{(2)} .$$

Since $f(c)$ and ξ_0 can now be calculated using the self-consistent KKR-CPA method, we have obtained a fully first-principles Cahn-Hilliard theory.

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