PHYSICAL REVIEW B VOLUME 35, NUMBER 9 15 MARCH 1987-II

Surface-sandwich segregation in Pt-Ni and Ag-Ni alloys: Two different physical origins for the same phenomenon

Guy Tréglia
Laboratoire de Physique des Solides, Université de Paris—Sud,
Bâtiment 510, Centre Universitaire d'Orsay, 91405 Orsay Cédex, France

Bernard Legrand
Section de Recherche de Métallurgie Physique, Centre d'Etudes Nucléaires de Saclay,
91191 Gif-sur-Yvette Cédex, France

(Received 14 July 1986)

We show that a simple mean-field approach, including simultaneously a correct size effect (treated atomistically), a surface-tension term and the alloy effect, is sufficient to account for the surface-"sandwich" segregation observed on the (111) faces of Pt-Ni and very dilute Ag:Ni alloys. We show that this phenomenon does not have the same physical origin in both cases.

I. INTRODUCTION

The study of the surface composition of binary alloys is interesting for many purposes. Actually, it has long been known experimentally that the concentration near the surface is usually different from the one in the bulk. The fundamental questions raised by these experiments are the following:

(i) existence or nonexistence of a superficial enrichment;

(ii) in the affirmative, nature of the segregating element;

(iii) number of layers affected by the segregation;

(iv) concentration profile (monotonous, oscillating);

(v) influence of temperature and bulk concentration;

(vi) and finally, possible anisotropy of these phenomena with the crystallographic orientation of the surface.

Most of the theoretical studies have been devoted to the prediction of a possible surface segregation and to the knowledge of the segregating element. The various calculations have put in evidence the influence of three predominant factors:[1] the differences in size and surface tension between the components and their mixing energy. On the other hand, the concentration profile has been related to this last term: monotonous (oscillating) profile when the alloy tends to segregate (to order) in the bulk.[1] For many authors, the first two effects are the most important; consequently they have established structural maps defining, as a function of the surface tensions and sizes of the two elements, the domains where surface segregation occurs.[2] In most cases, the surface tension argument is sufficient to explain the observed behavior. In one particular case (Fe-Zr) the size effect prevails unambiguously. However, this kind of map is too schematic to account for the experimental data collected for two particular systems: Pt-Ni (in the whole range of concentration) (Ref. 3) and Ag-Ni (in the limit of very small concentrations of Ni).[4]

In the first case, the segregation of Pt at any concentration can be explained neither by the difference in surface tension (quite negligible) nor by the elastic treatment of size effect which leads always to the segregation of the solute. In the other case, the strong enrichment of the surface sublayer in Ni associated with an almost pure Ag surface plane for a bulk concentration in Ni of some ppms, is out of the scope of this simple framework. The aim of this paper is to give a quantitative interpretation of the experimental results for these two systems using a mean field approximation in which the size effect is treated within a microscopic model.

II. FORMALISM

Let us consider an alloy A_cB_{1-c} described by the simple Ising Hamiltonian

$$H=\frac{1}{2}\sum_{n,m,i,j}\varepsilon_{nm}^{ij}p_n^ip_m^j \tag{1}$$

where ε_{nm}^{ij} is the interaction energy between an atom of type i at site n and an atom of type j ($i,j=A,B$) at site m. p_n^i is the occupation number which is equal to 1 (0) if the site is (not) occupied by an atom of type i. For a binary alloy, $p_n^A+p_n^B=1$, so that Eq. (1) can be written in terms of only one variable, $p_n=p_n^A$:

$$H=H_0+\sum_n p_n\sum_{m(\neq n)}(\tau_{nm}-V_{nm})+\sum_{\substack{n,m\\(m\neq n)}}p_np_mV_{nm}\ , \tag{2}$$

with

$$H_0=\frac{1}{2}\sum_{\substack{n,m\\(n\neq m)}}\varepsilon_{nm}^{BB},\quad \tau_{nm}=\frac{1}{2}(\varepsilon_{nm}^{AA}-\varepsilon_{nm}^{BB})\ ,$$

and

$$V_{nm}=\frac{1}{2}(\varepsilon_{nm}^{AA}+\varepsilon_{nm}^{BB}-2\varepsilon_{nm}^{AB})\ .$$

The quantity τ_{nm} can be related to the difference in surface tension between A and B metals whereas V_{nm} is the pair interaction which characterizes the tendency of the system to order or not. Let us note that we have assumed here that the energy could be written as a sum of pair interactions. This is not really justified for transition metal alloys. In fact, it has been shown that such a development is valid for the configuration dependent part of this energy [i.e., the term quadratic with respect to p_n in Eq. (2)].[5] Therefore the remaining problem lies in the coefficient of p_n in the linear term of (2). We will detail this point in the practical calculations. Moreover, we will consider only in Eq. (2) the interactions between first neighbors which is well justified for the fcc structure of Pt-Ni and Ag-Ni,[5] assuming in addition no modification of the interaction at the surface: $\tau_{nm}=\tau$ and $V_{nm}=V$. Then, we can write

$$H=H_0+(\tau-V)\sum_n p_n Z_n+V\sum_{\substack{n,m\\(m\neq n)}} p_n p_m \ , \tag{3}$$

where Z_n is the coordination number of site n.

Let us note that, with our sign convention, $V>0$ (<0) indicates a tendency of the alloy to order (segregate) in the bulk whereas $\tau>0$ (<0) means that the A (B) element has a surface energy lower than that of the other component.

The equation (3) does not account for a possible size effect. It can be done by introducing a third term ΔH_{se}. A first evaluation of this term has been given by McLean,[6] in the dilute case, assuming that the elastic energy associated with a solute atom vanishes when this atom in the bulk is exchanged with a solvent one at the surface. It gives:[7]

$$\Delta H_{\text{se}}=-\frac{24\pi K G r_0 r_1 (r_0-r_1)^2}{3Kr_1+4Gr_0} \ , \tag{4}$$

where K is the bulk modulus of the solute, G the shear modulus of the solvent and r_0 and r_1 are appropriate radii for solvent and solute, respectively. Such a formula leads always to a segregation of the solute, not dependent on the sign of the mismatch. This can be criticized since it assumes that the surface part of the size mismatch vanishes; more generally, the use of elasticity to evaluate the size mismatch energy is doubtful. These drawbacks can be avoided using simultaneously an atomistic model and a relaxation process to minimize the strain energy of one impurity successively in the bulk and at the surface of the solvent matrice.[8] Like Tománek,[9] we use the model proposed by Ducastelle[10] to write the total energy as a sum of an attractive d band term and a repulsive semiempirical one. The former is calculated in the tight-binding framework using densities of states exact up to the second moment.[11] The latter is assumed, as usual, of the Born-Mayer type.[10] We use here the same parameters as in Ref. 8. The resulting energies for Pt-Ni and Ag-Ni alloys are shown in Table I. We can now introduce this term into Eq. (3):

$$H=H_0+(\tau-V)\sum_n p_n Z_n+V\sum_{\substack{n,m\\(m\neq n)}} p_n p_m+\sum_n \Delta H^{n}_{\text{se}} p_n \ . \tag{5}$$

Let us consider a disordered alloy: for T sufficiently high compared with the critical temperature T_c, a mean-field approach is fully justified. In this case, the average of the two site correlation functions $\langle p_n p_m\rangle$ factorizes into the product of one site correlation functions $\langle p_n\rangle\langle p_m\rangle$. We can write $\langle p_n\rangle=c_n$ and $\langle p_n p_m\rangle=c_n c_m$.

In an infinite crystal, c_n does not depend on n: $c_n=c$. In presence of a surface, the concentration can be different for planes parallel to this surface. Therefore one must define p-plane concentrations c_p[$p=0$ (surface), $p=1$ (first underlayer), $\cdots$, $p=\infty$ (bulk plane)] so that

$$\forall n \epsilon p \text{ plane } c_n=c_p \ .$$

The internal energy is obtained by averaging the Hamiltonian (5) over all configurations:

$$\begin{aligned}\langle H\rangle=H_0&+N(\tau-V)\sum_p c_p(Z+Z_p^{+}+Z_p^{++}+Z_p^{-}+Z_p^{--})\\&+NV\sum_p c_p(Zc_p+Z_p^{+}c_{p+1}+Z_p^{-}c_{p-1}+Z_p^{++}c_{p+2}\\&+Z_p^{--}c_{p-2})+N\sum_p \Delta H^{p}_{\text{se}}c_p \ ,\end{aligned} \tag{6}$$

in which ΔH^{n}_{se}, as c_n, only depends on the index of the plane p where the site n lies; N is the number of atoms per plane; Z, Z_p^{+} (Z_p^{++}), Z_p^{-} (Z_p^{--}), are the numbers of first neighbors of a site n in the plane p, respectively, in the same plane, in the plane(s) "below" and the plane(s) "above." Averaging the entropy in the same way, we obtain the free energy:

$$F=\langle H\rangle+NkT\sum_p [c_p\ln c_p+(1-c_p)\ln(1-c_p)]-N\sum_p c_p\mu \ , \tag{7}$$

where μ is the chemical potential. Note that we have neglected the vibrational entropy. The minimization of the free energy ($\partial F/\partial c_p=0$, $\forall c_p$) leads to the following system of coupled equations:

$$\begin{aligned}\forall_p, \frac{c_p}{1-c_p}=\exp\{-\beta[&(\tau-V)(Z+Z_p^{+}+Z_p^{++}+Z_p^{-}+Z_p^{--})+V(2Zc_p+Z_p^{+}c_{p+1}+Z_p^{++}c_{p+2}+Z_p^{--}c_{p-2}+Z^{-}_{p+1}c_{p+1}\\&+Z^{--}_{p+2}c_{p+2}+Z^{+}_{p-1}c_{p-1}+Z^{++}_{p-2}c_{p-2})+\Delta H^{p}_{\text{se}}-\mu]\} \ .\end{aligned} \tag{8}$$

From a practical point of view, we let the concentrations vary on the three first planes (c_0, c_1, c_2) assuming $c_3=c_4=\cdots=c_\infty$. This point, which could be criticized if c_2—and to a less extent c_1 (in the case $Z_3^{--}=Z_1^{++}\neq 0$ only)—is very different from c_B, will be discussed in more details in the following sections. Then, Eqs. (8) reduce to three nonlinear equations which must be solved self-consistently:

$$\frac{c_0}{1-c_0}=\frac{c_B}{1-c_B}\exp(-\beta\{-(Z'+Z'')(\tau-V)+2V[Z(c_0-c_B)+Z'(c_1-2c_B)+Z''(c_2-2c_B)]+\Delta H^0_{\mathrm{se}}\})\,,$$

$$\frac{c_1}{1-c_1}=\frac{c_B}{1-c_B}\exp(-\beta\{-Z''(\tau-V)+2V[Z(c_1-c_B)+Z'(c_2+c_0-2c_B)-Z''c_B]+\Delta H^1_{\mathrm{se}}\})\,, \tag{9}$$

$$\frac{c_2}{1-c_2}=\frac{c_B}{1-c_B}\exp(-\beta\{2V[Z(c_2-c_B)+Z'(c_1-c_B)+Z''(c_0-c_B)]+\Delta H^2_{\mathrm{se}}\})\,,$$

in which Z' $(Z'')=Z_p^+$ $(Z_p^{++})=Z_p^-$ (Z_p^{--}) for $p>2$.

Let us recall that the values of ΔH^i_{se} given in Table I have been obtained for $c_B\to 0(1)$. For intermediate concentrations, we have used a sinusoidal shape to interpolate between these limits:

$$\Delta H^p_{\mathrm{se}}=\tfrac{1}{2}\{(\Delta H^p_1-\Delta H^p_0)\sin[(c-\tfrac{1}{2})\pi]+(\Delta H^p_1+\Delta H^p_0)\}\,,$$

where $\Delta H^p_0(1)$ is given in Table I for an impurity in the p plane ($p=0$ surface), for $c\to 0$ (1). The corresponding curves for PtNi are given in Fig. 1 where they are compared to the elastic term,[7] interpolated in the same way. One sees that, when the size of the impurity is larger than that of the solute ($c\to 0$) in Fig. 1, both approaches give similar results. On the contrary, when the impurity is the smallest, the sign of ΔH^0_{se} can be reversed. This shows the importance of an atomistic treatment of the size effect. It is obvious from Table I that ΔH^p_{se} is negligible for $p>2$.

III. APPLICATION TO Pt-Ni

Let us first recall the existing experimental data concerning the surface segregation of PtNi alloys. By means of low-energy electron diffraction (LEED), Gauthier *et al.* and Baudoing *et al.*[3] have put in evidence a short-wave large-amplitude composition oscillation across three layers at the (111) surface of $Pt_{50}Ni_{50}$, $Pt_{78}Ni_{22}$, and $Pt_{10}Ni_{90}$ at 850 °C. More precisely, they observed a well-developed Pt-Ni sandwich with platinum on top. The strong Pt enrichment of the first plane on the whole range of concentration has been confirmed by ion-scattering spectroscopy.[12] This oscillating behavior can be easily understood from the tendency of this alloy to order ($V>0$). It has been the subject of a previous paper[13] in which the authors used a simple nearest- neighbor interaction model which was not able to account for the Pt enrichment of the topmost plane. The surface composition was then selected from the experimental data. Our model does not suffer from this limitation since it takes into account, not only the ordering effect, but also the size effect (the surface tension effect being negligible for PtNi).

TABLE I. Energy of the size mismatch effect for Pt-Ni and Ag-Ni (in units of eV/at.) for the three low-index surfaces (111), (100), and (110). ΔH^p_i is the energy of segregation due to the size effect on the p plane [$p=0$ (surface), $p=1$ (first underlayer), and so on] in the limit $C_B\to 0$ ($i=0$) or $C_B\to 1$ ($i=1$), C_B being the bulk concentration of Pt (in Pt-Ni) or Ag (in Ag-Ni). In bracket is the nature of the segregant element.

Surface	Energy of segregation	Pt-Ni	Ag-Ni
(111)	ΔH^0_0	−0.26 (Pt)	−0.47 (Ag)
	ΔH^0_1	−0.04 (Pt)	0
	ΔH^1_0	0	−0.01 (Ag)
	ΔH^1_1	+0.02 (Ni)	+0.02 (Ni)
(100)	ΔH^0_0	−0.28 (Pt)	−0.52 (Ag)
	ΔH^0_1	+0.02 (Ni)	+0.05 (Ni)
	ΔH^1_0	0	−0.01 (Ag)
	ΔH^1_1	+0.03 (Ni)	+0.02 (Ni)
(110)	ΔH^0_0	−0.27 (Pt)	−0.52 (Ag)
	ΔH^0_1	+0.09 (Ni)	+0.09 (Ni)
	ΔH^1_0	−0.11 (Pt)	−0.21 (Ag)
	ΔH^1_1	−0.02 (Pt)	0
	ΔH^2_0	0	−0.01 (Ag)
	ΔH^2_1	+0.02 (Ni)	+0.01 (Ni)

The respective effects of the size mismatch ($\tau=0$, $V=0$) and of the ordering term ($\tau=0$, $\Delta H^i_{\mathrm{se}}=0$) are exhibited in Fig. 2, for the three low index faces of Pt-Ni. The value of V has been derived from the critical temperature of Pt-Ni ($T_c=635$ °C) in the mean-field approximation ($V=\frac{1}{2}kT_c=0.038$ eV, for an ordering of the $L1_0$ type). The mismatch effect is strongly asymmetric: it produces a strong Pt enrichment on the topmost plane for a concentration of Pt less than 70%. For larger concentration, this effect is weaker and even changes sign on the (110) face. Moreover, on that last face, it leads to a

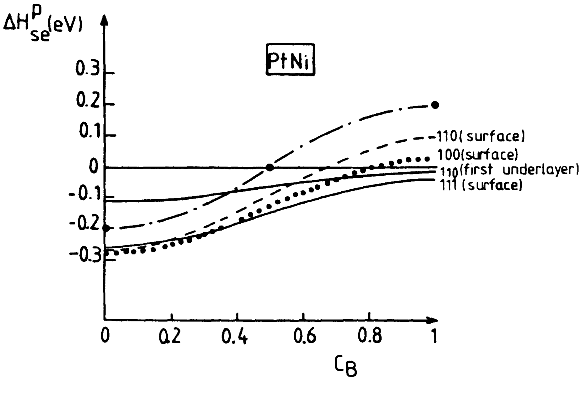

FIG. 1. Interpolation of the size mismatch energy between its extremal values (see Table I) as a function of Pt bulk concentration (c_B) for a Pt-Ni alloy [see formula (10)]. For the sake of comparison we have also plotted the prediction of elasticity theory [see formula (4)] which is face independent (—·—·—·)

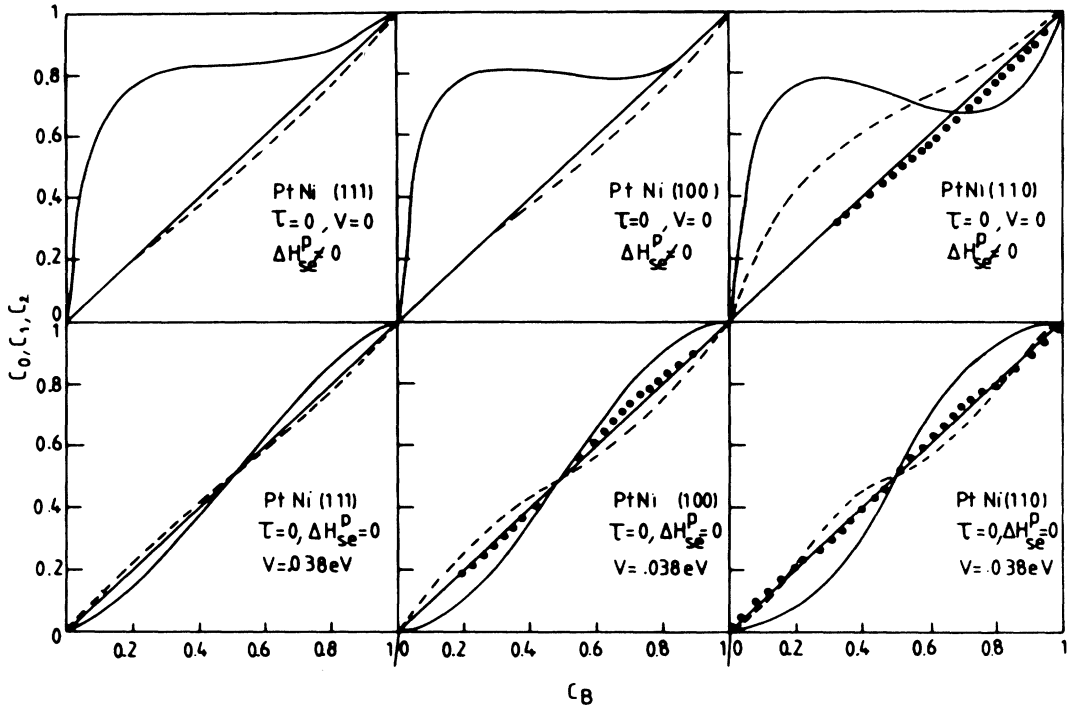

FIG. 2. Variation of the Pt concentration at the surface (c_0, ——), on the first (c_1, — — —) and second (c_2, · · · ·) underlayers as a function of the Pt bulk concentration (c_B) for the three low index faces of Pt-Ni at $T=850\,^{\circ}\mathrm{C}$: upper part, size effect alone; lower part, alloy effect alone.

segregation of Pt on the first underlayer. The ordering effect is symmetric with respect to $c_B=\frac{1}{2}$ and always favors the segregation of the majority species at the surface; it oscillates with depth.

When both effects are taken into account simultaneously in Eq. (9), the oscillating behavior is reinforced for the (111) and (100) faces (see Fig. 3). Moreover we obtain, in the whole range of concentrations, a strong Pt enrichment of the surface, a significant depletion on the first underlayer and again a slight enrichment on the second sublayer. This oscillation is much more damped for the (111) face than for the (100) one. These results are in qualitative agreement with the experiments[3] but the amplitude of the oscillation is underestimated in the calculation. The case of the (110) face is very exciting. Actually, essentially due to the size effect, one predicts an enrichment of Pt on the whole range of concentration for the first underlayer, the depletion appearing only for the second sub-

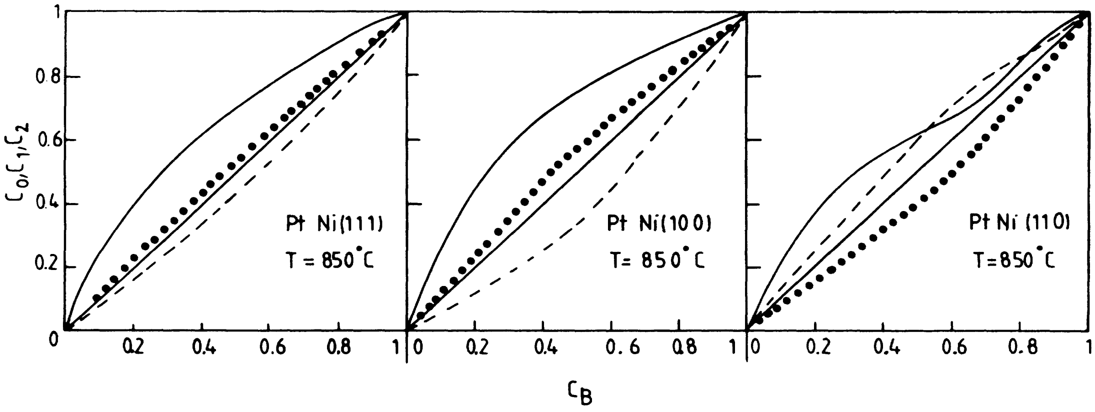

FIG. 3. Variation of the Pt concentration at the surface (c_0, ——), on the first (c_1, — — —) and second (c_2, · · · ·) underlayers as a function of the Pt bulk concentration (c_B) for the three low index faces of Pt-Ni at $T=850\,^{\circ}\mathrm{C}$, when size and alloy effects are taken into account simultaneously.

layer. On the topmost plane, the Pt segregation is less important than for the other faces particularly on the Pt-rich side for which this Pt segregation almost vanishes. This amazing behavior of the (110) face would deserve some experimental attention.

IV. APPLICATION TO Ag-Ni

The equilibrium segregation in AgNi (111) dilute solid solutions was studied using radiotracers ^{63}Ni, over the temperature range 500–700 °C.[4] In view of the very low solubility of Ni in solid Ag ($<2\times10^{-3}$ at./at.), the experiments were performed for some ppm of Ni. In these conditions, the authors found that Ni strongly segregates on silver with a very peculiar surface structure: the topmost layer consists purely of solvent (Ag), Ni being located under this layer in "sandwich" between silver planes. This original configuration presents some analogy with the "surface sandwich" observed in Pt-Ni and described in the preceding section. However, whereas the oscillating behavior of Pt-Ni was due to positive V (tendency to order), it is well known that Ag-Ni tends to segregate in the bulk ($V<0$). It is therefore very interesting to elucidate the origin of the phenomenon in this case.

As for Pt-Ni, we use the model developed in Sec. II, but in the present case the surface tension effect is no longer vanishing. The corresponding value of τ has been obtained by averaging over the cohesive energies and surface tensions of Ag and Ni.[14] This leads to $\tau=0.08$ eV. This procedure is not fully justified since it is known that these energies are not really pairwise[10] but is nevertheless sufficient for the semiquantitative treatment of interest here. As for the alloy parameter V, its determination from T_c is more difficult than for Pt-Ni, due to its high value. We have then chosen to derive V from Miedema's tables,[15] which gives

$$V^{\text{Ag-Ni}} \simeq -3V^{\text{Pt-Ni}} = -0.115 \text{ eV} .$$

Finally, the size effect is obtained with the same interpolation as for Pt-Ni, from Table I.

The respective effects of the size mismatch and surface tension are illustrated in Fig. 4(a). We have chosen a high value of the temperature to be sufficiently above the critical temperature ($T_c \simeq 2000$ °C) to be consistent with our mean-field approach. One sees that both effects lead to a segregation of Ag on the surface plane for the whole range of concentration. On an other hand, they do not lead to any significant variation of concentration on the underlayers. Note that the size effect is similar to that obtained for Pt-Ni but is damped by temperature.

Let us now consider the alloy effect. We have plotted in Fig. 4(b) the variation of the concentration on the three first planes due to this factor alone ($\tau=0$, $\Delta H_{\text{se}}=0$). The most striking feature is the strong segregation of the minority species on these planes contrasting with previous results for $V>0$. One can wonder whether the large difference between c_2 and c_B is consistent with our assumption to fix $c_3=c_B$. We have checked that our results for c_0, c_1, and c_2 are not changed if, instead of $c_3=c_B$, we assume $c_3=c_2$ which is the opposite assumption. The other peculiarity of Fig. 4(b) is the nonmonotonous behavior of c_1, c_2, c_3 as a function of c_B, compared to the monotonous one for very small V or very high temperatures.[1] We then have to vary the temperature between 5000 and 10 000 °C. This is illustrated in Fig. 5. We indeed observe for a temperature of about 7500 °C, a kind of phase transition induced by the surface which is characterized by a change in the behavior of c_0 versus c_B for $0.3<c_B<0.7$ The characterization of this transition would require more extensive calculations which are beyond the scope of this paper since we are interested here in studying the dilute limit ($c_B \rightarrow 1$).

We have then introduced the three effects simultaneously. This leads to the curves of Fig. 6 showing the vari-

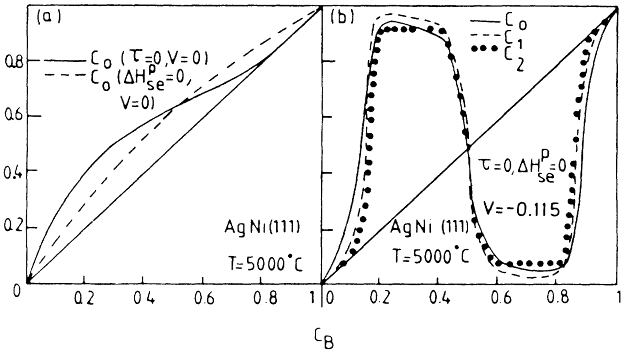

FIG. 4. (a) Variation of the surface (c_0) Ag concentration as a function of the Ag bulk concentration (c_B) for Ag-Ni (111) at $T=5000$ °C: ——, size effect alone; — — —, surface tension effect alone. (b) Variation of the Ag concentration at the surface (c_0, ——), on the first (c_1, — — —) and second (c_2, · · · ·) underlayers as a function of the bulk Ag concentration (c_B) for Ag-Ni (111) at $T=5000$ °C when only the alloy effect is considered.

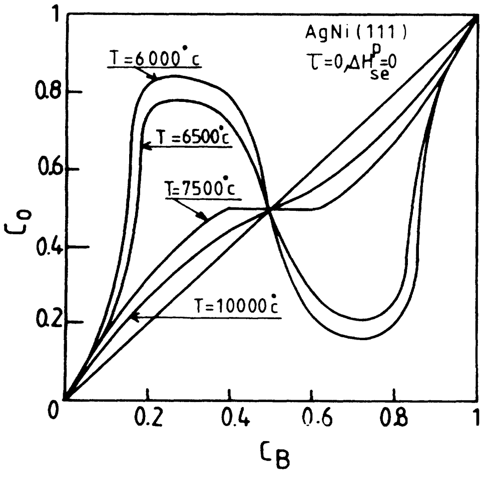

FIG. 5. Variation of the surface (c_0) Ag concentration as a function of the Ag bulk concentration (c_B) for Ag-Ni (111) at different temperatures when only the alloy effect is taken into account.

ation of c_0 and c_1 as a function of c_B, and of the temperature. Except for $T = 5000\,^{\circ}\mathrm{C}$ (which can be compared to Fig. 5), the curves are presented only for small Ni concentrations. In this domain we note two important features when the temperature is lowered. (i) The Ag segregation increases at the surface, the surface layer being of pure Ag for $T \lesssim 2000\,^{\circ}\mathrm{C}$.

(ii) on the contrary, a dramatic depletion is observed on the first underlayer leading, for $T \lesssim 2000\,^{\circ}\mathrm{C}$, to an almost pure Ni plane.

This spectacular behavior is differently illustrated in Fig. 7 in which c_0 and c_1 are plotted as a function of the temperature for $c_B = 0.9$ (for numerical stability reasons, it was difficult to mimic strictly the experiments with $c_B = 0.99999\ldots$,[4] but our results can be extrapolated up to this limit). This confirms that, below a "critical" temperature $T_c^s \sim 4000\,^{\circ}\mathrm{C}$ for $c_B = 0.9$, the surface layer tends to a pure-Ag plane whereas the first underlayer tends to a pure-Ni plane. We have also plotted in Fig. 7 the corresponding curve for the second underlayer (c_2). One sees that the value of c_2 is very close to that of c_B. This is an important point to justify our procedure of determining c_0, c_1, and c_2 with the boundary condition $c_3 = c_B$, which could be questionable, as mentioned by the referee, if c_2 is very different from c_B. Actually, it is obvious from Eq. (8) that, for a (111) face ($Z_3^{--} = Z_1^{++} = 0$), c_3 only depends on c_2, and not on c_1 so that $c_2 \simeq c_B$ implies $c_3 \simeq c_B$. It remains to check if our result ($c_2 \simeq c_B$, see Fig. 7 does not depend on our assumption of fixing $c_3 = c_B$. To answer this question, we have changed this boundary condition into $c_3 = c_2$. As in the previous case, c_2 is found to be almost equal to c_B. This proves that the curves plotted in Fig. 7 are indeed meaningful. From the extrapolation of these curves up to the experimental temperature and concentration, we then obtain a "sandwich" structure in which a pure-nickel plane (first underlayer) is placed between two silver planes (topmost and second underlayer).

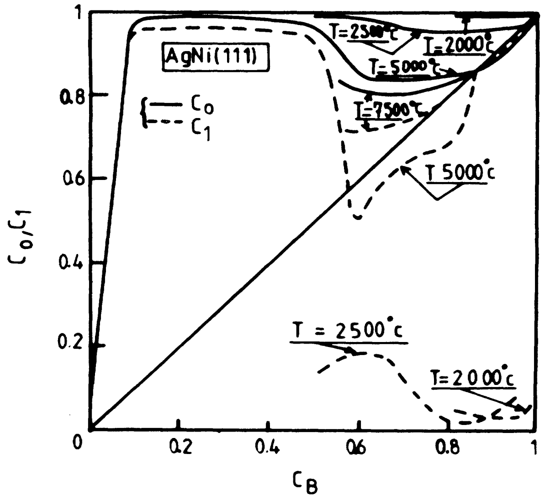

FIG. 6. Variation of the Ag concentration at the surface (c_0, ——) and on the first underlayer (c_1, — — —) as a function of the Ag bulk concentration (c_B) in Ag-Ni (111) for different temperatures when size, surface tension, and alloy effects are taken into account simultaneously.

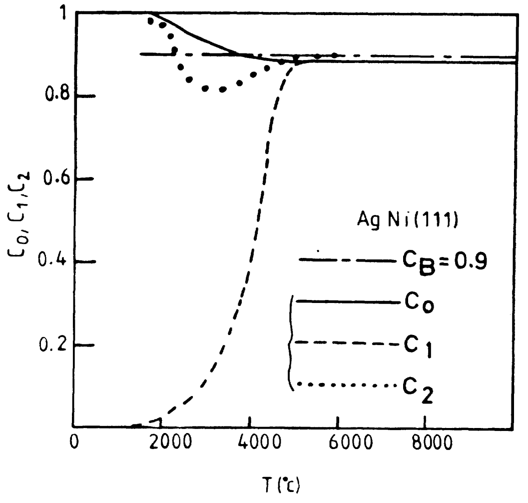

FIG. 7. Variation of the Ag concentration at the surface (c_0, ——), on the first underlayer (c_1, — — —) and second (c_2, · · · ·) underlayers for a given bulk concentration of Ag ($c_B = 0.9$, —·—·—·) as a function of temperature, for Ag-Ni (111).

One can wonder to what extent this phenomenon depends on the face orientation. We have then performed preliminary calculations indicating the same tendency for the (110) face with two small differences: T_c^s is lower and the topmost plane is not strictly a pure-Ag plane, some Ni segregation existing also at the surface [the first underlayer being of pure Ni as in the (111) case].

V. CONCLUSION

We have shown here that a simple mean-field approach, including simultaneously a correct size effect (treated atomistically), a surface tension term and the alloy effect, is sufficient to account for the surface-sandwich segregation observed on the (111) faces of Pt-Ni (Ref. 3) and Ag-Ni (Ref. 4) alloys. This model allows us to show that this phenomenon has not the same physical origin in both cases. For Pt-Ni, it is due to an oscillating behavior induced by the tendency of this alloy to order in the bulk, the nature of the first plane (strong Pt enrichment) being mainly determined by the size effect. For very dilute Ag-Ni, the tendency of the alloy to segregate in the bulk induces a strong segregation of Ni near the surface which is counteracted by surface tension and size mismatch effects. Taking into account all these effects indeed leads to the structure proposed by Rolland *et al.*,[4] i.e., a pure-Ni plane placed between two silver planes. From this point of view, the term of "surface sandwich" is more suited to Ag-Ni than to Pt-Ni.

Finally, let us suggest two experiments which could be interesting: (i) The study of the (110) face of Pt-Ni for which we predict a segregation of Pt on the first underlayer whereas the Pt enrichment is reduced at the surface and almost vanishing for the Pt-rich alloy, the Pt depletion occuring on the second sublayer. (ii) A study of the influence of temperature on the surface sandwich structure of Ag-Ni, which is expected to disappear for a critical temperature which depends on the bulk concentration.

ACKNOWLEDGMENTS

We are very indebted to F. Ducastelle for many enlightening discussions on the models and to A. Rolland, J. and F. Cabané, Y. Gauthier, and R. Baudoing for giving us useful information on their experimental data.

---

[1] F. L. Williams and D. Nason, Surf. Sci. **45**, 377 (1974); P. Wynblatt and R. C. Ku, *ibid.* **65**, 511 (1977); T. S. King and R. G. Donnelly, *ibid.* **141**, 417 (1984); S. M. Foiles, Phys. Rev. B **32**, 7685 (1985).

[2] F. F. Abraham, N. H. Tsai, and G. M. Pound, Surf. Sci. **83**, 406 (1979); F. F. Abraham, and C. R. Brundle, J. Vac. Sci. Technol. **18**, 506 (1981); A. R. Miedema, Z. Metall. **69**, 455 (1978); J. C. Hamilton, Phys. Rev. Lett. **42**, 989 (1979).

[3] Y. Gauthier, Y. Joly, R. Baudoing, and J. Rundgren, Phys. Rev. B **31**, 6216 (1985); R. Baudoing, Y. Gauthier, M. Lundberg, and J. Rundgren, J. Phys. C **19**, 2825 (1986).

[4] A. Rolland, B. Aufray, F. Cabané-Brouty, and J. Cabané, C. R. Acad. Sci. Paris **292**, 1477 (1981); A. Rolland, F. Cabané-Brouty, Nouv. J. Chem. **8**, 485 (1984); A. Rolland and B. Aufray, Surf. Sci. **162**, 530 (1985).

[5] F. Ducastelle and F. Gautier, J. Phys. F **6**, 2039 (1976); F. Ducastelle and G. Tréglia, *ibid.* **10**, 2137 (1980); A. Bieber, F. Gautier, G. Tréglia, and F. Ducastelle, Solid State Commun. **39**, 149 (1981).

[6] D. McLean, *Grain Boundaries in Metals* (Oxford University Press, London, 1957).

[7] J. Friedel, Adv. Phys. **3**, 446 (1954).

[8] B. Legrand (unpublished).

[9] D. Tománek, A. A. Aligia, and C. A. Balseiro, Phys. Rev. B **32**, 5051 (1985); a very similar model is the "embedded-atom method;" see, for instance, S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[10] F. Ducastelle, Thèse de Doctorat d'Etat, Université de Paris—Sud, Orsay (France), 1972; F. Ducastelle, J. Phys. (Paris) **31**, 1055 (1970).

[11] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2845 (1972); J. P. Gaspard and F. Cyrot-Lackmann, *ibid.* **6**, 3077 (1973).

[12] L. de Temmerman, C. Creemers, H. Van Hove, A. Neyens, J. C. Bertolini, and J. Massardier, Proceedings of ECOSS 8 [Surf. Sci (to be published)].

[13] M. Hillert and J. Rundgren, Phys. Rev. B **32**, 640 (1985).

[14] J. Friedel, J. Magn. Magn. Mater. **17-19**, 38 (1980).

[15] A. R. Miedema, P. F. de Châtel, and F. R. de Boer, Physica B **100**, 1 (1980).