PHYSICAL REVIEW B VOLUME 28, NUMBER 10 15 NOVEMBER 1983

Surface-orientation dependence on the segregation energies of impurities

H. Dreyssé and R. Riedinger
Laboratoire de Physique et de Spectroscopie Electronique (Jeune Equipe No. 03-40-70
du Centre National de la Recherche Scientifique), 4 rue des Frères Lumière, F-68093 Mulhouse Cedex, France
(Received 24 March 1983; revised manuscript received 11 July 1983)

We present the influence of the surface orientation on the band contribution to the segregation energy, within the tight-binding model, for fcc crystals. These results confirm that nondense surfaces favor the segregation, as experimentally observed. "Complex-energy-plane integration" for occupancy numbers, or energies, is also discussed.

I. INTRODUCTION

Concentration profiles can be obtained by different techniques such as Auger-electron spectroscopy (AES), ion spectroscopy, neutral retrodiffusion spectroscopy, x-ray photoelectron spectroscopy (XPS), secondary-ion mass spectroscopy (SIMS), and field-ion microscopy (FIM), each having its specific depth resolution. AES and XPS show integrated signals over several layers whose individual contribution cannot always be deconvoluted in an obvious and unique way. SIMS has the problem of different cross sections for sputtering different elements. Atom-probe FIM is able to count the individual atoms on each face of the tip atomic layer by atomic layer by field evaporation. Some of these techniques show a face orientation dependence of the surface segregation.[1,2] Ng *et al.*[1] fit a bond model and a macroscopic elastic strain model to their experimentally obtained concentration profiles.

In a recent paper,[3] the authors extended the theory of the electronic structure of a substitutional impurity versus the position to the surface which allows determination of the band contribution to the segregation enthalpy. Self-consistency for the perfect semi-infinite medium, as well as for the impurity potential (of finite spatial ranges assumed to be localized on one side in the applications) was imposed. The results for the segregation of impurities of the first transition-metal series in semi-infinite nickel bounded by a (111) surface were reported. In order to bring this problem into tractable form, the recursion methods for computing local Green's functions of Haydock *et al.*[4] and complex-energy-plane contour integration for quantities such as the total number of electrons on a site or the segregation energy were used. This technique was already known to Kohn and Sham.[5] It was rediscovered independently by Daniel,[6] and used by Koenig.[7] The full extensions to quantities such as charges, magnetic moments, spin-wave stiffness constant, and energies were done by one of the authors until 1975,[8] and later by others.[9–12] Working on dilute impurities in bulk by Korringa-Kohn-Rostoker (KKR) techniques,[13] Zeller, Deutz, and Dederichs realized that they could use this technique to reduce their computation time by a factor of about 100 instead of integrating, as is usually done, over the density of states for real energies. Others also realized the usefulness of this trick,[14] which introduces nothing new to physics, but makes possible precise and tractable applications.

We apply the method developed in Ref. 3 to (001) and (110) fcc surfaces; we have to build symmetry-adapted local orbitals, to the local symmetry broken by the surface plane, and to determine the corresponding independent Green's-function matrix elements (Sec. III). In conclusion, we show that the results confirm the experimental trend that segregation is favored in almost all of the cases toward open nondense surfaces.

II. COMPLEX-ENERGY-PLANE CONTOUR INTEGRATION

Often, one has to compute occupation numbers, energies, etc., for fermions,

$$A=\int r(E)f(E)dE\ , \tag{2.1}$$

where r represents some spectral density, and f the Fermi function. The contour integrals related to these quantities are well-known in the temperature-dependent Green's-function method,[15,16] and the remainder of this section can be considered as the limiting case for vanishing temperature; indeed, since f becomes a step function: 1 (0) below (above) the Fermi energy E_F:

$$A=\int_{-\infty}^{E_F} r(E)dE\ . \tag{2.2}$$

The spectral density has some analytical continuation in the complex-energy plane, called $R(z)$. The singularities of $R(z)$ consist of poles (bound states) and branch cuts (continuum spectrum), all on the real axis for Hermitian Hamiltonians H and having the conjugation property

$$R(z^*)=R^*(z)\ . \tag{2.3}$$

Thus

$$r(E)=\lim_{\epsilon\to 0}\left[-\frac{1}{2\pi i}[R(E+i\epsilon)-R(E-i\epsilon)]\right], \tag{2.4}$$

and (2.1) becomes a contour integral

$$A=\frac{1}{2\pi i}\int_{C_1} R(z)dz\ , \tag{2.5}$$

where C_1 is a contour around the real axis from $E_F+i\epsilon$ to $E_F-i\epsilon$, turning at $-\infty$ (regularly, since the spectrum has a lower bound) (Fig. 1). Via the Cauchy theorem, this

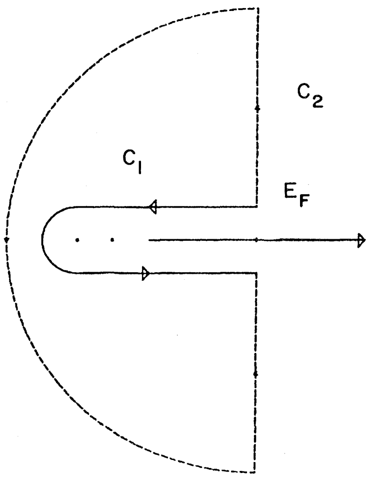

FIG. 1. Complex contour path for integration of (2.1).

path can be deformed into any path not crossing the singularities; among them, the most convenient is C_2, a Bromwitch line from $E_F-i\infty$ to $E_F+i\infty$, closed by a half-circle at infinity $[\mathrm{Re}(z)<E_F]$. This is the path which avoids, at best, the singularities on the real axis (branch cuts for continuous spectrum, poles for bound states).

Owing to the symmetry (2.3), A becomes

$$A=\frac{1}{2\pi i}\int_{\text{h.c.}} R(z)dz+\frac{1}{\pi}\int_0^{\infty}[\mathrm{Re}R(E_F+iy)]dy \quad (2.6)$$

The contributions of the half-circle (h.c.) and the fastness of convergence of the second term depend on the asymptotic form of $R(z)$; $R(z)$ may be expanded into a Laurent series at infinity,

$$R(z)=\sum_{n=\alpha}^{\infty}\mu_{n-1}z^{-n} \quad (2.7)$$

(moment expansion).

In the case of diagonal elements of Green's-function matrix, $\alpha=1$, and the contribution of the first term of (2.6) (residue at infinity) is $\frac{1}{2}\mu_0$ ($\mu_0=1$ for local orbital diagonal contribution). In the case of the energy, we obtain a similar result; if $G(z)$ is the continuation of the density of states $r(E)$, $zG(z)-1$ is a good candidate for the band energy $\mathrm{En}(E)$, the second moment μ_1 (center of gravity of the band) playing the role of μ_0. If the expansion (2.7) starts with $\alpha>2$, the contribution of the half-circle vanishes (Jordan's lemma[17]). The asymptotic form (2.7) may also be used to impose rigorous bounds on the precision of the second term of (2.7). We mention that the sampling on y should be made with the bandwidth as scale in (2.6); Gaussian integration may then be used.

III. SYMMETRY-ADAPTED ORBITALS FOR fcc (001) AND (110) SURFACES

As in Ref. 3, for the (111) semi-infinite medium, we built symmetry-adapted orbitals induced by the broken mirror symmetry for (001) and (110) surfaces. The residual point-group symmetry is, respectively, C_{4v} and D_2. In Table I, we report the corresponding orbitals. The selection rules for the Green's-function matrix elements of the ideal semi-infinite medium localized on a site are, respectively, with the convention of Table I,

$$g_1=G_{11}^0,\quad g_2=G_{22}^0=G_{33}^0,\quad g_4=G_{44}^0,\quad g_5=G_{55}^0\ , \quad (3.1)$$

and otherwise 0 for (001) surfaces,

$$g_1=G_{11}^0,\quad g_2=G_{22}^0,\quad g_3=G_{33}^0\ ,$$

$$g_4=G_{44}^0,\quad g_5=G_{55}^0,\quad g_6=G_{45}^0=G_{54}^0\ ,$$

and otherwise 0 for (110) surfaces.

We built them as continued fractions with the recursion method.[4] We mention that in the case of opened surfaces, the argument invoked in Ref. 3 is that for the prolongation of a_∞ and b_∞, the energy support of the spectrum cannot be further identified with the bulk one. In the case of opened surfaces, a surface-state continuum not strictly overlapping with the bulk one, is superimposed near the surface. We chose the best energy segment, in the sense of Pettifor.[18] We apply this formalism to Ni with the same convention as in Ref. 3 and the same set of parameters.

In Figs. 2 and 3, we report the corresponding spectral

Table I. fcc (001) and (110) surface-adapted d harmonics $[\alpha=(15/4\pi)^{1/2}]$. All irreducible representations are one dimensional, except Γ^5 (which is two dimensional).

Bulk symmetry	Bulk 0_h	Label	fcc (001) surface bounded semi-infinite C_{4v}	Comments	fcc (110) surface bounded-semi-infinite D_2	Comments
Γ'_{25}	αxy	1	αxy	Γ^4	$-\frac{\alpha}{2}(x^2-y^2)$	Γ^4
	αyz	2	αyz	Γ^5	$\frac{\alpha}{\sqrt{2}}(yz-zx)$	Γ^3
	αzx	3	αzx		$\frac{\alpha}{\sqrt{2}}(yz+zx)$	Γ^2
Γ_{12}	$\frac{\alpha}{2}(x^2-y^2)$	4	$\frac{\alpha}{2}(x^2-y^2)$	Γ^2	αxy	Γ^1
	$\frac{\alpha}{\sqrt{12}}(3z^2-r^2)$	5	$\frac{\alpha}{\sqrt{12}}(3z^2-r^2)$	Γ^1	$\frac{\alpha}{\sqrt{12}}(3z^2-r^2)$	Γ^1

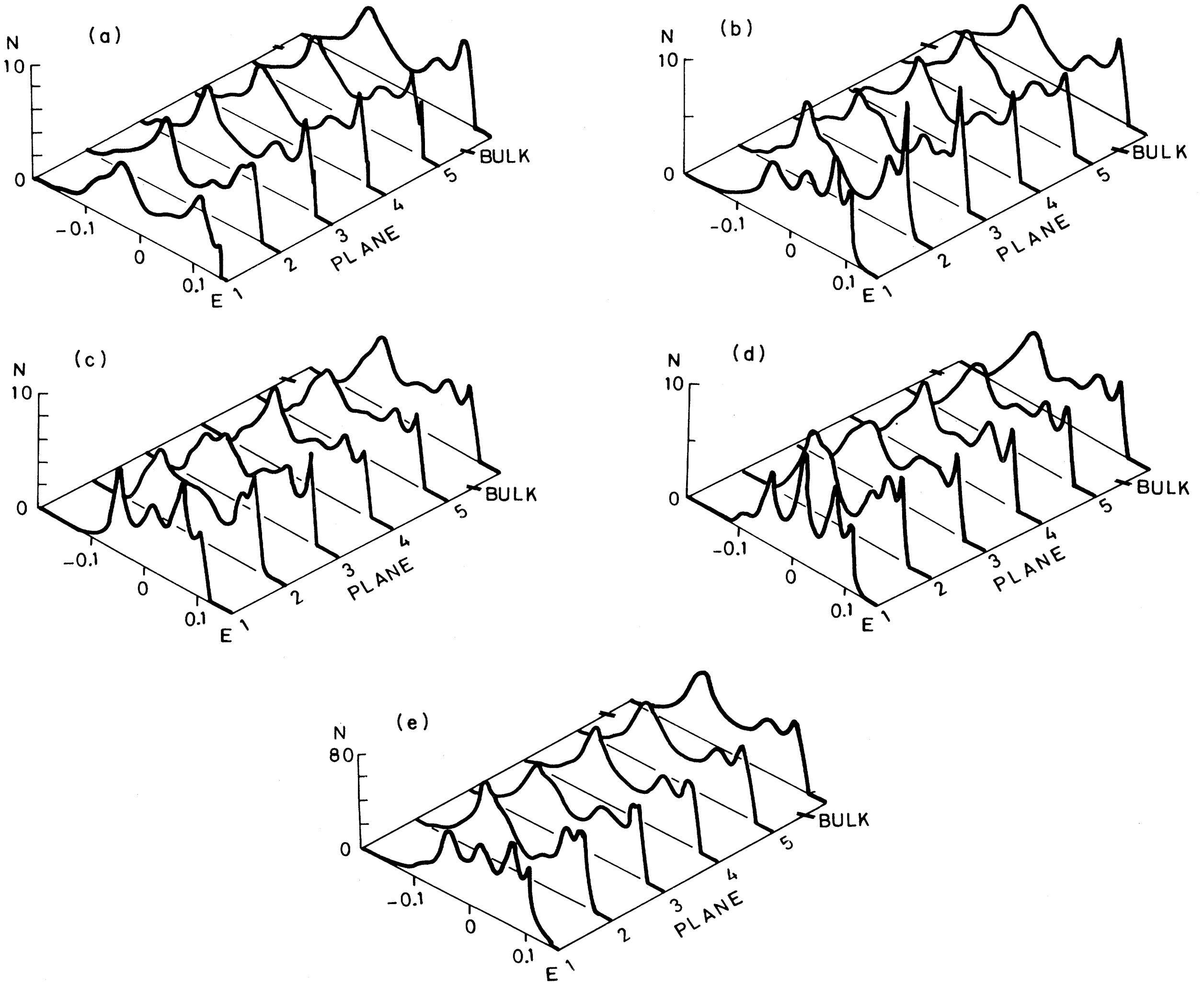

FIG. 2. Spectral densities ($-\pi^{-1}\mathrm{Im}g_i$), $i=1$, 2, 3, and 4 [(a), (b), (c), and (d)] and total density of states (e) vs the plane position relative to the surface (001) (first plane); the bulk is represented the sixth plane on up.

densities. We recover the surface state in the middle of the band for the (001) and (110) mainly on the first plane. This position corresponds to a dip of density of states for the bulk. These surface states appear only for the orbitals pointing out of the surface; the others [Figs. 2(c) and 2(a)] do not exhibit this surface state. The interorbital term g_6 for the (110) surface falls rapidly down with the distance to the surface. We also observe, in some cases, a peak on the top of the band which may not be physical, but related to the termination of continued-fraction coefficients.[18]

These matrix elements are needed for the determination of the phase shift induced by the perturbing potential of the substitutional impurity located at site R,

$$Z(R,z)=\mathrm{Tr}\ln[1-V_p(R)G^0(z)] \ . \tag{3.2}$$

The physical phase shift, $\eta(E)$, being in fact the imaginary part of it as $z\rightarrow E+i\epsilon$,

$$\eta(E)=\arg\det[1-V_p(R)G^0(E+i\epsilon)] \ . \tag{3.3}$$

This determinant factorizes according to the irreducible components [(3.1) and Table I].

With the auxiliary hypothesis that the extension of the potential is limited to its own site, only diagonal matrix elements survive; if we suppose further that these values are equal, the calculation becomes parameter-free, if completed with Friedel's sum rule.

The dissolution E_d and segregation E_s energies within the hypothesis of paper,[3] retain only one-electron contributions, which are given by

$$\begin{aligned} E_d(R)&=ZE_F-\frac{1}{\pi}\int_{-\infty}^{E_F}\eta(E,R)dE \ , \\ E_s(R)&=E_d(R)-E_d(\infty) \ , \end{aligned} \tag{3.4}$$

the infinity being located in the bulk, far from the surface; E_F is the Fermi energy of the system. We present in Table II the results for the self-consistent potentials and

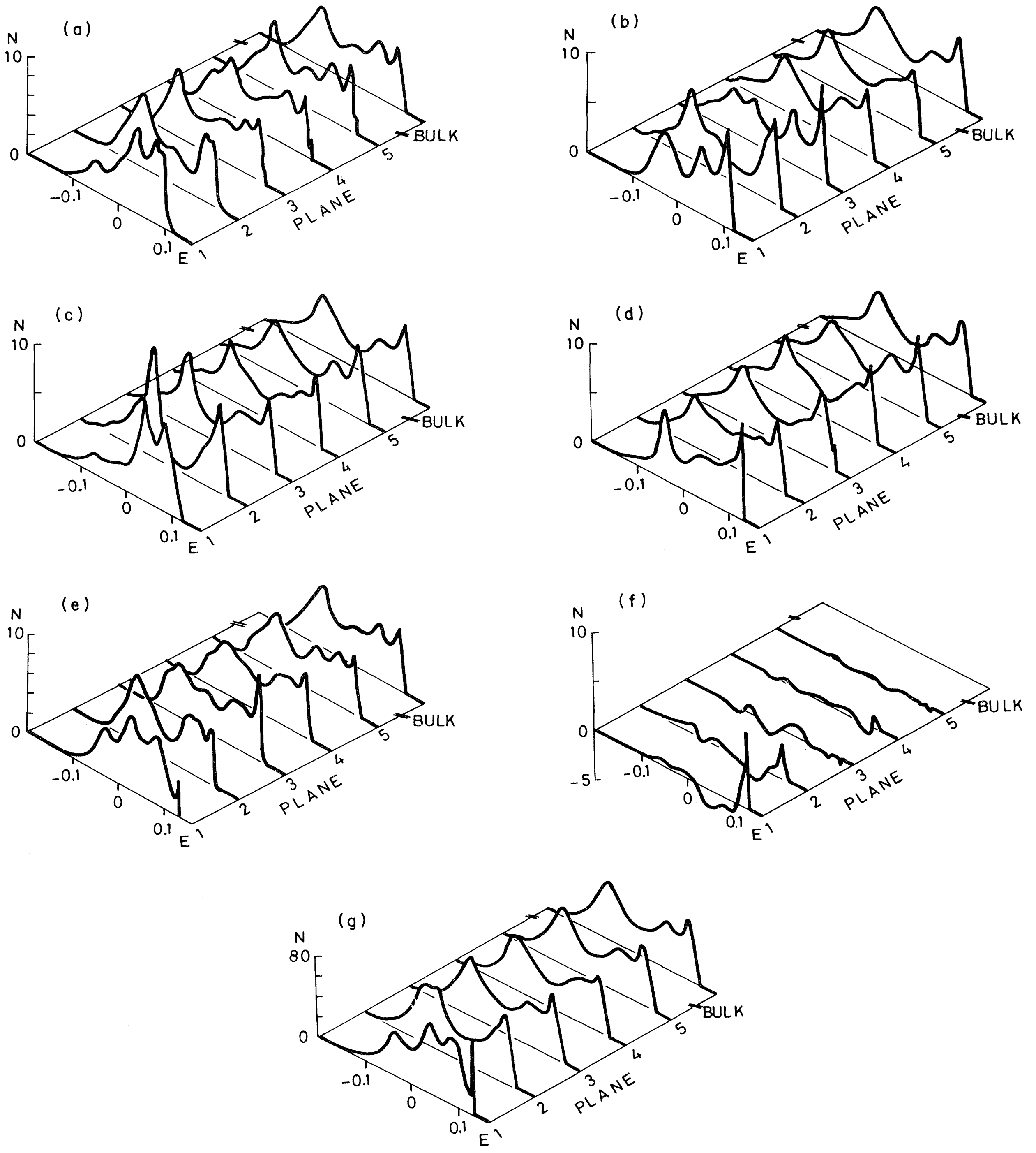

FIG. 3. Spectral densities $(-\pi^{-1}\text{Im}g_i)$, $i=1, 2, 3, 4, 5$, and 6 [(a), (b), (c), (d), (e), and (f), respectively] and total density of states (g) vs the plane position relative to the surface (110) (first plane); the bulk is represented from the sixth plane on up.

the segregation energy for (001) and (110) surfaces.

The comparison of the segregation energies obtained with Pettifor and Beer prescription[18] to the same quantities with the bulk termination (Ref. 3) shows that (i) there is no qualitative difference in the tendency to segregation (sign of the segregation energies), and also shows (ii) minor quantitative modifications for the (110) surface, but more significant variations for the (001) surface.

IV. APPLICATION TO SEGREGATION ON DIFFERENT Ni FACES

Our results show clearly a strong surface dependence to the surface-plane crystallographic orientation. It can even happen that the solute segregates on some faces, but not on others. This result cannot be obtained in the ideal solution model.[19] It appears that the more the surface is not

TABLE II. (a) Impurity-perturbing potentials and (b) segregation energies vs position in fcc (001) or (110) surface-bounded semi-infinite Ni (in Ry).

Impurity Plane	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Surface (001)				(a)				
1	0.087 065	0.058 341	0.041 785	0.028 824	0.015 946	0.000 000	−0.024 758	−0.080 553
2	0.125 252	0.065 539	0.040 990	0.025 896	0.013 480	0.000 000	−0.018 618	−0.051 412
3	0.207 322	0.089 193	0.051 478	0.030 843	0.015 380	0.000 000	−0.019 459	−0.050 277
4	0.155 682	0.080 058	0.050 190	0.031 658	0.016 281	0.000 000	−0.021 321	−0.056 915
5	0.119 986	0.067 117	0.043 765	0.028 317	0.014 805	0.000 000	−0.019 873	−0.054 967
Surface (110)								
1	0.059 993	0.041 325	0.030 955	0.022 586	0.013 316	0.000 000	−0.022 944	−0.078 699
2	0.091 252	0.056 219	0.039 179	0.025 964	0.013 415	0.000 000	−0.017 204	−0.047 788
3	0.163 859	0.075 359	0.045 299	0.027 934	0.014 093	0.000 000	−0.017 756	−0.045 994
4	0.116 367	0.067 711	0.044 583	0.029 113	0.015 515	0.000 000	−0.022 208	−0.064 560
5	0.124 192	0.068 097	0.043 981	0.028 312	0.014 772	0.000 000	−0.019 734	−0.054 141
Surface (001)				(b)				
1	−0.153 319	−0.065 894	−0.021 301	−0.000 107	0.007 467	0.000 000	−0.043 385	−0.244 189
2	0.007 566	−0.011 562	−0.020 244	−0.020 324	−0.012 615	0.000 000	0.013 914	0.038 896
3	0.156 592	0.100 054	0.049 078	0.017 253	0.002 812	0.000 000	0.007 210	0.052 868
4	0.085 869	0.066 746	0.044 384	0.025 295	0.011 199	0.000 000	−0.010 943	−0.012 832
5	0.008 490	0.007 013	0.003 698	0.000 621	−0.000 741	0.000 000	0.002 005	0.004 642
Surface (110)								
1	−0.268 414	−0.163 926	−0.095 691	−0.049 249	−0.014 596	0.000 000	−0.026 630	−0.227 870
2	−0.078 878	0.049 675	−0.026 455	−0.016 981	−0.012 029	0.000 000	0.025 977	0.071 285
3	−0.094 598	0.040 619	0.009 911	−0.004 531	−0.007 712	0.000 000	0.022 689	0.093 287
4	−0.000 597	0.011 118	0.010 441	0.007 811	0.005 796	0.000 000	−0.020 524	−0.089 869
5	0.018 814	0.011 473	0.004 841	−0.000 405	−0.001 112	0.000 000	−0.003 405	0.012 862

dense, the more the segregation is favored; this fact can be correlated to the existence of surface states below the Fermi level. Only noble-metal impurities do not comply to this rule in our pure tight-binding model without lattice strain.

We can summarize the following results for the Ni host.

(i) A strong segregation for vanadium and chromium solutes exists, which is enhanced on open surfaces. We found no experimental results for vanadium. In the case of chromium, our results agree with the results of Mosser and Werckmann,[20] who studied the (001) surface only.

(ii) Iron and manganese exhibit a similar behavior; segregation for the (110) and (001) surfaces, and none for (111). The *Ni*Mn system has not been experimentally studied; we dispose of extensive data on *Ni*Fe. We find a small negative segregation energy for the plane (100). This result may not be too significant due to the errors introduced in our calculation by the termination for the continued fraction, and also due to the fact that we neglected other contributions to the segregation energy (size effects). But this result agrees with Brundle *et al.*[21] and Greco *et al.*[22] results. The slight enrichment in Ni that Wandelt and Erlt found[23] on a polycrystalline sample may confirm our result, that segregation occurs for some faces only.

(iii) We find a cobalt segregation on the (110) surface, and none for (001) and (111). We found no experimental results for this system.

(iv) We obtain a strong surface segregation for zinc and copper for the three faces studied. There are no experimental results available for *Ni*Zn; *Ni*Cu is in agreement with the experimentals results (see Ref. 3), but contradicts result of the (111) surface of Wandelt and Brundle[2] and Ng, Tsong, and MacLane[1]; we found a stronger segregation for this surface as we did for the (001) one.

Our formalism also permits us to obtain concentration profiles.[3] The concentration profile is surface orientation dependent. It is very difficult to obtain experimental concentration profiles. In the case of the three orientations, (001), (110), and (111), we found a strong segregation of Cu on the surface plane and a Cu depletion on the next two planes. This agrees with the experimental results of Ng *et al.*[1] and Webber *et al.*[24] Ng *et al.*[1] found that the Cu enrichment on the surface plane as well as the Cu depletion on the next layers should be in the order of $(110)>(001)>(111)$. Our model fulfills the general concentration profile curve, but not the exact face orientation order shown above.

V. CONCLUSION

In this paper we have detailed the complex-energy-plane integration method which allows us to calculate directly integrated quantities in the most economical and accurate way (densities of states, total, number of electrons, band energies, magnetization, etc.).

We determined the band contribution to the segregation energy of an impurity in a semi-infinite medium within the tight-binding model. This microscopic model is completely parameter free and gives qualitative and quite quantitative results, which agree with the available experimental data. It has been shown for d impurities in semi-infinite Ni host, that the segregation is surface-orientation dependent; for some impurities we may observe segregation for certain faces and not for others. For transition impurity, the more the surface is open the more the segregation is favored. The concentration profiles are also surface-orientation dependent, and in all cases they present an oscillatory character. Our calculation neglects the lattice strain induced by the impurity, which needs to be introduced when solvent and atom sizes differ too much. A more complete study must take all these contributions into account.

---

[1] Y. S. Ng, T. T. Tsong, and S. B. Mc Lane, Jr., Phys. Rev. Lett. 42, 588 (1979). Y. S. Ng, S. B. Mc Lane, Jr., and T. T. Tsong, J. Vac. Sci. Technol. 17, 154 (1980).

[2] K. Wandelt and C. R. Brundle, Phys. Rev. Lett. 46, 1529 (1981).

[3] R. Riedinger and H. Dreyssé, Phys. Rev. B 27, 2073 (1983).

[4] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C 5, 2845 (1972); 8, 2591 (1975); V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35, p. 1; R. Haydock, in *Solid State Physics*, p. 216; M. J. Kelly, in *Solid State Physics*, p. 296.

[5] W. Kohn and L.J. Sham, Phys. Rev. A 137, 1697 (1965).

[6] E. Daniel (private communication).

[7] C. Koenig, thèse de troisième cycle, Université de Strasbourg (1972) [J. Phys. F 3, 1497 (1973)].

[8] R. Riedinger and M. Nauciel-Bloch, J. Phys. F 5, 732 (1975); M. Hennion, B. Hennion, M. Nauciel-Bloch, and R. Riedinger, *ibid.* 6, L303 (1976); R. Riedinger, M. C. Mokrani, H. Dreyssé, and M. A. Khan, *ibid.* 9, 337 (1979).

[9] Y. Khwaja and M. Nauciel Bloch, Phys. Status Solidi B 83, 473 (1977).

[10] M. Hennion-Bonfante, doctorat d'Etat, Orsay, 1978 (unpublished).

[11] H. Dreyssé, thèse de troisième cycle, Université Louis Pasteur et Université de Haute Alsace, 1980 (unpublished).

[12] H. Dreyssé and R. Riedinger, J. Phys. (Paris) 42, 437 (1981).

[13] R. Zeller, J. Deutz, and P. H. Dederichs, Solid State Commun. 44, 993 (1982).

[14] A. R. Williams, P. J. Feibelman, and N. D. Lang, Phys. Rev. B 26, 5433 (1982).

[15] L. A. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).

[16] A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, in *Methods of Quantum Field Theory in Statistical Physics*, edited by R. A. Silverman (Prentice-Hall, Englewood Cliffs, New Jersey, 1963).

[17] W. Rudin, *Real and Complex Analysis*, 2nd ed. (McGraw-Hill, New York, 1974).

[18] D. G. Pettifor and N. Beer, (a) ψ_K Newsletter—Darsbury Laboratory (United Kingdom) August 1982, Report No. 3 (unpublished); (b) in Electronic Structure of Complex Systems—NATO Advanced Study Institute, Gent (Plenum, New York, in press).

[19] F. F. Abraham, N. H. Tsai, and G. M. Pound, Surf. Sci. 83, 406 (1979).

[20] A. Mosser and J. Werckmann, in *Proceedings of the Fourth Colloquium on Solid Surface Physics and Chemistry, Antibes Juan les Pins, 1978*, in Revue Le Vide (French-American Society, Paris 1979).

[21] C. R. Brundle, E. Silvermann, and R. T. Madix, J. Vac. Sci. Technol. 16, 474 (1979).

[22] S. E. Greco, J. P. Roux, and J. M. Blakely, Surf. Sci. 120, 203 (1982).

[23] K. Wandelt and G. Ertl, J. Phys. F 6, 1607 (1976).

[24] P. R. Webber, C. E. Rojas, P. J. Dobson, and D. Chadwick, Surf. Sci. 105, 20 (1981).