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Lattice relaxation in high-temperature pure crystalline materials and substitutionally disordered alloys. II. Self-consistent treatment of distortion and related problems

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Using the formalism of the Korringa-Kohn-Rostoker method in conjunction with the coherent-potential approximation (KKR-CPA) for treating substitutional disorder and the embedded-cluster method, we describe the scattering from single displaced atoms and clusters of displaced atoms embedded in an effective medium. By means of a distribution function this approach leads to a self-consistent treatment of lattice relaxation. Introducing a supermatrix formulation for the KKR-CPA method and using the concept of the "renormalized interactor" allows us to reformulate the diagonal and off-diagonal elements of the Green function such that (i) impurities or clusters of impurities in an effective medium, displaced or not, can be treated properly and (ii) Bloch spectral functions can be obtained with no further assumptions beyond the level of the KKR CPA. The proposed method, for example, covers the case of lattice relaxation for pure matter at elevated temperatures and treats properly the effects of short-range order in substitutionally disordered materials. In general, it provides a solution to the problem of embedding impurities in pure materials or alloys describable within the muffin-tin approximation for the crystal potential.

I. INTRODUCTION

In the preceding paper[1], hereafter referred to as I, the Korringa-Kohn-Rostoker[2-4] (KKR) method for calculating the electronic structure of periodic solids was generalized to include deviations from structural periodicity confined to compact clusters of atoms. Specific prescriptions were given for the evaluation of the Green function for a single displaced atom and for a cluster of displaced atoms embedded in a pure host material with atoms fixed at the positions of a rigid, regular lattice. Two methods for treating lattice relaxation were presented in I. The first method relied on the evaluation of the renormalized interactor (RI) associated with a cluster of displaced atoms, while the second was based on the individual scattering matrices for displaced muffin-tin (MT) spheres and, assuming that a complete basis set of angular-momentum states is used, it is entirely equivalent to the RI approach. The generalization of the multiple-scattering formalism presented in I allows a first-principles study of physical properties of solid materials that are sensitive to interatomic separation, such as magnetic moments, NMR and ESR frequencies, and Dingle temperatures.

In this paper the methods presented in I and, in particular, the renormalized-interactor approach, are extended (i) to include the calculation of displaced-atom Green functions in concentrated substitutionally disordered alloys rather than just pure materials, (ii) to provide a self-consistent treatment of (small) lattice softening in otherwise pure, translationally invariant materials, and (iii) to provide a self-consistent treatment of small, but correlated, atomic displacements in substitutionally disordered alloys. Thus this paper provides a coherent scheme for the treatment of various and diverse cases involving the embedding of impurities and deviations from structural periodicity. In particular, the RI approach reduces the calculation of impurity Green functions to the evaluation of integrals over the first Brillouin zone (BZ) of the undistorted lattice. It is hoped that the detailed presentation of several applications may exemplify the general formalism given in I and indicate its possible utility.

As was the case in I, a MT-like approximation is employed. Thus the potentials associated with individual scattering centers are bounded by nonoverlapping spheres although they are not necessarily confined to being spherically symmetric. Deviations from spherical symmetry, indeed, are necessary if charge-transfer effects and broken translational and rotational symmetry are to be taken into account. The formalism presented in this paper allows the incorporation of charge-transfer effects in a straightforward manner.

In addition to the MT approximation, we also retain the concept of a rigid lattice. Thus we consider structural disorder confined to compact clusters of atoms or, in the self-consistent treatment of lattice relaxation, the *averaged* atomic positions are assumed to form a regular lattice. This allows us to reduce the treatment of many cases of physical interest to the general problem of calculating the Green functions associated with displaced atoms embedded in a translational invariant medium. A prototype system, namely displaced atoms in a pure host material, was discussed in some detail in the preceding paper. The choice of the embedding medium there was simple, being taken as the host medium itself. In this paper, the construction of the embedding medium is examined in detail for a variety of cases. Once such a medium has been specified and the various parameters entering a calculation properly identified, the formalism of I can be applied whole to the particular case under study.

The construction of an embedding medium in the case of substitutionally disordered alloys merits special attention. For such systems, we choose the effective medium determined in the coherent-potential approximation[5–8] (CPA), particularly as it is applied to potentials of the MT type (KKR CPA). We now briefly describe the ideas underlying the CPA and some of its cluster generalizations.

The CPA has proved to be the best single-site theory for studying the properties of substitutionally disordered alloys. In the CPA one considers the real disordered material as being replaced by an effective medium that possesses the translational invariance of the underlying lattice. The CPA medium is, in general, complex and energy dependent and is determined through the self-consistency condition that the scattering off of a real atom embedded in the medium vanishes on the average. The CPA has many desirable properties, such as analyticity of calculated self-energies and Green functions, and yields analytic, physically meaningful results. The theoretical aspects of the CPA and its many applications to the calculation of the physical properties of substitutional alloys have been amply discussed in review articles.[6–8]

The viability of the CPA as a general theory of substitutionally disordered alloys is severely limited, however, due to the single-site nature of the method. In order to take account of statistical correlations, i.e., short-range-order effects known to affect many of the physical properties of disordered materials, e.g., magnetic moments, it is necessary to extend the CPA to a multisite or cluster theory. Of the many such theories which have been proposed,[9–18] the embedded-cluster method[14–17] (ECM) appears to be the most satisfactory in terms of analytical and computational requirements. In particular, the ECM yields analytic cluster Green functions and hence nonnegative density-of-states (DOS) curves when used in conjunction with a proper single-site medium, such as the one determined in the CPA. The advantages as well as the limitations of the ECM have been discussed in a previous publication.[14] The KKR CPA and the ECM as applied to MT potentials provide the foundation upon which much of the formalism for treating lattice relaxation is constructed.

Now, a few comments about the potential function characterizing the impurity clusters as well as those of the surrounding medium are appropriate. All such potentials must be made electronically self-consistent within the context of local-density theory. Self-consistent MT potentials for pure materials have been used extensively in band-structure calculations.[19] The construction of self-consistent MT potentials for substitutionally disordered alloys also has been described in detail in the literature.[20,21] The results of numerical calculations[21] have clearly demonstrated that electronic self-consistency is essential for a fully satisfactory application of the KKR CPA. The formalism used in this and the preceding paper yields individual atomic Green functions and can be used in the construction of self-consistent potentials in connection with pure systems or substitutionally disordered alloys. However, it is to be expected that cluster self-consistent potentials will require much greater computational effort than their single-site counterparts.

The remainder of the paper is arranged as follows. In Sec. II we discuss the evaluation of the Green function for displaced atoms in substitutionally disordered alloys. A self-consistent treatment of uncorrelated displacements in pure materials and correlated displacements in alloys are given in Secs. III and IV, respectively. Section V contains a discussion of the non-site-diagonal Green function in a disordered material with or without distortion. The results of sample calculations are presented in Sec. VI. A final discussion of the methods presented in the body of the paper is given in Sec. VII.

II. DISPLACED ATOMS IN SUBSTITUTIONALLY DISORDERED ALLOYS

The KKR CPA and the ECM (for a review, see Refs. 7 and 8) are based on the premise of a rigid, translationally invariant lattice. Using the formal methods presented in I, it is straightforward to extend the KKR CPA and the ECM to the calculation of the Green function associated with either a single displaced atom or with a cluster of displaced atoms in substitutionally disordered alloys. All that is formally necessary is the replacement of the pure host quantities of I, such as $\underline{\tau}^{00}$, with the corresponding quantities evaluated in a KKR-CPA effective medium. That is to say, in substitutionally disordered alloys the CPA medium plays the role of a host material. To illustrate these comments we will derive the explicit formulas for the Green functions associated with displaced atoms in concentrated alloys. As in I, displaced quantities will be distinguished from their undisplaced counterparts by a circumflex. We begin by considering a single atom displaced from its equilibrium lattice position and surrounded by a KKR-CPA effective medium.

First, note that the quantity of interest is $\hat{\underline{\tau}}^{\alpha\alpha}$ $[=(\hat{\underline{\tau}}^{00})^{\alpha}]$ corresponding to a single displaced atom of type α. From Eq. (4.1) in I, we obtain

$$\hat{\underline{\tau}}^{\alpha\alpha}=(\hat{\underline{m}}^{\alpha}-\hat{\underline{\Delta}})^{-1} , \tag{2.1}$$

where $\hat{\underline{m}}^{\alpha}$ $[=(\hat{\underline{t}}^{\alpha})^{-1}]$ and $\hat{\underline{\Delta}}$ are, respectively, the inverse of the displaced MT scattering matrix, and the renormalized interactor for the *displaced* atom. Note that $\hat{\underline{m}}^{\alpha}$ may indeed be different from its undisplaced counterpart $\underline{m}^{\alpha}$ due to charge-transfer effects, and must be determined in a self-consistent evaluation of the displaced MT potential. The renormalized interactor $\hat{\underline{\Delta}}$ is given by expression (4.3) of I with $\underline{\tau}(\mathbf{k})$ replaced with the KKR-CPA quantity $\overline{\underline{\tau}}(\mathbf{k})$. Having obtained $\hat{\underline{m}}^{\alpha}$, we readily obtain the corresponding expression for the Green function,

$$\hat{\underline{G}}^{\alpha}(E,\mathbf{r},\mathbf{r}')=\sum_{L,L'}\hat{Z}^{\alpha}_{L}(E,\mathbf{r})\hat{\tau}^{\alpha\alpha}_{LL'}(E)\hat{Z}^{\alpha}_{L}(E,\mathbf{r}')-\sum_{L}\hat{Z}^{\alpha}_{L}(E,\mathbf{r})\hat{J}^{\alpha}_{L}(E,\mathbf{r}'),\quad r'>r . \tag{2.2}$$

The *averaged* Green function is then given by an average of $\hat{\underset{\sim}{G}}^{\alpha}$ over all possible components α of the alloy. Note the explicit use of circumflexes in $\hat{\mathbf{Z}}$ and $\hat{\mathbf{J}}$ to denote any possible differences between the solutions of the Schrödinger equation between displaced and undisplaced potentials.

The cluster-diagonal scattering-path operator $\hat{\underset{\sim}{\tau}}^{CC}$, and hence the Green function for a cluster of displaced atoms, can be calculated in an equally straightforward way through the use of the formalism of Sec. IV in I. In particular, $\hat{\underset{\sim}{\tau}}^{CC}$ is given by the expression

$$\hat{\underset{\sim}{\tau}}^{CC}=[(\hat{\underset{\sim}{t}}^{CC})^{-1}-\hat{\underset{\sim}{\Delta}}^{C}]^{-1}\;, \tag{2.3}$$

with $\hat{\underset{\sim}{t}}^{CC}$ defined in Eq. (4.6) in I, and $\hat{\underset{\sim}{\Delta}}^{C}$ evaluated in the manner prescribed by Eq. (4.10) of that section. Finally, the Green functions associated with the cluster C can be obtained through use of the matrix elements of $\hat{\underset{\sim}{\tau}}$ given in Eq. (2.3).

It is important to point out the existence of a certain discrepancy among the various potentials entering the discussion of this section and which the reader may have already noticed. These differences are due to the fact that, because of charge transfer, the displaced MT t matrices $\hat{\underline{t}}^{\alpha}$ are, in general, not equal to the undisplaced quantities $\underline{t}^{\alpha}$ that enter the construction of the KKR CPA medium. Thus, the self-consistent treatment of a displaced atom results in an impurity of a foreign kind, i.e., one whose potential is different from those entering the construction of the embedding medium. In many cases, such differences can be safely ignored. Also, for small displacements, such discrepancies can be removed in a self-consistent treatment of lattice relaxation, as will be shown in Secs. III and IV.

III. SELF-CONSISTENT TREATMENT OF LATTICE RELAXATION-UNCORRELATED DISPLACEMENTS

In this section we present a self-consistent treatment of lattice relaxation which, for small displacements, leads to full self-consistency between the potentials of displaced atoms and those of the surrounding medium. To this end, we first consider lattice relaxation in pure materials.

Let the position of a displaced atom in the material be described in terms of a distribution function $P(\boldsymbol{\rho})$, with $\boldsymbol{\rho}$ measured from the equilibrium position of the atom. In order to maintain the conditions of validity of multiple-scattering expressions, the function $P(\boldsymbol{\rho})$ is taken as nonzero only for displacements which restrict the MT potential inside a bounding sphere centered on the lattice site. For small displacements we can consider lattice distortion to be isotropic and the atomic displacements uncorrelated. A particular configuration of the material consists of each atom j being displaced by a vector $\boldsymbol{\rho}_j$ from its equilibrium lattice position. Any quantity, e.g., the Green function, is a function of a particular configuration $\{\boldsymbol{\rho}_j\}$, and its exact configurational average is given formally by the expression

$$\langle G(\boldsymbol{\rho}_1,\boldsymbol{\rho}_2,\ldots,\boldsymbol{\rho}_j,\ldots)\rangle=\int\left[\prod_k d^3\rho_k\right]\left[\prod_j P(\boldsymbol{\rho}_j)\right]G(\boldsymbol{\rho}_1,\boldsymbol{\rho}_2,\ldots,\boldsymbol{\rho}_j,\ldots)\;. \tag{3.1}$$

As was the case for random substitutional alloys, Eq. (3.1) can be evaluated only approximately. Consistent with the spirit of the CPA, we replace the exact site-diagonal element of $\langle G\rangle$ by the quantity

$$\langle G(E,\mathbf{r},\mathbf{r}')\rangle=\int d^3\rho\,P(\boldsymbol{\rho})\left[\sum_{L,L'}Z_L(\boldsymbol{\rho};E,\mathbf{r})\tau_{LL'}(\boldsymbol{\rho})Z_{L'}(\boldsymbol{\rho};E,\mathbf{r}')-\sum_L Z(\boldsymbol{\rho};E,\mathbf{r})J_L(\boldsymbol{\rho};E,\mathbf{r}')\right],\quad r'>r \tag{3.2}$$

with the following definitions of the various quantities. The scattering-path operator $\underline{\tau}(\boldsymbol{\rho}_j)$ is associated with the MT sphere displaced through $\boldsymbol{\rho}_j$ from its equilibrium lattice site, but it is referred to the lattice site rather than the center of the displaced MT. The solutions $\underline{Z}(\boldsymbol{\rho})$ and $\underline{J}(\boldsymbol{\rho})$ are those for the individual, displaced MT spheres at $\boldsymbol{\rho}$, expressed in terms of coordinates also centered at the lattice site.

In order to evaluate Eq. (3.2), a method for evaluating $\underline{\tau}(\boldsymbol{\rho})$ must be devised. Consider the exact disordered material as replaced by an effective medium characterized by a translationally invariant lattice with an effective single-site scattering matrix $\underline{\bar{m}}$ associated with each lattice site. To determine $\underline{\bar{m}}$ we impose the CPA condition

$$\langle\underline{\tau}(\boldsymbol{\rho})\rangle=\underline{\bar{\tau}}^{00}\;, \tag{3.3}$$

or, explicitly,

$$\int d^3\rho\,P(\boldsymbol{\rho})[\underline{m}(\boldsymbol{\rho})-\underline{\bar{\Delta}}^{0}]^{-1}=(\underline{\bar{m}}-\underline{\bar{\Delta}}^{0})^{-1}\;. \tag{3.4}$$

Equation (3.4) also can be written in the form

$$\int d^3\rho\,P(\boldsymbol{\rho})[\underline{m}(\boldsymbol{\rho})-\underline{\bar{m}}+(\underline{\bar{\tau}}^{00})^{-1}]^{-1}=\underline{\bar{\tau}}^{00}=\frac{1}{\Omega_{\mathrm{BZ}}}\int[\underline{\bar{m}}-\underline{G}(\mathbf{k})]^{-1}d^3k\;. \tag{3.5}$$

It should be noted that $\underline{\bar{\tau}}^{00}$ in these equations is the scattering-path operator of the translationally invariant effective medium determined in the KKR CPA. This approach leads naturally to the use of the displaced MT t matrix rather than the displaced-atom structure constants. The CPA self-consistency condition can also be expressed in terms of the displaced renormalized interactor, but in that form it is somewhat less transparent and it is less useful for calculational purposes. Note also that, in its present form, Eq. (3.5) involves only the structure constants of the undistorted lattice, a convenient circumstance since these constants can be taken as well known.

The discussion given above for lattice distortion in pure materials can be extended to random small displacements in substitutionally disordered alloys. In this case the CPA condition, Eq. (3.5), takes the form

$$\sum_{\alpha} C_\alpha \int d^3\rho P(\rho)[\underline{m}^{\alpha}(\rho)-\overline{\underline{m}}+(\underline{\tau}^{00})^{-1}]^{-1} = \underline{\tau}^{00} = \frac{1}{\Omega_{\mathrm{BZ}}}\int [\overline{\underline{m}}-\underline{G}(\mathbf{k})]^{-1} d^3k \; , \qquad (3.6)$$

where $\underline{m}^{\alpha}(\boldsymbol{\rho})$ is the (inverse) scattering matrix of a displaced atom of type α referred to the lattice site rather than the displaced position corresponding to $\boldsymbol{\rho}$.

There are several comments that should be made about the CPA self-consistency conditions, Eqs. (3.5) and (3.6). First, these equations lead to an effective medium consistent with the potentials of the displaced atoms. Once such a medium has been constructed, the formalisms of I can be used to calculate the Green functions associated with single displaced atoms or clusters of displaced atoms. Second, the BZ integrals occurring in Eqs. (3.5) and (3.6) should be approached with care; the corresponding quantities for pure materials involve divergent integrands. Such integrals have been evaluated in the past, however, using various techniques. Finally, the insistence on complete self-consistency for each position $\boldsymbol{\rho}$ can quickly lead to an extraordinarily difficult computational task. It may be a good approximation for many systems, e.g., metals, to forego complete self-consistency at each value of $\boldsymbol{\rho}$, and to calculate self-consistent potentials only for selected positions $\boldsymbol{\rho}$ to determine $\overline{\underline{m}}$.

IV. CORRELATED DISPLACEMENTS IN SUBSTITUTIONALLY DISORDERED ALLOYS

The formalism of the preceding section provided a self-consistent treatment of small, random atomic displacements such as may be caused by elevated temperatures in crystalline solids. In this section we consider correlated displacements that can occur in concentrated, substitutionally disordered alloys even in zero temperature. As can be verified experimentally[22,23] in many alloys, nearest-neighbor (NN) and often next-nearest-neighbor (NNN) distances are functions of the chemical nature of the neighbor atoms. Thus, we seek a generalization of the KKR CPA equations that takes into account correlated lattice relaxation.

We begin with the equation of motion for the scattering-path operator[24] [see Eq. (3.8) in I],

$$\underline{\tau}^{ij}=\underline{t}^{i}\delta_{ij}+\underline{t}^{i}\sum_{k\,(\neq i)}\underline{G}^{ik}\underline{\tau}^{kj} \; . \qquad (4.1)$$

The free-electron propagators $\underline{G}^{ij}$, as well as the t matrices $\underline{t}^{i}$, depend on the configuration of the disordered material. In particular, $\underline{G}^{ik}$ can take on various values, $\underline{G}^{ik}_{\alpha\beta}$, for an atom of type α at site i and an atom of type β at site k. In fact, each alloy configuration is characterized by a distribution of values for $\underline{G}^{ik}_{\alpha\beta}$, through the dependence of $|\mathbf{R}^{ik}|$ on the occupation of the sites in the alloy. However, we will assume for the sake of simplicity that $\underline{G}^{ik}_{\alpha\beta}$ depends only on the distance between sites i and k, which is a function of the chemical occupation of those sites, and is independent of their local environment. The variation of $\underline{G}^{ik}_{\alpha\beta}$ with the occupation of sites i and k will be referred to as off-diagonal disorder (ODD). As it is usually assumed, $\underline{t}^{i}$ will be taken to be a function of the chemical occupation of the site i and independent of the local environment of that site.

In order to apply the KKR CPA method to the treatment of Eq. (4.1), we follow the approach used by Blackman, Esterling, and Berk[25] (BEB) in their treatment of ODD within a tight-binding (TB) formulation of the CPA. For definiteness we consider explicitly the case of binary A_cB_{1-c} alloys; the generalization to multicomponent alloys is straightforward. Thus, we introduce projection operators x_i and y_i ($=1-x_i$), where

$$x_i=\begin{cases}1 & \text{if there is an } A \text{ atom at site } i,\\ 0 & \text{otherwise.}\end{cases} \qquad (4.2)$$

Now we multiply Eq. (4.1) on the left and on the right by all combinations of x_i and y_j, i.e., consider all possible occupations of sites i and j, and insert the identity $x_k+y_k=1$ in the product $\underline{G}^{ik}\underline{\tau}^{kj}$. The resulting equations can be written in the form

$$\underset{\sim}{\tau}^{ij}=\underset{\sim}{t}^{i}\delta_{ij}+\underset{\sim}{t}^{i}\sum_{k\,(\neq i)}\underset{\sim}{G}^{ik}\underset{\sim}{t}^{kj} \qquad (4.3)$$

in terms of the following matrix quantities:

$$\underset{\sim}{\tau}^{ij}=\begin{bmatrix} x_i(\underline{\tau}^{ij})^{AA}x_j & x_i(\underline{\tau}^{ij})^{AB}y_j \\ y_i(\underline{\tau}^{ij})^{BA}x_j & y_i(\underline{\tau}^{ij})^{BB}y_j\end{bmatrix} , \qquad (4.4)$$

$$\underset{\sim}{t}^{i}=\begin{bmatrix} x_i\underline{t}^{A} & 0 \\ 0 & y_i\underline{t}^{B}\end{bmatrix} , \qquad (4.5)$$

and

$$\underset{\sim}{G}^{ij}=\begin{bmatrix} \underline{G}^{ij}_{AA} & \underline{G}^{ij}_{AB} \\ \underline{G}^{ij}_{BA} & \underline{G}^{ij}_{BB}\end{bmatrix} . \qquad (4.6)$$

Note that the projection operators which represent the disorder are not present in the matrix representing $\underset{\sim}{G}^{ij}$, but occur only in the site-diagonal matrix $\underset{\sim}{t}$. Thus, Eq. (4.5) corresponds to simple diagonal disorder in the matrices $\underset{\sim}{t}^{i}$ and can be treated formally in a manner analagous to that used in the usual formulation of the CPA. The KKR CPA formalism can be transcribed in its entirety to the case of 2×2 supermatrices ($n\times n$ supermatrices for n-component alloys). We will quote some specific results. The KKR CPA condition[7,8] takes the form

$$\sum_{\alpha} C_\alpha\{\underset{\sim}{\mathbb{1}}-\underset{\sim}{t}^{\alpha}[\underset{\sim}{\overline{t}}^{-1}-(\underset{\sim}{\tau}^{00})^{-1}]\}^{-1}\underset{\sim}{t}^{\alpha}=\underset{\sim}{\tau}^{00} , \qquad (4.7)$$

where $\underset{\sim}{\overline{t}}$ is a 2×2 supermatrix, and the site-diagonal element $\underset{\sim}{\overline{\tau}}^{00}$ of the scattering-path operator is given by the expression

$$\begin{aligned}\underset{\sim}{\bar{\tau}}^{00}&=\frac{1}{\Omega_{\rm BZ}}\int_{\rm BZ}\underset{\sim}{\bar{\tau}}(k)d^3k\\&=\frac{1}{\Omega_{\rm BZ}}\int_{\rm BZ}[\underset{\sim}{t}^{-1}-\underset{\sim}{G}(\mathbf{k})]^{-1}d^3k\\&=\frac{1}{\Omega_{\rm BZ}}\int_{\rm BZ}\left[\begin{bmatrix}(\underline{\bar{\tau}}^{00})^{AA} & \underline{0}\\ \underline{0} & (\underline{\bar{\tau}}^{00})^{BB}\end{bmatrix}^{-1}+\begin{bmatrix}\underline{\bar{\Delta}}^{AA} & \underline{\bar{\Delta}}^{AB}\\ \underline{\bar{\Delta}}^{BA} & \underline{\bar{\Delta}}^{BB}\end{bmatrix}-\begin{bmatrix}\underline{G}^{(\mathbf{k})}_{AA} & \underline{G}^{(\mathbf{k})}_{AB}\\ \underline{G}^{(\mathbf{k})}_{BA} & \underline{G}^{(\mathbf{k})}_{BB}\end{bmatrix}\right]^{-1}d^3k\ .\end{aligned} \tag{4.8}$$

In this equation the matrix renormalized interactor can be evaluated from the expression

$$\underset{\sim}{\Delta}=\underset{\sim}{t}^{-1}-(\underset{\sim}{\bar{\tau}}^{00})^{-1}\ , \tag{4.9}$$

as follows easily from the CPA condition, Eq. (4.7).

The matrix structure constants $\underset{\sim}{G}(\mathbf{k})$ entering Eq. (4.8) are the Fourier transforms (FT's) of $\underset{\sim}{G}$ and must be evaluated using the methods presented in I. For example, consider $\underline{G}_{AA}(\mathbf{k})$. Let the nth-neighbor distance between two A atoms in the material be given (on the average) by $\mathbf{R}_n{}^{AA}=\mathbf{R}^0+\rho_n{}^{AA}$, where $\mathbf{R}_n{}^0$ denotes the equilibrium separation and $\rho_n{}^{AA}$ are occupation-dependent deviations from this equilibrium value. The corresponding $\underline{G}^{\mathbf{R}_n}_{AA}$ can be obtained from the structure constants $\underset{\sim}{G}^{\mathbf{R}_n}$ by the methods discussed in I. If the $\rho_n{}^{AA}$ are nonzero for n extending to a maximum of Nth-nearest neighbors, usually $N\leq 2$, we can write $\underline{G}_{AA}(\mathbf{k})$ in the form

$$\underline{G}_{AA}(\mathbf{k})=\underline{G}(\mathbf{k})+\sum_{n=1}^{N}(\hat{\underline{G}}^{\mathbf{R}_n}_{AA}-\underline{G}^{\mathbf{R}_n})e^{i\mathbf{k}\cdot\mathbf{R}_n}\ , \tag{4.10}$$

where $\hat{\underline{G}}^{\mathbf{R}_n}_{AA}$ is a displaced-atom structure constant corresponding to the displacement $\rho_n{}^{AA}$. Similar expressions hold for all $G_{\alpha\beta}(\mathbf{k})$.

Once $\underline{\tau}^{\alpha\alpha}$ (omitting the superscripts 0) has been determined, the full Green function can be obtained through the expression

$$\begin{aligned}\langle G(E,r,r')\rangle&=\sum_{\alpha}\langle G^{\alpha\alpha}(E,r,r')\rangle\\&=\sum_{\alpha}C_\alpha\left[\sum_{L,L'}Z^{\alpha}_{L}(E,\mathbf{r})\tau^{\alpha\alpha}_{LL'}Z^{\alpha}_{L'}(E,\mathbf{r})\right.\\&\qquad\left.-\sum_{L}Z^{\alpha}_{L}(E,\mathbf{r})J^{\alpha}_{L}(E,\mathbf{r}')\right]\ ,\end{aligned} \tag{4.11}$$

where Z^α and J^α correspond to a MT of type α. The $\underline{\tau}^{\alpha\alpha}$ are given by the usual expression,

$$\underline{\tau}^{\alpha\alpha}=[(\underline{t}^{\alpha})^{-1}-\underline{\bar{\Delta}}^{\alpha\alpha}]^{-1}=(\underline{m}^{\alpha}-\underline{\bar{\Delta}}^{\alpha\alpha})^{-1}\ . \tag{4.12}$$

Note that even though the off-diagonal element of the single-site renormalized interactor $\underline{\bar{\Delta}}^{AB}$ is nonzero, corresponding in a sense to the nonphysical situation of a site being occupied by both A and B atoms, it never appears in a real-space expansion of $\underline{\tau}^{\alpha\alpha}$. Its main function is to guarantee the satisfaction of the self-consistency condition, Eq. (4.7).

There are several features of the formalism just presented which warrant special attention. First, note that each element $A^{ij}_{LL'}$ of any matrix entering the expression in Eqs. (4.3)–(4.12) is a 2×2 matrix in the space of the operators x and y. Physical quantities are obtained[25] as the sum

$$(A^{ij}_{LL'})=\sum_{\alpha,\beta}(A^{ij}_{LL'})^{\alpha\beta},\ \ \alpha,\beta=A\text{ or }B\ . \tag{4.13}$$

In particular, we have

$$\bar{\tau}^{00}_{LL'}=(\bar{\tau}^{00}_{LL'})^{AA}+(\bar{\tau}^{00}_{LL'})^{BB}\ , \tag{4.14}$$

with a corresponding expression for the Green function. Finally, in the limit of all $\underline{G}^{ij}_{\alpha\beta}$ becoming equal to $\underline{G}^{ij}$, the formalism of BEB reduces to the usual CPA.

The matrix single-site expressions of the KKR CPA with ODD can be readily generalized to clusters of impurity atoms. The method of this extension is essentially identical to that used[26] in the cluster generalization of the BEB formalism in connection with TB Hamiltonians, so the details will not be given here.

Throughout the discussion of this section it was assumed implicitly that the alloy can be described by a common Brillouin zone even though the atomic positions in the direct lattice are correlated with the type of atoms occupying these sites. This leads to no discrepancies, provided that the deviations of neighboring positions from the overall lattice constant of the alloy are small, a few percent. In this case the formalism is conceptually similar to that used in I to treat small displacements in pure systems that may arise from elevated temperatures. However, for large displacements the single-site approach of this section breaks down. It is still possible to take larger position correlations into account by considering the behavior of large clusters embedded in an averaged medium in the manner discussed in I. Such a procedure, carried to self-consistency, may yield accurate information about the behavior of alloy systems with strongly correlated atomic positions.

V. THE NON-SITE-DIAGONAL GREEN FUNCTION

The discussion in the preceding sections was exclusively concerned with the calculation of the site-diagonal element of the Green function in solid materials in various cases, characterized by the absence of full translational invariance. In many instances, however, a knowledge of the non-site-diagonal Green function is required. In particular, a generalization of the Bloch-density function[27] for periodic solids,

$$A^B(E;\mathbf{k})=\sum_{\alpha}\delta(E-E_\alpha(\mathbf{k}))\ , \tag{5.1}$$

to disordered materials is necessary for a discussion of transport properties in such materials. In Eq. (5.1) $\delta(x)$ is the Dirac δ function and α is a band index, with $E_\alpha(\mathbf{k})$ the energy eigenvalues obtained in a band-structure calculation.

The appropriate generalization of the Bloch-density function to substitutionally disordered alloys describable by MT Hamiltonians has been shown[28] to be the trace of the imaginary part of the lattice FT, $G(E;\mathbf{k},\mathbf{k})$, of the averaged Green function $\langle G\rangle$. The evaluation of $G(E;\mathbf{k},\mathbf{k})$ is a simple matter for systems characterized by TB Hamiltonians due to the fact that the eigenfunctions associated with an atom in the alloy are independent of the chemical nature of that atom. This condition is clearly not fulfilled in MT systems. By considering approximations consistent with the single-site KKR CPA, Faulkner and Stocks[28] derived an expression for the Bloch spectral density of disordered alloys of the form

$$A^B(E;\mathbf{k})=-\frac{1}{\pi}\mathrm{Im}G(E;\mathbf{k},\mathbf{k}) \;, \tag{5.2}$$

where $G(E;\mathbf{k},\mathbf{k})$ is the Fourier transform of $G(E;\mathbf{r},\mathbf{r}')$ obtained in the CPA.

The derivation of Eq. (5.2) given in Ref. 28 was complicated by the circumstance that the wave function associated with different scatterers in the alloy depends on the atomic species occupying the scattering centers. The formalism presented in the preceding section allows for such a dependence and leads naturally to the expression

$$\begin{aligned}\underline{G}(E;\mathbf{k},\mathbf{k})=&\left\langle\int\begin{bmatrix}x_i\underline{Z}^A/c_A & \underline{0}\\ \underline{0} & y_i\underline{Z}^B/c_B\end{bmatrix}\begin{bmatrix}\underline{\overline{\tau}}^{AA}(\mathbf{k}) & \underline{\overline{\tau}}^{AB}(\mathbf{k})\\ \underline{\overline{\tau}}^{BA}(\mathbf{k}) & \underline{\overline{\tau}}^{BB}(\mathbf{k})\end{bmatrix}\begin{bmatrix}x_i\underline{Z}^A/c_A & \underline{0}\\ \underline{0} & y_i\underline{Z}^A/c_B\end{bmatrix}d^3r\right\rangle\\ &+\int\begin{bmatrix}(1-c_A)\underline{Z}^A\underline{\overline{\tau}}^{AA}\underline{Z}^A & \underline{0}\\ \underline{0} & (1-c_B)\underline{Z}^B\underline{\overline{\tau}}^{BB}\underline{Z}^B\end{bmatrix}d^3r\\ =&\begin{bmatrix}\underline{\xi}^{AA}\underline{\tau}^{AA}(\mathbf{k}) & \underline{\xi}^{AB}\underline{\tau}^{AB}(\mathbf{k})\\ \underline{\xi}^{BA}\underline{\tau}^{BA}(\mathbf{k}) & \underline{\xi}^{BB}\underline{\tau}^{BB}(\mathbf{k})\end{bmatrix},\end{aligned} \tag{5.3}$$

for the Fourier transform of $\underline{G}$. In this expression, $\underline{\xi}^{\alpha\beta}\underline{\overline{\tau}}^{\alpha\beta}(\mathbf{k})$ is a symbolic quantity denoting a matrix defined through its elements

$$(\underline{\xi}^{\alpha\beta}\underline{\tau}^{\alpha\beta})_{LL'}=\int_{\mathrm{WS}}Z_L^\alpha(E,r)\overline{\tau}_{LL'}^{\alpha\beta}(\mathbf{k})Z_{L'}^\beta(E,\mathbf{r})d^3r \;. \tag{5.4}$$

The Bloch-density function can be obtained directly from Eqs. (5.4) and (4.13),

$$A^B(E;k)=-\frac{1}{\pi}\mathrm{Im}\,\mathrm{Tr}\sum_{\alpha,\beta}\underline{G}^{\alpha\beta}(E;\mathbf{k},\mathbf{k}),\quad \alpha,\beta=A\text{ or }B\;. \tag{5.5}$$

It is a matter of some straightforward, although lengthy, algebra to show that Eq. (5.5) is entirely equivalent to Eq. (5.2). Thus the results of this section are equivalent to those of Faulkner and Stocks.[28] However, the method of derivation used here is based directly on the KKR CPA and requires no further arguments than those underlying that approximation.

One advantage in writing the Bloch spectral density in the form of Eq. (5.3) is that it allows the species decomposition of the band structure of a substitutionally disordered alloy. In particular, the components $\underline{G}^{\alpha\alpha}(E;\mathbf{k},\mathbf{k})$ can be compared with the band structure of the pure α species, which may yield detailed information on the effects of disorder on each of the constituents of an alloy.

VI. NUMERICAL RESULTS

Of the formalisms presented in this paper, the easiest one to implement using existing technology is that of the preceding section. In addition, it is straightforward to compare the sum of the component Bloch spectral functions in Eq. (5.5) to the total Bloch density obtained in the ordinary version of the KKR CPA using the formalism of Faulkner and Stocks.[28]

Figures 1—3 depict the total and component Bloch

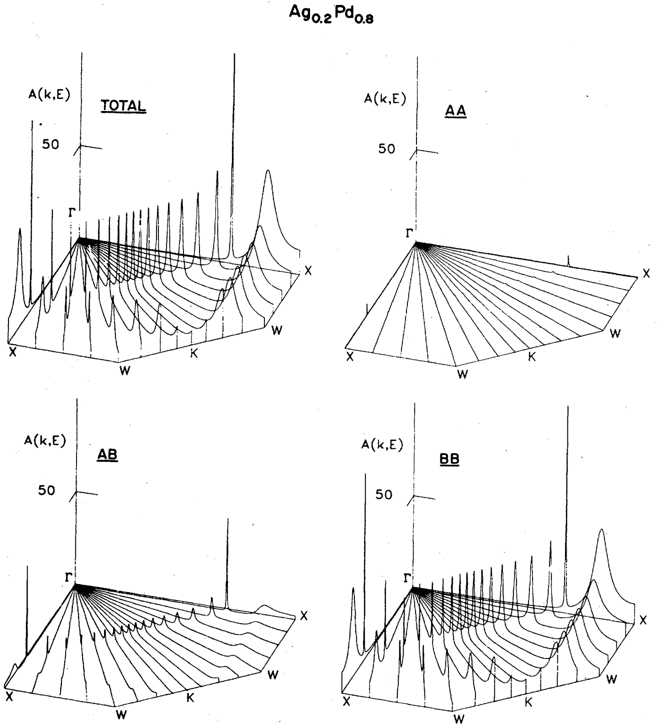

FIG. 1. Total and component (species resolved) Bloch spectral densities discussed in the text for a Ag_cPd_{1-c} alloy, with $c=0.2$.

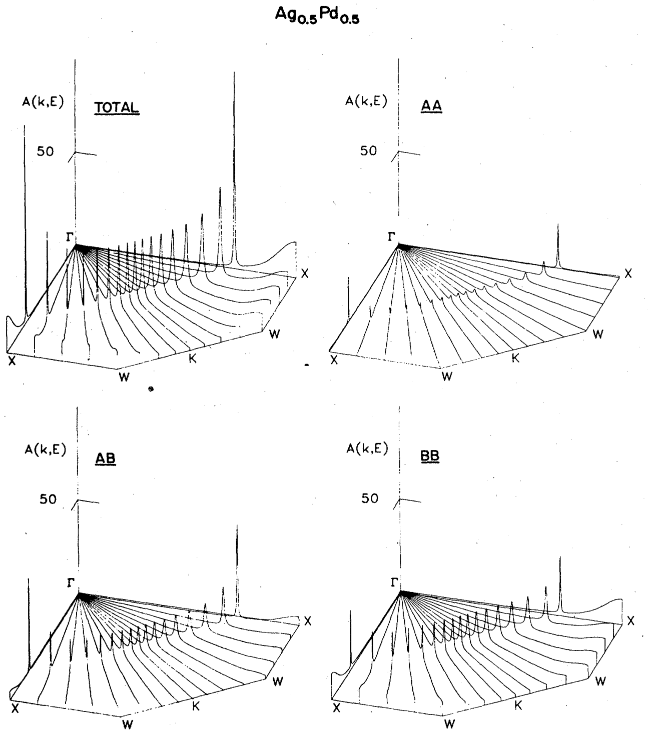

FIG. 2. Results analogous to those depicted in Fig. 1, but for $c = 0.5$.

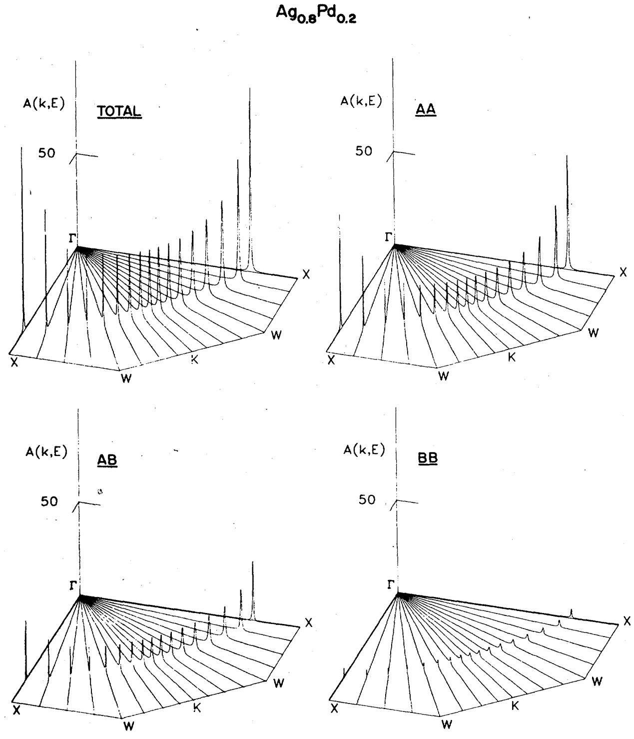

FIG. 3. Results analogous to those depicted in Fig. 1, but for $c = 0.8$.

spectral densities on the ΓXW plane of the Brillouin zone and at the Fermi energy for several Ag_cPd_{1-c} alloys, with $c = 0.2$, 0.5, and 0.8. In these figures, A denotes Ag and B the Pd atoms. The results for the total Bloch spectral functions were obtained in two ways, using the formalism of this section as well as that of Ref. 28. In each case the sum of the component densities, evaluated using Eq. (5.5), equals exactly the total Bloch density obtained in the KKR CPA.[28]

The component Bloch densities AA, AB, and BB shown in Figs. 1–3 can be interpreted as the component band structures associated with an alloy. In each case they show rather clearly the effect that alloying has on the band structure of the individual constituents. The results are consistent with those that can be obtained by calculating component densities of states, but are much more descriptive in character. As an example, we may examine the band structure of the Pd component in these three alloys, designated as the BB Bloch density in the figures. We see that in the $Ag_{0.2}Pd_{0.8}$ alloy the Pd Bloch density resembles closely that of pure Pd, clearly showing the presence of the s and d sheets of the Fermi surface. Increased concentration of Ag atoms gradually and consistently transforms the band structure to one resembling that of pure Ag, in the form of a practically spherical Fermi surface.

The species decomposition of the Bloch spectral density opens up an interesting prospect for examining the ordering effects that may be present in multicomponent alloys, such as ternary alloys. Although in a binary system the behavior of either component is tied in intimately with that of the other, in a multicomponent alloy each species may behave in a more independent fashion from the others. For example, in the so-called pseudobinary alloys one element forms an ordered sublattice while atoms of two other elements form a disordered substitutional alloy on a lattice interpenetrating the first one. One may perform a KKR CPA calculation as if the entire system formed a disordered substitutional alloy on a common lattice, and then use the component Bloch densities to examine the behavior of the different species separately. Such a calculation is currently being contemplated by us and any results obtained will be communicated in a future publication.

VII. CONCLUSIONS

In the set comprised by this paper and I we have presented a general and unified multiple-scattering approach which allows the treatment—on an equal footing—of a variety of problems associated with defects in solid materials. The formalism relies on the evaluation of the renormalized interactor for a MT potential, which represents the influence of the surrounding material on the scattering off an individual center. The present formulation encompasses many previous treatments of related problems and goes beyond them in several respects. The method is applicable to a great variety of physical problems of an embedding character, including substitutional defects in pure materials or concentrated substitutionally disordered alloys with any accompanying lattice distortion in the region surrounding the impurities, vacancies and interstitial defects in such materials, and the self-consistent treatment of (small) lattice relaxation caused by elevated temperatures or substitutional defects. Many of these problems were treated in detail in these two papers. Others, for example, lattice distortion due to defects in materials with a polyatomic basis, can be discussed within a straightforward generalization of the methods presented here. An extension of the nonrelativistic expressions of this work to include relativistics effects is also straightforward.

Many quantities of physical interest in solid materials depend strongly on the effects of local environment and the formalism presented in these papers was developed with the objective of determining such quantities. In addition to the immediate calculation of charge densities and DOS's, this approach can be used to obtain more remotely related quantities, such as the electron-phonon interaction in metals as well as metallic alloys, interatomic forces in solid materials, interatomic distances in alloys, magnetic moments, and others.

One cannot overemphasize the importance of carrying all alloy calculations to electronic self-consistency. This is an essential feature which guarantees that the Green function is continuous across the boundary of an atomic cell in the material. Self-consistent potentials for substitutionally disordered alloys have indeed been reported,[21] and were, in fact, used to obtain the numerical results of the preceding section. It is hoped that the day is drawing near when developments in supercomputer technology will alloy similar self-consistent calculations to be performed on the basis of some of the more general, and computationally more difficult, considerations presented in these papers.

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