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Lattice relaxation in high-temperature pure crystalline materials and substitutionally disordered alloys. I. Multiple-scattering formalism for displaced atoms

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A unified theory is presented which allows the calculation of the Green function for atoms in solid matter displaced from positions defined by a regular lattice. This theory is based (1) on the construction of Korringa-Kohn-Rostoker (KKR) type structure constants for displaced atoms, and (2) on the quantity termed "renormalized interactor," which arises from a reformulation of the well-known KKR theory. It is shown that the concept of the renormalized interactor can be extended to scattering from clusters and also yields the Green function for arbitrarily displaced atoms. The formalism can also be expressed in terms of the T matrix (scattering matrix) of single displaced atoms or of clusters of such atoms. The proposed method can be extended readily to the treatment of displaced atoms in substitutionally disordered alloys or to interstitial impurities in pure metals or alloys.

I. INTRODUCTION

Most band-structure calculations of solid materials, whether ordered or disordered, are based on the concept of a rigid, translationally invariant lattice. The lattice constants used in such calculations are usually found experimentally through x-ray diffraction, or are determined by other means. For example, in connection with concentrated substitutionally disordered alloys, the virtual-crystal approximation[1] (VCA) is often used, in which the lattice constant of a material is assumed to vary linearly with concentration, i.e., to obey Vegard's law.[2]

The concept of an underlying translationally invariant lattice has been a great aid to the theoretical understanding of solid materials. This concept allows the use of powerful mathematical tools, e.g., group theory and lattice Fourier transforms, which facilitate advances in both theory and computation. As a consequence of the assumption of a translationally invariant lattice, current theories for studying the properties of substitutionally disordered alloys are rapidly approaching the level of rigor of theories dealing with pure crystalline materials. In contrast, structurally (topologically) disordered materials, e.g., liquids and amorphous materials such as glasses, possess no regular lattice and, consequently, our theoretical understanding of such materials is comparatively low. The general mathematical treatment of structural disorder presents a formidable problem which, to date, remains largely unsolved.

The concept of an underlying translationally invariant lattice, however, is by no means rigorously valid on a microscopic scale in all cases of physical interest. It is well known that elevated temperatures, as well as the presence of impurities even at zero temperature, induce deviations in atomic positions away from the sites of a regular lattice, with temperature effects on the x-ray spectra being described largely in terms of the Debye-Waller factor. In the case of alloys, standard x-ray methods average the structure over distances large on the scale of a lattice constant and thus yield only averaged, or VCA-like values for interatomic distances. Deviations of nearest-neighbor (NN) as well as next-nearest-neighbor (NNN) distances from VCA values can be detected experimentally[3,4] by the use of x-ray-absorption fine-structure (EXAFS) methods, and are found to amount to from less than 1% in the case of some metallic alloys[3] to several percent in certain semiconducting alloys.[4] In the former case the deviations have been found[3] to conform to well-understood elastic models, while in some semiconducting alloys, such as the pseudobinary $\mathrm{Ga}_x\mathrm{Al}_{1-x}\mathrm{As}$, lattice distortions obey[5] Bragg's[6] classical principle of conservation of tetrahedral bonds.

Since many physical properties, e.g., magnetic moments, Dingle temperatures, and NMR and ESR frequencies, may be quite sensitive to interatomic-distance fluctuations, it is necessary to devise band-structure methods which take such fluctuations into account. It is the purpose of this and the following paper (labeled II) to show how lattice relaxation can be incorporated into the structure of multiple-scattering formalism in the rigid muffin-tin (MT) approximation. Specifically, by modifying the well-known Korringa-Kohn-Rostoker[7-10] (KKR), or Green-function, method for calculating the electronic structure of translationally invariant materials, we derive expressions for the Green function associated with a single atom or a cluster of atoms displaced in arbitrary directions from their equilibrium lattice positions. The amount of displacement is limited only by the requirement that the multiple-scattering formalism remains valid, i.e., that the displaced MT spheres do not overlap.

For the sake of clarity, it may be useful to keep in mind a simple prototype of the systems to which the formalism presented in this paper can be applied. Consider a substitutional impurity embedded in an otherwise pure host, say Ni in Cu. Due to differences between host atoms and the impurity, e.g., differences in size and potential, the impurity perturbs the potentials of the surrounding atoms and distorts the lattice in its vicinity. In metallic alloys[11,12] it is reasonable to assume that these perturbations are confined to a compact cluster of atoms which will be referred to as the impurity cluster. Beyond the cluster, the host atoms are assumed to be unperturbed and to occupy the sites of a translationally invariant lattice. We seek expressions for the Green functions associated with the various sites of the impurity cluster, from which one can calculate the effects produced by lattice relaxation. Clearly, the formalism for calculating such impurity-cluster Green functions can also be applied to the case of a finite number of substitutional impurities and their "could" of perturbed atoms.

Certain problems connected with impurities in a pure host, including lattice distortion, do not require the use of the multiple-scattering formalism as developed here. Lodder[13] and co-workers[14] have evaluated the transition rate due to impurity clusters between two Bloch states by using the wave functions associated with the host and the impurity potentials. Their approach is exact—within the MT approximation—and well suited for the calculation of such physical properties as Dingle temperatures, to which it has been applied. However, any method based on wave functions cannot be applied to many systems of physical interest, such as concentrated substitutionally disordered alloys. For such systems the wave function is not a useful concept since no Schrödinger equation corresponding to the averaged material can be constructed. On the other hand, the Green function retains its character and provides a powerful tool for investigating substitutionally disordered systems. In fact, it appears that a real-space formulation of multiple-scattering theory, along the lines proposed in this paper, may be the most convenient approach if lattice relaxation is to be taken properly into account.

Calculations based on MT potentials yield much more accurate results when the potentials are made self-consistent within the context of local-density theory. The use of self-consistent MT potentials is almost routine in connection with pure crystalline materials.[15] The formalism presented in this paper allows the calculation of the Green function and hence the charge density associated with displaced atoms, so that it can be used in the construction of self-consistent potentials through well-known means.

The remainder of the paper takes the following form. In Sec. II we summarize certain expansion formulas for spherical functions, i.e., products of Bessel, Neumann, and Hankel functions with spherical harmonics. In Sec. III some basic elements of the KKR method are reviewed and the concept of the defective-medium scattering-path operator is introduced. These concepts are used in Sec. IV to derive expressions for the scattering-path operator and hence the Green function associated with displaced atoms. An alternative but entirely equivalent formalism is presented in Sec. V. Finally, a discussion of the formalism and of its possible applications is given in Sec. VI.

II. TRANSLATION PROPERTIES OF SPHERICAL FUNCTIONS

Much of the ensuing formalism is based on a set of convenient formulas which allow the evaluation of spherical functions, $A_L(\mathbf{r})=a_l(kr)Y_L(\hat{\mathbf{r}})$, under translations (shifts) of the origin. Here, $a_l(kr)$ denotes one of the spherical Bessel, Neumann, or Hankel functions, $Y_L(\hat{\mathbf{r}})$ is a spherical harmonic or an appropriate real linear combination of spherical harmonics, $L\ [=(l,\mu)]$ is an angular-momentum index, and $k=\sqrt{E}$, where E is the energy parameter. It can easily be shown[16-18] that under a displacement of the origin the displaced functions $A(\mathbf{r}+\boldsymbol{\rho})$ can be obtained in terms of their undisplaced counterparts by means of the expressions

$$\begin{aligned} J_L(\mathbf{r}+\boldsymbol{\rho}) &= \sum_{L'} g_{LL'}(\boldsymbol{\rho}) J_{L'}(\mathbf{r}) \\ &= \sum_{L'} J_{L'}(\mathbf{r}) g_{L'L}(\boldsymbol{\rho}) \quad \text{for all } \mathbf{r} \text{ and } \boldsymbol{\rho} \end{aligned} \tag{2.1}$$

and

$$\begin{aligned} kH_L(\mathbf{r}+\boldsymbol{\rho}) &= \sum_{L'} G_{LL'}(\boldsymbol{\rho}) J_{L'}(-\mathbf{r}) \\ &= \sum_{L'} J_{L'}(-\mathbf{r}) G_{L'L}(\boldsymbol{\rho}) \quad \text{for } |\boldsymbol{\rho}| \geq |\mathbf{r}| \ , \end{aligned} \tag{2.2}$$

where $J_L(\mathbf{r})=j_l(kr)Y_L(\hat{\mathbf{r}})$ and $H_L(\mathbf{r})=h_l^+(kr)Y_L(\hat{\mathbf{r}})$ are the spherical Bessel and Hankel functions of the first kind, respectively. The Newmann functions and the Hankel functions of the second kind obey equations similar to Eq. (2.2). We now introduce a vector-matrix notation in terms of which Eqs. (2.1) and (2.2) can be expressed in the forms

$$|J(\mathbf{r}+\boldsymbol{\rho})\rangle = \underline{g}(\boldsymbol{\rho})\,|J(\mathbf{r})\rangle \tag{2.3}$$

and

$$|H(\mathbf{r}+\boldsymbol{\rho})\rangle = \underline{G}(\boldsymbol{\rho})\,|J(-\mathbf{r})\rangle, \quad |\boldsymbol{\rho}| \geq |\mathbf{r}| \tag{2.4}$$

with analogous expressions holding for the ket vectors $\langle J(\mathbf{r})|$ and $\langle H(\mathbf{r})|$. The expansion coefficients $g_{LL'}(\boldsymbol{\rho})$ and $G_{LL'}(\boldsymbol{\rho})$ are given explicitly by the relations

$$g_{LL'}(\boldsymbol{\rho}) = 4\pi \sum_{L''} i^{l-l'+l''} C(L,L',L'') J_{L''}(\boldsymbol{\rho}) \tag{2.5}$$

and

$$G_{LL'}(\boldsymbol{\rho}) = -4\pi k i \sum_{L''} i^{l-l'+l''} C(L,L',L'') H_{L''}(\boldsymbol{\rho}) \ , \tag{2.6}$$

where $C(L,L',L'')$ are Gaunt numbers. The coefficients $G_{LL'}(\mathbf{R})$ for $\mathbf{R}$ a direct-lattice vector are the real-space expressions for the familiar KKR structure constants. It follows easily from Eqs. (2.4) and (2.6) that the $\underline{G}(\mathbf{R})$ and $\underline{g}(\boldsymbol{\rho})$ satisfy the relations

$$\underline{G}(\mathbf{R}-\boldsymbol{\rho}) = \underline{G}(\mathbf{R})\underline{g}(\boldsymbol{\rho}) = \underline{g}(\boldsymbol{\rho})\underline{G}(\mathbf{R}), \quad |\mathbf{R}| \geq |\boldsymbol{\rho}| \ . \tag{2.7}$$

These expressions describe the behavior of the real-space structure constants under a shift of the origin and are fundamental to the following discussion.

III. ELEMENTS OF THE KKR METHOD

In this section we review certain aspects of the KKR formalism for crystal potentials bounded by nonoverlapping spheres which will be used in our subsequent development, and introduce the useful concept of the defective-medium scattering path operator.

The electronic Hamiltonian of a solid is taken to be of the form

$$H=-\nabla^2+V\ , \tag{3.1}$$

where the potential function V corresponds to a collection of nonoverlapping spherically bounded, but not necessarily spherically symmetric, potentials,

$$V(\mathbf{r})=\sum_n v(\mathbf{r}-\mathbf{R}_n)=\sum_n v(\mathbf{r}_n)\ . \tag{3.2}$$

Here, $v(\mathbf{r}-\mathbf{R}_n)$ is the potential at $\mathbf{r}$ due to an atom centered at site $\mathbf{R}_n$ and is assumed to vanish for $|\mathbf{r}-\mathbf{R}_n|$ greater than the MT-sphere radius S_n. The single-particle properties of the material are given in terms of the one-particle Green function

$$\begin{aligned}G(E,\mathbf{r},\mathbf{r}')=&\sum_{L,L'} Z_L^n(E,\mathbf{r}_n)\tau_{LL'}^{nm}(E)Z_{L'}^m(E,\mathbf{r}'_m)\\&-\sum_L Z_L^n(E,\mathbf{r}_n^<)J_L^n(E,\mathbf{r}_n'^>)\delta_{nm}\ ,\end{aligned} \tag{3.3}$$

where $\mathbf{r}^<$ $(\mathbf{r}'^>)$ denotes the smaller (qreater) of the vectors $\mathbf{r}$ and $\mathbf{r}'$. In this expression, $\mathbf{r}$ $(\mathbf{r}')$ is within the cell centered at $\mathbf{R}_n$ $(\mathbf{R}_m)$. The functions $Z_L^n(E,\mathbf{r}_n)$ and $J_L^n(E,\mathbf{r}_n)$ are solutions of the Schrödinger equation for a single MT potential $v(\mathbf{r}_n)$ corresponding to angular-momentum indices L. $Z_L^n(E,\mathbf{r}_n)$ is regular at the origin and joins smoothly to the function

$$Z_L^n(E,\mathbf{r}_n)=[j_l(kr)m_L^n-ikh_l^+(kr)]Y_L(\hat{\mathbf{r}}) \tag{3.4}$$

at $r_n=S_n$. The function $J_L^n(E,\mathbf{r}_n)$ joins smoothly to $j_l(kr_n)Y_L(\hat{\mathbf{r}}_n)$ at $r_n=S_n$ and is not regular at the origin, in general. The $\tau_{LL'}^{nm}(E)$ are the on-the-energy-shell matrix elements of the scattering-path operator defined by Gyorffy and Stott,[19] and are given by the inverse of the matrix $\underline{M}$,

$$\tau_{LL'}^{nm}=(\underline{M}^{-1})_{LL'}^{nm}\ , \tag{3.5}$$

where

$$M_{LL'}^{nm}=m_L^n\delta_{nm}-G_{LL'}^{nm}\ . \tag{3.6}$$

In Eqs. (3.4) and (3.6), m^n is the inverse of the site-diagonal t matrix, $m^n={t_n}^{-1}$, which for a spherically symmetric MT potential is diagonal in the angular-momentum indices, and $G_{LL'}^{nm}\equiv G_{LL'}(\mathbf{R}_{nm})$. Several quantities of physical interest, such as the density of states (DOS), can be obtained directly from the Green function in Eq. (3.3).

It is clear from Eq. (3.3) that in order to evaluate the site matrix elements of the Green function one must evaluate the corresponding element of the scattering-path operator. The matrix elements of this operator satisfy the equation of motion

$$\tau_{LL'}^{nm}=t_{LL'}^n\left[\delta_{nm}+\sum_{k\ (\neq n)}G_{LL''}^{nk}\tau_{L''L'}^{km}\right]\ , \tag{3.7}$$

or

$$\underline{\tau}^{nm}=\underline{t}^n\left[\delta_{nm}+\sum_{k\ (\neq n)}\underline{G}^{nk}\underline{\tau}^{km}\right]\ , \tag{3.8}$$

where the symbol $\underline{A}$ denotes a matrix in angular-momentum indices.

For a translationally invariant material, $\underline{m}^n$ is independent of n and Eq. (3.8) can be solved by means of Fourier transforms,

$$\begin{aligned}\underline{\tau}^{nm}&=\frac{1}{\Omega_{\mathrm{BZ}}}\int_{\mathrm{BZ}}[\underline{m}-\underline{G}(\mathbf{k})]^{-1}e^{i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_m)}d^3k\\&=\frac{1}{\Omega_{\mathrm{BZ}}}\int_{\mathrm{BZ}}\underline{\tau}(\mathbf{k})e^{i\mathbf{k}\cdot(\mathbf{R}_n-\mathbf{R}_m)}d^3k\ ,\end{aligned} \tag{3.9}$$

where Ω_{BZ} denotes the volume of the first Brillouin zone (BZ) of the material and $\underline{G}(\mathbf{k})$ are the well-known lattice structure constants of KKR. When Eq. (3.9) is used in Eq. (3.3), it yields the desired expression for the Green function.

Even though Eqs. (3.3) and (3.9) provide a complete description for constructing the Green function of a translationally invariant material described by MT potentials, they are not general enough to apply to disordered systems. To effect this generalization we consider a slightly different approach for evaluating Eq. (3.3). The starting point is the expression for $\underline{\tau}^{nn}$, which is obtained from Eq. (3.8). With the second term on the right-hand side of Eq. (3.8) treated formally as a perturbation, one can express τ^{nn} in the form

$$\underline{\tau}^{nn}=(\underline{m}^n-\underline{\Delta}^n)^{-1}\ , \tag{3.10}$$

where the renormalized interactor (RI), $\underline{\Delta}^n$, has the real-space expansion

$$\begin{aligned}\underline{\Delta}^n=&\sum_{k\ (\neq n)}\underline{G}^{nk}\underline{m}^k\left[\delta_{km}+\sum_{i\ (\neq n)}\underline{G}^{ki}\underline{m}^i\right.\\&\qquad\left.\times(\delta_{im}+\cdots)\right]\underline{G}^{mn}\\=&\sum_{\substack{k\ (\neq n),\\ m\ (\neq n)}}\underline{G}^{nk}\underline{\Gamma}_{km}^{(n)}\underline{G}^{mn}\ .\end{aligned} \tag{3.11}$$

Here, $\underline{\Gamma}_{km}^{(n)}$ is the defective-medium scattering-path operator corresponding to a material from which site n has been removed, or, equivalently, replaced by vacuum. The expansion in Eq. (3.11) represents the sum of all paths through the material that start and end on site n but that avoid state n at all intermediate steps. Note that Eq. (3.10) is valid generally and is not restricted to materials with translational invariance. For such materials, however, the quantity $\underline{\Delta}^n$ can be explicitly obtained from Eq. (3.10),

$$\underline{\Delta}^n=\underline{m}^n-(\underline{\tau}^{nn})^{-1}\ , \tag{3.12}$$

where $\underset{\sim}{\tau}^{nn}$ is obtained from Eq. (3.9). We now generalize the preceding discussion of single-site quantities to the corresponding quantities associated with a cluster of atoms.

To effect this generalization, consider a cluster C of atoms and introduce the corresponding cluster (matrix) quantities,

$$(\underset{\sim}{\tau}^{CC'})^{nm}_{LL'}=\tau^{nm}_{LL'},\quad n\in C,\ m\in C' \tag{3.13a}$$

$$(\underset{\sim}{G}^{CC'})^{nm}_{LL'}=G^{nm}_{LL'},\quad n\in C,\ m\in C' \tag{3.13b}$$

and

$$(\underset{\sim}{t}^{C})^{nm}_{LL'}=[(\underset{\sim}{m}^{C}+\underset{\sim}{G}^{CC})^{-1}]^{nm}_{LL'},\quad n,m\in C \tag{3.13c}$$

where $\underset{\sim}{A}$ denotes a matrix in both site and angular-momentum indices, and $\underset{\sim}{m}^{C}$ is a site-diagonal matrix, $(\underset{\sim}{m}^{C})^{nm}_{LL'}=m^{C}_{LL'}\delta_{nm}$. With these definitions, the equation of motion of the scattering-path operator, Eq. (3.8), can be written in the form

$$\underset{\sim}{\tau}^{CC'}=\underset{\sim}{t}^{C}\left[\delta_{CC'}+\sum_{C''\,(\neq C)}\underset{\sim}{G}^{CC''}\underset{\sim}{\tau}^{C''C'}\right], \tag{3.14}$$

which is formally identical to Eq. (3.8). This equation can be treated in a manner analogous to that of Eq. (3.8), which yields the cluster generalization of Eq. (3.12). In particular, the cluster-diagonal scattering-path operator can be written in the form

$$\underset{\sim}{\tau}^{C}=[(\underset{\sim}{t}^{C})^{-1}-\underset{\sim}{\Delta}^{C}]^{-1} \tag{3.15}$$

in terms of the cluster renormalized interactor $\underset{\sim}{\Delta}^{C}$. This last quantity has site-matrix elements

$$\begin{aligned}(\underset{\sim}{\Delta}^{C})^{nm}&=[(\underset{\sim}{t}^{C})^{-1}-(\underset{\sim}{\tau}^{C})^{-1}]^{nm}\\&=\sum_{\substack{k\notin C,\\ l\notin C}}\underset{\sim}{G}^{nk}\underset{\sim}{\Gamma}^{(C)}_{kl}\underset{\sim}{G}^{lm},\quad n,m\in C\end{aligned} \tag{3.16}$$

where $k\notin C$ implies that k may not assume a value corresponding to a site in C, and $\underset{\sim}{\Gamma}^{(C)}$ is the defective-medium cluster scattering-path operator for a material in which all sites in cluster C have been removed. We now turn to an explicit determination of the defective-medium scattering-path operators $\underset{\sim}{\Gamma}^{(C)}$.

The displacement of an atom, or more generally, the introduction of an impurity into an otherwise translationally invariant material, can be thought of as taking place in two steps. First, an atom, or a cluster of atoms for extended defects, of the host material is removed leaving a "hole" in the material. The defective material left behind can be described in terms of the quantities $\underset{\sim}{\Gamma}^{(C)}$. Second, an impurity is introduced to fill the vacancy left by the removed atom. The impurity can either be placed at positions defined by lattice sites or be displaced away from them.

To obtain $\underset{\sim}{\Gamma}^{(C)}$ in terms of the host quantities $\underset{\sim}{m}$ and $\underset{\sim}{G}$, we begin by introducing impurity potentials at the sites of the cluster. Upon denoting by $\delta\underset{\sim}{m}$ the scattering difference between host and impurity atoms, we can write

$$\underset{\sim}{\tau}^{(C)}=\underset{\sim}{\tau}+\underset{\sim}{\tau}\underset{\sim}{X}^{(C)}\underset{\sim}{\tau} \tag{3.17}$$

for the scattering-path operator of the material containing a cluster C of impurities. The "scattering matrix" $\underset{\sim}{X}^{(C)}$ has site-matrix elements confined to the space of the cluster C and has the form

$$\underset{\sim}{X}=\delta\underset{\sim}{m}(1-\underset{\sim}{\tau}\,\delta\underset{\sim}{m})^{-1}=(1-\delta\underset{\sim}{m}\,\underset{\sim}{\tau})^{-1}\delta\underset{\sim}{m}\ . \tag{3.18}$$

Taking cluster matrix elements in Eq. (3.17), we obtain the expression

$$\underset{\sim}{\tau}^{(C)}_{CC'}=\underset{\sim}{\tau}^{CC'}+\underset{\sim}{\tau}^{C0}\underset{\sim}{X}^{00}\underset{\sim}{\tau}^{0C'}\ , \tag{3.19}$$

where the impurity cluster has been designated by 0. An expression for $\underset{\sim}{\Gamma}^{(C)}$ is now obtained by taking the limit $\delta\underset{\sim}{m}\rightarrow\infty$, which yields the result

$$\underset{\sim}{\Gamma}^{(0)}_{C'C''}=\underset{\sim}{\tau}^{C'C''}-\underset{\sim}{\tau}^{C'0}(\underset{\sim}{\tau}^{00})^{-1}\underset{\sim}{\tau}^{0C''} \tag{3.20}$$

for the scattering-path operator of the defective medium. Note that $\underset{\sim}{\Gamma}^{(C)}$ has the desired property $\underset{\sim}{\Gamma}^{(0)}_{00}=\underset{\sim}{0}$.

IV. LATTICE RELAXATION

A. A single displaced atom

Figure 1(a) is a schematic diagram of the case under consideration. The atom at site 0 has been displaced by a vector $\boldsymbol{\rho}$ from its lattice position, while the atoms of the surrounding material have been held fixed at the sites of a lattice. We are interesting in obtaining an expression for $\hat{\underset{\sim}{\tau}}^{00}$, the site-diagonal element of the scattering-path operator associated with the displaced atom. From Eq. (3.10) we immediately have

$$\hat{\underset{\sim}{\tau}}^{00}=(\hat{\underset{\sim}{m}}^{0}-\hat{\underset{\sim}{\Delta}}^{0})^{-1}\ , \tag{4.1}$$

where $\underset{\sim}{m}^{0}$ and $\hat{\underset{\sim}{\Delta}}^{0}$ are the scattering matrix and the renormalized interactor (RI), respectively, associated with the displaced atom and are denoted, along with all displaced-atom quantities, by a circumflex. Note that $\underset{\sim}{m}^{0}$ can change upon displacement, a fact that can be incorporated into a self-consistent calculation of the potentials. That Eq. (4.1) is valid follows from the real-space derivation of Eq. (3.10), which contains no assumptions regarding the positions of the atoms in the material.

The RI $\hat{\underset{\sim}{\Delta}}^{0}$ is now given by an equation analogous to Eq. (3.11),

$$\hat{\underset{\sim}{\Delta}}^{0}=\sum_{\substack{k\,(\neq 0),\\ n\,(\neq 0)}}\hat{\underset{\sim}{G}}^{0k}\underset{\sim}{\Gamma}^{(0)}_{kn}\hat{\underset{\sim}{G}}^{n0}\ , \tag{4.2}$$

where $\hat{\underset{\sim}{G}}^{0k}$ is the displaced-atom structural Green function between the displaced atom at 0 and an undisplaced atom at $\mathbf{R}_k$, and is given explicitly in Eq. (2.7). The matrix elements $\underset{\sim}{\Gamma}^{(0)}_{kn}$ are not affected by the displacement, since sites k and n remain fixed on the lattice. Equation (4.2) can be directly evaluated in real space through the use of Eqs. (2.7) and (3.11),

$$\hat{\underset{\sim}{\Delta}}^{0}=\underset{\sim}{g}(\boldsymbol{\rho})\underset{\sim}{\Delta}^{0}\underset{\sim}{g}(-\boldsymbol{\rho})\ , \tag{4.3}$$

in terms of the undisplaced quantities $\underset{\sim}{\Delta}^{0}$. Finally, use of Eq. (3.3) now yields the displaced-atom Green function

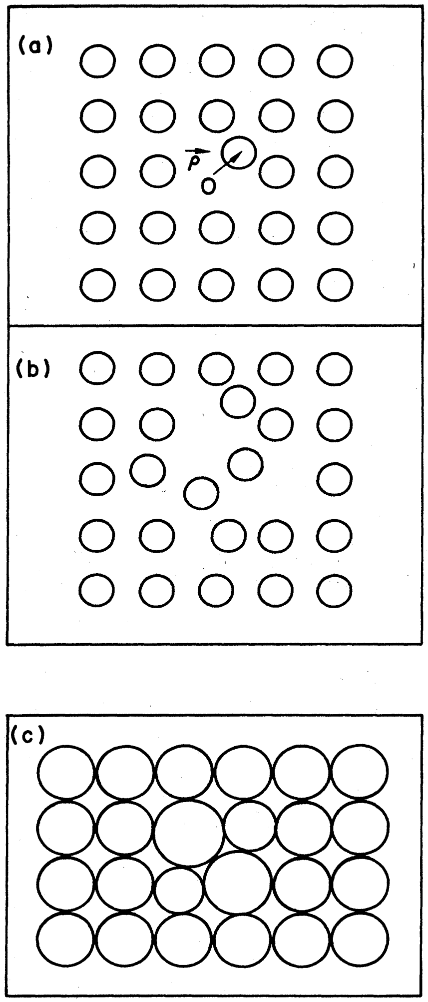

FIG. 1. Various configurations of displaced atoms surrounded by a material of atoms rigidly fixed at the sites of a lattice.

$$\hat{\mathbf{G}}(E,\mathbf{r},\mathbf{r}')=\sum_{L,L'}\hat{\mathbf{Z}}_L^0(E,\mathbf{r}_0)\hat{\tau}_{LL'}^{00}(E)\hat{\mathbf{Z}}_{L'}^0(E,\mathbf{r}_0') - \sum_L \hat{\mathbf{Z}}_L^0(E,\mathbf{r}_0)\hat{\mathbf{J}}_L^0(E,\mathbf{r}_0') , \tag{4.4}$$

where $\hat{\mathbf{Z}}_L^0$ and $\hat{\mathbf{J}}_L^0$ are the solutions to the Schrödinger equation for the displaced MT potential at 0, and are equal to Z_L^0 and J_L^0, respectively, when deviations between the undisplaced and displaced spherical potentials are neglected.

B. A cluster of displaced atoms

Figure 1(b) depicts a cluster C of atoms j each displaced from its equilibrium lattice position by a set of corresponding vectors $\boldsymbol{\rho}_j$ (not shown). We seek to evaluate the quantity $\hat{\underset{\sim}{\tau}}^{CC}$ associated with this cluster of displaced atoms. Through a straightforward generalization of the corresponding single-site quantities, we obtain

$$\hat{\underset{\sim}{\tau}}^{CC}=[(\hat{\underset{\sim}{t}}^{C})^{-1}-\hat{\underset{\sim}{\Delta}}^{C}]^{-1} , \tag{4.5}$$

where the definition

$$[\hat{\underset{\sim}{t}}^{C}]_{LL'}^{nm}=[(\hat{\underset{\sim}{m}}^{C}+\hat{\underset{\sim}{\mathbf{G}}}^{CC})^{-1}]_{LL'}^{nm}, \quad n,m\in C \tag{4.6}$$

has been used and where $\hat{\underset{\sim}{\mathbf{G}}}^{C}$ is the matrix of the intracluster displaced-atom structural Green function with matrix elements

$$(\hat{\underset{\sim}{\mathbf{G}}}^{CC})_{LL'}^{nm}=G_{LL'}(\mathbf{R}_m-\mathbf{R}_n+\boldsymbol{\rho}_{nm}) , \tag{4.7}$$

$\boldsymbol{\rho}_{nm}$ being the difference in displacement between the atoms at $\mathbf{R}_n$ and $\mathbf{R}_m$, $\boldsymbol{\rho}_{nm}=\boldsymbol{\rho}_m-\boldsymbol{\rho}_n$. The site-matrix elements of the renormalized interactor $\hat{\underset{\sim}{\Delta}}^{C}$ are given by the expression

$$\hat{\underline{\Delta}}_{ij}^{C}=\sum_{\substack{k\notin C ,\\ n\notin C}}\hat{\underline{\mathbf{G}}}^{ik}\underline{\Gamma}_{kn}^{(C)}\hat{\underline{\mathbf{G}}}^{nj}, \quad i,j\in C \tag{4.8}$$

which is an immediate generalization of the undisplaced-atom expression, Eq. (3.16).

Equation (4.8) can be evaluated through a straightforward generalization of Eq. (4.4),

$$(\hat{\underline{\Delta}}_{ij}^{C})_{LL'}=\sum_{L_1,L_2} g_{LL_1}(\boldsymbol{\rho}_i)\Delta_{L_1L_2}^{C}g_{L_2L'}(-\boldsymbol{\rho}_j) , \tag{4.9}$$

or, in matrix notation,

$$(\hat{\underset{\sim}{\Delta}}^{C})_{ij}=\underline{g}(\boldsymbol{\rho}_i)\underline{\Delta}^{C}\underline{g}(-\boldsymbol{\rho}_j) . \tag{4.10}$$

Here, $\underline{\Delta}^{C}$ is the RI for the undisplaced atoms in C and is given by Eq. (3.16). (An expression for $\hat{\underset{\sim}{\Delta}}^{C}$ in $\mathbf{k}$ space can also be constructed, but it is not particularly convenient for computational purposes.)

V. SCATTERING-MATRIX FORMALISM

In this section we consider an approach to the evaluation of the displaced-atom Green function which is based on the scattering matrix of displaced MT potentials and uses the structural Green functions for the *undistorted* underlying lattice. As we will show, this approach is equivalent to the RI formalism presented thus far, provided that the various expansions remain valid, i.e., the displaced MT spheres do not overlap and that all angular momentum summations are carried to convergence. The transition from the RI to the t-matrix approach, and vice versa, involves straightforward matrix transformations of the multiple-scattering expansion for the Green function associated with an assembly of scatterers. The following considerations are therefore justified when a complete basis set as indexed by L is used in the calculation.

The site-diagonal element of the scattering-path operator, $\underset{\sim}{\tau}^{00}$, referred to the site $\mathbf{R}_0$ but with the MT sphere displaced to the position $\mathbf{R}_0+\boldsymbol{\rho}_0$, is given by the expression

$$\underset{\sim}{\tau}^{00}=(\underline{m}'-\underline{\Delta})^{-1} , \tag{5.1}$$

where $\underline{\Delta}$ is the single-site RI associated with an undisplaced center at $\mathbf{R}_0$. The matrix $\underline{m}'$ is the inverse of the scattering matrix

$$t'_{LL'}=\sum_{L_1,L_2} g_{LL_1}(-\boldsymbol{\rho}_0)\hat{t}_{l_1} g_{L_1L_2}(\boldsymbol{\rho}_0) , \tag{5.2}$$

or

$$\underline{t}'=\underline{g}(-\boldsymbol{\rho}_0)\underline{\hat{t}}\,\underline{g}(\boldsymbol{\rho}_0) , \tag{5.3}$$

associated with the displaced atom. Equation (5.2) follows easily from Eq. (2.3) and the usual definition of the t matrix in the L representation. Using Eqs. (4.11) and (5.3) we can write Eq. (5.1) in the form

$$\underline{\tau}^{00}=\underline{g}(\boldsymbol{\rho}_0)(\underline{\hat{m}}-\underline{\hat{\Delta}})^{-1}\underline{g}(-\boldsymbol{\rho}_0)=\underline{g}(\boldsymbol{\rho}_0)\underline{\hat{\tau}}^{00}\underline{g}(-\boldsymbol{\rho}_0) . \tag{5.4}$$

The quantity $\underline{\tau}^{00}$ is that occurring in Eq. (3.5); it is the scattering-path operator centered at the displaced atom at $\mathbf{R}_0+\boldsymbol{\rho}_0$. The generalization of these results to clusters of displaced atoms is straightforward. Thus, a RI formalism (based on $\hat{\mathbf{G}}$) leads to a scattering-path operator $\underline{\hat{\tau}}^{00}$ and a corresponding Green function $G(\mathbf{r},\mathbf{r}')$, with $\mathbf{r}$ and $\mathbf{r}'$ measured from the instantaneous displaced position of the MT center, located at $\mathbf{R}_0+\boldsymbol{\rho}_0$. To obtain the corresponding expression centered at $\mathbf{R}_0$, a final shift is necessary through the translation operator $\underline{g}(\boldsymbol{\rho})$.

VI. DISCUSSION AND CONCLUSIONS

In this paper we have presented two equivalent formalisms which allow the calculation of the Green function associated with atoms in a material that have been displaced from the positions defined by a regular lattice. Our aim was to develop a unified approach for calculating the effects of lattice relaxation that may occur in pure materials at nonzero temperature, or in substitutionally disordered alloys. For the sake of clarity, we discussed explicitly only the case of displaced atoms in a pure host. In paper II we show how this formalism can be generalized to substitutionally disordered alloys, as well as to a self-consistent treatment of some types of structural disorder. Either of the two formalisms presented here can be used in conjunction with the local-density approximation to construct charge self-consistent potentials for displaced atoms.

As is discussed in more detail in II, this formalism has a rather wide range of applications. In addition to the case of the displaced atom (or atoms) in a pure host, the following cases can be treated.

(i) A cluster consisting of substitutional impurities, displaced or not, embedded in a pure host lattice, and the host atoms whose potentials and positions are affected by the impurities.

(ii) Displaced atoms in concentrated, random substitutionally disordered alloys.

(iii) Impurities, displaced or not, embedded in a concentrated substitutional alloy, i.e., atoms of type X embedded in an A_cB_{1-c} alloy.

(iv) Correlated displacements in substitutionally disordered alloys.

In presenting our discussion in terms of MT potentials, we have chosen not to discuss explicitly Hamiltonians of a tight-binding (TB) character. This choice was made because the treatment of TB Hamiltonians, even with lattice relaxation included, is much simpler mathematically and computationally than that of MT Hamiltonians and can be considered to be well known. In fact, all that is necessary in order to incorporate lattice distortion into band-structure calculations based on TB potentials is a redefinition of the various site-matrix elements of the Hamiltonian. However, the determination of such matrix elements is very often basis dependent and therefore of questionable accuracy, even for ordered translationally invariant systems. Thus, even though the TB formalism is conceptually and computationally much simpler than that based on MT potentials, it does not provide, in general, a rigorous method for band-structure calculations. On the other hand, certain techniques originally developed in relation to TB Hamiltonians, particularly that of the renormalized interactor, will be useful in some aspects of incorporating lattice relaxation into the multiple-scattering formalism, especially in the self-consistent treatment of correlated atomic displacements in substitutional alloys which is presented in II.

In electronic band-structure calculations based on spherical MT potentials, it is customary to consider the bounding MT spheres as large as possible, adjacent ones often being in contact. Such large spheres minimize the interstitial region in which the crystal potential is treated much more approximately than it is inside the MT spheres. For many real systems, e.g., transition metals and their alloys, calculations based on MT potentials yield reliable and physically accurate results. Now, for atom displacement to be possible within a MT formalism, the radii of the MT spheres must be either smaller than half the NN distance, or the displaced atoms must be described by spheres of varying radii. These alternatives are depicted schematically in Fig. 1. Note that in Fig. 1(c) the centers of the displaced spheres do not coincide with the sites of the lattice. Thus, the MT approximation becomes somewhat more restrictive (smaller radii for some atoms) when used to discuss lattice relaxation than it does when rigid lattices are considered. However, since experience indicates that calculated quantities are not very sensitive to small changes in the MT radius, whereas atomic displacements can produce[14] significant differences in such quantities, the restriction on the MT radii can be expected to have effects smaller than those caused by the displacement itself. A more important consideration is the loss of symmetry which accompanies atomic displacements. As a consequence, the usual approach of spherically averaging the charge inside the MT sphere may lead to serious discrepancies between calculated quantities and experimental results. The formalism presented is valid for general (not spherically averaged) MT potentials with a concomitant increase in computational effort in applying it.

The second aspect of this work, namely the treatment of only finite clusters of displaced atoms, is based on two precepts. First, as was already mentioned, the treatment of general topological disorder is very difficult. Second, there is growing computational evidence[11] as well as theoretical justifcation[12] that the single-particle properties of a disordered material are primarily of a local character. For example, charge-transfer effects in metals extend only to finite distances away from an impurity. Thus, it is sufficient for most purposes to take into account fluctuations, either chemical or topological, that are confined within a compact cluster of atoms embedded in a translationally invariant medium. This medium must be chosen in some optimal way so as to guarantee the preservation of several mathematical and physical properties. In the case of displaced atoms in a pure crystalline host, the obvious choice of the embeddeding medium is the host material. For substitutionally disordered alloys the optimal choice of embedding medium is obtained in a self-consistent way which is described in detail in paper II. In either case it is necessary to calculate the interaction of a cluster of impurity atoms—such as displaced atoms forming a "liquid bubble"—with the surrounding translationally invariant material. However, even though for arbitrary displacements the formalism is applicable to compact clusters of impurities, for small displacements it is possible to treat lattice relaxation throughout the material in a self-consistent way, as is discussed in detail in paper II.

The two formalisms presented are based on the embedded-cluster method (ECM), which has been presented previously[20–24] in connection with substitutionally disordered alloys,[20–22] or with clusters of extended substitutional defects[23,24] embedded in pure, translationally invariant materials. In none of these works was lattice relaxation considered. Lattice relaxation can be taken into account within the ECM by exploiting the properties of the interaction of the electrons on a single impurity with the surrounding material. In particular, the method relies on expressing the structural Green function for a displaced atom in terms of the structure constants of the rigid lattice. This method is exact, within the MT approximation, and is applicable to arbitrary displacements subject to the conditions already stated.

The second formalism makes use of expansions of the t matrix associated with a single MT potential about a point other than the MT center. As shown in Sec. V, this formalism is equivalent to the first, and both are of comparable computational difficulty.

Finally, a word regarding the convergence properties of the various displaced quantities introduced in this paper is in order. Expansions of the type displayed in Eqs. (2.7) represent Taylor-series expansions and, strictly speaking, require the use of infinite sums. Failure to achieve convergence in such expansions can affect the precision of any band-structure calculation. Such failure can have particularly serious effects on calculations aiming at self-consistent potentials. For small (infinitesimal) displacements one can expect the various sums to converge sufficiently rapidly to provide a viable computational method for the calculation of the effects of lattice relaxation. In addition, the truncation of L values must be done with care, as it may have different effects depending on the stage in which it is performed. In any case the use of supercomputers can be expected to facilitate implementation of these formal results to atomic displacements of arbitrary magnitude.

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