PHYSICAL REVIEW B VOLUME 50, NUMBER 11 15 SEPTEMBER 1994-I

Relativistic electronic structure of random alloys and their surfaces by linear band-structure methods

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(Received 21 October 1993; revised manuscript received 4 March 1994)

An efficient Green's-function method is developed to calculate electronic and ground-state properties of heavy-elements containing random alloys and their surfaces. Based on the local-density approximation, the all-electron fully relativistic linear-muffin-tin-orbital method in the tight-binding representation is used to describe disorder within the coherent-potential approximation and the semi-infinite geometry of surfaces. As a first application the electronic and ground-state properties of a random fcc-$Cu_{75}Au_{25}$ alloy and its (001) surface are evaluated.

I. INTRODUCTION

Metallic alloys and their surfaces, particularly those containing heavy transition- and noble-metal elements, exhibit a number of properties interesting from both the physical and technological point of view. The phenomena of surface ordering and disordering,[1] of the face-dependent segregation in NiPt alloys,[2] or the use of platinum and other heavy transition metals and their alloys in heterogeneous catalysis are just few examples. The interrelation between electronic and structural properties is a key to a microscopic understanding of physical processes in the bulk and at the surface. Consequently, the use of efficient relativistic schemes to determine the electronic structure and related ground-state properties of alloys and their surfaces is of considerable interest. For such studies, *ab initio* methods based on the local-density approximation (LDA) are of particular importance since they also yield the parameters for an alloy Ising model, which in turn can be used in statistical mechanics studies of bulk and surface phase diagrams,[3] or surface segregation and ordering phenomena.[4]

Several *ab initio* methods for both ordered and disordered alloys and their surfaces were developed recently. They fall into two categories: (i) methods using slab or supercell geometry to simulate random alloys[5] or ordered surfaces,[6,7] and (ii) Green's-function methods[8–15] which take properly into account the semi-infinite geometry and perform configurational averaging for random systems in a systematic way. Methods based on slab or supercell geometry are of limited use for random surfaces or bulk alloys with complex lattice structures because they require an excessive number of atoms in the elementary cell.

For random bulk alloys charge self-consistent techniques based on the coherent potential approximation (CPA) and the LDA were developed within the Korringa-Kohn-Rostoker (KKR-CPA) method[8,9] and the linear muffin-tin orbital (LMTO-CPA) approach.[10] Recently, a fully relativistic self-consistent study of the electronic structure of random bulk alloys was performed within the KKR-CPA approach.[11]

The situation is much less satisfactory for surfaces of random alloys. A self-consistent Green's-function theory of ideal[12] as well as disordered[13–15] surfaces was up to now only developed for the nonrelativistic (scalar-relativistic) case. The only presently available fully relativistic approach is the layer KKR (LKKR) method for pure systems,[16] which, however, is non-self-consistent. At present, no relativistic theory is available for random surfaces.

The main aim of this paper is to develop a fully relativistic self-consistent Green's-function method that describes both ordered and disordered alloys and particularly their surfaces from a unified point of view. The main features of this method can be summarized as follows: (i) application of the all-electron fully relativistic linear-muffin-tin-orbital method in the tight-binding representation (R-TB-LMTO); (ii) application of the local-density approximation; (iii) description of the semi-infinite geometry of the system using the surface Green's function (SGF) formalism; (iv) use of the coherent potential approximation (CPA) extended to inhomogeneous systems; (v) simulation of the vacuum region by empty spheres which represent the continuation of the semi-infinite solid to infinity on the vacuum side; (vi) description of the component potentials within the atomic sphere approximation (ASA); and (vii) inclusion of monopole and dipole terms of the charge density for the calculation of the Madelung potential in the surface region.

The feasibility of the present approach is illustrated by an evaluation of the electronic and ground-state properties of a typical alloy containing a heavy metal element, namely, the fcc-based $Cu_{75}Au_{25}$ random alloy and its (001) surface. The corresponding results for pure fcc-Cu

0163-1829/94/50(11)/7903(12)/$06.00

and Au crystals and their fcc(001) surfaces are as well presented.

II. FORMALISM

In this section we summarize the basic ingredients of our approach. The potential is assumed to be a superposition of atomic sphere (AS) potentials of radius $s_{\mathbf{R}}$ centered at site $\mathbf{R}$ such that $\sum_{\mathbf{R}}(4/3)\pi s_{\mathbf{R}}^3 = N(4/3)\pi w^3$, where N is the number of spheres, and w is the averaged Wigner-Seitz radius. We shall use atomic Rydberg units, so that $\hbar = 1$, $m = 1/2$, and $c = 274.071\,979$.

A. Relativistic LMTO method

The relativistic LMTO method is a straightforward generalization of the nonrelativistic LMTO method.[17] It has been developed by Godreche,[18] Nemoshkalenko *et al.*,[19] and Christensen.[20] The advantage of the present approach is the unified treatment of both bulk alloys and their surfaces. This is achieved by using the same starting Hamiltonian in both cases, which in the so-called orthogonal MTO representation γ is of the form[21–23]

$$\begin{aligned} H^{\gamma}_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'} &= C_{\mathbf{R}\Lambda}\delta_{\mathbf{R}\mathbf{R}'}\,\delta_{\Lambda\Lambda'} \\ &\quad +\Delta^{1/2}_{\mathbf{R}\Lambda}\,[\,S^0\,(\,1-\gamma\,S^0)^{-1}\,]_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}\,\Delta^{1/2}_{\mathbf{R}'\Lambda'}\,, \\ O^{\gamma}_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'} &= \delta_{\mathbf{R}\mathbf{R}'}\,\delta_{\Lambda\Lambda'}\,. \end{aligned} \qquad (1)$$

In Eq. (1), H^{γ} and O^{γ}, is the Hamiltonian and the overlap matrix, respectively, $\mathbf{R}$ and $\mathbf{R}'$ are site indices, and Λ, Λ' refer to relativistic quantum numbers $\Lambda = (\kappa\mu)$ (see Appendix). The geometry of the problem enters the Hamiltonian via the structure constant matrix S^0 of elements $S^0_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}$, which can be obtained from their nonrelativistic counterparts, $S^{0,\,\mathrm{nr}}_{\mathbf{R}L,\mathbf{R}'L'}$, by means of a transformation.[18] Here we shall consider the simplest case, namely, an ideal periodic lattice randomly occupied by atoms A and B. We thus neglect lattice relaxations in the bulk, which can occur due to the different size of the alloy constituents, as well as possible inward or outward shifts of the surface layers. We can then use the ideal bulk structure constant matrix S^0 for both the bulk and the surface problem.

The potential parameters $X_{\mathbf{R}\Lambda}$ ($X = C, \Delta$, and γ) are obtained from the Dirac equation for a spherically symmetric potential centered at site $\mathbf{R}$ and confined to the atomic sphere of radius $s_{\mathbf{R}}$ (see Appendix). They can be combined into the potential function matrix

$$\begin{aligned} P^0_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}(E) &= P^0_{\mathbf{R}\Lambda}(E)\,\delta_{\mathbf{R}\mathbf{R}'}\,\delta_{\Lambda\Lambda'} \equiv P^0_{\mathbf{R}\kappa}(E)\,\delta_{\mathbf{R}\mathbf{R}'}\,\delta_{\Lambda\Lambda'}\,, \\ P^0_{\mathbf{R}\kappa}(E) &= (E - C_{\mathbf{R}\kappa})/\,[\,\Delta_{\mathbf{R}\kappa} + \gamma_{\mathbf{R}\kappa}\,(E - C_{\mathbf{R}\kappa})\,]\,, \end{aligned} \qquad (2)$$

which describes the scattering properties of the individual constituents.

The LMTO method can be formulated in various representations[21] characterized by a diagonal screening matrix α with elements $\alpha_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'} = \delta_{\mathbf{R}\mathbf{R}'}\,\delta_{\Lambda\Lambda'}\,\alpha_{\mathbf{R}\Lambda}$, $\alpha_{\mathbf{R}\Lambda} \equiv \alpha_{\mathbf{R}\kappa}$. When switching from the canonical representation (superscript 0) to the corresponding representation α, the potential function matrix is transformed according to

$$\begin{aligned} P^{\alpha}_{\mathbf{R}\kappa}(z) &= P^0_{\mathbf{R}\kappa}(z)\,[\,1 - \alpha_{\mathbf{R}\kappa}\,P^0_{\mathbf{R}\kappa}(z)\,]^{-1} \\ &= (z - C_{\mathbf{R}\kappa})\,[\,\Delta_{\mathbf{R}\kappa} + (\gamma_{\mathbf{R}\kappa} - \alpha_{\mathbf{R}\kappa})\,(z - C_{\mathbf{R}\kappa})\,]^{-1}\,, \end{aligned} \qquad (3)$$

and similarly the structure constants transform by

$$S^{\alpha}_{\mathbf{R}\Lambda,\,\mathbf{R}'\Lambda'} = [S^0\,(\,1 - \alpha\,S^0)^{-1}]_{\mathbf{R}\Lambda,\,\mathbf{R}'\Lambda'}\,. \qquad (4)$$

The canonical structure constant matrix S^0 is long-ranged because for large $|\mathbf{R} - \mathbf{R}'|$ its elements behave like $|\mathbf{R} - \mathbf{R}'|^{-l-l'-1}$. On the other hand, by a proper choice of the screening matrix α one can achieve a fast decay of S^{α} in real space. It has been found[22] that for close-packed lattices, the so-called tight-binding muffin-tin-orbital (TB-MTO) representation β, which is site independent, but l dependent, and specified by $\beta_s = 0.3485, \beta_p = 0.0530$, and $\beta_d = 0.0107$ ($\beta_l = 0$ for $l > 2$) gives the fastest and an essentially monotonic decay in real space. In fact, S^{β} vanishes beyond the second coordination shell for close-packed lattices.

In particular, the orthogonality of the basis set in the γ-MTO representation allows one to express all the relevant quantities in a simple and physically transparent way. The corresponding Green's function (GF) is given then by

$$G^{\gamma}_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}(z) = [\,(\,z - H^{\gamma}\,)^{-1}\,]_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}\,. \qquad (5)$$

In the following the superscript γ is omitted. Using the relation between the GF's in different MTO representations,[22] one can express $G(z)$ in terms of a general MTO representation α as

$$\begin{aligned} G_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}(z) &= \lambda^{\alpha}_{\mathbf{R}\Lambda}(z)\,\delta_{\mathbf{R}\mathbf{R}'}\,\delta_{\Lambda\Lambda'} \\ &\quad +\mu^{\alpha}_{\mathbf{R}\Lambda}(z)\,g^{\alpha}_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}(z)\,\mu^{\alpha}_{\mathbf{R}'\Lambda'}(z)\,, \end{aligned} \qquad (6)$$

where

$$g^{\alpha}_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}(z) = [\,(\,P^{\alpha}(z) - S^{\alpha})^{-1}\,]_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'} \qquad (7)$$

is the so-called auxiliary or nonphysical Green's function, and $\lambda^{\alpha}_{\mathbf{R}\Lambda}(z)$, $\mu^{\alpha}_{\mathbf{R}\Lambda}(z)$ are matrices diagonal in $\mathbf{R}$ and Λ, which in turn can be expressed in terms of the potential parameters.[10,21,22]

B. Configurational averaging

In general the configurational averaging of the Green's function for an inhomogeneous disordered alloy is performed within the CPA. The site-diagonal potential parameters $X_{\mathbf{R}\Lambda}$, $X = C, \Delta$, and γ, randomly take on two values, $X^A_{\mathbf{R}\Lambda}$ with the probability $c^A_{\mathbf{R}}$, and $X^B_{\mathbf{R}\Lambda}$ with the probability $c^B_{\mathbf{R}} = 1 - c^A_{\mathbf{R}}$, whereby the site dependency of the potential parameters is a consequence of the inhomogeneity of the system. Due to the randomness in $\Delta_{\mathbf{R}}$ and $\gamma_{\mathbf{R}}$, the Hamiltonian (1) exhibits a complicated off-diagonal randomness. Consequently, the CPA,[24] which can treat only site-diagonal randomness, cannot be applied to $G(z)$ in the form given by Eq. (5). The remedy[10,25] is to express $G(z)$ in the form of Eqs. (6, 7) with a nonrandom screening matrix α. A possible choice for the corresponding representation α may be either the tight binding ($\alpha = \beta$), or the canonical ($\alpha = 0$) representation, but also any other nonrandom representation can be used. The structure constants S^α are then nonrandom, and the only random quantities that enter the expression for $G(z)$, namely, $P^\alpha(z)$, $\lambda^\alpha(z)$, and $\mu^\alpha(z)$, are all site-diagonal quantities.

The on-site element of the configurationally averaged auxiliary Green's function $\langle g^\alpha(z) \rangle$ is of primary importance for both the CPA equations and for the charge self-consistency. By definition,

$$\begin{aligned}\Phi^\alpha_{\mathbf{R},\,\Lambda\Lambda'}(z) &= \langle g^\alpha(z) \rangle_{\mathbf{R}\Lambda,\mathbf{R}\Lambda'} \\ &= [\,(\mathcal{P}^\alpha(z) - S^\alpha)^{-1}]_{\mathbf{R}\Lambda,\mathbf{R}\Lambda'}\,. \end{aligned} \tag{8}$$

In (8), $\mathcal{P}^\alpha(z)$ is the coherent potential function with elements $\mathcal{P}^\alpha_{\mathbf{R},\,\Lambda\Lambda'}(z)$. The scattering of electrons by individual atoms is then described by the following site diagonal t matrices:

$$\begin{aligned}\tau^{\alpha Q}_{\mathbf{R},\,\Lambda\Lambda'}(z) = (&[P^{\alpha Q}_{\mathbf{R}}(z) - \mathcal{P}^\alpha_{\mathbf{R}}(z)] \\ &\times\{1 + \Phi^\alpha_{\mathbf{R}}(z)\,[P^{\alpha Q}_{\mathbf{R}}(z) - \mathcal{P}^\alpha_{\mathbf{R}}(z)]\}^{-1})_{\Lambda\Lambda'} \end{aligned}$$

$$(Q = A, B)\,, \quad (9)$$

such that within the single-site approximation for the CPA

$$\sum_{Q=A,B} c^Q_{\mathbf{R}}\, \tau^{\alpha Q}_{\mathbf{R},\,\Lambda\Lambda'}(z) = 0\,. \tag{10}$$

Since (10) has to be solved for all the lattice sites $\mathbf{R}$, and since $\Phi^\alpha_{\mathbf{R}}(z)$ depends on all $\mathcal{P}^\alpha_{\mathbf{R}}(z)$, (10) represents a set of mutually coupled CPA equations for an inhomogeneous effective medium characterized by the coherent potential functions $\mathcal{P}^\alpha_{\mathbf{R}}(z)$.

Finally, the conditionally averaged on-site element of the physical Green's function[10]

$$\begin{aligned}\langle G(z)\rangle^Q_{\mathbf{R}\Lambda,\,\mathbf{R}\Lambda'} = {}&\lambda(z)^{\alpha Q}_{\mathbf{R}\Lambda}\delta_{\Lambda\Lambda'} \\ &+(\dot{P}^{\alpha Q}_{\mathbf{R}\Lambda}(z))^{1/2}\,\Phi^\alpha_{\mathbf{R}}\,(z)\,\{1 + \Phi^\alpha_{\mathbf{R}}(z) \\ &\times[P^{\alpha Q}_{\mathbf{R}}(z) - \mathcal{P}^\alpha_{\mathbf{R}}(z)]^{-1}\}_{\Lambda\Lambda'}\,(\dot{P}^{\alpha Q}_{\mathbf{R}\Lambda'}(z))^{1/2} \end{aligned} \tag{11}$$

is used to calculate component resolved and averaged density matrices, $D^Q_{\mathbf{R},\,\Lambda\Lambda'}(E)$ and $D_{\mathbf{R},\,\Lambda\Lambda'}(E)$, respectively,

$$\begin{aligned} D^Q_{\mathbf{R},\,\Lambda\Lambda'}(E) &= -\frac{1}{\pi}\,\mathrm{Im}\,\langle G(E+i0)\rangle^Q_{\mathbf{R}\Lambda,\,\mathbf{R}\Lambda'}\,, \\ D_{\mathbf{R},\,\Lambda\Lambda'}(E) &= \sum_Q c^Q_{\mathbf{R}}\, D^Q_{\mathbf{R},\,\Lambda\Lambda'}(E)\,. \end{aligned} \tag{12}$$

These density matrices have to be used for charge self-consistent calculations. The diagonal elements of the density matrices, $D^Q_{\mathbf{R},\,\Lambda\Lambda}(E)$ and $D_{\mathbf{R},\,\Lambda\Lambda}(E)$, are simply the corresponding densities of states.

C. Evaluation of Green's function for inhomogeneous systems

The Green's function $\langle g^\alpha(z) \rangle$ can be easily calculated for homogeneous systems, like ideal bulk alloys, because $\mathcal{P}^\alpha_{\mathbf{R},\,\Lambda\Lambda'}(z) = \mathcal{P}^\alpha_{\Lambda\Lambda'}(z)$ and $S^\alpha_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'} = S^\alpha_{\Lambda\Lambda'}(\mathbf{R}-\mathbf{R}')$ for all $\mathbf{R}, \mathbf{R}'$:

$$\begin{aligned}\langle g^\alpha(z) \rangle_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'} = {}&\frac{1}{N}\sum_{\mathbf{k}} e^{i\mathbf{k}(\mathbf{R}-\mathbf{R}')} \\ &\times\{[\mathcal{P}^\alpha(z) - S^\alpha(\mathbf{k})]^{-1}\}_{\Lambda\Lambda'}\,, \end{aligned} \tag{13}$$

where

$$S^\alpha_{\Lambda\Lambda'}(\mathbf{k}) = \frac{1}{N}\sum_{\mathbf{R},\mathbf{R}'} e^{-i\mathbf{k}(\mathbf{R}-\mathbf{R}')}\, S^\alpha_{\mathbf{R}\Lambda,\mathbf{R}'\Lambda'}\,, \tag{14}$$

and $\mathbf{R}$ and $\mathbf{R}'$ are direct lattice vectors. The evaluation of $\langle g^\alpha(z) \rangle$ for inhomogeneous systems, like solids with surfaces or interfaces, disordered superlattices, or complex lattices is more difficult. Suppose that the set of direct lattice vectors can be decomposed into M subsets $\mathcal{R}_p$, ($p = 1, 2, \ldots, M, M \leq +\infty$) specifying geometrically and electronically equivalent sites such that each subset $\mathcal{R}_q$ is obtained from a generating subset $\mathcal{R}_p$ by some translation T_{pq}. A site $\mathbf{R} \in \mathcal{R}_p$ will be denoted by $\mathbf{R}_p$. The effective medium $\mathcal{P}^\alpha_{\mathbf{R}}(z)$ has to be identical for all sites belonging to one and the same subset $\mathcal{R}_p$, $\mathcal{P}^\alpha_{\mathbf{R}_p}(z) = \mathcal{P}^\alpha_p(z)$. For example, the subsets $\mathcal{R}_p$ can represent inequivalent sublattices of a complex lattice (finite M, T_{pq} is a nonprimitive translation), or atomic layers of a solid with a surface or an interface (infinite M). All subsets $\mathcal{R}_p$ have the same number N_0 of sites ($N = MN_0$), and the same translational (and point group) symmetry. The corresponding first Brillouin zone (BZ) will be denoted by $\mathcal{K}$. In the case of a solid with the surface, $\mathcal{K}$ is the surface BZ (SBZ) and the elements of $\mathcal{K}$ are denoted by $\mathbf{k}_{\|}$. The elements of the averaged Green's function can then be formulated as

$$\langle g^\alpha(z) \rangle_{\mathbf{R}_p\Lambda,\,\mathbf{R}'_q\Lambda'} = \frac{1}{N_0}\sum_{\mathbf{k}\in\mathcal{K}} e^{i\mathbf{k}(\mathbf{R}_p-\mathbf{R}'_q)}\,\langle g^\alpha(\mathbf{k},z)\rangle_{p\Lambda,\,q\Lambda'}\,, \tag{15}$$

where

$$\{\langle g^\alpha(\mathbf{k},z)\rangle^{-1}\}_{p\Lambda,\,q\Lambda'} = \mathcal{P}^\alpha_{p,\,\Lambda\Lambda'}(z)\,\delta_{pq} - S^\alpha_{p\Lambda,\,q\Lambda'}(\mathbf{k})\,, \tag{16}$$

and

$$S^\alpha_{p\Lambda,\,q\Lambda'}(\mathbf{k}) = \sum_{\mathbf{R}\in\mathcal{R}_{pq}} e^{-i\mathbf{k}\mathbf{R}}\, S^\alpha_{\Lambda\Lambda'}(\mathbf{R})\,. \tag{17}$$

In Eq. (17) $\mathcal{R}_{pq}$ denotes a set of vectors $\mathbf{R}_p - \mathbf{R}'_q$ such that $\mathbf{R}_p \in \mathcal{R}_p$ is fixed, and $\mathbf{R}_q^{'}$ runs over the whole subset $\mathcal{R}_q$.

The on-site elements $\Phi^{\alpha}_{p,\,\Lambda\Lambda'}(z) \equiv \langle g^{\alpha}(z)\rangle_{\mathbf{R}_p\Lambda,\,\mathbf{R}_p\Lambda'}$, which are needed for the CPA equations (10) as well as for the density matrices $D^{\alpha}_{p,\,\Lambda\Lambda'}$, Eq. (12), are obtained by integrating the (p,p) block of $\langle g^{\alpha}(\mathbf{k},z)\rangle$ over the bulk or surface Brillouin zone $\mathcal{K}$

$$\Phi^{\alpha}_{p,\,\Lambda\Lambda'}(z) = \frac{1}{N_o} \sum_{\mathbf{k}\in\mathcal{K}} \langle g^{\alpha}(\mathbf{k},z)\rangle_{pp} \,. \tag{18}$$

In the bulk case, $S^{\alpha}_{p\Lambda,\,q\Lambda'}(\mathbf{k})$ is the Fourier transform of the sublattice off-diagonal structure constants $S^{\alpha}_{\mathbf{R}_p\Lambda,\,\mathbf{R}'_q\Lambda'}$ that describe the coupling between sublattices p and q. The matrix $\langle g^{\alpha}(\mathbf{k},z)\rangle$ is then finite, and its (p,q) block is obtained by a simple inversion.

In the surface case, the matrix elements $S^{\alpha}_{\mathbf{R}_p\Lambda,\,\mathbf{R}'_q\Lambda'}$ describe intralayer $(p = q)$ or interlayer $(p \neq q)$ coupling, and the matrix $\langle g^{\alpha}(\mathbf{k}_{\parallel},z)\rangle$ is infinite. Consequently, special techniques and additional approximations are needed to evaluate $\langle g^{\alpha}(\mathbf{k}_{\parallel},z)\rangle$. A detailed derivation need not to be given, since it is formally equivalent to the nonrelativistic case.[26,27] In the following only the main results are summarized. The solid system is thought to be partitioned into three regions: (i) a homogeneous semi-infinite bulk alloy; (ii) a homogeneous vacuum region characterized by empty spheres with flat potentials (see the Appendix), which represents the continuation of the lattice to infinity; and (iii) an intermediate region consisting of several layers where all inhomogeneities (chemical, structural, and electronic) are located, and which contains also a few layers of empty spheres of the vacuum-solid interface. Consequently, the coherent potential function $\mathcal{P}^{\alpha}_{\mathbf{R},\,\Lambda\Lambda'}(z)$ is of the following form:

$$\mathcal{P}^{\alpha}_{\mathbf{R},\,\Lambda\Lambda'}(z) = \begin{cases} \mathcal{P}^{\alpha,v}_{\Lambda\Lambda'}(z) & \text{for layers in the vacuum region} \\ \mathcal{P}^{\alpha}_{p,\,\Lambda\Lambda'}(z) & \text{for layers in the intermediate region } (p = 1,2,...,P) \\ \mathcal{P}^{\alpha,b}_{\Lambda\Lambda'}(z) & \text{for layers in the bulk alloy region,} \end{cases} \tag{19}$$

where the superscripts v, and b refer to the vacuum and bulk alloy regions, respectively. The values of $\mathcal{P}^{\alpha}_{p,\,\Lambda\Lambda'}(z)$ are obtained by solving the set of coupled CPA equations (10) for the P layers in the intermediate region. The layer independent quantities $\mathcal{P}^{\beta,v}_{\Lambda\Lambda'}(z)$ and $\mathcal{P}^{\beta,b}_{\Lambda\Lambda'}(z)$ are found from separate calculations for the corresponding infinite systems.

By using the most localized representation $(\alpha = \beta)$, one can introduce the concept of principal layers (PL) (Ref. 28) which allows one to simplify the problem significantly. The semi-infinite solid can now be partitioned into PL's such that only nearest-neighbor PL's are coupled by the structure constants. A principal layer can include one or more atomic layers depending on the indices of the surface and the lattice type. The use of S^{β} justifies a limitation to first nearest neighbors for a fcc lattice and first and second nearest neighbors for a bcc lattice. The simplest case, when the PL consists of one atomic layer with one atom per primitive cell, already includes a number of important low-index surfaces [e.g., fcc(001), fcc(111), and bcc(110)]. A generalization to more complex PL's is given in Ref. 29.

The partitioning of a semi-infinite solid into PL's reflects the (block) tridiagonal form of $S^{\beta}_{pq}(\mathbf{k}_{\parallel})$, namely,

$$S^{\beta}_{pq}(\mathbf{k}_{\parallel}) = S^{\beta}_{00}(\mathbf{k}_{\parallel})\,\delta_{pq} + S^{\beta}_{01}(\mathbf{k}_{\parallel})\,\delta_{p+1,q} + S^{\beta}_{10}(\mathbf{k}_{\parallel})\,\delta_{p-1,q}\,, \tag{20}$$

which is of the same formal structure as in a nonrelativistic approach. Here, $S^{\beta}_{00}(\mathbf{k}_{\parallel})$, $S^{\beta}_{01}(\mathbf{k}_{\parallel})$, and $S^{\beta}_{10}(\mathbf{k}_{\parallel})$ denote the only nonzero blocks of the structure constant matrix. According to Eq. (16) the configurationally averaged Green's function $\langle\, g^{\beta}(\mathbf{k}_{\parallel},z)\,\rangle_{pq}$ is given by the inverse of an infinite tridiagonal matrix. The intermediate region is coupled to the homogeneous semi-infinite systems (bulk alloy and vacuum) via the surface Green's functions

$$\begin{aligned} \mathcal{G}^{\beta,\lambda}(\mathbf{k}_{\parallel},z) &= [\mathcal{P}^{\beta,\lambda}(z) - S^{\beta}_{00}(\mathbf{k}_{\parallel}) - \Gamma^{\beta,\lambda}(\mathbf{k}_{\parallel},z)]^{-1} \\ &\qquad (\lambda = b, v)\,, \\ \Gamma^{\beta,v}(\mathbf{k}_{\parallel},z) &= S^{\beta}_{10}(\mathbf{k}_{\parallel})\,\mathcal{G}^{\beta,v}(\mathbf{k}_{\parallel},z)\,S^{\beta}_{01}(\mathbf{k}_{\parallel})\,, \\ \Gamma^{\beta,b}(\mathbf{k}_{\parallel},z) &= S^{\beta}_{01}(\mathbf{k}_{\parallel})\,\mathcal{G}^{\beta,b}(\mathbf{k}_{\parallel},z)\,S^{\beta}_{10}(\mathbf{k}_{\parallel}) \end{aligned} \tag{21}$$

that can be determined directly in real space.[26] The (p,q) block $(1 \leq p,q \leq P)$ of the inverse configurationally averaged Green's function $\langle\, g^{\beta}(\mathbf{k}_{\parallel},z)\,\rangle$ is then given by[27]

$$\{\langle\, g^{\beta}(\mathbf{k}_{\parallel},z)\,\rangle^{-1}\}_{pq} = \mathcal{P}^{\beta}_{p}(z) - S^{\beta}_{00}(\mathbf{k}_{\parallel}) - \Gamma^{\beta,v}(\mathbf{k}_{\parallel},z)\,\delta_{p,1} - \Gamma^{\beta,b}(\mathbf{k}_{\parallel},z)\,\delta_{p,P}\,. \tag{22}$$

In this way the original problem of infinite order in PL indices is reduced to an effective problem of finite order P. It should be noted that the present formalism allows to include layer relaxations in the intermediate region, because the only assumption made regards the translational symmetry of the sets $\mathcal{R}_p$ which does not restrict the choice of interlayer distances.

D. Charge density and one-electron potentials

The charge density in an atomic sphere centered at site $\mathbf{R} \in \mathcal{R}_p$ and occupied by an atom of type Q is given by

$$\varrho_p^Q(\mathbf{r}) = \sum_{\Lambda\Lambda'} \int_{-\infty}^{E_F} \phi_{p\Lambda}^Q(E,\mathbf{r})\, D^Q_{p,\,\Lambda\Lambda'}(E)\, \phi^Q_{p\Lambda'}(E,\mathbf{r})\, dE + \varrho_p^{Q,\mathrm{core}}(\mathbf{r}), \tag{23}$$

where the $\phi^Q_{p\Lambda}(E,\mathbf{r})$ are normalized to unity within the atomic sphere of radius s^Q (see the Appendix) and $\varrho_p^{Q,\mathrm{core}}(\mathbf{r})$ is the spherically symmetric core charge density. The spherically averaged charge density $\tilde{\varrho}_p^Q(r)$ is then simply given by

$$\tilde{\varrho}_p^Q(r) = \frac{1}{4\pi} \sum_{\Lambda} \int_{-\infty}^{E_F} D^Q_{p,\,\Lambda\Lambda}(E)\, [(f^Q_{p\kappa}(E,r))^2 + (g^Q_{p\kappa}(E,r))^2]\, dE + \varrho_p^{Q,\mathrm{core}}(r)\,. \tag{24}$$

The radial functions $g^Q_{p\kappa}(E,r)$ and $f^Q_{p\kappa}(E,r)$ are regular solutions of the radial Dirac equation (see the Appendix) corresponding to the effective one-electron potential given by

$$V_p^Q(r) = -\frac{2Z^Q}{r} + V_p^{Q,H}(r) + \mu_{\mathrm{xc}}(\tilde{\varrho}_p^Q(r)) + V_p^{\mathrm{Mad}}. \tag{25}$$

The first term in (25) describes the Coulomb attraction to the nucleus with atomic number Z^Q, the second term is the Hartree potential due to the spherical electronic charge density $\tilde{\varrho}_p^Q(r)$, and the third term is the exchange-correlation contribution. The last term in Eq. (25), the Madelung term, is the spherically averaged electrostatic potential generated by the nonspherical charge density $\varrho_p^Q(\mathbf{r})$ from all other atomic spheres. Quite generally, this term can be expressed as

$$V_{\mathbf{R}}^{\mathrm{Mad}} = -2 \sum_{\mathbf{R}'}{}' \frac{Z_{\mathbf{R}'}}{|\mathbf{R}-\mathbf{R}'|} + 2 \sum_{\mathbf{R}'}{}' \sum_{L'} \mathcal{M}^{sL'}_{\mathbf{R}\mathbf{R}'}\, Q^{L'}_{\mathbf{R}'}\,, \tag{26}$$

where

$$Q_{\mathbf{R}}^{LQ} = \sqrt{\frac{4\pi}{2l+1}} \int_{s_{\mathbf{R}}} d^3r\, r^l\, \varrho^Q_{\mathbf{R}}(\mathbf{r})\, Y_L^*(\widehat{\mathbf{r}-\mathbf{R}}) \tag{27}$$

is the multipole moment of the nonspherical charge density in a sphere centered at $\mathbf{R}$, and the constants $\mathcal{M}^{LL'}_{\mathbf{R}\mathbf{R}'}$ are closely related to the nonrelativistic canonical structure constants

$$\mathcal{M}^{LL'}_{\mathbf{R}\mathbf{R}'} = -\frac{1}{2}\, [(2l+1)(2l'+1)]^{-1/2}\, w^{-l-l'-1}\, i^{l-l'} \times S^{0,\,nr}_{\mathbf{R}L,\,\mathbf{R}'L'}\,. \tag{28}$$

Within the CPA, the Madelung potential at a site $\mathbf{R} \in \mathcal{R}_p$ is then given by

$$V_p^{\mathrm{Mad}} = \sum_L \sum_q M^{sL}_{pq}\, \langle q_q^L \rangle\,, \tag{29}$$

where

$$\langle q_q^L \rangle = \sum_Q c_q^Q\, q_q^{LQ}, \quad q_q^{LQ} = Q_q^{LQ} - Z^Q\, \delta_{l,0}\,, \tag{30}$$

and Q_q^{LQ} is defined in Eq. (27) with $\varrho^Q_{\mathbf{R}}(\mathbf{r})$ replaced by its CPA value. It should be noted that the Madelung term at a site $\mathbf{R} \in \mathcal{R}_p$ is a linear combination of the configurationally averaged multipole moments $\langle q_q^L \rangle$ at all other sites $\mathbf{R}' \in \mathcal{R}_q$. The quantities M^{sL}_{pq} are the so-called Madelung constants for surface problems.[12,14]

In bulk systems corresponding to simple lattices (e.g., in substitutionally disordered fcc or bcc alloys), the condition of overall charge neutrality leads within the CPA to a vanishing Madelung term. However, the local environment effects can modify the charge distribution in the alloy and thus influence the Madelung fields and Madelung energies.[30] A correct description of such charge correlation effects goes beyond the single-site CPA. The problem can be solved approximately and basically two methods were proposed: (i) The atomic sphere radii s^Q are changed such that each atomic sphere is charge neutral while preserving the total volume of the random alloy.[10,31] In this way the average value of the Madelung term, Eq. (29), is zero and also the local fluctuations around this value are minimized. The absence of the Madelung contribution to the one-electron potentials, Eq. (25), is then compensated by a change of potential parameters due to changes of the sphere radii s^Q. (ii) The atomic radii are kept fixed, but charge correlations are explicitly included. This can be done at various levels of sophistication ranging from a mean-field theory[32] that employs local Madelung fields to the charge-correlated CPA,[33] which takes into account all possible environments of a central site leading thus to an effective problem for a $2(N_{1\mathrm{nn}}+1)$ component alloy, where $N_{1\mathrm{nn}}$ is the number of first nearest neighbors. Both these approaches improve the agreement of the alloy formation energy[31,33] with experiment.

In a bulk system consisting of several sublattices with at least one sublattice occupied randomly (e.g., quasibinary alloys), the averaged net charges $\langle q_p^{l=0} \rangle$ are in general nonzero. If the configurationally averaged environment of each site is characterized by some local point group symmetry (e.g., tetrahedral), the higher multipole moments can probably be neglected and the monopole-monopole interaction [term $L \equiv s$ ($l = m = 0$) in Eq. (29)] plays the decisive role.

For surface problems, the Madelung term describes not only the charge redistribution between different layers, but reflects also the strong deviations from the spherical symmetry for the charge density at the surface. It has been shown[12–15] that it is necessary to include the ($l = 1, m = 0$) term in Eq. (29), corresponding to the dipole moment perpendicular to the surface, in order to get results comparable to full-potential slab or supercell calculations.[6,7] In addition to the Madelung term in Eq. (29), the nonzero net charges and dipole moments in the surface layers lead to an electrostatic potential barrier B_d across the solid-vacuum interface. This quantity (and the closely related work function) is also very sensitive with respect to the nonspherical contributions to the charge density.[6,7,12–15]

In the surface case the sphere radii s_p^Q can be varied such that the net charges in each layer are the same, $q_p^{sA} = q_p^{sB} = \langle q_p^s \rangle$. The local charge fluctuations vanish then in each layer separately, the net charges, however, remain nonzero in the surface region.

E. Total energy

Within the density functional theory, the total energy of a system composed of electrons and fixed nuclei is in the relativistic case of the same form as in the nonrelativistic case because the one-particle kinetic energy term can be expressed in the same manner. For one configuration of the system the total energy is given within the ASA by[34]

$$\begin{aligned}\mathcal{E}^{\mathrm{tot}} &= \sum_i^{\mathrm{occ}} E_i - \sum_{\mathbf{R}} \int_{s_{\mathbf{R}}} d^3r \int_{s_{\mathbf{R}}} d^3r' \, \frac{\varrho_{\mathbf{R}}(\mathbf{r})\, \varrho_{\mathbf{R}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \\ &\quad + \sum_{\mathbf{R}} \int_{s_{\mathbf{R}}} d^3r \, \varrho_{\mathbf{R}}(r) \left[\epsilon_{\mathrm{xc}}(\varrho_{\mathbf{R}}(\mathbf{r})) - \mu_{\mathrm{xc}}(\varrho_{\mathbf{R}}(\mathbf{r}))\right] \\ &\quad + \sum_{\mathbf{R}\neq\mathbf{R}'} \frac{Z_{\mathbf{R}} Z_{\mathbf{R}'}}{|\mathbf{R}-\mathbf{R}'|} - \sum_{\mathbf{R}\neq\mathbf{R}'} \sum_{LL'} (Q_{\mathbf{R}}^{L})^{*} \mathcal{M}_{\mathbf{R}\mathbf{R}'}^{LL'} \, Q_{\mathbf{R}'}^{L'} \,, \end{aligned} \tag{31}$$

where the summation runs over the occupied one-particle states. The first term in (31) can be rewritten within the ASA as

$$\begin{aligned}\sum_i^{\mathrm{occ}} E_i &= \mathcal{E}^{\mathrm{core}} + \mathcal{E}^{\mathrm{band}} \\ &= \sum_{\mathbf{R}} \sum_j \epsilon_{\mathbf{R}j}^{\mathrm{core}} + \sum_{\mathbf{R}} \sum_{\Lambda} \int_{E_b}^{E_F} E \, D_{\mathbf{R},\,\Lambda\Lambda}(E) \, dE \,, \end{aligned} \tag{32}$$

where j runs over the core states with energies $\epsilon_{\mathbf{R}j}^{\mathrm{core}}$, $D_{\mathbf{R},\,\Lambda\Lambda}(E)$ is the valence density of states, and E_b is the bottom of the valence band. The second and third terms in (31) represent corrections for the electrostatic and exchange-correlation double-counting terms, $\epsilon_{\mathrm{xc}}(\varrho_{\mathbf{R}}(\mathbf{r}))$ is the local density of the exchange-correlation energy, and $\mu_{\mathrm{xc}}(\varrho_{\mathbf{R}}(\mathbf{r}))$ is the exchange-correlation potential. The fourth term corresponds to the electrostatic energy of the nuclei, and the fifth term describes the electrostatic energy of interacting electron densities in different Wigner-Seitz spheres, expressed via their multipole expansion. The sum of the fourth and fifth terms is usually called the Madelung energy, $\mathcal{E}^{\mathrm{Mad}}$. The first three terms can be written as a sum of contributions from individual atoms; however, not the Madelung energy, which arises from electrostatic interactions of pairs of atoms. In the case of disordered systems, the total energy $\mathcal{E}^{\mathrm{tot}}$, Eq. (31), has to be averaged over all configurations.[9]

Besides the total energy $\mathcal{E}^{\mathrm{tot}}$ of the whole system, one can also define in general a total energy normalized per atom $E^{\mathrm{tot}} = \mathcal{E}^{\mathrm{tot}}/N$ for a homogeneous system, or per one atom in a given subset $\mathcal{R}_p$, $E^{\mathrm{tot}} = \mathcal{E}^{\mathrm{tot}}/N_0$ for inhomogeneous systems.

The configurationally averaged sum of the first three terms, $\langle\mathcal{E}^{\mathrm{ind}}\rangle$, is given within the CPA as

$$\begin{aligned}\langle\mathcal{E}^{\mathrm{ind}}\rangle &= N_0 \sum_p \langle E_p^{\mathrm{ind}}\rangle \,, \quad \langle E_p^{\mathrm{ind}}\rangle = \sum_Q c_p^Q \, E_p^{\mathrm{ind},\,Q} \,, \\ E_p^{\mathrm{ind},\,Q} &= \sum_j \epsilon_{pj}^{\mathrm{core},\,Q} + \sum_{\Lambda} \int_{E_b}^{E_F} E \, D_{p,\,\Lambda\Lambda}^{Q}(E) \, dE \\ &\quad + \int_{s_p^Q} d^3r \, \tilde{\varrho}_p^Q(r) \left[\epsilon_{\mathrm{xc}}(\tilde{\varrho}_p^Q(r)) - \mu_{\mathrm{xc}}(\tilde{\varrho}_p^Q(r)) \right. \\ &\quad \left. - \int_{s_p^Q} d^3r' \, \frac{\tilde{\varrho}_p^Q(r')}{|\mathbf{r}-\mathbf{r}'|} \right] , \end{aligned} \tag{33}$$

where $\mathbf{R} \in \mathcal{R}_p$.

For homogeneous isotropic alloys the configurationally averaged total energy can easily be calculated, because the multipoles $Q_{\mathbf{R}}^{L}$ for $l > 0$ vanish on average, and the averaged Madelung energy $\langle\mathcal{E}^{\mathrm{Mad}}\rangle$ is given as

$$\langle\mathcal{E}^{\mathrm{Mad}}\rangle = \sum_{\mathbf{R}\neq\mathbf{R}'} \frac{\langle Z_{\mathbf{R}} Z_{\mathbf{R}'}\rangle - \langle Q_{\mathbf{R}}^{s} Q_{\mathbf{R}'}^{s}\rangle}{|\mathbf{R}-\mathbf{R}'|} \,, \tag{34}$$

since $\mathcal{M}_{\mathbf{R}\mathbf{R}'}^{ss} = |\mathbf{R}-\mathbf{R}'|^{-1}$. In this case $\langle\mathcal{E}^{\mathrm{Mad}}\rangle = 0$, because the $Z_{\mathbf{R}}$'s and the $Q_{\mathbf{R}}^{s}$'s average independently, $\langle Z_{\mathbf{R}} Z_{\mathbf{R}'}\rangle = \langle Z_{\mathbf{R}}\rangle \langle Z_{\mathbf{R}'}\rangle$ and $\langle Q_{\mathbf{R}}^{s} Q_{\mathbf{R}'}^{s}\rangle = \langle Q_{\mathbf{R}}^{s}\rangle \langle Q_{\mathbf{R}'}^{s}\rangle$ for $\mathbf{R} \neq \mathbf{R}'$, and $\langle Q_{\mathbf{R}}^{s}\rangle = \langle Z_{\mathbf{R}}\rangle$ for all $\mathbf{R}$.

The energy of formation for a homogeneous disordered alloy $A_x B_{1-x}$ is then defined by $\Delta E^{\mathrm{alloy}} = E^{\mathrm{tot}}(A_x B_{1-x}) - x\, E^{\mathrm{tot}}(A) - (1-x)\, E^{\mathrm{tot}}(B)$, namely, as a difference between the total energy $E^{\mathrm{tot}}(A_x B_{1-x})$ of the random alloy $A_x B_{1-x}$ and the properly weighted total energies $E^{\mathrm{tot}}(Q)$ of the pure constituent metals $Q = A, B$.

For inhomogeneous systems the electronic multipoles and the nuclear charges at different sites are again averaged independently, but their averages $\langle Z_{\mathbf{R}}\rangle = \langle Z_p\rangle$ and $\langle Q_{\mathbf{R}}^{L}\rangle = \langle Q_p^{L}\rangle$ depend on their position $\mathbf{R} \in \mathcal{R}_p$. In this case one finds that the Madelung energy can be expressed in terms of the layer dependent Madelung constants $M_{pq}^{LL'}$ with the monopole-monopole term $L = L' = s$ being excluded from the (L, L') sum

$$\begin{aligned}\langle\mathcal{E}^{\mathrm{Mad}}\rangle = -\frac{1}{2} \sum_{pq} \Bigg[& [2\langle Z_p\rangle + \langle Q_p^{s}\rangle] \, M_{pq}^{ss} \, \langle q_q\rangle \\ & + {\sum_{L,L'}}' \langle Q_p^{L}\rangle \, M_{pq}^{LL'} \, \langle Q_q^{L'}\rangle \Bigg] . \end{aligned} \tag{35}$$

The configurationally averaged total energy $\langle\mathcal{E}^{\mathrm{tot}}\rangle$ for a disordered alloy with a surface is then given by the sum of $\langle\mathcal{E}^{\mathrm{ind}}\rangle$ and of $\langle\mathcal{E}^{\mathrm{Mad}}\rangle$. A similar expression for the crystal surface using the frozen-core approximation and a nonrelativistic approach was given in Ref. 12.

The surface energy, i.e., the energy that leads to the formation of a surface, is defined then by $\Delta E^{\mathrm{surf}} = E^{\mathrm{tot}}(\mathrm{surf}) - nE^{\mathrm{tot}}(\mathrm{bulk})$, namely, as the difference of the total energy $E^{\mathrm{tot}}(\mathrm{surf})$ of a system with surface represented by n atomic layers in the intermediate region (excluding the layers of empty spheres), and the n multiple of the total energy $E^{\mathrm{tot}}(\mathrm{bulk})$ of the corresponding bulk system per one site.

III. RESULTS AND DISCUSSION

A. Computational details

In all calculations use is made of the point symmetry of the lattice. The **k** space integration in Eq. (18) is performed over the irreducible part of the Brillouin zone (BZ). In the bulk case we integrate over 1/48 of the fcc BZ using typically 110 **k** points. For the fcc(001) surface we integrate over 1/8 of the surface BZ using typically 21 special $\mathbf{k}_{\parallel}$ points.[35] Energy integrations are performed using a semicircle contour in the complex energy plane starting at an energy well below the bottom of the valence spectrum and ending at the Fermi level E_F. The integration is performed using the Gaussian quadrature method, which does not require the knowledge of the integrand at E_F. Typically 10 to 15 energy points are sufficient for an accurate energy integration over the energy interval of about 1 Ry. In the bulk case, we adjust a value of the Fermi level E_F in each iteration step using the approximate value of the total density of states and its slope in the neighborhood of E_F, which can be found by extrapolation from the values corresponding to the last two points on the complex contour. In the surface case the Fermi energy is that of the corresponding bulk systems and it remains unchanged during self-consistent calculations. Once self-consistency is achieved, the quantities of interest (e.g., the layer densities of states) are evaluated on a dense mesh of points parallel to the real axis and then continued analytically to the real axis.[36]

The CPA equations (10) are a set of coupled nonlinear equations for the coherent potential functions $\mathcal{P}_p^{\beta}(z)$ and the method for their solution is similar to the nonrelativistic case.[10] The use of the symmetry-adapted spin spherical harmonics reduces the number of off-diagonal elements of $\mathcal{P}^{\beta}_{\Lambda\Lambda'}(z)$ and $\Phi^{\beta}_{\Lambda\Lambda'}(z)$. For example, for $l \leq 2$, the irreducible representations of the O_h group to be considered are $\Gamma_6^+(s^{1/2})$, $\Gamma_6^-(p^{1/2})$, $\Gamma_7^+(d^{3/2})$, $\Gamma_8^-(d^{3/2})$, and $\Gamma_8^+(d^{3/2}$ and $d^{5/2})$. There are 26 nonzero matrix elements, and 8 (7) of them are independent for non-Hermitian (Hermitian) matrices.[37] In the (001)-surface case (group C_{4v}) with only two irreducible representations, Δ_6 and Δ_7, the number of nonzero elements is significantly higher (82) and also the number of independent elements (38).

In order to achieve a maximum internal consistency in the bulk and the surface calculations, which is important for total energy calculations, we determine the Green's function for bulk by coupling the isolated layer of bulk alloy atoms to the ideal "left" and "right" semi-infinite alloy subspaces characterized by the corresponding SGF's.[13] The surface Green's functions $\mathcal{G}^{\beta,v}(\mathbf{k}_{\parallel},z)$ and $\mathcal{G}^{\beta,b}(\mathbf{k}_{\parallel},z)$ are calculated by solving Eqs. (21) similarly as in the nonrelativistic case.[26]

The problem of charge self-consistency is essentially the same for both bulk disordered alloys and their surfaces and is similar to the case of ordered systems. The basic quantity is the local density of states matrix $D^{Q}_{p,\,\Lambda\Lambda'}(E)$, Eq. (12), which is used to solve a coupled system of the LDA equations[17] for all inequivalent atoms (constituent atoms in the bulk case and constituent atoms in all layers of the intermediate region in the surface case). The intermediate region consists of three layers of an alloy and two layers of empty spheres which describe the solid-vacuum interface. The exchange correlation is described by the functional of Ceperley and Alder[38] as parametrized by Perdew and Zunger.[39] In all calculations the maximum angular momentum quantum number l is restricted to 2 and the core orbitals are determined self-consistently (all-electron case).

The implemented codes are very efficient and can be run even on the low cost workstations. For example, a fcc-$\mathrm{Cu}_{75}\mathrm{Au}_{25}$ relativistic bulk calculation including total energy requires about two hours on the DEC 5000/20 personal station. A similar calculation for fcc(001) surface requires approximately ten hours.

In the following results for a random bulk fcc-$\mathrm{Cu}_{75}\mathrm{Au}_{25}$ alloy and its (001) surface are presented together with corresponding results for pure fcc-Cu and Au and their fcc(001) surface. For fcc-Au and its surface we have also performed analogous calculations in the nonrelativistic limit by putting c to 10^{12}.

B. Ground-state properties of fcc bulk constituents

We have calculated the equilibrium volumes of the fcc Cu and fcc Au by minimizing the corresponding total energies with respect to the crystal volume. The equilibrium values of the Wigner-Seitz radius w in the fully relativistic cases are w^{Cu}=2.646 a.u. and w^{Au}=3.070 a.u., and w^{Au}=3.23 a.u. in the nonrelativistic case. These values agree rather well with the corresponding experimental data w^{Cu}=2.670 a.u. and w^{Au}=3.013 a.u., as well as with recent theoretical calculations using the full-potential linearized augmented-plane-wave (LAPW) method[40] by which values of w_{Cu}=2.631 a.u., w_{Au}=3.023 a.u. were obtained in the scalar-relativistic case, and w_{Au}=3.164 a.u. in the nonrelativistic case. The slightly higher value of w^{Au} in the present case is due to the restriction to $l \leq 2$.[41] Also the bulk moduli estimated from fitting a parabola to $E_{\mathrm{tot}} = f(w)$, using typically 5–7 values of w, agree reasonably with the scalar-relativistic LAPW calculations (in brackets): $B_{\mathrm{Cu}} = 1.44$ Mbar and $B_{\mathrm{Au}} = 1.84(1.83)$ Mbar. In agreement with (Ref. 40) it is thus obvious that scalar-relativistic corrections reduce the equilibrium crystal volume and thus stiffen the bulk modulus significantly.

C. fcc-Cu and its (001) surface

Nonrelativistic surface calculations were performed recently[14] at the experimental value for the Wigner-Seitz radius s^{Cu}=2.669 a.u., which is close to the one determined theoretically, and need not be repeated here. The fully relativistic layer-resolved densities of states (DOS) for the top three layers of Cu(001) are compared with the corresponding bulk DOS in Fig. 1. The top-layer DOS shows a significant narrowing due to the lowering of the coordination number at the surface. The second

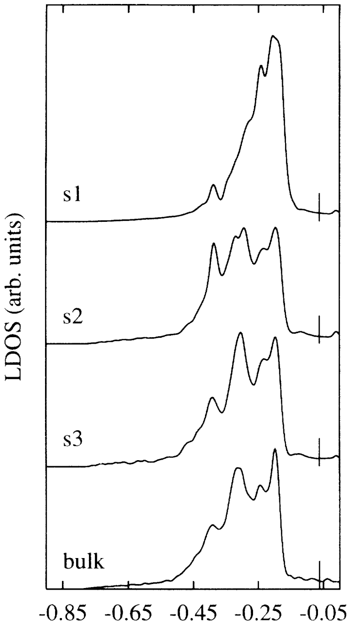

FIG. 1. Layer-resolved densities of states for a clean relativistic Cu(001) surface. The top three layers are denoted by $s1$, $s2$, and $s3$, respectively. The bulk density of states is given for a comparison. The vertical lines denote the position of the bulk Fermi level.

layer DOS is still influenced by the presence of the surface while the third layer DOS is already close to that of the bulk layer. It should be noted that the shapes of the layer-resolved DOS's agree very well with their nonrelativistic counterparts (see Fig. 1 of Ref. 14).

The surface-core level shift (SCLS) is connected with a different local coordination of atom at the surface and in the bulk. In the present case, the surface and bulk coordination numbers are 8 and 12, respectively. In the so-called initial state model, the SCLS is identified with the difference of calculated core levels for the bulk and its surface as obtained from corresponding self-consistent all-electron calculations. By neglecting screening effects it is frequently assumed that the core level shifts follow rigidly the shifts for the corresponding valence levels. Screening effects are at least partially included in the so-called final state models, of which an especially simple one is the equivalent core model.[42] In the present paper we determined the SCLS within the initial state model. For the Cu($2p_{3/2}$) level the SCLS amounts to 0.34 eV, which is in a reasonably good agreement with the experimentally observed value of 0.24 eV.[43]

The calculated work functions Φ (defined as $\Phi = B_d - E_F$, where B_d is the dipole barrier, i.e., the value of potential in the vacuum region[12]) are similar for the nonrelativistic and the relativistic case, namely, Φ=4.75 eV and Φ=5.0 eV, respectively. We used in both calculations the same atomic radius $w^{\mathrm{Cu}} = 2.646$ a.u. as found from the fully relativistic total energy calculations. The experimental value is Φ=4.64 eV. The fully relativistic value agrees reasonably with a recent scalar-relativistic calculations of Ref. 44.

D. fcc-Au and its (001) surface

We assumed an ideal, unreconstructed Au(001) (1x1) surface, similarly as in a recent scalar-relativistic full-potential LAPW (FLAPW) calculation.[45] The results for the layer-resolved DOS are compared with their bulk counterparts in Figs. 2 and 3 for the non-relativistic and fully relativistic cases, respectively. Similarly to the previous case, we have used in both calculations the same atomic radius $w^{\mathrm{Au}} = 3.070$ a.u. which was determined theoretically from the fully relativistic total energy calculations. In both cases one can see narrowing and an energetic upward shift of the top layer DOS, and a fast convergence to the bulk DOS. The shape of the layer-resolved DOS's are, however, significantly determined by relativistic effects, namely, a large downward shift of the s band with respect to the d band (corresponding to the Darwin and mass-velocity shift in a scalar-relativistic approach), and a significant splitting into $d^{3/2}$ and $d^{5/2}$ contributions. It should be noted that the bottom of the s and the d band nearly coincides in the nonrelativistic case, whereas in the fully relativistic case the bottom of the s-band is about 2 eV below the bottom of the d band. The calculated bulk DOS agrees very well with the scalar-relativistic LAPW results with spin-orbit corrections included [see Fig. 2(c) of Ref. 40].

The spin-orbit splitting of 1.6 eV as estimated from the difference $C(d^{5/2}) - C(d^{3/2})$, is not influenced by the presence of the surface, i.e., the energetic upward shift of 0.8 eV for the $5d^{3/2}$ and $5d^{5/2}$ levels in the surface layer is

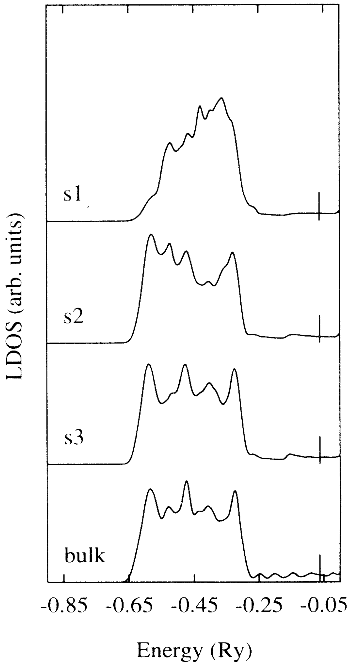

FIG. 2. Nonrelativistic layer-resolved densities of states for a clean Au(001) surface. The top three layers are denoted by $s1$, $s2$, and $s3$, respectively. The bulk density of states is given for a comparison. The vertical lines denote the position of the bulk Fermi level.

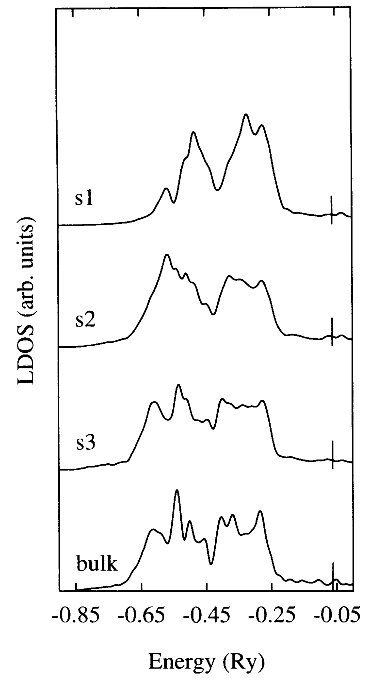

FIG. 3. Relativistic layer-resolved densities of states for a clean Au(001) surface. The top three layers are denoted by *s*1, *s*2, and *s*3, respectively. The bulk density of states is given for a comparison. The vertical lines denote the position of the bulk Fermi level.

almost rigid. Due to the reduced coordination, however, the dispersion of the $5d^{3/2}$ and $5d^{5/2}$ bands near and at the surface is considerably reduced. Quite clearly a fully relativistic treatment is needed to describe the details of the electronic structure for Au(001).

Within the initial state model the calculated values for the SCLS for the Au($4f_{7/2}$) level are 0.23 eV and 0.39 eV in the nonrelativistic and the fully relativistic case, respectively. A comparable value of 0.5 eV (for a shift of the center of gravity of surface bands) was estimated from scalar-relativistic FLAPW calculations.[45] The experimentally measured value[43] is 0.39 eV.

The inclusion of relativistic effects influences significantly the calculated work function for an ideal fcc-Au(001) surface. The nonrelativistic and fully relativistic values are Φ =5.16 eV and Φ =6.15 eV, respectively. The main reason for this increase of Φ is the downward shift of the Fermi level (from a nonrelativistic value of −0.053 Ry to −0.135 Ry in the relativistic case). A similar value of 6.16 eV was obtained in the scalar-relativistic frozen core calculations of Ref. 44, while a slightly smaller value of 5.39 eV was found in the scalar-relativistic FLAPW calculations for nine-layer slab. The experimental value is 5.47 eV.[44]

E. fcc-$Cu_{75}Au_{25}$ alloy and its (001) surface

The case of substitutionally disordered random CuAu alloys is more involved due to the very different sizes of constituent atoms. The present approach allows in principle an approximate inclusion of lattice relaxations around larger and smaller atoms by scaling locally the ideal, unperturbed structure constants and thus modeling lattice relaxations via additional off-diagonal disorder.[10,46] The effect of charge correlations can be also included (see discussion in Sec. II D). In the present paper, however, the above effects are neglected and the case of an ideal undistorted lattice with equal atomic radii $w^{\mathrm{Cu}} = w^{\mathrm{Au}} = w^{\mathrm{all}}$ is discussed, where a common Wigner-Seitz radius of a random alloy is determined by minimizing the corresponding alloy total energy. Such an alloy model is commonly used in state-of-the-art bulk KKR-CPA calculations.[11,37,48–50] The calculated value of the equilibrium Wigner-Seitz radius for random fcc $Cu_{75}Au_{25}$ is 2.807 a.u. and the estimated value of the alloy bulk modulus amounts to 1.56 Mbar. Both are therefore close to corresponding values for pure Cu. The calculated value of w^{all} is larger than its Vegard value (w^{all} = 2.76 a.u.). This is in agreement with experiment and a recent self-consistent fully relativistic KKR-CPA calculation.[47] The present values are systematically slightly larger in comparison with Ref. 47 as a result of restriction $l \leq 2$.[41]

There are quite a few relativistic KKR-CPA studies of the bulk fcc-$Cu_{75}Au_{25}$ random alloy in the literature[48–50] whereby only Ref. 49 was an early attempt of includ-

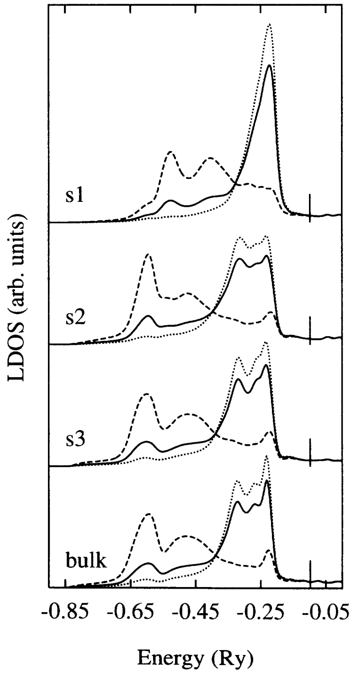

FIG. 4. Relativistic layer-resolved densities of states for a random $Cu_{75}Au_{25}$(001) surface. The top three layers are denoted by *s*1, *s*2, and *s*3, respectively. The bulk alloy densities of states are given for a comparison. Shown are the total densities of states (full lines), and the componentlike densities of states for Cu (dotted lines) and Au (dashed lines). The vertical lines denote the position of the bulk alloy Fermi level.

ing charge self-consistency. In all other calculations the Cu- and Au-alloy potentials were either adjusted[50] or taken from self-consistent calculations for the corresponding ordered Cu_3Au alloy.[48] The self-consistent scalar-relativistic calculations of Ref. 40 with spin-orbit corrections were performed for artificially ordered so-called special quasirandom structures (SQS) simulating a random fcc-$Cu_{75}Au_{25}$ alloy. The results for total and component-resolved layer DOS's are summarized in Fig. 4 together with their corresponding bulk counterparts. The layer-resolved and bulk Cu-component DOS's are similar to those for a pure Cu (Fig. 1) but extend below the bottom of the Cu *d* band due to hybridization between Cu and Au states. The effect of disorder can be seen from the broadening of the DOS below the bottom of the Cu *d* band. The Au DOS's differ significantly from those of the pure system (Fig. 3), because of (i) the different lattice spacing, and (ii) the effect of strong disorder for the impuritylike Au atoms. As a result, the Au DOS's in a random alloy are broadened and rather structureless. A strong reduction of the Au DOS's in the energy region of Cu *d* states can be seen indicating presence of strong disorder. The narrowing and the upward shift of the top layer DOS for Cu and Au reflect the reduced coordination at the surface. Similarly to pure crystals, the subsurface DOS is still influenced by the presence of the surface while the third sample layer is already close to the bulk DOS. The present results for the bulk DOS's of random $Cu_{75}Au_{25}$ alloy agree well with those of KKR-CPA (Refs. 48 and 50) as well as with the SQS results of Ref. 40. In the latter case, not surprisingly, additional features in the DOS missing in alloy calculations are present due to the artificially ordered structures used.

The calculated work function for disordered $Cu_{75}Au_{25}(001)$ alloy is Φ =5.29 eV, which almost corresponds to the concentration weighted values of Φ for the pure Cu and Au fcc(001) surfaces. Finally, within the initial state model, the value of the SCLS for the Au $4f_{7/2}$ level is 0.36 eV, which is slightly reduced in comparison with the pure Au value.

IV. SUMMARY

A numerically efficient self-consistent Green's-function formalism needed to calculate electronic properties of disordered alloys and their surfaces from a unified point of view was presented. This approach is based on the fully relativistic all-electron LMTO method in the tight-binding representation. The applied surface Green's function concept allows one to reduce the problem, originally infinite in the layer indices, to an effective problem of finite order in layer indices. Charge self-consistency is described within the ASA by using the monopole and dipole components of the charge density at the surface and thus facilitates a proper description of surface states and of the work function. In addition to the CPA derivations expressions for the total energies of the bulk and surface alloys are given.

The results of self-consistent calculations can be used to determine a number of physically relevant electronic (densities of states, x-ray and photoelectron spectra, bulk- and surface-core level shifts, work functions, etc.) and ground-state (equilibrium lattice constants, bulk moduli, heats of mixing, surface energies, etc.) properties of random alloys and their surfaces. The applicability of the present method was illustrated in terms of the fcc-$Cu_{75}Au_{25}$ random alloy and its (001) surface, whereby the corresponding results for the pure constituents were also discussed. The necessity of a relativistic approach for fcc Au and its (001) surface was demonstrated by comparing with corresponding nonrelativistic results.

ACKNOWLEDGMENTS

The financial support for this work was provided by the Academy of Sciences of Czech Republic (Project No. 11015), the Grant Agency of Czech Republic (Project No. 202/93/0688), the Austrian Ministery of Science (Project No. GZ 45.123./1-II/A/4/91) and the Austrian Science Foundation (P8918).

APPENDIX: RADIAL DIRAC EQUATION AND POTENTIAL PARAMETERS

A solution $\phi_\Lambda(E,\mathbf{r})$ of the Dirac equation for a spherically symmetric potential $V(r)$ confined to an atomic sphere of radius s and energy E is given by[51,37]

$$\phi_\Lambda(E,\mathbf{r}) = i^{\,l} \begin{pmatrix} g_\kappa(E,r)\,\Omega_{\kappa\mu}(\hat{\mathbf{r}}) \\ i\,f_\kappa(E,r)\,\Omega_{-\kappa\mu}(\hat{\mathbf{r}}) \end{pmatrix}, \quad \Lambda = (\kappa\mu)\,, \tag{A1}$$

whereby within the ASA it is assumed that $\phi_\Lambda(E,\mathbf{r}) = 0$ for $r = |\mathbf{r}| > s$. The $\Omega_{\kappa\mu}(\hat{\mathbf{r}})$ are spin-spherical harmonics corresponding to the relativistic quantum numbers $\kappa = -l-1$ for $j = l+1/2$, $\kappa = l$ for $j = l-1/2$, and $-j \leq \mu \leq j$. Because of spherical symmetry, the functions $\phi_\Lambda(E,\mathbf{r})$ are orthonormal in the Wigner-Seitz sphere

$$\int_s d^3\mathbf{r}\,\phi^+_\Lambda(E,\mathbf{r})\phi_{\Lambda'}(E,\mathbf{r}) = \delta_{\Lambda\Lambda'}\,. \tag{A2}$$

The radial functions $g_\kappa(E,r)$ and $f_\kappa(E,r)$ are solutions to the radial Dirac equation

$$\left(\frac{d}{dr} + \frac{1+\kappa}{r}\right) g_\kappa(E,r) - \left(1 + \frac{E-V(r)}{c^2}\right) \times c\,f_\kappa(E,r) = 0\,, \tag{A3}$$

$$\left(\frac{d}{dr} + \frac{1-\kappa}{r}\right) c\,f_\kappa(E,r) + [E - V(r)] \times g_\kappa(E,r) = 0\,, \tag{A4}$$

where for matters of simplicity the site index $\mathbf{R}$ is omitted. These solutions are regular at the origin, i.e., $\lim_{r\to 0} r g_\kappa(E,r) = \lim_{r\to 0} r f_\kappa(E,r) = 0$, and are normalized within the Wigner-Seitz sphere $\int_0^s dr\, r^2 \left[g_\kappa^2(E,r) + f_\kappa^2(E,r) \right] = 1$.

In the case of potentials with the leading term $V(r) \cong -2Z/r$, $Z > 0$, the regular solution $g_\kappa(E,r)$ behaves for small r like r^a, where $a = -1 + [\kappa^2 - (2Z/c)^2]^{1/2}$. For $r \to 0$ the initial condition for the radial Dirac equation is then given by

$$\frac{c\, f_\kappa(E,r)}{g_\kappa(E,r)} = \frac{c^2}{2Z} \left\{ \kappa + \left[\kappa^2 - \left(\frac{2Z}{c} \right)^2 \right]^{1/2} \right\} , \qquad \text{(A5)}$$

while in the case of an empty sphere, for which $Z = 0$ and thus $V(r)$ is finite at $r = 0$, the initial condition (A5) is defined by

$$\frac{c\, f_\kappa(E,r)}{g_\kappa(E,r)} = \begin{cases} 0 & \text{for } \kappa = -l - 1 < 0 \\ +\infty & \text{for } \kappa = l > 0 \, . \end{cases} \qquad \text{(A6)}$$

The logarithmic derivative of the wave function and the logarithmic derivative of its energy derivative (denoted by tilde) evaluated at the sphere radius s are defined for the upper (big) components as $D_\kappa(E) = s\, g'_\kappa(E,s)/g_\kappa(E,s)$ and $\tilde{D}_\kappa(E) = s\, \dot{g}'_\kappa(E,s)/\dot{g}_\kappa(E,s)$. Here, $g'_\kappa(E,s)$ denotes the derivative with respect to r evaluated at the sphere radius s and the overdot denotes the derivative with respect to the energy. They are approximately given by

$$D_\kappa(E) = s\, c\, \frac{f_\kappa(E,s)}{g_\kappa(E,s)} - \kappa - 1 \, , \qquad \text{(A7)}$$

$$\tilde{D}_\kappa(E) = s\, c\, \frac{\dot{f}_\kappa(E,s)}{\dot{g}_\kappa(E,s)} - \kappa - 1 \, , \qquad \text{(A8)}$$

as follows from Eqs. (A3), (A4), if $[E - V(r)]/c^2$ is neglected as compared to 1.

The so-called canonical potential function

$$P^0_\kappa(E) = 2(2l+1) \left(\frac{w}{s} \right)^{2l+1} \frac{D_\kappa(E) + l + 1}{D_\kappa(E) - l} \qquad \text{(A9)}$$

is within the TB-LMTO method approximated by

$$P^o_\kappa(E) = \frac{E - C_\kappa}{\Delta_\kappa + \gamma_\kappa \, (E - C_\kappa)} \, , \qquad \text{(A10)}$$

where C_κ, Δ_κ, and γ_κ are the potential parameters.

The potential parameters in the relativistic case are determined essentially in the same way as in the nonrelativistic case, namely,

$$\begin{aligned} \gamma_\kappa &= \frac{1}{2(2l+1)} \left(\frac{s}{w} \right)^{2l+1} \frac{D_{\dot\nu\kappa} - l}{D_{\dot\nu\kappa} + l + 1} \, , \\ \Delta_\kappa &= \gamma_\kappa \frac{g_{\nu\kappa}}{\dot{g}_{\nu\kappa}} \left(\frac{D_{\nu\kappa} - l}{D_{\dot\nu\kappa} - l} - \frac{D_{\nu\kappa} + l + 1}{D_{\dot\nu\kappa} + l + 1} \right) , \\ C_\kappa &= E_{\nu\kappa} - \frac{g_{\nu\kappa}}{\dot{g}_{\nu\kappa}} \frac{D_{\nu\kappa} + l + 1}{D_{\dot\nu\kappa} + l + 1} \, , \end{aligned} \qquad \text{(A11)}$$

where $g_{\nu\kappa} = g_\kappa(E_{\nu\kappa}, s)$, $\dot{g}_{\nu\kappa} = \dot{g}_\kappa(E_{\nu\kappa}, s)$, $D_{\nu\kappa} = D_\kappa(E_{\nu\kappa})$, and $D_{\dot\nu\kappa} = \tilde{D}_\kappa(E_{\nu\kappa})$.

The potential parameters for empty spheres can be determined analytically (see Ref. 17), since $V(r) = V = \text{const}$,

$$g_\kappa(E,r) = A\, j_l(pr) \, ,$$

$$c\, f_\kappa(E,r) = \begin{cases} -A\, (p/\gamma)\, j_{l+1}(pr) & \text{for } \kappa = -l - 1 < 0 \\ A\, (p/\gamma)\, j_{l-1}(pr) & \text{for } \kappa = l > 0 \, , \end{cases} \qquad \text{(A12)}$$

where A is the normalization constant, $\gamma = 1 + (E - V)/c^2$, $p = \{(E - V)\gamma\}^{1/2}$, and $j_l(x)$ is a spherical Bessel function.

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