

Calculation of elastic strain and electronic effects on surface segregation

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(Received 19 October 1984; revised manuscript received 27 June 1985)

We present an electronic theory for calculating the heat of impurity segregation at metal surfaces by considering both the electronic contribution to the surface energy and the size-mismatch energy. The attractive part of the total energy is described by a multiband tight-binding Hartree Hamiltonian, and for the repulsive part Born-Mayer-type interatomic repulsions are assumed, which may depend on charge transfer. With simplifying assumptions about the density of states and the charge transfer, the heat of segregation and the equilibrium geometry can be obtained from an expression which depends only on the bulk cohesive energy, the bulk modulus, and the atomic size of the alloy components. Using this theory, we calculate the heat of segregation of Rh, Cu, and Au impurities on different Pt single-crystal surfaces and make a comparison with existing experimental data.

I. INTRODUCTION

It is well established¹⁻⁵ that the surface-segregation behavior in binary alloys is determined mainly by the different surface energies of the pure constituents and the size-mismatch energy. While both these effects have been considered in phenomenological theories of surface segregation,¹⁻³ existing electronic theories restricted themselves to systems with components of same atomic size^{6,7} and treated the size-mismatch energy in a rather crude way within the continuum theory.^{4,5} Only recently has bulk strain energy due to interstitial impurities been calculated within an electronic model.⁸ Of course, an accurate estimate of both effects is necessary in systems where one component tends to segregate to the surface because of its lower surface energy and the other component due to its larger atomic size. In contrast to previous calculations, which assumed the surface part of the size-mismatch energy to vanish,^{4,5} it seems necessary to consider such terms and their dependence on the surface considered. Hence, in Sec. II we present a theory which describes the electronic and the size-mismatch parts of the surface energy on a microscopic footing. In Sec. III we use this theory to calculate the heat of segregation of Rh, Cu, and Au impurities in Pt, where the electronic and the size-mismatch effects compete, and compare the results with experimental observations. In Sec. IV we discuss the limitations and a possible generalization of our theory.

II. THEORY

For low concentrations x of the solute A in the alloy A_xB_{1-x} , its surface concentration x_s is given by⁴

$$\frac{x_s}{1-x_s} = \frac{x}{1-x} e^{-Q_{\text{seg}}/kT}, \quad (2.1)$$

where the heat of segregation Q_{seg} is the work involved in exchanging a surface B atom and a bulk A atom. In the dilute case, Q_{seg} is given by

$$Q_{\text{seg}} = E^{\text{tot}}(A \text{ impurity at the surface of } B) - E^{\text{tot}}(A \text{ impurity in the bulk of } B). \quad (2.2)$$

For a given geometry, the total energy E^{tot} of the system is given by the band-structure energy $E_{\text{BS}}^{\text{tot}}$ and the repulsive energy E_R^{tot} , as^{8,9}

$$E^{\text{tot}} = E_{\text{BS}}^{\text{tot}} + E_R^{\text{tot}}. \quad (2.3)$$

The conduction electrons are described by a multiband tight-binding Hartree Hamiltonian with intra-atomic Coulomb interactions U^α as⁶

$$H = \sum_{i,\alpha,\sigma} \epsilon_{i\sigma}^\alpha n_{i\sigma}^\alpha + \sum_{i,j,\alpha,\beta,\alpha} t_{ij}^{\alpha\beta} c_{i\sigma}^{\alpha\dagger} c_{j\sigma}^\beta - \sum_i E_{ee}(i), \quad (2.4)$$

where $c_{i\sigma}^\alpha$ ($c_{i\sigma}^{\alpha\dagger}$) is the creation (annihilation) operator of an electron in the Wannier state corresponding to the site i (occupied by an A or B atom), the band α and spin σ , and $n_{i\sigma}^\alpha = c_{i\sigma}^{\alpha\dagger} c_{i\sigma}^\alpha$. $t_{ij}^{\alpha\beta}$ is the hopping integral between the site i , band α , and the nearest-neighbor site j , band β . $\epsilon_{i\sigma}^\alpha$ is the Hartree-Fock single-site energy in the alloy. The latter can be related to its value $\epsilon_{i\sigma}^{\alpha 0}$ in the pure metal atoms by

$$\epsilon_{i\sigma}^\alpha = \epsilon_{i\sigma}^{\alpha 0} + U_i^\alpha \langle n_{i-\sigma}^\alpha \rangle, \quad (2.5)$$

where U_i^α takes the value U_A^α (U_B^α), if the site i is occupied by an A (B) atom. The quantity $E_{ee}(i)$ is given by

$$E_{ee}(i) = \frac{1}{2} \sum_{\alpha,\sigma} (\epsilon_{i\sigma}^\alpha - \epsilon_{i\sigma}^{\alpha 0}) \langle n_{i\sigma}^\alpha \rangle. \quad (2.6)$$

The local density of states $N_i^\alpha(E)$ for the band α at the site i is determined by the corresponding diagonal element of the one-particle Green's function as

$$N_i^\alpha(E) = -\frac{1}{\pi} \text{Im} \sum_\sigma G_{ii,\sigma}^{\alpha\alpha}(E). \quad (2.7)$$

For nonmagnetic elements, the average occupancy of the band α and spin σ at the site i can be obtained from

$$\langle n_{i\sigma}^\alpha \rangle = \frac{1}{2} \int_{-\infty}^{E_f} N_i^\alpha(E) dE, \quad (2.8)$$

and the band-structure energy $E_{\text{BS}}^{\text{tot}}$ is given up to a constant by

$$E_{\text{BS}}^{\text{tot}} = \sum_{i,\alpha} \int_{-\infty}^{E_F} E N_i^\alpha(E) dE - \sum_i E_{ee}(i). \quad (2.9)$$

The repulsive energy E_R^{tot} is assumed to consist of pairwise Born-Mayer-type repulsive interactions between nearest neighbors,¹⁰

$$E_R^{\text{tot}} = \frac{1}{2} \sum_{\substack{i,j \\ (i \neq j)}} E_{R,ij}. \quad (2.10)$$

In order to account for possible atomic relaxations near the impurity and at the surface, we assume an exponential distance dependence for both the hopping integrals $t_{ij}^{\alpha\beta}(r)$ and the pair bond energies $E_{R,ij}(r)$, given by¹⁰

$$t_{ij}^{\alpha\beta}(r) = t_{ij}^{\alpha\beta}(r_{ij}^0(\delta Q = 0)) \exp(-q_{ij}^{\alpha\beta} \{ [r/r_{ij}^0(0)] - 1 \}) \quad (2.11)$$

and

$$E_{R,ij}(r) = E_{R,ij}(r_{ij}^0(\delta Q)) \exp(-p_{ij} \{ [r/r_{ij}^0(\delta Q)] - 1 \}). \quad (2.12)$$

In these equations, i and j denote solely the type of atom occupying the respective sites.

Generally, a charge transfer δQ has to be considered between the alloy components, which will modify the equilibrium distances. Since the hopping integrals in Eq. (2.11) are assumed independent of δQ , the equilibrium distance $r_{ij}^0(\delta Q = 0)$ is given by the sum of the atomic radii $r_i(0), r_j(0)$ of the respective pure alloy components, as

$$r_{ij}^0(0) = r_i(0) + r_j(0). \quad (2.13)$$

On the other hand, charge transfer is expected to affect the repulsive interactions in Eq. (2.12) due to its origin in the compression of valence electrons. We assume that for the charge-transfer-dependent equilibrium distance

$$r_{ij}^0(\delta Q) = r_i(\delta Q_i) + r_j(\delta Q_j). \quad (2.14)$$

Here, the charge transfer δQ_i at the site i is given relative

to the valence charge in pure element i by

$$\delta Q_i = \sum_{\alpha,\sigma} (\langle n_{i\sigma}^\alpha \rangle - \langle n_{i\sigma}^{\alpha 0} \rangle). \quad (2.15)$$

The charge-dependent atomic radii can be estimated from

$$r_i(\delta Q_i) \approx r_i(0) - \delta Q_i \Delta r_i \quad (i = A, B) \quad (2.16)$$

where $r_i(0)$ is the atomic radius in the pure component and Δr_i is the change in radius from the neutral element i to a $(1 +)$ -charged ion.

In order to obtain Q_{seg} from Eq. (2.2) for the general case of an impurity with different electronic structure and atomic size than the solvent, one has to calculate the total energy of the system from Eqs. (2.3), (2.9), and (2.10) for the relaxed equilibrium geometry corresponding to the A impurity at the surface and in the bulk.

Clearly, a self-consistent electronic calculation determining both the relaxed geometry and the electronic structure of the alloy is computationally very tedious. Hence we show how introducing some assumptions that are not too restrictive can greatly simplify the calculation of Q_{seg} .

We first assume that the Hartree Hamiltonian in Eq. (2.4) consists of a single "effective" band. Further assuming $\delta Q = 0$ and local-charge neutrality at all sites, each energy term E^{tot} determining Q_{seg} can be expressed by

$$E^{\text{tot}} = \sum_i \left[\int_{-\infty}^{E_F} (E - \epsilon_i) N_i(E) dE + \frac{1}{2} \sum_{j (\neq i)} E_{R,ij} \right]. \quad (2.17)$$

Without specific assumptions about the band shape $N_i(E)$, the first term, which is the band-structure energy, is proportional to the square root of the second moment⁹ $M_{2,i}$ of $N_i(E)$, which is given by¹¹

$$M_{2,i} = \sum_{j (\neq i)} t_{ij}^2. \quad (2.18)$$

For a pure alloy component we further require that Eq. (2.17) should reproduce the bulk cohesive energy $E_{\text{coh}}(\text{bulk})$ and the nearest-neighbor distance r_{ij}^0 . Then, this equation can be simplified to^{9,10}

$$E^{\text{tot}} = \sum_i \left[- \left[\sum_{i \neq j} \xi^2 \exp\{-2q[r_{ij}/r_{ij}^0(0)] - 1\} \right]^{1/2} + \frac{q/p}{(Z_{\text{bulk}})^{1/2}} \sum_{j (\neq i)} \xi \exp\{-p[r_{ij}/r_{ij}^0(0)] - 1\} \right], \quad (2.19)$$

where j is nearest neighbor of i , and

$$\xi = \frac{E_{\text{coh}}(\text{bulk})}{(1 - q/p)(Z_{\text{bulk}})^{1/2}}. \quad (2.20)$$

Here, Z_{bulk} is the bulk coordination number. q and p describe the distance dependence of the "effective" hopping integrals and the repulsive pair bonds, respectively, and are related to bulk elastic constants. Note, Eq. (2.19) relates the total energy to the (correct) bulk cohesive energy by assuming local-charge neutrality and the same band shape as in the bulk. The latter seems to avoid some

problems arising from the use of the model Gaussian or rectangular bands.^{8,10}

In dilute alloys, p and q corresponding to the solvent can be used in a good approximation. The quantity ξ , which from comparing Eqs. (2.18) and (2.19) is essentially a hopping integral, can be modified in the alloy as

$$\xi_{ij} = \frac{[E_{\text{coh}}(\text{bulk } i) E_{\text{coh}}(\text{bulk } j)]^{1/2}}{(1 - q/p)(Z_{\text{bulk}})^{1/2}}, \quad i = A, B. \quad (2.21)$$

The use of the total energy expression in Eq. (2.19), which

contains essentially only thermodynamic parameters, strongly simplifies the calculation, first by allowing for geometry optimization. In pure metals, this formula has been successfully used to predict atomic relaxations at the surface.^{10,12} For alloys with a small charge transfer we further expect good predictions for the heat of segregation, since this expression treats the electronic and size-mismatch effects on the same microscopic footing. Hence, it also seems reasonable to use this simplified formalism in systems with large charge transfer in order to first determine the atomic structure. In a second step, a more refined electronic calculation of Q_{seg} can be performed with the full multiband Hamiltonian, e.g., by using the recursion technique.

III. CALCULATION OF SEGREGATION IN Pt-BASED ALLOYS

In order to show the usefulness of the presented theory, in the following we calculate the heat of segregation of substitutional Rh, Cu, and Au impurities in Pt. Of special interest are the first two systems, since the competition of size mismatch and electronic forces (solvent segregation due to the solute's smaller atomic size, solute segregation due to its smaller surface energy) leads to Pt segregation in $\text{Rh}_x\text{Pt}_{1-x}$ and to Rh segregation in $\text{Rh}_x\text{Pt}_{1-x}$. For $\text{Au}_x\text{Pt}_{1-x}$ reliable experimental data exist on the heat of segregation.

Before determining the equilibrium geometry from Eq. (2.19) and calculating the heat of segregation from Eq. (2.2), we first estimate the parameters p and q . In fcc lattices, p and q are related to the bulk modulus B and the nearest-neighbor distance r_{ij}^0 by

$$pq = \frac{9(r_{ij}^0)^3}{\sqrt{2}} \frac{B}{E_{\text{coh}}(\text{bulk})} \quad (3.1)$$

From $B(\text{Pt}) = 2.88 \times 10^{12} \text{ dyn/cm}^2$ and the previously assumed ratio¹³ $p/q = 3$, we obtain $p = 11.1$ and $q = 3.7$ for the "single band solid" Pt, in qualitative agreement with earlier calculations.^{12,14} The lattice constants and bulk cohesive energies of the considered alloy components are listed in Table I.

When calculating Q_{seg} at different Pt surfaces, we modeled the surface and the bulk of the semi-infinite crystals by corresponding clusters. These clusters, embedded

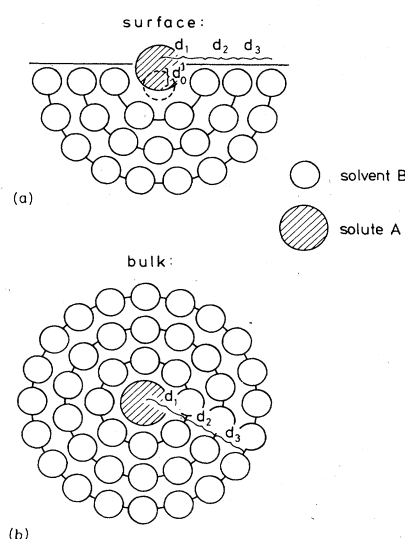


FIG. 1. Relaxations near the impurity.

in the solid, consisted of a central atom and a variable number of nearest-neighbor shells [Figs. 1(a) and 1(b)]. Since the only energy changes occur within the finite surface and bulk clusters upon exchanging a surface A and a bulk B atom, Eq. (2.2) can be rewritten as

$$Q_{\text{seg}} = [E^{\text{tot}}(B \text{ surface}) + E^{\text{tot}}(A \text{ in bulk } B)] - [E^{\text{tot}}(A \text{ at } B \text{ surface}) + E^{\text{tot}}(B \text{ bulk})] \quad (3.2)$$

The relaxed geometry is obtained by minimizing E^{tot} given by Eq. (2.19) with respect to the atomic positions at the surface and in the bulk. The effect of the matrix is taken into account by inhibiting the cluster boundary to relax. In order to keep the number of variational parameters reasonable, we assumed only radial shell displacements Δd_i ($i = 1, 2, \dots$) with respect to the cluster center, and at the surface in addition an in-out relaxation d_0 [see Figs. 1(a) and 1(b)].

The results of our calculation for the heat of segregation of Rh, Cu, and Au impurities at the Pt(111) surface are given in Table I. We consider clusters with six nearest-neighbor shells, but decreasing the cluster size to four shells had only a very small effect on Q_{seg} . In all

TABLE I. Segregation at the Pt(111) surface.

Solute	Lattice constant a (Å)	$E_{\text{coh}}(\text{bulk})^a$ (kJ/mol)	Segregating element and Q_{seg} (kJ/mol)				Ref.
			Only size mismatch ^b	Only surface energy ^c	Our calculation	Expt.	
Rh	3.80	553.9	Pt, 3.8	Rh, -1.2	Pt, 2.8	Pt	15
Cu	3.61	336.8	Pt, 2.7	Cu, -23.1	Cu, -12.6	Cu, moderate segregation	16
Au	4.08	368.6	Au, -11.6	Au, -19.8	Au, -33.9	Au, -38.6±4.8	17
Pt	3.92	565.5					

^aR. Hultgren *et al.*, *Selected Values of the Thermodynamic Properties of the Elements* (American Society for Metals, Cleveland, 1973).

^b $E_{\text{coh}}(\text{solute}) = E_{\text{coh}}(\text{solvent})$ assumed.

^c $r_{\text{solute}}^0 = r_{\text{solvent}}^0$ assumed.

three cases we obtain agreement with experimental data, which is even quantitative in $\text{Au}_x\text{Pt}_{1-x}$, where Q_{seg} has been measured. Also included in this table are calculated results for Q_{seg} for the special case that solute and solvent have the same surface energy (only size-mismatch effects) or the same atomic size (only surface-energy difference). These data illustrate the competing role of these forces in the first two alloys.¹⁵⁻¹⁷

Since on more open surfaces the role of elastic and electronic effects on Q_{seg} can change, we calculated the segregation behavior also at the (100) and (110) surfaces of these alloys. The results are presented in Table II. While for Cu and Au impurities Q_{seg} only increases in magnitude towards the more open surfaces, in dilute Rh alloys we predict changes in the segregating component between close packed and open surfaces.¹⁵⁻¹⁷

Table III shows typical relaxations near Rh, Cu, and Au impurities in Pt(bulk) and at different Pt surfaces. For the sake of comparison, we also included results for pure-Pt systems in this table. In contrast to the bulk, where the relaxations of the matrix are small, the surface displacements of the impurities are comparatively large.

IV. DISCUSSION

The correct prediction of the segregating component and of Q_{seg} in alloys with competing electronic and size-mismatch contributions is a remarkable success of the simple total energy expression (2.19). Obviously, the second moment of the density of states contains the essential information for the band-structure part of Q_{seg} . Note that we avoid the assumption of a band shape (Gaussian, rectangular, etc.) as done previously,^{8,10} but rather relate the hopping integrals to the bulk cohesive energy in Eqs. (2.20) and (2.21). Clearly, an impurity atom can lead to split-off states and never will form an alloy band. In Eq. (2.19) we assume that the second-moment approximation

TABLE II. Segregation at different Pt surfaces.

Solute	Segregating element and Q_{seg} (kJ/mol)		
	(111) surface	(100) surface	(110) surface
Rh	Pt, 2.8	Pt, 1.7	Rh, -0.2
Cu	Cu, -12.6	Cu, -25.1	Cu, -39.6
Au	Au, -33.9	Au, -46.5	Au, -58.0

correctly reproduces the weight and position of these states by allowing for a modification of the ξ_{ij} parameters near the impurity according to Eq. (2.21). Further correction terms would be necessary especially in the case when the difference between the hybridizing levels of the solute and the solvent is large. While these corrections have been discussed before,¹⁸ we neglected such terms for the sake of a theory relying solely on thermodynamic parameters.

Charge-transfer effects, at least on the elastic terms, can be approximately accounted for in Eq. (2.19) by using Eq. (2.16) for the atomic radii and estimating δQ_i from the electronegativity difference of the alloy components. Such effects are expected to be small in the alloys considered and will mainly affect the local relaxations.

We also want to point out the importance of elastic terms in Q_{seg} at the surface which have been neglected in similar calculations.⁵ These surface-specific terms can be responsible for effects such as the segregation trend reversal between close-packed and open $\text{Rh}_x\text{Pt}_{1-x}$ surfaces. Also, the continuum model predicts negative contributions to Q_{seg} for both oversized and undersized impurities,⁴ while our theory (more correctly) gives a negative strain contribution only for oversized impurities, e.g., for Au in Pt, but not for Cu in Pt.

It is generally difficult to obtain reliable data for the heat of segregation in alloys. It has been shown¹⁹ that

TABLE III. Relaxations of the Pt solvent near Rh, Cu, and Au impurities in Pt in the bulk and at different surfaces. Δd_i (d_i^0) are the changes of intershell distances (unrelaxed intershell distances) shown in Fig. 1, and a is the lattice constant of the solvent.

System	d_0/a	$\Delta d_1/d_1^0$	$\Delta d_2/d_2^0$	$\Delta d_3/d_3^0$	$\Delta d_4/d_4^0$
Rh/Pt(bulk)		-0.0%	+0.0%	+0.0%	+0.0%
Rh/Pt(111)	-2.2%	-0.3%	-0.3%	-0.1%	-0.1%
Rh/Pt(100)	-3.1%	-0.4%	-0.3%	-0.1%	-0.1%
Rh/Pt(110)	-3.9%	-0.4%	-0.4%	-0.1%	-0.1%
Cu/Pt(bulk)		-0.1%	+0.0%	+0.1%	+0.0%
Cu/Pt(111)	-3.2%	-0.4%	-0.3%	-0.0%	-0.1%
Cu/Pt(100)	-4.1%	-0.4%	-0.4%	+0.0%	-0.1%
Cu/Pt(110)	-4.9%	-0.5%	-0.5%	+0.0%	-0.0%
Au/Pt(bulk)		+0.1%	-0.1%	+0.0%	+0.0%
Au/Pt(111)	+3.1%	-0.3%	-0.4%	-0.1%	-0.1%
Au/Pt(100)	+2.5%	-0.4%	-0.4%	-0.0%	-0.1%
Au/Pt(110)	+1.5%	-0.4%	-0.5%	-0.0%	-0.1%
Pt/Pt(bulk)		0.0%	0.0%	0.0%	0.0%
Pt/Pt(111)	-0.9%	-0.3%	-0.3%	-0.1%	-0.1%
Pt/Pt(100)	-1.6%	-0.4%	-0.3%	-0.1%	-0.1%
Pt/Pt(110)	-2.5%	-0.4%	-0.4%	-0.1%	-0.1%

within the equivalent cores approximation the surface core-level binding-energy shift Δ_c^s observed in photoemission is equal to the heat of segregation of an impurity of the element which follows next in the Periodic Table. The results of this method, which is restricted to alloys of neighboring elements in the Periodic Table and which was applied here to $\text{Au}_x\text{Pt}_{1-x}$, showed good agreement with the predicted value for Q_{seg} .

The relaxation data presented in Table III confirm local lattice expansion in the bulk and an out-of-surface movement of large (Au) impurities and the reverse behavior of small (Rh,Cu) atoms. Also the trends in the calculated values confirm larger relaxations in systems with large size mismatch and/or open surfaces. As shown in Table III, our model also predicts an inward relaxation of Pt "impurities" at Pt surfaces, which is indicative of the observed surface contraction. The relatively small contraction values result from the fact that in our simplified geometry, relaxations perpendicular to the surface can occur only at the impurity site, while the rest of the surface is considered as unrelaxed in this way.

The calculated nearest-neighbor relaxations $\Delta d_1/d_1^0$ in the bulk of -0.04% for Pt(Rh), -0.08% for Pt(Cu), and $+0.06\%$ for Pt(Au) are only $\leq 10\%$ of those expected from a local addition of atomic radii, namely, -0.7% for Pt(Rh), -2.0% for Pt(Cu), and $+1.0\%$ for Pt(Au). These smaller relaxations are confirmed by x-ray-absorption fine-structure (EXAFS) measurements²⁰ of nearest-neighbor distances in semiconductors. In these systems, whose lattice constants accurately follow Vegard's law, the corresponding values of $\Delta d_1/d_1^0$ have been found to be only 20% of those expected from the virtual-crystal approximation.²⁰ While still smaller distortions are expected in the relatively hard transition-metal solvents, in agreement with our predictions, it would be very valuable to perform similar EXAFS experiments in the above studied systems.

In this paper we tested the presented theory on substitutional impurities in Pt single crystals, but its application to interstitial alloys is straightforward. In this case, however, the atomic relaxations might be more far reaching. The calculation of Q_{seg} in interstitial alloys also requires a detailed knowledge of bulk and surface impurity sites and a careful analysis of possible relaxations in the surrounding matrix. In amorphous structures and in small metallic clusters the elastic terms are expected to play a minor role, due to the possibility of local stress release by local

reordering of the matrix in the first case, and by the absence of a rigid boundary in the second case. Similar to the case of interstitial impurities, model assumptions have to be made here about the local structure of the solvent.

This is also the case in concentrated alloys in general. Here, in addition, the simplifying assumptions for the entropy leading to Eq. (2.1) lose validity. Instead of

$$S = k[x \ln x + (1-x) \ln(1-x)] , \quad (4.1)$$

an expression depending on the short-range order is required. In this case, an approximate expression given by Kikuchi can be used.²¹

At adsorbate-covered alloy surfaces or at interfaces the inclusion of overlayer-substrate coupling in the Hamiltonian (2.4) will account for the modification of Q_{seg} and changes in the segregation behavior, which have been discussed previously in a phenomenological model.²² Our formalism can be further used to calculate Q_{seg} in ternary alloys. The hydrogen-absorption-induced segregation in $\text{Zr}_x\text{Pd}_{1-x}$ alloys, previously explained by the different heat of solution of hydrogen in the alloy components,²² can be now described within an electronic model.

In summary, we presented a microscopic theory for the surface segregation in dilute alloys. The electronic contribution to the heat of segregation was described within a multiband tight-binding Hamiltonian; size-mismatch energies, which were considered in the bulk and at the surface, were described by Born-Mayer-type interactions. It has been shown, that under reasonable assumptions a simple formula for the heat of segregation can be obtained, which uses only thermodynamic parameters such as the bulk cohesive energy and the atomic size. This theory, applied to dilute Pt-based alloys of Rh, Cu, and Au, showed good agreement with experimental data. It has also been shown, that competing size mismatch and electronic forces can lead to the segregation of different alloy components in $\text{Rh}_x\text{Pt}_{1-x}$ at different surfaces.

ACKNOWLEDGMENTS

We acknowledge stimulating discussions with K. H. Bennemann. One of us (D.T.) acknowledges financial support from the Kernforschungszentrum Karlsruhe and the Comisión Nacional de Energía Atómica (CNEA) through the Centro Atómico Bariloche.

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