

Surface segregation in jellium binary solid solutions

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The electron-density-functional method is applied to a jellium model for the surface-segregated binary (single-phase) solid solution. The segregation potential, thickness of the segregated layer, and the segregating component are determined and the following rule is derived for a binary (single-phase) solid solution of substitutional type: Atoms of the component which has the larger Wigner-Seitz radius segregate to the surface. The present theoretical predictions are completely compatible with those determined by Miedema's method and agree reasonably well with various experimental data.

I. INTRODUCTION

Surface segregation has experimentally been confirmed in various binary-alloy systems.¹⁻³ It has been emphasized⁴ that the surface segregation may occur at the surface of an alloy if it is in a single-phase region of the phase diagram and must be distinguished from the precipitation of the second phase.

It is well known that the first theoretical treatment of surface segregation was given by Gibbs about a century ago. However, it is only within the last decade that the theoretical investigation of surface segregation has become active and various theories have been offered.^{2,3} Most such theories are based on the Gibbs thermodynamics which relates the surface composition to the bulk composition and uses the heat of segregation as a criterion of segregation, assuming that the entropy contribution is negligible. (At least, it was shown³ that the vibrational entropy contribution to the free energy of segregation was negligible for a harmonic solid and the free energy of segregation may well be approximated by the potential energy of segregation or the heat of segregation.)

In the present work, a jellium model of the surface segregation is discussed, using the density-functional formula for the ground state of inhomogeneous electrons.^{5,6} That is, zero absolute temperature is assumed in the present theory despite the fact that another major assumption that the alloy be a single-phase solid solution may not be valid at zero degree. It should be emphasized that the primary purpose of the present theory is not to explain a variety of experimental data of surface segregation, but to investigate the validity of an electron-density-functional approach when it is applied to a jellium model, which was successfully utilized in the theory of work-function change due to adsorption by metals.^{7,8} Nonetheless, it will also be demonstrated that a simple rule derived from the present model works well for explaining the majority of experimental data.

II. JELLIUM MODEL

A simple jellium model or uniform-positive-background model (as shown in Fig. 1) was employed theoretically to

calculate the work function and surface energy of metals using the electron-density-functional theory.⁹⁻¹² The distribution of the positive charge is assumed to be

$$n_+(x) = \begin{cases} n_b, & x \leq 0 \\ 0, & 0 < x \end{cases} \quad (1)$$

if the x axis is taken perpendicular to the surface and the surface is located at position $x=0$. n_b is the average density of quasifree electrons and is related to the Wigner-Seitz radius r_s :

$$r_s = (3/4\pi n_b)^{1/3}. \quad (2)$$

The theoretical values of the work function^{9,11} were in reasonable agreement with experimental data for $r_s \geq 2.5$ a.u. but were lower than experimental values for $r_s \leq 2.5$ a.u. It should, however, be noted that the general dependence of the experimental data on r_s was sufficiently well reproduced by the theory for r_s in the range of $\sim 1.2-6.0$ a.u. (Refs. 9 and 11) in which all the actual metals may be located. On the contrary, the same model failed to reproduce the dependence of experimental surface energy on r_s when r_s was smaller than 3.0 a.u.^{9,10,12} This is apparently because the present jellium model does not consider the discreteness of the ion cores.¹⁰ Thus one must realize that the jellium model is not always valid for all metals. Nonetheless, it should be pointed out that the model is

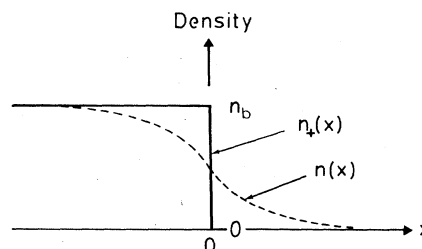


FIG. 1. Jellium model for clean metallic surface. The positive-charge-density distribution $n_+(x)$ is constant and equal to the average charge density in the bulk, n_b , up to the surface located at $x=0$. Electron-density distribution $n(x)$ is obtained so that the ground-state energy is a minimum.

simple enough to describe physical quantities such as the work function and surface energy in terms of only a single variable, r_s , and can still provide us with theoretical values which agree reasonably well with experimental data if the range of r_s is carefully chosen. Similar arguments were valid when a jellium model was applied with the electron-density-functional formula to spherical voids in metals¹³⁻¹⁵ and to composition-modulated metallic systems.¹⁶⁻¹⁸

Lang⁷ utilized the electron-density-functional approach to evaluate the work-function change due to adsorption by metals. Lang's jellium model,⁷ or a two-step jellium model, for the adsorbed metallic surface is shown in Fig. 2 and the positive-charge distribution in it is defined as

$$n_+(x) = \begin{cases} n_b, & x \leq 0 \\ n_s, & 0 < x \leq t \\ 0, & t < x \end{cases} \quad (3)$$

where n_b , as defined above, is the average density of quasifree electrons in the bulk and n_s is the average density of quasifree electrons in the adsorbed surface layer of thickness t . Lang⁷ showed, using a numerical, self-consistent calculation, that the work-function change due to adsorption of alkali metals on the surfaces of transition metals such as W was quantitatively well described by this two-step jellium model despite the fact that the quantitative agreement of the theoretical values for the work function of transition metals with experimental values was poor. Yamauchi *et al.*⁸ showed that a simple approximate but analytical calculation was possible for solving the Lang model to obtain an analytical expression for the work-function change.

Among various possible reasons for the surface segregation, the Gibbs-type adsorption where the reduction in surface energy is the driving force may simply be the dominant mechanism in many alloys.¹ If so, it may be quite natural to employ as a simple model to describe the segregated metallic surface the same two-step jellium model as that defined by Eq. (3) (and Fig. 2). If the

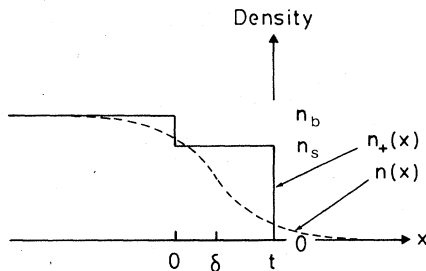


FIG. 2. Two-step jellium model for a segregated metallic surface. The positive-charge density distribution, $n_+(x)$ is constant and equal to the average charge density in the bulk, n_b , up to the bottom of the segregated layer located at $x=0$, and is then a constant equal to the average charge density in the segregated layer, n_s , of thickness equal to t . Electron-density distribution $n(x)$ is obtained so that the ground-state energy is a minimum. δ represents the position of the electronic surface.

ground-state energy of such a model, $E^{(s)}$, is obtained as a function of the average charge densities, n_b for the initial (unsegregated) bulk and n_s for the segregated surface layer and of the surface-layer thickness t , i.e.,

$$E^{(s)} = E^{(s)}(n_b, n_s, t), \quad (4)$$

and the ground-state energy of the same bulk but without surface segregation, $E^{(0)}$, is obtained [using the model defined by Eq. (1)] as a function of the same average charge density n_b , i.e.,

$$E^{(0)} = E^{(0)}(n_b), \quad (5)$$

then the energy difference ΔE defined by

$$\Delta E \equiv E^{(s)} - E^{(0)} \quad (6)$$

becomes a function of n_b , n_s , and t . It is apparent that for

$$\Delta E > 0, \text{ there is no segregation,}$$

$$\Delta E < 0, \text{ there is segregation,} \quad (7)$$

when a set of (n_b, n_s, t) is given: ΔE defined by Eq. (6) can be used as the criterion of surface segregation for the present jellium model.

When z_I and ω_I denote, respectively, the number of quasifree electrons and the volume per atom in the pure metal of I type ($I=A, B$), its lattice structure being the same as that of the (single-phase) solid solution under consideration, the average charge density in the bulk solid solution may be given by¹⁷

$$n_b \simeq [z_A(1-c_B) + z_B c_B] / [\omega_A(1-c_B) + \omega_B c_B], \quad (8)$$

where c_B is the composition of B atoms in the bulk solid solution. Similarly,

$$n_s \simeq [z_A(1-c_B^{(s)}) + z_B c_B^{(s)}] / [\omega_A(1-c_B^{(s)}) + \omega_B c_B^{(s)}], \quad (9)$$

where $c_B^{(s)}$ is the composition of B atoms in the segregated surface layer. It should be noted that Eqs. (8) and (9) are valid only in single-phase alloys of the substitutional type and, more strictly speaking, when the alloys are dilute.

III. DENSITY-FUNCTIONAL APPROACH

According to Hohenberg and Kohn,⁵ the ground-state energy E of a nonuniform electron-gas system may be given by

$$E[n] = E_{\text{es}}[n] + T_s[n] + E_x[n] + E_c[n], \quad (10)$$

where E_{es} , T_s , E_x , and E_c are energy functionals of the electron-density-distribution function $n(\mathbf{r})$ at position \mathbf{r} and denote, respectively, the electrostatic, kinetic, exchange, and correlation energy of the electrons:

$$E_{\text{es}}[n] = \frac{1}{2} \int \int \{ [n(\mathbf{r}) - n_+(\mathbf{r})] \times [n(\mathbf{r}') - n_+(\mathbf{r}')] / |\mathbf{r} - \mathbf{r}'| \} d\mathbf{r} d\mathbf{r}', \quad (11)$$

$$T_s[n] = \frac{3}{10} (3\pi^2)^{2/3} \int n(\mathbf{r})^{5/3} d\mathbf{r} + \frac{1}{12} \int \{ [\nabla n(\mathbf{r})]^2 / n(\mathbf{r}) \} d\mathbf{r}, \quad (12)$$

$$E_x[n] = -\frac{3}{4}(3/\pi)^{1/3} \int n(\mathbf{r})^{4/3} d\mathbf{r}, \quad (13)$$

and

$$E_c[n] - 0.056 \int \{n(\mathbf{r})^{4/3} / [0.079 + n(\mathbf{r})^{1/3}]\} d\mathbf{r}. \quad (14)$$

Atomic units (a.u.) are used in Eqs. (11)–(14) and will be used throughout. Apparently, Eq. (12) has a term which depends on ∇n . This indicates that the present approach is an expansion method. A test function will be used to obtain $n(\mathbf{r})$ which minimizes $E[n]$, instead of a numerical self-consistent calculation.^{6,10,11} Such a choice of the correlation energy as given by Eq. (14) may be obsolete,¹⁹ but Eq. (14) is employed in the present work in order to be consistent with previous works for the clean^{9–12} and adsorbed surfaces.^{7,8}

Smith⁹ utilized the following test function for the electron-density-distribution function in the jellium model as defined by Eq. (1) and in Fig. 1:

$$h(z) = z(0.1300 - 0.5874z - z^2 \ln[z/(0.7937 + z)] + \{0.06837 - 0.1450z - z^5 \ln[(1+z)/(0.7937 + z)]\} / (1 + z^3)). \quad (19)$$

Yamauchi *et al.*⁸ utilized the following test function for the electron-density distribution function $n(\mathbf{r})$ in the two-step jellium model as defined by Eq. (3) (and in Fig. 2):

$$n(x; \beta_s) = \begin{cases} \frac{1}{2} n_b (2 - e^{\beta_s(x-\delta)}), & x \leq \delta \\ \frac{1}{2} n_b e^{-\beta_s(x-\delta)}, & \delta < x \end{cases} \quad (20)$$

where δ is given by

$$\delta = (n_s / n_b) t \quad (21)$$

to satisfy the electroneutrality condition, and β_s is obtained so that $E^{(s)}[n]$ may be minimized:

$$dE^{(s)}(\beta_s) / d\beta_s = 0. \quad (22)$$

That is,

$$\frac{3}{2} \pi n_b^2 - g(n_b) \beta_s^2 - [f(\beta_s, n_b, n_s, t) + (\ln 2 / 72) n_b] \beta_s^4 = 0, \quad (23)$$

where $g(x)$ is already given by Eq. (18) and f is given by

$$f(\beta, n_b, n_s, t) = (\pi/2) n_b \{ n_s (t - \delta) t \beta^{-2} + (n_b - n_s) (-12 + 12\beta\delta - \beta^2 \delta^2 + 12e^{-\beta\delta} + 4\beta\delta e^{-\beta\delta}) \beta^{-4} + n_s [-12 + 4\beta(t - \delta) - \beta^2(t - \delta)^2 + 12e^{-\beta(t - \delta)} + 4\beta(t - \delta) e^{-\beta(t - \delta)}] \beta^{-4} \}. \quad (24)$$

It is straightforward to calculate ΔE defined by Eq. (6) using β_0 and β_s which are solutions of Eqs. (17) and (23), respectively:

$$\Delta E / A = (\pi_b / 2) (\beta_s^{-3} - \beta_0^{-3}) - g(n_b) (\beta_s^{-1} - \beta_0^{-1}) + \phi(\beta_s) + (\ln 2 / 72) n_b (\beta_s - \beta_0), \quad (25)$$

in which A is the total surface area and

$$\begin{aligned} \phi(\beta) = & (\pi/2) \{ -n_b n_s (t - \delta) t / \beta + n_b (n_b - n_s) [4 - 6\delta\beta + (\delta\beta)^2 - 4e^{-\beta\delta}] / \beta^3 \\ & + n_b n_s [4 - 2(t - \delta)\beta + (t - \delta)^3 \beta^2 - 4e^{-\beta(t - \delta)}] / \beta^3 - \frac{2}{3} (n_b - n_s)^2 \delta^3 \\ & + 2n_s (n_b - n_s) (t - \delta) t \delta + (2/3) n_s (\delta - t)^3 \}. \end{aligned} \quad (26)$$

$$n(x; \beta_0) = \begin{cases} \frac{1}{2} n_b (2 - e^{\beta_0 x}), & x \leq 0 \\ \frac{1}{2} n_b e^{-\beta_0 x}, & 0 < x \end{cases} \quad (15)$$

where β_0 is obtained so that $E^{(0)}[n]$ may be minimized with respect to β_0 , after substituting Eqs. (1) and (15) in Eq. (10) via Eqs. (11)–(14):

$$dE^{(0)}(\beta_0) / d\beta_0 = 0. \quad (16)$$

That is,

$$\frac{3}{2} \pi n_b^2 - g(n_b) \beta_0^2 - (\ln 2 / 72) n_b \beta_0^4 = 0, \quad (17)$$

where⁸

$$\begin{aligned} g(x) = & \frac{3}{10} (3\pi^2)^{2/3} (0.5719) x^{5/3} \\ & - \frac{3}{4} (3/\pi)^{1/3} (0.3389) x^{4/3} \\ & - 0.168 x h(0.079/x^{1/3}), \end{aligned} \quad (18)$$

and

The criterion of surface segregation, $\Delta E/A$, is now a function of only three variables, n_b , n_s , and t . It can also be regarded as a function of c_B , $c_B^{(s)}$, and t when z_I and ω_I ($I=A, B$) are given and Eqs. (8) and (9) are employed.

IV. SEGREGATION CRITERION

The segregation criterion ΔE defined by Eq. (6) has now been written as a function of n_b , n_s , and t or of c_B , $c_B^{(s)}$, and t , as given by Eq. (25). The composition c_B of the bulk solid solution must be given as an experimental parameter. Thermodynamics might suggest that the surface composition $c_B^{(s)}$ be either 1.0 or 0.0 and the segregated layer thickness t be one monolayer at absolute zero.²⁰ However, no such thermodynamical principles are installed in the present electron-density-functional approach. It is assumed only that the principle of minimum energy be applied to the present segregation criterion: in the actual ground state, ΔE must be minimum with respect to $c_B^{(s)}$ and t :

$$(\Delta E/A)^* = \min_{c_B^{(s)}, t} [\Delta E(c_B, c_B^{(s)}, t)/A]. \quad (27)$$

Thus, given z_I and ω_I or z_I and $(r_s)_I$ ($I=A$ and B) as well as c_B , $(\Delta E/A)^*$ and corresponding values of $c_B^{(s)}$ and t , i.e., $c_B^{(s)*}$ and t^* , are uniquely determined by Eq. (27).

Figure 3 shows the segregation criterion $(\Delta E/A)^*$ in terms of the ratio of the Wigner-Seitz radii of solute atom A and solvent atom B ,

$$\rho \equiv (r_s)_A / (r_s)_B, \quad (28)$$

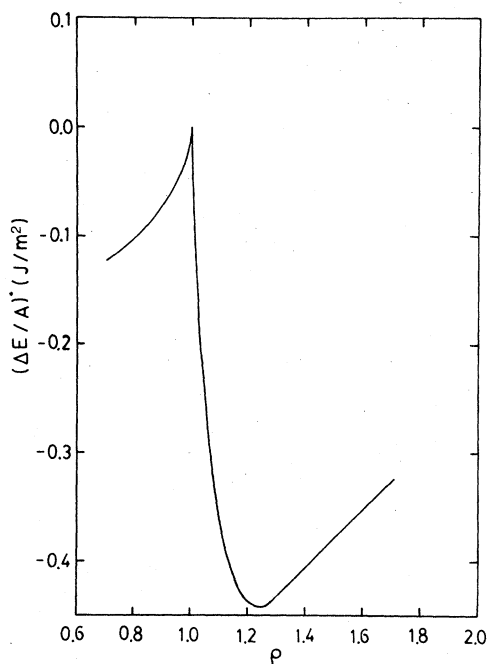


FIG. 3. Segregation criterion or segregation potential per unit area, $(\Delta E/A)^*$, with respect to the ratio of the Wigner-Seitz radii of solute and solvent, $\rho \equiv (r_s)_A / (r_s)_B$. Here, $(r_s)_B = 2.67$ a.u., the valence numbers $z_A = z_B = 1$, and the bulk composition $c_B = 0.95$ are assumed.

when it is assumed that $z_A = z_B = 1$, $(r_s)_B = 2.67$ a.u., and $c_B = 0.95$. That is, Cu-based solid solutions having a solute composition c_A of five atomic percent are now considered. It is shown that $(\Delta E/A)^*$ is always negative except at $\rho = 1$, which indicates the occurrence of surface segregation, according to the criterion given by Eq. (7). The type of segregation can immediately be found out from Fig. 4 where $c_A^{(s)*}$ ($= 1 - c_B^{(s)*}$) is plotted with respect to ρ : $c_A^{(s)*} = 0.0$ for $\rho < 1$ and $c_A^{(s)*} = 1.0$ for $1 < \rho < 1.35$, resulting in the solvent segregation and the solute segregation, respectively. For $\rho > 1.35$, $c_A^{(s)*}$ decreases and asymptotically approaches the average bulk concentration c_A ($= 0.05$). Apparently, in this situation there is also the solute enrichment at the surface, although intermediate values between 0.0 and 1.0 for $c_A^{(s)*}$ do not satisfy the thermodynamical requirement at absolute zero. This may result from the basic assumption in the present model that the bulk is a solid solution in which A and B atoms are always randomly distributed (even at $T = 0$). Or this may be an artifact due to an approximation based on the trial functions given by Eqs. (15) and (20), or an artifact inherent to the present jellium model. A fully self-consistent calculation using the electron-density functional formula would provide us with a certain insight to this problem. The minimum in $(\Delta E/A)^*$ about $\rho \sim 1.23$ may well have a certain physical meaning analogous to the minimum in the work-function change of transition metals due to alkali-atom surface adsorption.²¹

It must be strongly emphasized that the qualitative feature of the $(\Delta E/A)^*$ -versus- ρ curve given in Fig. 3 is common whatever the values of z_A , z_B , $(r_s)_B$, and c_B . In other words, the only decisive parameter that determines whether a solute or solvent segregation occurs is the Wigner-Seitz radii ratio ρ , defined by Eq. (28). This leads us to the following rule:

Rule A: Atoms of the component which has the larger Wigner-Seitz radius segregate to the surface.

It should be noted that this rule has been derived strictly from the present electron-density-functional calculation using the jellium models shown in Figs. 1 and 2.

Figure 5 shows the segregated surface-layer thickness t^* [which corresponds to $(\Delta E/A)^*$] with respect to ρ .

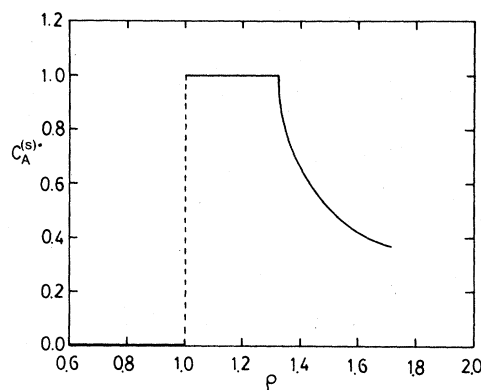


FIG. 4. Surface composition of solute, $c_A^{(s)*}$, with respect to the ratio of the Wigner-Seitz radii of solute and solvent, ρ . The same conditions as in Fig. 3 are assumed.

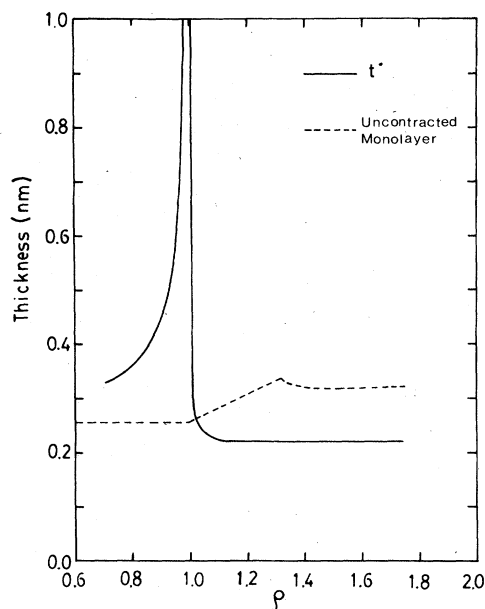


FIG. 5. Segregated-surface-layer thickness t^* , with respect to the ratio of the Wigner-Seitz radii of solute and solvent, ρ . The same conditions as in Fig. 3 are assumed. Dashed line represents uncontracted monolayer thickness on the most dense atomic plane.

For the solvent segregation ($\rho < 1$), t^* monotonically approaches the monolayer thickness of solvent atoms as ρ decreases. When $(r_s)_A$ and $(r_s)_B$ are nearly equal, i.e., $\rho \sim 1.0$, t^* becomes large. This is simply because the en-

ergy reduction per unit thickness of the segregated layer is small when $\rho \sim 1.0$ and, therefore, a large thickness is required to achieve an energy minimum. For the solute segregation ($\rho > 1$), t^* is almost constant for $\rho \geq 1.1$. This behavior is a contrast to the dependence of the monolayer thickness on ρ , as seen in Fig. 5. Should this have any actual physical meaning, the segregated surface layer would be contracted about 20% (if $\rho \geq 1.1$).

V. COMPARISON WITH EXPERIMENTAL DATA

In the preceding section, a criterion of surface segregation was obtained using Eq. (27) for the jellium model [as defined by Eqs. (1) and (3) and in Figs. 1 and 2], and a simple rule for the surface segregation in the "jellium solid solution" was determined which was stated as Rule A with the assumption that Eqs. (8) and (9) be valid. Any jellium models do not take into account the detailed structure of each ion core as well as core arrangement or the energy bands. This is why one must be careful in a comparison of the theoretical results for a jellium model with the experimental data, as discussed in Sec. II.

Most of the available data of surface segregation are for binary alloys of transition (and noble) metals which belong to groups IVA–VIII A and IB (in the Periodic Table of the elements). The major question is if the results, especially Rule A, obtained for the present jellium model are applicable to such alloys.

Let us first compare the value of $(\Delta E/A)^*$ obtained in Fig. 3 to the experimental value. In Table I of Ref. 2, the heat of adsorption of the solute Au in a Cu(Au) alloy [express as solvent(solute)] is given to be -6.1 kcal/mole.

TABLE I. Wigner-Seitz radii $r_s^{(fcc)}$ of alloy components with fcc structure using standard values of nearest-neighbor (NN) distance (Ref. 22) d and of the valence number (Ref. 23) z of the most stable oxidation state. Note that $r_s^{(bcc)} = (4\sqrt{6}/9)^{1/3} r_s^{(fcc)}$ and $r_s^{(fcc)} = (3\sqrt{2}/8\pi)^{1/3} d/z^{1/3}$.

Component	NN Distance (a.u.) ^a	Valence number ^b	$r_s^{(fcc)}$ (a.u.)
Ag	5.46	1	3.02
Al	5.40	3	2.07
Au	5.44	1	3.01
Ca	7.46	2	3.27
Cr	4.72	3	1.81
Cu	4.84	1 ^c	2.67
Fe	4.69	3	1.80
In	6.14	3	2.35
Ir	5.12	4	1.78
Li	5.71	1	3.16
Mn	4.23	2	1.86
Na	6.92	1	3.82
Ni	4.71	2	2.07
Os	5.06	4	1.76
Pb	6.61	2	2.90
Pd	5.20	2	2.28
Pt	5.23	4	1.82
Rh	5.08	3	1.95
Sn	5.31	4	1.85
V	4.95	5	1.60
Zr	5.99	4	2.09

^aReference 22, Table 4.

^bReference 23.

^c $z(\text{Cu})=2$ is recommended in Ref. 23.

This corresponds to -0.51 J/m^2 if a monolayer of Au is considered on the (100) plane of Cu. Using the values of the Wigner-Seitz radii for Cu and Au which are listed in Table I, $\rho=1.13$ is obtained. From Fig. 3, the theoretical value of $(\Delta E/A)^*$ for $\rho=1.13$ is now estimated at $\sim -0.39 \text{ J/m}^2$. Thus the agreement between the theoretical and experimental values of $(\Delta E/A)^*$ is fair. This is,

however, astonishingly good if the bases of the present theory are taken into consideration: *no adjustable parameters are employed* in the present calculation, other than standard values of the nearest-neighbor distance²² and of the valence number of the most stable oxidation state.²³ It is easily seen that the range of $\sim 0.0-0.5 \text{ J/m}^2$ for $|(\Delta E/A)^*|$ (shown in Fig. 3) is coincident with the

TABLE II. Segregated behavior of binary solid solutions. Experimental data are those listed in Table I of Ref. 3. Theoretical predictions are due to Rule A given in Sec. IV when the Wigner-Seitz radii listed in Table I are utilized.

Solvent (solute)	Segregating component		Comment ^a
	Experimental	Theoretical	
Ag(Au)	Ag	Ag or None	$\Delta=0.3\%$
Ag(Cu)	Ag	Ag	
Ag(Pb)	Pb	Ag	ESO
Au(Ag)	Ag	Ag or None	$\Delta=0.3\%$
Au(Ca)	Ca	Ca	
Au(Cu)	Au	Au	
Au(In)	In	Au	D
Au(Ni)	None	Au	ENC
Au(Pd)	Au	Au	
Au(Sn)	Sn	Au	D
Cu(Ag)	Ag	Ag	
Cu(Al)	Al	Cu	ENC
Cu(Au)	Au	Au	
Cu(Ni)	Cu	Cu	
Cu(Sn)	Sn	Cu	D
Fe(Al)	Al	Al	
Fe(Cr)	Cr	Cr	
Fe(Cu)	Cu	Cu	
Fe(Ni)	Ni	Ni	None ($\Delta=0.5\%$) if $z(\text{Fe})=2$
Fe(Sn)	Sn	Sn	
Fe(Zr)	Zr	Zr	None ($\Delta=1.4\%$) if $z(\text{Fe})=2$
In(Pb)	Pb	Pb	
Ir(Pt)	Pt	Pt	
Li(Na)	Na	Na	
Ni(Au)	Au	Au	
Ni(Cu)	Cu	Cu	
Ni(Fe)	Fe	Ni	None ($\Delta=0.5\%$) if $z(\text{Fe})=2$
Ni(Pd)	Pd	Pd	
Os(Pt)	Pt	Pt	
Pb(In)	Pb	Pb	
Pd(Ag)	Ag	Ag	
Pd(Au)	Au	Au	
Pd(Ni)	Pd	Pd	
Pd(V)	None	Pd	ENC
Pt(Au)	Au	Au	
Pt(Cu)	Cu	Cu	
Pt(Cr)	None	Pt or None	$\Delta=0.5\%$
Pt(Fe)	None	Pt or None	$\Delta=1.1\%$
Pt(Ir)	Pt	Pt	
Pt(Ni)	None	Ni	Pt if $z(\text{Pt})=2$
Pt(Rh)	Pt	Rh	Pt if $z(\text{Pt})=2$, ENC
Pt(Sn)	Sn	Sn	
Rh(Ag)	Ag	Ag	
Rh(Pt)	Pt	Rh	Pt if $z(\text{Pt})=2$, ENC
Zr(Fe)	Fe	Zr	None ($\Delta=1.4\%$) if $z(\text{Fe})=2$

^aESO: Experimental result is "speculation only."

ENC: Experimental result "needs confirmation." [Results from Ref. (3).]

D: Experimental and theoretical results disagree.

$\Delta \equiv |\Delta r_s / r_s|$.

range for the surface energy of alkali and alkaline-earth metals (except Be), i.e., $\sim 0.07\text{--}0.57\text{ J/m}^2$,^{10,13,15} for which Smith's jellium model⁹ with the electron-density-functional approach sufficiently worked.^{9,10,15} It is therefore predicted that Rule A for the surface segregation would be effective for alloys whose heat of segregation may not exceed much more than the range of $\sim -0.5\text{--}0.0\text{ J/m}^2$.

Most of previous theories of surface segregation^{2-4,24,25} have demonstrated the agreement of their predictions with experimental data using score tables. The present score table for Rule A is given in Table II using the same 45 experimental results cited in Table I of Ref. 3. The theoretical predictions are based on the Wigner-Seitz radii listed in Table I. In some cases, experimental data are not entirely reliable.³ In other cases, valence numbers other than those listed in Table I could be employed to change the theoretical predictions. If all such ambiguous cases are excluded, only three cases remain where experimental results disagree with the theoretical ones. Each of them is a combination of components from group IB and group IV A. It is apparent that the components of group IB and group IV A have totally different kinds of bonding. Thus, Rule A would easily fail for such combinations. It should be noted that the present predictions agree with those given by Miedema for all the 22 solid solutions listed in Table 3 of his paper,²⁵ including the Fe(Mn) (which is not listed in Table II). Even though both the present theory and Miedema's theory^{4,25} are based on similar electronic considerations of metallic components, Miedema's theory employs two independent parameters, while the present theory has only one parameter, i.e., the Wigner-Seitz radius ratio ρ , defined by Eq. (28). Compared with Abra-

ham and Brundle's parameter γ^* ,³ the present parameter for the surface segregation is much easier to calculate using only standard values for the nearest-neighbor distances and valence number of the components.

VI. CONCLUSIONS

The electron-density-functional method was utilized in a jellium model for a surface-segregated binary solid solution. A segregation criterion which corresponded to the segregation potential was analytically derived. Full minimization of the segregation potential gave rise to a simple rule.

Rule A: In a binary (single-phase) solid solution of substitutional type, atoms of the component which has the larger Wigner-Seitz radius segregate to the surface.

This indicated that the ratio of the Wigner-Seitz radii of the solute and solvent was the unique segregation parameter. The predictions by the above rule agreed reasonably well with the experimental data. The present theoretical predictions totally agreed with those found by Miedema's method for all the 22 binary systems which Miedema had listed. The present theory also predicted that the solute segregated layer in a solid solution might be contracted when the Wigner-Seitz radius ratio was larger than ~ 1.1 .

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