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Electronic structure of dilute impurities near surfaces. An approach to dissolution and segregation energies

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We present the extension of the electronic structure of bulk substitutional impurity to the surface in the tight-binding model. Self-consistency is assumed as well for the surface as for the impurity potential. The band contribution to the dissolution energy is obtained for Ni(111) surface, versus the valence and the position of the impurity to the surface in a localized potential model. Good agreement with experiment is obtained for $|Z| < 4$.

I. INTRODUCTION

The knowledge of the surface composition of transition- and noble-metal-based alloys is essential in metallurgy or catalysis. The progress of vacuum science and technology has allowed many authors to analyze in a reliable way the composition of surface of the alloys [by Auger, x-ray photoemission spectroscopy (XPS), ion, and neutral retrodiffusion, etc.]. It has been demonstrated that the surface composition may differ strongly from the bulk one; some authors even tried to obtain concentration profiles.[1,2] Many approaches to explain these phenomena have been used: phenomenological ones, such as bond models (Defay *et al.*[3]), elastic models based on the strain created by the atomic-size discrepancy (McLean[4]), or a combination of electronic and size effects (Miedema,[5] Hamilton,[6] Abraham,[7] Kumar[8]). The first-principles approaches to the segregation problem are more limited, the coherent-potential approximation for bulk concentrated alloys have been adapted in an approximate way to surface.[9,10]

More recently, another way to compute directly the segregation energy in an alloy *AB* has been developed; it is the energy variation shown by the exchanging of positions of a pair of atoms *A*, *B*, respectively, near the surface and in the bulk. Lambin and Gaspard[11] obtained trends for transition-metal alloys with a very simplified band structure, the tight binding up to the second moment. Muscat[12] applied the same principle to an impurity within a metallic cluster treated within the muffin-tin potential approximation, the whole being immersed in a free-electron gas. Let us focus more precisely on the dilute alloy case which will be our subject of study in the remainder of this paper. It is known that impurities in the bulk, even traces, may segregate strongly at surfaces or grain boundaries, producing effects such as temper embrittlement.[13,14] These effects are often difficult to observe reliably, due to the extreme condition of cleanliness required for the sample. Other traces of impurities (S, C, N, O, etc.) may mask the binary effect we try to study.[13–15] Gewinner[16] observed that at the end of nitrogen elimination from chromium, an important surface segregation of vanadium occurs, although traces only are present in the bulk. In Sec. II, we develop the theory of the electronic structure of a substitutional impurity in the tight-binding model with the aid of a Green-function theory and show that the band contribution to the dissolution energy can be expressed in terms of phase shifts requiring only local Green functions limited to the nonvanishing perturbing impurity potential region.

In Sec. III we perform a calculation of impurities within the localized potential model, using the Friedel sum rule[17] and the self-consistent dense Ni (111) surface band-structure parameters.[18] We report our results of the band contribution to the segregation energy versus the atomic number of the impurity and its position relative to surface.

In Sec. IV we discuss the equilibrium concentrations and a simple model for segregation kinetics, which we compare to experience, neglecting in the numerical application all contributions except that of the electronic band structure. Lattice distortion contributions to the segregation energies and the ion-ion repulsion modifications are not considered here.

II. ELECTRONIC STRUCTURE OF AN IMPURITY NEAR A SURFACE

The results for the dilute substitutional impurities in the bulk case are well established. Within the tight-binding models or interpolation schemes, we may refer to Friedel,[17] Wolff,[19] Clogston,[20] Riedinger.[21] There is still active research being done in the muffin-tin-model field today.[22,23] The study of the electronic structure of dilute impurities in semiconductors with the tight-binding formalism near surfaces and interfaces is also an active research field, owing to the technological implications on the electronic properties of devices,[24,25] but we have not found in the literature an extensive application of this study to the segregation energies. In this section we will present the most concise formalism for this problem.

The Hamiltonian describing our ideal semi-infinite medium with a surface is the following:

$$\underline{H}^0=\sum_{\sigma}\left[\sum_{Rm}|Rm\sigma\rangle\epsilon_R^{m\sigma}\langle Rm\sigma| + \sum_{\substack{m',m\\ R',R}}|R'm'\sigma\rangle t_{R'R}^{m'm}\langle Rm\sigma|\right] . \tag{2.1}$$

$|Rm\sigma\rangle$ is an atomic spin orbital of orbital symmetry m, centered at R; R is limited to the semi-infinite medium bounded by the surface plane; $\epsilon_R^{m\sigma}$ is the renormalized self-consistent level, comprising an *a priori* crystal shift, intra-atomic Coulomb and exchange, and electrostatic dipolar contribution[26]; $t_{R'R}^{m'm}$ are the hopping integrals, supposed to be rapidly decreasing with distance. We will not expand further here on the difficult problem of obtaining a self-consistent band structure for the ideal semi-infinite tight-binding medium because this problem has been tackled by the authors elsewhere.[26]

From this work it was found that the simplified model of Allan and Lenglart,[27] adjusting the surface level in order to achieve the global charge neutrality, gives satisfactory qualitative results in most of the cases, and this simplified prescription of a surface ideal medium will be used in the application of Sec. III. The substitutional impurity is described by a perturbing potential of finite range V_p, the perturbed Hamiltonian being

$$\underline{H}=\underline{H}^0+\underline{V}_p . \tag{2.2}$$

This potential may include within it a finite neighborhood of the impurity intrasite level modifications as well as the hopping integral ones. The latter may reflect the chemical difference and the distortion of the lattice around the impurity.

It is usual to introduce the Green operator

$$\underline{G}(z)=(z-\underline{H})^{-1} \tag{2.3}$$

for the perturbed or unperturbed case (the latter, labeled by 0). It is possible to obtain explicit representation for the unperturbed surface Green function G^0.[9,26,27] We obtain the perturbed function with the aid of Dyson's equation,

$$\underline{G}=\underline{G}^0+\underline{G}^0\underline{V}_p\underline{G} , \tag{2.4}$$

which can be solved in a matrixlike form as

$$\underline{G}=\underline{G}^0+\underline{G}^0\underline{T}_p\underline{G}^0 , \tag{2.5}$$

with

$$\underline{T}_p=\underline{V}_p(\underline{1}-\underline{G}^0\underline{V}_p)^{-1} , \tag{2.6}$$

$\underline{T}_p$ being the $\underline{T}$ matrix. The case of a perturbing potential limited to the impurity cell is particularly simple, the size of $\underline{T}_p$ being reduced by symmetry. In the case of the dense Ni(111) surface that we are studying, the same formulas as in bulk are valid; the Green-function matrix elements are just the local formula on the impurity site p. But the reduction by symmetry is lower than in bulk, as we will see in Sec. III.

From the Green function it is usual to define the total density of states as

$$n(E)=\lim\left[-\frac{1}{\pi}\operatorname{tr}\operatorname{Im}\underline{G}(z)\right],\quad z\rightarrow E+i0 \tag{2.7a}$$

the trace being peformed over any complete orthonormal basis. The local density of states on orbital $|Rm\sigma\rangle$ is given by the projection of $\underline{G}$ on this orbital,

$$n_\sigma(E,R)=\lim\left[-\frac{1}{\pi}\operatorname{Im}\langle Rm\sigma|\underline{G}(z)|Rm\sigma\rangle\right] . \tag{2.7b}$$

The last matrix element is notated $G^{mm}(z,R)$ for the sake of brevity. As in the bulk, it is mandatory to impose the Friedel sum rule, i.e., the global neutrality of the system. The increment of the total number of occupied states under the Fermi level E_F produced by the impurity potential must be equal to the difference of the number of electrons introduced by it, i.e., Z, the difference of atomic numbers (impurity host),

$$\int^{E_F}[n(E)-n^0(E)]dE=Z . \tag{2.8}$$

From (2.5), it is easy to show that the first member of (2.8) can be written as a phase shift; indeed, since

$$\operatorname{tr}[\underline{G}^0(\underline{1}-\underline{G}^0\underline{V}_p)^{-1}\underline{V}_p\underline{G}^0]=\frac{d}{dz}\operatorname{tr}\ln(\underline{1}-\underline{G}^0\underline{V}_p) ,$$

we obtain

$$\frac{1}{\pi}\eta(E_F)=Z \tag{2.9}$$

with

$$\eta(E)=-\operatorname{Im}\operatorname{tr}\ln(\underline{1}-\underline{G}^0\underline{V}_p) . \tag{2.10}$$

Owing to the localized nature of V_p, the most adequate basis is the symmetry-adapted atomic-orbital basis in which the phase shift appears as

$$\eta(E)=-\operatorname{Arg}\operatorname{Det}(1-\underline{G}^0\underline{V}_p) . \tag{2.11}$$

Let us discuss now the electronic band contribution to the dissolution energy of a substitutional impurity located at site R. In the framework of random-phase approximation (RPA) the total band contribution can be written as

$$E_d=E_{d_1}+E_{d_2} . \tag{2.12}$$

E_{d_1} is the one-electron contribution:

$$E_{d_1}=\int^{E_F}[n(E)-n^0(E)]E\,dE . \tag{2.13}$$

With the introduction of the phase shift and by integration by parts, this is

$$E_{d_1}=Z\,E_F-\frac{1}{\pi}\int^{E_F}\eta(E)dE . \tag{2.14}$$

Only the knowledge of a finite amount of ideal Green-function matrix elements of the semi-infinite medium at the sites of nonvanishing impurity potential are required. Moreover, if one assumes V_p to be localized and the same for the five d orbitals, this single potential matrix element is entirely determined by Friedel's rule (2.9).

The electron-electron contributions are counted twice in E_{d_1}, thus

$$E_{d_2}=-\langle H_{e\text{-}e}\rangle . \tag{2.15}$$

They comprise intra-atomic Coulomb and exchange long-range electrostatic interactions (of a dipolar Coulombic nature near the surface) and correlations. It is not possible in this simple model to obtain reliable estimations of this term, and it will, therefore, be neglected in the following. Even the computation of the local ionicities which can be computed along the same lines as those of the ideal surface would lead to a prohibitive computer cost. In conclusion, we showed that the localized impurity problem can be generalized formally from bulk to surface; only the matrix elements of the ideal self-consistent semi-infinite medium sensitive to the position of the surface appear instead of the bulk ones. In Sec. III we will see, however, that the realization is not completely trivial.

III. BAND CONTRIBUTION TO THE DISSOLUTION AND SEGREGATION ENERGIES OF IMPURITIES NEAR THE Ni(111) SURFACE

In this section we discuss a specific case with the preceding model; impurities described by a potential localized on one site in semi-infinite paramagnetic fcc Ni bounded by a (111) dense plane. Our choice is justified by the following reasons:

(i) A lot of experimental and theoretical information exists for this system.

(ii) It allows us to perform significant calculations with our very limited computer time and size allocations for cases where the elastic strain effects can be neglected.

The point-group symmetry of bulk fcc O_h is reduced by the (111) surface to C_{3v}. Therefore, we have to reconsider the symmetry-adapted d orbital. It is easy to check that the cubic harmonics belonging to representation Γ_{12} from an irreducible representation of dimension two of C_{3v}, and that $\Gamma_{25'}$ splits into a two-dimensional irreducible representation we constructed isomorphic to the preceding one, and a one-dimensional identity representation. We report in Table I the set of parameters for self-consistent semi-infinite Ni(111), and in Table II the C_{3v} adapted d harmonics.

From the selection rules applied to C_{3v} adapted orbitals, we check that we have to compute three diagonal matrix elements of Green function, $G^0_{11}=g_1$, $G^0_{22}=G^0_{33}=g_2$, and $G^0_{44}=G^0_{55}=g_3$, and a nondiagonal one, $G^0_{24}=G^0_{35}=g_4$, which vanishes in the bulk. The latter matrix elements do not infer on the determination of the density of states and Fermi level, but are present in the phase shift and the dissolution energy.

We used Desjonquères and Cyrot-Lackmann[18] first-neighbor parameters $dd\sigma, dd\pi, dd\delta$ and checked their self-consistent surface level V_0. The overlap matrix is assumed to be unity. We adapted the Haydock, Heine, and Kelly recursion method[28] for calculating the local Green-function matrix elements on the different planes parallel to the (111) surface as continued fractions:

$$\begin{aligned} &G(z)=G_1(z) ,\\ &G_n(z)=1/[z-a_n-b_n^2G_{n+1}(z)] . \end{aligned} \tag{3.1}$$

TABLE I. Parameters (in Ry) for self-consistent Ni(111) (Ref. 18).

$dd\sigma=-0.041\,676$	$dd\pi=0.018\,842$	$dd\delta=-0.002\,331$
$E_F=0.101\,81$	$a_\infty=-0.033\,022$	$b_\infty=0.080\,190$
$V_0=0.016$		

TABLE II. cfc(111) surface-adapted d harmonics $[\alpha=(15/4\pi)^{1/2}]$.

Symmetry	Bulk O_h	Label	cfc(111) surface bounded semi-infinite C_{3V}	Comments
$\Gamma_{25'}$	αxy	1	$\frac{\alpha}{\sqrt{3}}(xy+yz+zx)$	Identity representation
	αyz	2	$\frac{\alpha}{\sqrt{2}}(yz-zx)$	Two-dimensional irreducible representation
	αzx	3	$\frac{\alpha}{\sqrt{6}}(2xy-zx-yz)$	
Γ_{12}	$\frac{\alpha}{2}(x^2-y^2)$	4	$\frac{\alpha}{2}(x^2-y^2)$	Two dimensional representation isomorphic to (2-3)
	$\frac{\alpha}{\sqrt{12}}(3z^2-R^2)$	5	$\frac{\alpha}{\sqrt{12}}(3z^2-R^2)$	

We were able to obtain eight levels of coefficients a_n and b_n for the local Green function. We stop the continued fraction by assuming that the coefficients are constant, equal to their asymptotic values $a_\infty b_\infty$, i.e.,

$$G_{n+1}(z)=G_\infty(z)=1/[z-a_\infty b_\infty^2 G_\infty(z)] ,$$

thus

$$G_\infty(z)=\{(z-a_\infty)-[(z-a_\infty)^2-(2b_\infty^2)]^{1/2}\}/2b_\infty , \tag{3.2}$$

with the correct determination of the square root. We determined the coefficients a_∞ and b_∞ from the bulk band extension by calculating $E_n(k)$ at three-dimensional Brillouin-zone high-symmetry points[28]: a_∞ is the middle of the band, $b_\infty=W/4$, the fourth of the bandwidth.

We know that this procedure is fair since there exist no surface states for Ni(111) with the set of parameters of Desjonquères *et al.*,[18] and the spectral domain is thus the same as in bulk. The nondiagonal elements of the Green function are also brought into a form similar to the diagonal elements, i.e., the difference of continued fractions by a trick devised by Heine[28(c)]:

$$g_4=\tfrac{1}{2}(\langle X1|G|X1\rangle-\langle X2|G|X2\rangle) , \tag{3.3}$$

with

$$|X1\rangle=(\tfrac{1}{2})^{1/2}(|2\rangle+|4\rangle) ,$$
$$|X2\rangle=(\tfrac{1}{2})^{1/2}(|2\rangle-|4\rangle) . \tag{3.4}$$

In Fig. 1 we report the local density of states on the different planes and also the interorbital transfer spectral density $-(1/\pi)\mathrm{Im}g_4$. In Fig. 2 we trace the phase shifts. It is easy to check that the phase shift becomes

$$\eta(z)=-\arg\{(1-g_1V_p)\times[(1-g_2V_p)(1-g_3V_p)-(g_4V_p)^2]^2\} \tag{3.5}$$

per spin. The heat of dissolution is known to be

$$H=E_d-Ts_{\rm nc}+Pv , \tag{3.6}$$

where $s_{\rm nc}$ represents the variation of entropy not of purely random configuration type and v the variation of volume of the sample occurring by the substitution of one host by an impurity atom. E_d is the total energy variation associated with such a substitution, and comprises an electronic band contribution, as well as a lattice distortion and ion-ion contribution.[29] It may be conceivable to generalize a calculation of the type developed by the authors in Refs. 30 and 31 for the relaxation and recontruction of pure surfaces (or for impurities in the bulk[32] or adsorbates on surfaces[33]) to the present problem, but

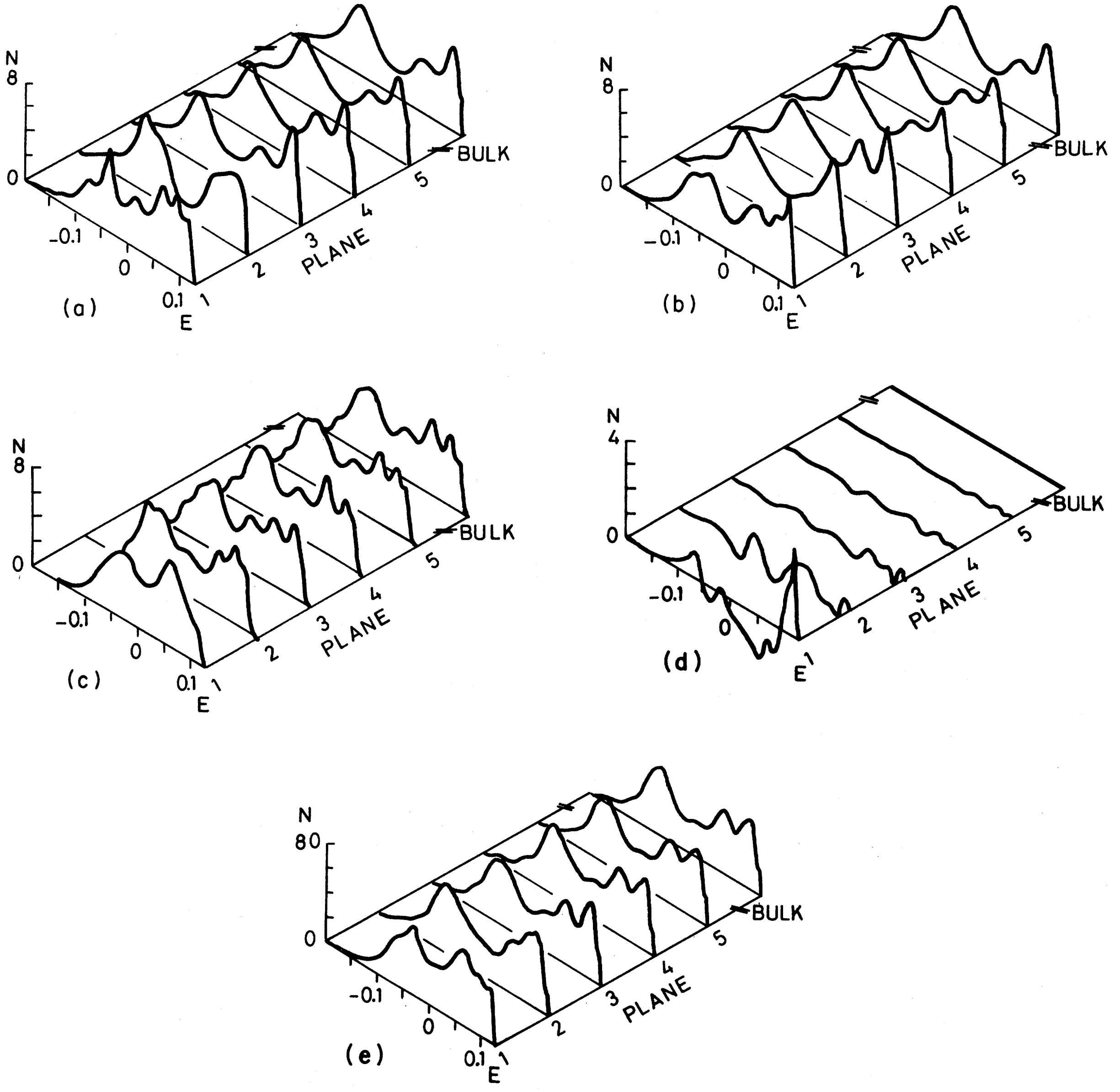

FIG. 1. Spectral densities $[-(1/\pi)\mathrm{Im}g_i]$, $i=1,4$ [(a), (b), (c), and (d), respectively], and total local density of states (e) vs the plane position relative to the surface (1st plane); the bulk is represented up from the 6th plane.

at a prohibitive cost. We do not believe that a macroscopic evaluation within linear elasticity, versus the position of the impurity to the surface, may be reliable. Thus, in the following, we suppose that the lattice is undistorted; we neglect, therefore, volume term v in (3.6). The entropy term (requiring a phonon impurity calculation along the same lines as the one developed here for electrons) is also neglected, and in the energy term E_d the elastic and two-electron contributions are neglected. Thus with these approximations and (3.6) we identify the heat of dissolution with E_{d_1}. Since the segregation energy is the energy associated with an exchange of position between a host atom on a plane near the surface and an impurity dissolved in the bulk, we obtain simply these quantities as the difference of dissolution energies of the impurity at site R and in the bulk:

$$E_{\mathrm{segr}}(R)=E_{d_1}(R)-E_{d_1}(\mathrm{bulk}) \; . \tag{3.7}$$

Thus we obtain as far as the electronic contribution is concerned, a much finer description than those currently existing in the literature which are limited

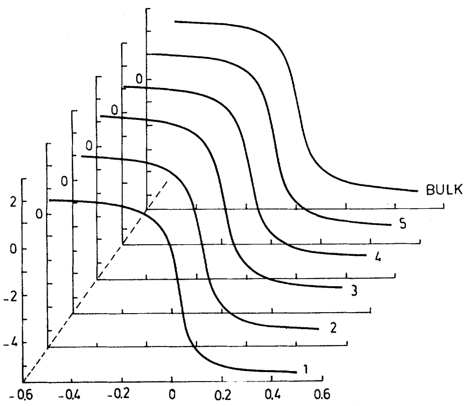

FIG. 2. Total displaced charge [renormalized phase shifts $(1/\pi)\eta(E_F,R,V)$ vs location (y) and the impurity potential (Ry)].

to "surface" and bulk only, since the position-dependent segregation energies obtained here may be used to construct an equilibrium concentration profile (Sec. IV). In Table III we report the dissolution and segregation energies on the different planes. The main qualitative features deduced from this table are the following:

(i) The oscillatory behavior of segregation energy versus the distance to the surface.

(ii) The sign of the segregation energy for an atom localized on the surface plane agrees with the experimental values available. We note a segregation on the surface for chromium,[15] copper,[1,2] vanadium, and zinc, but we did not find reliable studies for the latter alloys. With the positive value of E_{segr} for iron, we predict an enrichment of the surface by the host Ni, as observed by Wandelt and Ertl.[34] A similar result is expected for cobalt and manganese.

(iii) The influence of the off-diagonal matrix element of the Green function g_4 in (3.5) is sensitive on the surface plane, and for big valence differences $|Z|$ only (of second order in V_p).

(iv) Our model is much more detailed than the existing surface and bulk models. The order of magnitude of the segregation energy agrees with other existing data; for instance, our segregation energy at the surface of Ni-Cu is about three times that of Muscat's.[12]

For high values of $|Z|$, the localized model may not be reliable, even when brought to self-consistency, due to the extended nature of the impurity potential. For the determination of E_F and band contribution to dissolution energies, we used complex integration, deforming the contour from a lace around the real axis from $-\infty$ up to Fermi level into a vertical path $(E_F+iy), y\in[0,+\infty]$, and using Gaussian integration.[26] A great advantage is that there is no problem of phase determination; the real part involved in the calculation is uniform and a high accuracy necessary for significant energies is obtained. Let us mention that it is possible to compute directly the segregation energy as an impurity pair problem, on the semi-infinite system, with one impurity in the bulk. The perturbing potential is

TABLE III. (A) Impurity perturbing potentials, (B) segregation energies versus position in cfc(111) surface bounded semi-infinite Ni, and (C) dissolution energy in bulk Ni (in Ry).

Impurity Z Plane	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	−5	−4	−3	−2	−1	0	+1	+2
				(A)				
1	0.090 271	0.060 183	0.044 893	0.032 647	0.018 770	0.000 000	−0.028 161	−0.084 341
2	0.080 687	0.051 380	0.036 023	0.024 605	0.013 439	0.000 000	−0.019 600	−0.059 685
3	0.124 175	0.067 679	0.044 571	0.029 305	0.015 411	0.000 000	−0.019 749	−0.052 058
4	0.114 143	0.068 193	0.046 439	0.031 006	0.016 507	0.000 000	−0.022 361	−0.063 074
5	0.102 914	0.064 165	0.044 766	0.030 251	0.016 142	0.000 000	−0.021 926	−0.063 147
Bulk	0.102 810	0.063 411	0.044 120	0.029 909	0.016 056	0.000 000	−0.021 905	−0.062 680
				(B)				
1	−0.075 215	−0.028 930	0.000 393	0.018 302	0.021 301	0.000 000	−0.057 479	−0.208 700
2	−0.086 974	−0.070 446	−0.056 272	−0.040 681	−0.021 526	0.000 000	0.020 551	0.026 200
3	0.056 989	0.018 818	0.000 723	−0.006 038	−0.006 121	0.000 000	0.020 919	0.104 600
4	0.033 781	0.024 108	0.014 773	0.007 956	0.003 570	0.000 000	−0.004 036	−0.003 200
5	0.000 596	0.004 105	0.004 330	0.002 599	0.000 721	0.000 000	−0.000 221	−0.004 600
				(C)				
Bulk	0.111 720	0.055 382	0.045 297	0.046 791	0.037 963	0.000 000	−0.101 067	−0.393 320

$$V=V_p(n')\,|\,n'\rangle\langle n'\,|-V_p(n)\,|\,n\rangle\langle n\,|\ .$$

(The positions of a host atom with the impurity, initially at n' and n, are exchanged.)

We must also mention a puzzling problem: The number of levels on the calculation (8) is not yet sufficient to ensure the convergence of the segregation energies. Unfortunately, we cannot further increase the number of levels due to our limited computer size and time allocations. This fact may shed some doubts about the validity of the results existing in the literature where even cruder approximations to the densities of states than the one here are used.

IV. EQUILIBRIUM CONCENTRATIONS, DIFFUSION KINETICS

In the usual segregation model comprising two "phases," the bulk and the surface, we are led to the McLean formula[4] for the surface to bulk concentration,

$$\frac{c_s}{1-c_s}=\frac{c_{b_\infty}}{1-c_{b_\infty}}\exp\left[\frac{-h}{kT}\right], \tag{4.1}$$

where h is the segregation enthalpy and c_∞ the concentration in the bulk. It is easy to extend this relation to our case by minimizing the free energy with respect to the local concentration on each plane c_i and imposing conservation of the total number of impurity atoms. Within our approximations,

$$G=\sum_i c_iE_i+kT[c_i\ln c_i+(1-c_i)\ln(1-c_i)]\ , \tag{4.2}$$

$$\sum_i(c_i-c_\infty)=0\ . \tag{4.3}$$

[E_i is the segregation energy $E_{\text{segr}}(i)$ defined in (3.7).] Thus we obtain, as long as the bulk acts as an impurity atom reservoir,

$$\frac{c_i}{1-c_i}=\frac{c_\infty}{1-c_\infty}\exp\left[\frac{-E_i}{kT}\right], \tag{4.4}$$

and the usual Arrhenius law for concentration versus temperature, as long as $c_i \ll 1$.

We expect this relation to be valid in the dilute regime; otherwise, we should modify the model in order to include concentrated alloy layers in the very enriched regions. This relation may be used to check equilibrium concentration profiles. As far as we know, the experimental determination of individual concentration on each plane is a very difficult challenge, since usually, one observes an integrated signal over a few planes by Auger spectroscopy, or only related to the surface plane (ion and neutral low-energy backscattering). If the plane by plane crystal growth is well controlled by molecular-beam epitaxy, the reverse secondary-ion mass-spectroscopy analysis technique does not work due to a difference in the sputtering cross section. For Ni-Cu alloys, Ling *et al.*[1] predicted at least one oscillation in the concentration profile. More recently, Webber *et al.*,[2] with a combined XPS and/or Auger electron spectroscopy study for a 5 at. % Cu alloy, found a very strong segregation of Cu at the surface plane (85–100 at. %) followed by a depletion region with less than 5 at. % over 3–6 Å and an enriched region Cu (8–17 at. %) around 12 Å depth. By (4.4) we find a Cu concentration profile very similar (Fig. 3). As mentioned by Webber *et al.*,[2] no oscillation was expected from regular solution models treated by free-energy minimization[35] or Monte Carlo methods.[36] We hope that many other concentration profiles of Ni-based alloys will be available.

In general, we note that in case of a strong segregation on a plane ($E_{\text{segr}} \gg kT$), the concentrations on these planes are not very sensitive to the bulk value since the segregation energy in the exponential factor (4.4) dominates the bulk concentration prefactor. In any case, our model presented here can only be qualitatively valid in the case of strong enrichment. A combined model of concentrated alloy planes coupled to a dilute system may be constructed.

Our point is that alternative information about the energies on the different planes may be obtained from segregation kinetics, with the knowledge of the time dependence of the concentration on the first plane only. This is in a certain sense a time-space converter. It widens also the temperature range for the study of segregation, allowing one to analyze nonequilibrium situations.

One of the simplest models of diffusion adapted to the present study is

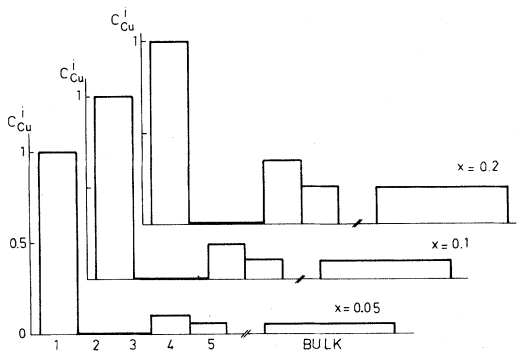

FIG. 3. Cu equilibrium concentration profile in Cu_x,Ni_{1-x} alloys ($x=0.20$, 0.10, 0.05) at $T=900$ K.

$$\begin{aligned}\frac{d}{dt}c_1 &= -W(1\to 2)c_1 + W(2\to 1)c_2\ ,\\ \frac{d}{dt}c_i &= W(i-1\to i)c_{i-1}\\ &\quad -[W(i\to i+1)+W(i\to i-1)]c_i\\ &\quad + W(i+1\to i)c_{i+1}\ .\end{aligned} \tag{4.5}$$

$W(i\to j)$ is the probability per unit time that an impurity diffuses from ith to jth plane. We associate these probability rates with those of an activation barrier; $W(i\to j)=0$ if i,j are not first-neighbor planes,

$$W(i\to j) = W_0 \exp[-\beta(E_j - E_i)] \times \frac{1+r\exp(-\beta E_i)}{1+r\exp(-\beta E_j)}\ , \tag{4.6}$$

with

$$r = c_\infty/(1-c_\infty)\ , \tag{4.7}$$

$$\beta = 1/kT\ , \tag{4.8}$$

and

$$W_0 = D/L^2\ . \tag{4.9}$$

D is the bulk heterodiffusion coefficient and L the distance separating two neighboring planes; the energies are the segregation energies. The last relation is simply derived by identifying the difference system to a partial differential diffusion equation in the limit $L\to 0$.

The last ratio in (4.6) has been introduced here in a heuristic manner; with this term, the thermodynamic equilibrium solution (4.4) becomes the exact stationary solution of (4.5). In practice, this factor is often negligible in dilute systems. In order to sketch the arguments developed in this section, let us simply show that from the knowledge of $c_1(t)$ one is able to obtain the difference of segregation energies on the neighboring planes, starting from an uniform concentration distribution $c_i = c_\infty$, whatever i, $\vec{c}(t)$ can be written as a Taylor series (a way to obtain formally the matrix exponential general solution),

$$\vec{c}(t) = \vec{c}(t=0) + \frac{d}{dt}\vec{c}(t=0)t + \frac{1}{2!}\frac{d^2}{dt^2}\vec{c}(t=0)t^2 + \cdots\ ,$$

with

$$\frac{d^n}{dt^n}\vec{c}(t=0) = W^n \vec{c}(t=0)\ .$$

The experimental data may be fitted to such a polynomial. It is easy to check that from the rate $(d/dt)c_1(t)$; for instance, one obtains $E_2 - E_1$ within the approximation of this paper,

$$2W_0 c_\infty \sinh(\beta(E_2 - E_1)) = \frac{dc_\infty}{dt}c_1(t=0)\ .$$

Other properties of this system of equations will be discussed elsewhere.

V. CONCLUSION

We studied the electronic structure of a substitutional impurity in a semi-infinite medium in the tight-binding model. We showed that the band contribution to the dissolution energy can be expressed by phase shifts which require only the knowledge of a finite number of matrix elements in the atomic-orbital basis. The segregation energy at a given site R is obtained as the difference of dissolution energies at this site and in the bulk; this gives us a much finer description than the usual surface and bulk models. Within the localized potential approximation, brought to self-consistency in the Friedel sense, we computed the segregation energies of impurities dissolved in a semi-infinite Ni crystal bounded by a (111) plane versus the difference of atomic number and the distance to the surface. This calculation is completely parameter free. It neglects, however, the lattice strain induced by the impurity, which needs to be considered when solvent and solute atom sizes differ too much. For the alloys reported in this paper, this approximation may not be too crucial. These energies are in good agreement with the existing experimental data and allow one to construct concentration profiles with an oscillatory character not predicted by a regular solution model.[35,36] In case of a strong enrichment ($E_{\mathrm{segr}} \gg kT$), the bulk concentration prefactor in the concentration on these planes is of minor importance, since the exponential term $\exp(-E_{\mathrm{segr}}/kT)$ is dominating. We suggested also that full information on the segregation energies on the different planes may be extracted from the kinetics by monitoring the time dependence on a single plane of the concentration (the surface plane, for instance). The study of bcc iron alloys, that we could not yet realize since a cluster eight times larger is required for the same accuracy (next-nearest-neighbor interactions are important), is in progress. The fact that we used a paramagnetic band structure is not a restriction to this work since the effects are sensitive at a sufficient high temperature.

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