PHYSICAL REVIEW B VOLUME 44, NUMBER 12 15 SEPTEMBER 1991-II

Electronic properties of surfaces of disordered alloys

J. Kudrnovský* and P. Weinberger
Institute of Theoretical Electrochemistry, Technical University, Getreidemarkt 9, A-1060 Vienna, Austria

V. Drchal
Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 Praha, Czechoslovakia

(Received 15 March 1991)

An approach to the electronic properties of surfaces of disordered metals is developed that combines the tight-binding linear-muffin-tin-orbital method with the surface Green's-function formalism and the coherent-potential approximation. The actual composition in the top surface layers can differ from that in the bulk layers. The method is applied to evaluate component- and layer-projected densities of states for the $Ag_{50}Pd_{50}(001)$ surface, assuming both uniform and nonuniform concentration profiles in the sample surface.

I. INTRODUCTION

Surfaces of bulk alloys are of great interest from both the theoretical point of view and the standpoint of probable technical applications such as, e.g., catalysis or multilayered metallic structures. One of the most interesting features of such systems is the segregation behavior at surfaces or interfaces. The oscillatory behavior of the concentration in the top alloy surface layers is, e.g., characteristic for low-index faces of Ni/Pt alloys. In order to explain such behavior, an empirical tight-binding Ising model[1] coupled with a mean-field approximation was developed and used successfully for a qualitative understanding of this phenomenon.

The detailed knowledge of the underlying electronic structure is a necessary first step in any such study. Until now, however, only oversimplified models have been used to describe the underlying electronic structure of imperfect alloy surfaces. Also, the true semi-infinite geometry is usually only modeled by a cluster of atoms and recursion methods are then used to evaluate the corresponding Green's functions. The only paper which properly takes into account the semi-infinite geometry of the system and also possible concentration variations at the surface is that of Berk.[2] The simpler but physically relevant case of a disordered overlayer on an otherwise perfect substrate was studied in Ref. 3. In both papers, however, a simplified band-structure model was adopted, namely the theoretical *s*-cubium model. The present authors developed recently an approach[4] that allows one to study the electronic structure of disordered overlayers with the accuracy common to contemporary first-principles alloy theories. This approach describes the underlying band structure from first principles within the local-density approximation using the tight-binding (TB) linear-muffin-tin-orbital (LMTO) method[5] by taking into account the effect of the surface via the surface Green's-function approach[6,7] and by describing the disorder within the framework of the coherent-potential approximation (CPA). The main purpose of this paper is to extend this approach to alloy systems with concentration oscillations in the vicinity of the surface. As will become clear later, our method is not limited to low-Miller-index faces as is the case in some of the contemporary first-principles electronic-structure theories for surfaces.

II. FORMALISM

Let $H_{\mathbf{R}L,\mathbf{R}'L'}$ be the Hamiltonian in the orthogonal muffin-tin orbital (MTO) representation[5] written usually as

$$H_{\mathbf{R}L,\mathbf{R}'L'}=C_{\mathbf{R}L}\delta_{\mathbf{R}\mathbf{R}'}\delta_{LL'}+\Delta_{\mathbf{R}L}^{1/2}[S^0(1-\gamma S^0)^{-1}]_{\mathbf{R}L,\mathbf{R}'L'}\Delta_{\mathbf{R}'L'}^{1/2}\;, \tag{1}$$

where $\mathbf{R}$ denotes atomic sites and $L=(l,m)$ the angular momenta. The quantities $X=C,\Delta,\gamma$ are the so-called potential parameters, which are diagonal matrices with elements $X_{\mathbf{R}L}$. The potential parameters can be combined into matrices of potential functions of the complex energy $z=\varepsilon+i\delta$, $\delta>0$,

$$P^0(z)=(z-C)[\Delta+\gamma(z-C)]^{-1}\;, \tag{2}$$

whose elements $P^0_{\mathbf{R}L}(z)$ are proportional, for $\delta=0$, to the cotangents of the phase shifts at the Wigner-Seitz sphere centered at site the $\mathbf{R}$. The canonical structure constants S^0 in (1) are represented by a matrix of elements $S^0_{\mathbf{R}L,\mathbf{R}'L'}=S^0_{LL'}(\mathbf{R}-\mathbf{R}')$, which depend only on the lattice structure of the system and hence are nonrandom.

By switching from the orthogonal MTO representation to the so-called most-localized MTO representation[5,8] characterized by a nonrandom site and angular momentum diagonal matrix β ($\beta_{\mathbf{R}L}=\beta_l$, $\forall\mathbf{R}$), the Green's function (GF) in the original representation

$$G(z)=(z-H)^{-1} \tag{3}$$

is related to the Green's function $g(z)$ in the new representation β by a simple scaling transformation[4,5,8]

$$G(z)=\lambda(z)+\mu(z)g(z)\mu(z)\;, \tag{4}$$

$$g(z)=[P(z)-S]^{-1}\;, \tag{5}$$

$$P(z)=P^0(z)[1-\beta P^0(z)]^{-1}\ ,\quad S=S^0(1-\beta S^0)^{-1}\ . \tag{6}$$

The matrices $\lambda(z)$ and $\mu(z)$ are site and angular momentum diagonal:

$$\begin{aligned}\lambda(z)&=\Delta^{-1/2}(\gamma-\beta)\mu(z)\ ,\\ \mu(z)&=[dP(z)/dz]^{1/2}\ .\end{aligned} \tag{7}$$

It should be noted, that because of $P(z)$, now only site diagonal disorder is present in $g(z)$, allowing, therefore, a direct application of the CPA.[8]

The main problem in treating theoretically surfaces of disordered alloys is of course the simultaneous occurrence of a surface and disorder. The effect of the surface can be formalized by using the surface Green's-function (SGF) technique,[6,7] while the configurational averaging can be performed using a properly modified CPA method. Note that there is a crucial difference between the case of an infinite bulk alloy and the case of a semi-infinite alloy, since, in the latter case, applying the CPA condition to each layer gives rise to an infinite system of coupled CPA equations to be solved self-consistently.[2] The problem is made tractable, however, by assuming that, from a certain layer on, the (electronic) properties of all subsequent layers are those for the infinite system. Note also that the related case of a disordered overlayer on a nonrandom substrate allows one to solve the CPA equations without any additional approximation.[3,4]

Let $L_t=\{\mathbf{a}_{nt}\,|\,\mathbf{a}_{nt}=n_1\mathbf{a}_1+n_2\mathbf{a}_2\}$ be the two-dimensional lattice spanned by primitive two-dimensional lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$. Then, quite clearly, each atomic position vector $\mathbf{R}_n$ can be expressed in terms of a vector $\mathbf{c}_n$ and a lattice vector $\mathbf{a}_{nt}\in L_t$:

$$\mathbf{R}_n=\mathbf{c}_n+\mathbf{a}_{nt}\ . \tag{8}$$

By neglecting surface relaxations effects these $\mathbf{c}_n$ are nothing but multiples of a generating vector $\mathbf{c}_0$, which connects two neighboring atomic layers,

$$\mathbf{c}_n=n\mathbf{c}_0\ . \tag{9}$$

In binary disordered alloys of components A and B the potential parameters are given randomly by $X_l^{A,n}$ and $X_l^{B,n}$ with probabilities $c^{A,n}$ and $c^{B,n}=1-c^{A,n}$, where the superscript n refers to (different) atomic layers parallel to the surface, labeled by $\mathbf{c}_n$. The $X_l^{\alpha,n}$, $\alpha=A$ or B, are in general different from the corresponding bulk values $X_l^{A,b}$ or $X_l^{B,b}$, whose probabilities are given by the (macroscopical) bulk concentrations $c^{A,b}$ and $c^{B,b}=1-c^{A,b}$. Practically, however, the layer-dependent potential parameters and concentrations deviate from the bulk ones only in the first N top layers, where N typically is about 2 or 3. The set $\{c_n^\alpha\,|\ n=1,2,\ldots,N;\ \alpha=A,B\}$ characterizes, therefore, the surface concentration profile.

Because of the two-dimensional periodicity all quantities related to the Green's function can be viewed[9] as matrices with rows and columns labeled in terms of $\mathbf{c}_n$, Eqs. (8) and (9). Depending on the actual "screening length" of the screened structure constants

$$S_{LL'}(\mathbf{R}_m-\mathbf{R}_n)\equiv 0\ ,\quad \forall|\mathbf{R}_m-\mathbf{R}_n|>|\mathbf{d}_0|=M|\mathbf{c}_0|\ , \tag{10}$$

these matrices are tridiagonal supermatrices with rows and columns labeled by $\mathbf{d}_i$, $\mathbf{d}_{i+1}$, etc., where $|\mathbf{d}_{i+1}-\mathbf{d}_i|=|\mathbf{d}_0|$,

$$\mathsf{S}=\begin{bmatrix} & & & 0 & 0 & 0 & 0\\ 0 & \underline{S}_{i-1,i} & \underline{S}_{i,i} & \underline{S}_{i,i+1} & 0 & 0 & 0\\ 0 & 0 & \underline{S}_{i+1,i} & \underline{S}_{i+1,i+1} & \underline{S}_{i+1,i+2} & 0 & 0\\ 0 & 0 & 0 & \underline{S}_{i+2,i+1} & \underline{S}_{i+2,i+2} & \underline{S}_{i+2,i+3} & 0\\ 0 & 0 & 0 & 0 & 0 & & \end{bmatrix}. \tag{11}$$

Each element $\underline{S}_{ij}$ is a matrix with rows and columns labeled by atomic layers, i.e., by $\mathbf{c}_n$, $\mathbf{c}_{n+1}$, $\mathbf{c}_{n+2}$, etc,

$$\underline{S}_{ij}=\begin{bmatrix} S_{i_1,j_1} & S_{i_1,j_2} & S_{i_1,j_M}\\ S_{i_2,j_1} & S_{i_2,j_2} & S_{i_2,j_M}\\ S_{i_M,j_1} & S_{i_M,j_2} & S_{i_M,j_M}\end{bmatrix}\ , \tag{12}$$

where the terminating index M is defined by (10). The semi-infinite crystal can therefore be partioned into principal layers[6] (PL's) such that only nearest-neighboring PL's are coupled by the structure constants [see Eq. (11)]. In principle, of course, these PL's can comprise also the situation for complex lattices, namely if also nonprimitive translations characterize the two-dimensional periodicity. By using bulk-derived structure constants the form of (11) is even simpler, namely,

$$\underline{S}_{ij}=\underline{S}_{01}\delta_{j,i+1}+\underline{S}_{10}\delta_{j,i-1}\ ,\quad \underline{S}_{ii}=\underline{S}_{00}\ . \tag{13}$$

The potential functions can be written as PL-diagonal supermatrices

$$\mathsf{P}^\alpha(z)=\begin{bmatrix}\underline{P}_i^\alpha(z) & 0 & 0\\ 0 & \underline{P}_{i+1}^\alpha(z) & 0\\ & & \\ 0 & 0 & \underline{P}^{\alpha,b}(z)\end{bmatrix}\ ,\quad \alpha=A,\ B,\ \text{or}\ c \tag{14}$$

whose elements are also diagonal with respect to atomic layers,

$$\underline{P}_i^\alpha(z)=\begin{bmatrix}P_{i_1}^\alpha & 0 & 0\\ 0 & P_{i_2}^\alpha(z) & 0\\ 0 & 0 & P_{i_M}^\alpha(z)\end{bmatrix}\ , \tag{15}$$

and where the suffix $\alpha=c$ denotes the (nonrandom and complex) coherent potential functions.[8]

The above setup can be viewed in the following way: starting with an arbitrary PL i inside the semi-infinite system, "epitaxially" further PL's are added until the PL in the surface of the system ($i=1$) is reached. Similarly in the opposite direction PL's are added until that PL is reached, whose properties (potential parameters or layer concentrations) still differ from the bulk ones. Finally, the remainder of the semi-infinite system with bulk characteristics in all layers ("ideal" substrate) is attached. This procedure is easily formalized using partitioning technique[3,10] and is a direct consequence of the tridiagonal structure of S. Due to the inhomogeneity of the problem, the $\underline{P}_i^c(z)$ differ from each other in the first N atomic layers, while for all others they are identical to the infinite bulk coherent potential functions $\underline{P}^{c,b}(z)$ determined within the standard TB-LMTO-CPA method.[8] It should be noted that, while for cubic lattices and $l \leq 2$ the bulk $\underline{P}^{c,b}(z)$ are diagonal matrices with respect to L, L', due to the lowering of the symmetry close to the surface, this in general is not the case for the surface-related coherent potential functions $\underline{P}_i^c(z)$.

By defining in formal analogy to (14) and (15) diagonal matrices for the concentration profiles of A and B atoms

$$\mathsf{C}^\alpha = \begin{bmatrix} \underline{c}_i^\alpha & 0 & 0 & 0 & 0 \\ 0 & \underline{c}_{i+1}^\alpha & 0 & 0 & 0 \\ & 0 & \underline{c}_{i+2}^\alpha & 0 & 0 \\ & 0 & 0 & 0 & \underline{c}^{\alpha,b} \end{bmatrix} \quad \alpha = A \text{ or } B \ , \tag{16}$$

where $\underline{c}^{\alpha,b}$ refers to the corresponding bulk concentrations, the CPA condition is given by the following set of equations:

$$\begin{aligned} \mathsf{P}^c(z) &= \mathsf{C}^A \mathsf{P}^A(z) + \mathsf{C}^B \mathsf{P}^B(z) \\ &\quad + [\mathsf{P}^A(z) - \mathsf{P}^c(z)] \mathsf{F}(z) [\mathsf{P}^B(z) - \mathsf{P}^c(z)] \ , \end{aligned} \tag{17}$$

where the supermatirix $\mathsf{F}(z)$ is diagonal with respect to atomic layers. The nonvanishing subblocks are defined by

$$F_{i_p i_p}(z) = \frac{1}{N_\parallel} \sum_{\mathbf{k}_\parallel} \langle g(\mathbf{k}_\parallel, z) \rangle_{i_p i_p} \ , \tag{18}$$

$$\langle \underline{g}(\mathbf{k}_\parallel, z) \rangle_{ii} = [\underline{P}_i^c(z) - \underline{S}_{00}(\mathbf{k}_\parallel) - \underline{\Gamma}_{ii}(\mathbf{k}_\parallel, z) - \underline{\tilde{\Gamma}}_{ii}(\mathbf{k}_\parallel, z)]^{-1} \ , \tag{19}$$

$$\begin{aligned} \underline{\Gamma}_{ii}(\mathbf{k}_\parallel, z) &= \underline{S}_{01}(\mathbf{k}_\parallel) [\underline{P}_{i+1}^c(z) - \underline{S}_{00}(\mathbf{k}_\parallel) \\ &\quad - \underline{\Gamma}_{i+1,i+1}(\mathbf{k}_\parallel, z)]^{-1} \underline{S}_{10}(\mathbf{k}_\parallel) \ , \end{aligned} \tag{20}$$

$$\begin{aligned} \underline{\tilde{\Gamma}}_{ii}(\mathbf{k}_\parallel, z) &= \underline{S}_{10}(\mathbf{k}_\parallel) [\underline{P}_{i-1}^c(z) - \underline{S}_{00}(\mathbf{k}_\parallel) \\ &\quad - \underline{\tilde{\Gamma}}_{i-1,i-1}(\mathbf{k}_\parallel, z)]^{-1} \underline{S}_{01}(\mathbf{k}_\parallel) \ . \end{aligned} \tag{21}$$

It should be noted that (17) represents a set of CPA equations for individual layers of an inhomogenous system. All equations are mutually coupled via $\mathsf{F}(z)$ because, as follows from (19)–(21), $\mathsf{F}(z)$ depends on the whole supermatrix $\mathsf{P}^c(z)$.

In (18)–(21) $\langle \ \rangle$ denotes a configurational average and $\mathbf{k}_\parallel$ a vector in the surface Brillouin zone (SBZ). The set of above recursive equations is terminated by the following "boundary" conditions:

$$\underline{\Gamma}_{kk}(\mathbf{k}_\parallel, z) = \underline{S}_{01}(\mathbf{k}_\parallel) \underline{g}^{c,b}(\mathbf{k}_\parallel, z) \underline{S}_{10}(\mathbf{k}_\parallel) \ , \tag{22}$$

$$\underline{\tilde{\Gamma}}_{00}(\mathbf{k}_\parallel, z) = \underline{\tilde{\Gamma}}^{\text{vac}}(\mathbf{k}_\parallel, z) \ , \tag{23}$$

where the subscript k refers to the last PL in which the potential parameters or concentrations are different from the bulk ones. In (23) $\underline{\tilde{\Gamma}}^{\text{vac}}(\mathbf{k}_\parallel, z)$ characterizes the surface boundary condition. Its specific form depends on the surface barrier in the vacuum.[7,11] In the simplest case of the so-called natural boundary condition (no electrons outside the system) $\underline{\tilde{\Gamma}}^{\text{vac}}(\mathbf{k}_\parallel, z) = 0$, $\forall \mathbf{k}_\parallel \in$ SBZ.

The quantity $\underline{g}^{c,b}(\mathbf{k}_\parallel, z)$ in (22) is the GF of a semi-infinite system with the bulk coherent potential functions $\underline{P}^{c,b}(z)$ on each site. Due to the tridiagonal structure of the structure constants (11), $\underline{g}^{c,b}(\mathbf{k}_\parallel, z)$ can be determined directly[7,12] by means of the following self-consistent condition:

$$\begin{aligned} \underline{g}^{c,b}(\mathbf{k}_\parallel, z) &= [\underline{P}^{c,b}(z) - \underline{S}_{00}(\mathbf{k}_\parallel) \\ &\quad - \underline{S}_{01}(\mathbf{k}_\parallel) \underline{g}^{c,b}(\mathbf{k}_\parallel, z) \underline{S}_{10}(\mathbf{k}_\parallel)]^{-1} \ . \end{aligned} \tag{24}$$

Finally, the configurationally averaged physical GF $\langle G(z) \rangle$ corresponding to (3) has to be expressed in terms of $\langle g(z) \rangle$ (19). Since, in principle, three random quantities [see Eq. (4)] are involved, this is a nontrivial step. The method developed in Ref. 8 is used here according to which for the pth atomic layer in the ith principle layer $\langle G(z) \rangle$ is given by

$$\langle G(\mathbf{a}_{nt}, z) \rangle_{i_p, i_p} = \frac{1}{N_\parallel} \sum_{\mathbf{k}_\parallel} \langle G(\mathbf{k}_\parallel, z) \rangle_{i_p, i_p} \exp(i \mathbf{k}_\parallel \cdot \mathbf{a}_{nt}) \ , \tag{25}$$

$$\langle G(\mathbf{k}_\parallel, z) \rangle_{i_p, i_p} = \Lambda_{i_p}(z) + M_{i_p}(z) \langle g(\mathbf{k}_\parallel, z) \rangle_{i_p, i_p} M_{i_p}(z) \ , \tag{26}$$

where $\Lambda_{i_p}(z)$ and $M_{i_p}(z)$ are site diagonal matrices related to $P_{i_p}^c(z)$. Dropping the indices i_p, their explicit forms are given by

$$\begin{aligned} \Lambda(z) &= \langle \lambda(z) \rangle + [\mu^A(z) - \mu^B(z)]^2 \\ &\quad \times [\langle P(z) \rangle - P^c(z)] / [P^A(z) - P^B(z)]^2 \ , \end{aligned} \tag{27}$$

$$\begin{aligned} M(z) &= \{\mu^A(z) [P^B(z) - P^c(z)] \\ &\quad - \mu^B(z) [P^A(z) - P^c(z)]\} / [P^A(z) - P^B(z)] \ . \end{aligned} \tag{28}$$

Quite clearly any one-electron property of interest related to the surface of a disordered alloy can be determined now from $\langle G(z) \rangle$. The atomic layer-projected density of states[8] $n_{i_p}(\varepsilon)$ is, for example, given by the corresponding concentration weighted component densities of states $n_{i_p}^\alpha(\varepsilon)$,

$$n_{i_p}(\varepsilon) = \sum_{\alpha = A,B} c_{i_p}^\alpha n_{i_p}^\alpha(\varepsilon) \ , \tag{29}$$

$$\begin{aligned} n_{i_p}^\alpha(\varepsilon) &= -\pi^{-1} [dP_{i_p}^\alpha(\varepsilon)/d\varepsilon] \\ &\quad \times \operatorname{Im}\{[\mathsf{P}^\alpha(\varepsilon) - \mathsf{P}^c(\varepsilon) + \mathsf{F}(\varepsilon + i0)^{-1}]_{i_p, i_p}^{-1}\} \ , \end{aligned} \tag{30}$$

which, because of the properties of the potential functions (2), can be further decomposed into l-like layer-projected component densities of states

$$n_{i_p}^{\alpha}(\varepsilon)=\sum_{l} n_{i_p,l}^{\alpha}(\varepsilon)\ . \tag{31}$$

It should be noted that (i) in principle, surface relaxation effects can be included by allowing a few atomic layers for which the layer vectors $\mathbf{c}_n$ are not multiples of the generating vector $\mathbf{c}_0$; (ii) the formulation leading to (24) is quite general and applicable therefore also to high-Miller-index surfaces; and (iii) the same formal structure retains in principle a fully relativistic description.

III. NUMERICAL ILLUSTRATION AND DISCUSSION

The above formalism is applied in the present paper to evaluate the electronic structure of the (001) face of fcc $Ag_{50}Pd_{50}$ random alloy. Despite the fact that this system is not known to exhibit a pronounced nonuniform layer composition near the surface, it is an excellent test of our theory since the bulk behavior of the Ag/Pd system is well known (see Ref. 8, and references therein).

For fcc lattice the use of the screened structure constants S in (11) allows a restriction to first-nearest-neighbor interactions.[5,7] A principal layer consists therefore only of a single atomic layer ($M=1$) and, consequently, the above presented formalism simplifies significantly. Consequently, for $l_{\max}\le 2$ all occurring matrices are of order 9.

In the present calculations we used the self-consistent bulk potential parameters X_l^{α} ($\alpha=$Ag, Pd) evaluated at their equilibrium Wigner-Seitz radii by the scalar-relativistic LMTO method.[5] As discussed in Ref. 8, for bulk alloys this corresponds to an approximate treatment of charge self-consistency and lattice relaxations due to the different sizes of the constituent atoms. This is a reasonable choice to illustrate the applicability of our approach. In the future, however, potential parameters derived from charge-self-consistent film or supercell calculations will be used, since such calculations not only supply layer-dependent potential parameters, but also a more realistic description of the boundary condition at the surface [see Eq. (23)].

The equation for the $\mathbf{k}_{\parallel}$-projected SGF (24) was solved self-consistently parallel to the real axis. For the integration in the irreducible part of the SBZ [see Eq. (18)] the 55 special $\mathbf{k}_{\parallel}$ points of Cunningham[13] were used. As it turned out, essentially the same results were obtained also with only 21 $\mathbf{k}_{\parallel}$ points or even with 10 $\mathbf{k}_{\parallel}$ points. Finally, in order to evaluate the densities of states (DOS) $\mathsf{F}(z)$ (18) is analytically continued to the real axis.

In the present calculations we allow the layer-dependent concentrations to differ from the corresponding bulk concentrations in the top two layers and the coherent potential parameters to be different in the first three layers ($N=3$). This approximation, for which Berk[2] introduced the term "surface-bulk approximation," was verified on the basis of test calculations (see also the discussion corresponding below to Fig. 1).

In Fig. 1, in terms of the DOS for the top layer in $Ag_{50}Pd_{50}$ the "surface bulk" approximation ($N=3$) is compared with the so-called "homogeneous approximation"[2] assuming uniform alloy composition. This homogeneous approximation, which is defined by the condition that $P_n^c(z)=P^{c,b}(z)$, is valid in each layer of the semi-infinite system. The overall good agreement between both approaches is quite obvious. This agreement justifies in turn the contemporary use of first-principles alloy theories in angle-resolved photoemission[14] in which the validity of the homogeneous approximation is implicitly assumed. In other words, for the case of uniform alloy composition the coherent potential functions are not strongly layer dependent.

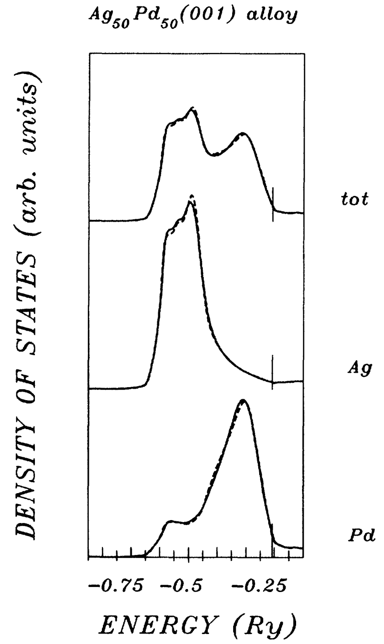

FIG. 1. Total and componentlike densities of states for the top surface layer $Ag_{50}Pd_{50}(100)$. Dashed lines correspond to the ($N=3$) "surface-bulk approximation," solid lines to the "homogeneous approximation." Both cases refer to the uniform bulk concentration. Long vertical lines denote the bulk-alloy Fermi energy.

The situation is, however, different in the case of nonuniform alloy composition, i.e., in the case with concentration oscillations in surface near layers. The use of bulk coherent potential functions of corresponding compositions in given layers seems to be too speculative and in fact even unnecessary from the computational point of view.

In the following two cases of an oscillatory enrichment of one of the components near the surface are considered within the ($N=3$) surface-bulk approximation, namely (i) a Pd-enriched surface: $c_1^{\mathrm{Ag}}=10$, $c_1^{\mathrm{Pd}}=90$; $c_2^{\mathrm{Ag}}=75$, $c_2^{\mathrm{Pd}}=25$; $c_3^{\mathrm{Ag}}=50$, $c_3^{\mathrm{Pd}}=50$ and (ii) an Ag-enriched surface: $c_1^{\mathrm{Ag}}=90$, $c_1^{\mathrm{Pd}}=10$; $c_2^{\mathrm{Ag}}=25$, $c_2^{\mathrm{Pd}}=75$; $c_3^{\mathrm{Ag}}=50$, $c_3^{\mathrm{Pd}}=50$. Experimentally[15] both kinds of enrichment are known to occur in Ni/Pt, although not for the same face.

In Fig. 2 the total and the componentlike layer-projected DOS for these two concentration profiles are shown together with the uniform concentration case ($c_n^{\mathrm{Ag}}=0.5$, $c_n^{\mathrm{Pd}}=0.50$, $n=1,2,3$) and the corresponding bulk DOS as obtained from a (bulk) TB-LMTO-CPA cal-

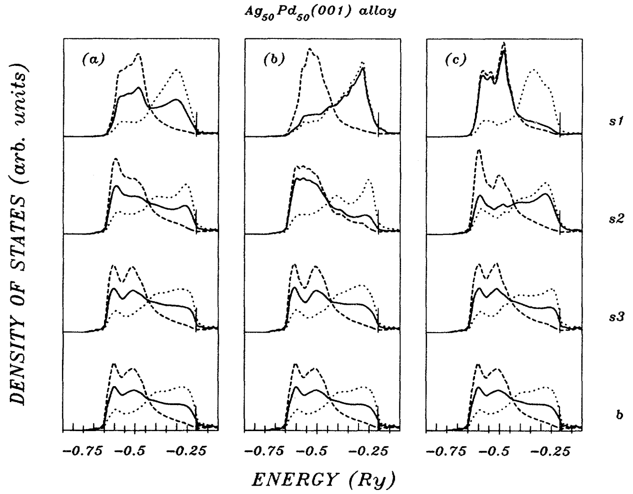

FIG. 2. Layer-resolved total (solid lines) as well as Ag-like (dashed lines) and Pd-like (dotted lines) component DOS for $Ag_{50}Pd_{50}(100)$. The bulk and first three top layers are denoted by b, $s1$, $s2$, and $s3$, respectively. The compositions in the layers $s1$, $s2$, and $s3$ are (a) $Ag_{50}Pd_{50}$, $Ag_{50}Pd_{50}$, $Ag_{50}Pd_{50}$; (b) $Ag_{10}Pd_{90}$, $Ag_{75}Pd_{25}$, $Ag_{50}Pd_{50}$; (c) $Ag_{90}Pd_{10}$, $Ag_{25}Pd_{75}$, $Ag_{50}Pd_{50}$. In all cases the $(N=3)$ surface-bulk approximation is used. Long vertical lines denote the bulk-alloy Fermi energy.

culation.[8] The peaks in the local bulk Ag and Pd DOS are well separated from each other in energy, thus indicating a strong local disorder in this alloy system. The lower part of the total DOS is thus dominated by Ag d-like states and the upper part by the PD d-like states. The features characteristic of the pure crystals are smeared out in the disordered phase. The Pd d-like states are strongly suppressed in the energy region of the Ag d-like states. Note also the Pd-induced Ag states in the upper part of the total DOS.

This behavior is qualitatively preserved also in the case of the alloy surface with uniform composition [Fig. 2(a)]. In comparison with the bulk we note a pronounced narrowing of the component DOS at the surface due to the reduced number of first neighbors (8 versus 12). The ratio δ/w (δ-level separation, w-averaged bandwidth) increases at the surface, thus leading to an additional smearing and, at the same time, in comparison with the bulk case to a better resolution of Ag- and Pd-related features. Remarkable also is the fast convergence of the layer DOS to the bulk values.

On the contrary, due to the varying component layer concentrations in the top two layers, the total top-layer DOS for the alloy surface with oscillatory enrichments [Figs. 2(b) and 2(c)] is distinctly different from the bulk case. The local Ag DOS for the Pd-rich surface [Fig. 2(b)] and the Pd DOS for the Ag-rich surface [Fig. 2(c)] behave like impurities. The enrichment of the surface by one component is reflected in the corresponding DOS in the layer beneath. Note that the second sublayer DOS ($s3$) is already very similar to the corresponding bulk DOS, but small deviations are still observable.

It should be noted that similarly as in bulk alloys, the concept of energy bands has to be replaced by generalized Bloch spectral functions[4] $A_p(k_{\|},E)$, related to a given atomic layer p. Their shapes can vary in a complicated manner.[4,8,9] Their study, though possible, is beyond the scope of the present work.

IV. CONCLUSIONS

We have presented a method of studying the electronic structure of surfaces of substitutionally disordered alloys. Our approach combines the linear-muffin-tin-orbital method, the coherent-potential approximation, and the surface Green's function formalism. Our method is able to describe properly both nonuniform compositions at the surface and the semi-infinite nature of the problem within the framework of the density functional theory. The formalism can easily be implemented numerically. Its accuracy is comparable to that of contemporary bulk alloy theories. It offers a number of interesting applications, such as the interpretation of experimental data of surface sensitive spectroscopies, the study of heterojunctions at crystall-alloy or grain boundaries, etc. Realistic calculations of surface energies and interatomic effective interactions are feasible, which, as parameters in effective Ising Hamiltonians,[1] are necessary for quantitative studies of surface compositional inhomogeneities, surface ordering, segregation, and related phenomena. Work in this direction is now in progress. The theory can be improved in some technical aspects, namely, by including the effect of the top-layer relaxation, by considering a more realistic boundary condition for the sample-vacuum interface, by the use of layer-dependent potential parameters, as obtained from slab or supercell calculations, or by the inclusion of the relativistic effects, necessary for a correct description of alloys containing heavy elements. The theory is presently limited by the use of spherically averaged muffin-tin atomic potentials, and therefore it is not suitable, for example, to calculate alloy work functions. Although the main purpose of this paper was to develop the formalism and to demonstrate its feasibility, one interesting result should be mentioned here: for a uniform alloy composition we have verified in the case of a realistic system the validity of the so-called homogenous approximation, i.e., the use of the same effective scattering potentials for sites within surface layers and in the bulk. This approximation is commonly used in contemporary *ab initio* theories of photoemission.

ACKNOWLEDGMENTS

This paper was supported by a grant by the Austrian Ministery of Science (Project No. GZ 45.123/4-II/A/4/90) and by a grant of the Czechoslovak Academy of Science (Project No. 11015).

[*] Permanent address: Institute of Physics, Czechoslovak Academy of Sciences, Na Slovance 2, 180 40 Praha, Czechoslovakia.

[1] B. Legrand, G. Tréglia, and F. Ducastelle, Phys. Rev. B **41**, 4422 (1990).

[2] N. F. Berk, Surf. Sci. **48**, 289 (1975).

[3] B. Velický and J. Kudrnovský, Surf. Sci. **64**, 411 (1977).

[4] J. Kudrnovský, B. Wenzien, V. Drchal, and P. Weinberger, Phys. Rev. B **44**, 4068 (1991).

[5] O. K. Andersen and O. Jepsen, Phys. Rev. Lett. **53**, 2571 (1984); see also Andersen, O. Jepsen, and M. Šob, in *Electronic Band Structure and Its Applications,* edited by M. Yussouff (Springer-Verlag, Heidelberg, 1987), p. 1.

[6] F. García-Moliner and R. Velasco, Prog. Surf. Sci. **64**, 96 (1986).

[7] B. Wenzien, J. Kudrnovský, V. Drchal, and M. Šob, J. Phys. Condens. Matter **1**, 9893 (1989).

[8] J. Kudrnovský, V. Drchal, and J. Mašek, Phys. Rev. B **35**, 2487 (1987); J. Kudrnovský and V. Drchal, *ibid.* **41**, 7515 (1990).

[9] P. Weinberger, *Electron Scattering Theory for Ordered and Disordered Matter* (Clarendon, Oxford, 1990).

[10] J. Kudrnovský and B. Velický, Czech. J. Phys. B **35**, 1017 (1985).

[11] W. R. L. Lambrecht and O. K. Andersen, Surf Sci. **178**, 256 (1986).

[12] J. Kudrnovský and V. Drchal, in *Studies in Surface Science and Catalysis,* Vol. 36 of *Physics of Solid Surfaces 1987,* edited by J. Koukal (Elsevier, Amsterdam, 1988), p. 74.

[13] S. L. Cunningham, Phys. Rev. B **10**, 4988 (1974).

[14] P. J. Durham, J. Phys. F **11**, 2475 (1981); see also J. Redinger, P. Weinberger, and A. Neckel, Phys. Rev. B **35**, 5647 (1987); J. Redinger and P. Weinberger, *ibid.* **35**, 5652 (1987).

[15] D. Dufayard, R. Baudoing, and Y. Gauthier, Surf. Sci. **233**, 223 (1990).