

Surface heat of segregation from surface core-level binding-energy shifts

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The surface core-level shift for the Z (Z being the atomic number) component in a $Z_x(Z+1)_{1-x}$ metallic alloy is shown to be directly related to the surface heat of segregation of the $(Z+1)$ component. Measurements of surface core-level shifts can therefore be an accurate means to obtain this important thermodynamic quantity, which also enters as a crucial parameter in the quasichemical theory for surface segregation. The possibility to use the surface core-level binding energies for a determination of the energetics of the surface is also pointed out.

I. INTRODUCTION

Surface segregation has in recent years been in the focus of interest for several reasons, one, of course, being its importance in many fields of science and technology, including catalysis, corrosion, and chemisorption. This phenomenon, manifesting itself as the equilibrium alloy surface composition being different from the bulk composition, was anticipated already by Gibbs.¹ The analogous phenomenon of grain boundary segregation is of great importance in metallurgy, causing the problems of grain boundary fracture in temper brittleness, creep embrittlement, stress-relief cracking of weldments, grain-boundary corrosion, intergranular stress corrosion cracking, hydrogen embrittlement, and environmentally assisted fatigue.² However, the main reason for the renewed interest in surface segregation is due to the recent development of new measurement techniques for surface analysis. Such techniques are, for example, Auger electron spectroscopy (AES), low-energy ion scattering (LEIS), and ultraviolet photoemission spectroscopy (UPS). The interpretation of measurements made with them is, however, somewhat hampered by the question of the region of sampling. So although most measurements with different techniques do agree upon whether there is segregation or not, there are appreciable differences in the extraction of an absolute composition depth profile. This is, for example, clearly demonstrated by measurements made on NiCu alloys.³⁻⁵ A technique which according to Ref. 6 is able to provide such profiles is time-of-flight atom-probe field ion microscopy. With these developments in measurement techniques there exists today a bulk of experimental data for theory to be tested against.

Theory has, over the past few years, been developing along mainly two lines, known as the

quasichemical approach⁷⁻⁹ and the strain theory.¹⁰ According to the first one the alloy constituent having the lower heat of vaporization segregates at the surface in order to minimize the surface free energy; according to the second one the minority component atoms segregate at the surface in order to minimize the strain energy. There have also been efforts to combine these theories.^{11,12} One problem of these approaches is to determine the parameters entering the theory and their temperature and concentration dependence.

The main purpose of the present paper is to show that for a special class of metallic alloys the heat of segregation can be accurately determined from surface core-level shifts (SCS), i.e., from the shifts in the core-level binding energies of surface atoms relative to bulk atoms. The heat of segregation is, of course, of interest in itself, but also enters in a crucial way in the theoretical models for segregation. Therefore, with this parameter available, a better assessment of the validity of the models can be made. The systems for which this determination is possible are alloys between a Z and a $(Z+1)$ metal (Z = atomic number). Although this is certainly a severe restriction it includes important systems such as Ni-Cu, Pd-Ag, and Ir-Pt. For a general but dilute alloy system A_xB_{1-x} (dilute in the A component), the surface core-level shifts of the A -component atoms will correspond to the difference between the heat of segregation of a substitutional $(A+1)$ impurity ($A+1$ being the $Z+1$ element relative to A) and the A atom itself, and will thus also provide here important segregation data for special types of dilute species. Today such surface core-level shifts have been measured for only a few metals,¹³⁻¹⁵ but it is expected that in the near future much more data will become available. Furthermore, since the surface core-level shift will depend on the surface plane,¹⁶⁻¹⁸ the anisotropy of the heat of segregation can be

determined. This should hopefully stimulate studies on the surface dependence of the degree of segregation, a subject which up to now has been practically untreated experimentally.

The division of this paper is as follows. In Sec. II we very briefly review the fundamental equations of the quasichemical approach to surface segregation. In Sec. III we derive an expression for the SCS for an alloy of two metals with atomic number Z and $Z+1$ and show that if the two metals have the same atomic volume this shift is almost exactly the heat of segregation. We also make some remarks on the bulk heat of formation of the alloy as well as on its surface counterpart. The last section, Sec. IV, contains a discussion and some concluding remarks.

II. THE QUASICHEMICAL APPROACH

To provide some background material for the next section we will here briefly review some of the basic results of the quasichemical approach. We will closely follow the paper and notation by Kumar *et al.*⁹ In the simplest version of this approach the system is treated as an ideal solution in which case segregation occurs only in the topmost layer. In more advanced versions of the theory the system is assumed to be a regular or nonregular solution and in these cases the composition is studied at the surface and in the layers parallel to the surface.

In our short description below, the usual assumptions will be made, i.e., we assume that the system is a semi-infinite solid binary alloy in thermodynamical equilibrium with atomistically plane surfaces, and that the total configuration energy U can be written as a sum of interaction energies between nearest-neighbor atom pairs only, i.e.,

$$U = \sum_{\lambda=0}^{\infty} \left[\epsilon_{AA} (N_{AA}^{\lambda\lambda} + N_{AA}^{\lambda\lambda+1}) + \epsilon_{AB} (N_{AB}^{\lambda\lambda} + N_{AB}^{\lambda\lambda+1} + N_{BA}^{\lambda\lambda+1}) + \epsilon_{BB} (N_{BB}^{\lambda\lambda} + N_{BB}^{\lambda\lambda+1}) \right], \quad (1)$$

where ϵ_{AA} , ϵ_{BB} , and ϵ_{AB} are the bond enthalpies for nearest-neighbor (NN) pairs of A and B atoms, $N_{ij}^{\lambda\mu}$ is the number of NN pairs in which an atom of type i lies in the λ th layer and an atom of type j in the μ th layer. Short-range order parameters α_λ , β_λ , and β'_λ are introduced in the following way:

$$N_{AB}^{\lambda\lambda} = 2x_\lambda y_\lambda \alpha_\lambda N^{\lambda\lambda}, \quad (2a)$$

$$N_{AB}^{\lambda\lambda+1} = x_\lambda y_{\lambda+1} \beta_\lambda N^{\lambda\lambda+1}, \quad (2b)$$

$$N_{BA}^{\lambda\lambda+1} = y_\lambda x_{\lambda+1} \beta'_\lambda N^{\lambda\lambda+1}, \quad (2c)$$

where $N^{\lambda\lambda}$ is the number of NN pairs within the

λ th layer, $N^{\lambda\lambda+1}$ the total number of NN pairs between the two adjacent layers λ and $\lambda+1$, and x_λ and y_λ are the concentrations of type A and type B atoms in layer λ . Leaving out the configuration-independent terms the configuration energy can be rewritten as

$$U = \sum_{\lambda=0}^{\infty} N^{\lambda\lambda} \left\{ \epsilon [Z_{LL} x_\lambda y_\lambda \alpha_\lambda + Z_{IL} (x_\lambda y_{\lambda+1} \beta_\lambda + x_{\lambda+1} y_\lambda \beta'_\lambda)] - 2B [Z_{LL} x_\lambda + Z_{IL} (x_\lambda + x_{\lambda+1})] \right\}, \quad (3)$$

where N^λ is the number of atoms in the λ th layer, Z_{LL} and Z_{IL} denote the number of nearest neighbors of an atom in the same layer and in the adjacent layer, respectively, and where

$$\epsilon = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2 \quad (4)$$

and

$$B = (\epsilon_{BB} - \epsilon_{AA})/4. \quad (5)$$

Kumar *et al.* then derive the configurational entropy of the system in the Bethe-Peierls approximation and determine x_λ and the short-range order parameters by minimizing the free energy under the constraint that the overall concentration of the alloy constituents is fixed.⁹ The minimization with respect to x_0 and x_1 leads to the following equations:

$$x_0/y_0 = (x_b/y_b) \exp(-\Delta H_0/kT) \exp(\Delta S_0/k), \quad (6)$$

where

$$\Delta H_0 = 2BZ_{IL} + \epsilon [Z_{LL} \alpha_0 (y_0 - x_0) + Z_{IL} (\beta_0 y_1 - \beta'_0 x_1) - Z \alpha_B (y_b - x_b)] \quad (7)$$

and

$$x_1/y_1 = (x_b/y_b) \exp(-\Delta H_1/kT) \exp(\Delta S_1/k), \quad (8)$$

where

$$\Delta H_1 = \epsilon [Z_{LL} \alpha_1 (y_1 - x_1) + Z_{IL} (\beta_1 y_2 - \beta'_1 x_2 + y_0 \beta'_0 - x_0 \beta_0) - Z \alpha_B (y_b - x_b)]. \quad (9)$$

Here x_b and y_b denote bulk concentrations of type- A atoms and type- B atoms, respectively. Equations (6) and (8) thus give the deviations from the bulk composition for the topmost and second-topmost layer, respectively.

Just as we did not specify the configurational entropy earlier we neither specify ΔS_0 nor ΔS_1 , and the reader interested in those details is referred to Ref. 9. We note that ΔH_0 in the case of an ideal solution ($\epsilon = 0$) reduces to $2BZ_{IL}$ which in the broken bond picture is $E_s(A) - E_s(B)$, i.e., the difference in surface energy between the pure

metals A and B . The discussion of the thermodynamic interpretation of the second term of Eq. (7) is deferred to Sec. III, and here we only note that $-\Delta H_0$ by means of Eq. (3) can be rewritten as the energy it will cost to exchange a B atom from the bulk with an A atom at the surface, i.e., $-\Delta H_0$ is the heat of segregation. In exactly the same way, $-\Delta H_1$ can be rewritten as the energy it costs to exchange a B atom from the bulk with an A atom in the first layer below the surface.

III. THE SURFACE CORE-LEVEL SHIFT

In this section we derive an expression for the core-level shift for a surface atom relative to a bulk atom. This is done for the case of a binary alloy where the two metallic constituents have atomic numbers Z and $Z+1$, respectively. This is a generalization of the treatments in Refs. 16–18, where only the case of pure metals was considered and where the heat of segregation interpretation was only briefly mentioned. Such surface core-level shifts for metals have only recently been experimentally confirmed.^{13–15} There is one assumption and one approximation vital to the derivation: (i) the final core-ionized state is assumed to be fully screened by valence electrons; (ii) the $(Z+1)$ approximation is made, i.e., the final-state screening valence electron distribution resulting from the photoejection of a deep core electron of a Z atom can be described by the valence electron distribution of a $(Z+1)$ substitutional atomic site. That is, we treat the core-ionized site as (i) a charge neutral Z^* impurity (where $*$ means the core-ionized atom) and (ii) the Z^* impurity is approximated by a $(Z+1)$ impurity.

The derivation is made by means of the Born-Haber cycle shown in Fig. 1. Let us start with an alloy of atoms with atomic number Z and $Z+1$, the atoms are called A and B , respectively, and the numbers are N_A and N_B . This is the initial state (Fig. 1). Then we separate the alloy into its pure metal constituents, which by definition will cost the alloy formation energy $E_{\text{alloy}}(N_A, N_B)$. After this we bring one atom from the so-obtained A metal to infinity. The cost of this process is the cohesive energy $E_{\text{coh}}(A)$. This atom is then core ionized, the energy involved being E_c^A . The core-ionized A^* atom is then neutralized by letting it acquire one electron in its lowest valence-shell state (in the presence of the core hole). This involves the energy I_{A^*} . The valence electrons of the so-prepared A^* atom can now, according to the $(Z+1)$ approximation, be treated as those of a $(Z+1)$ atom. This $(Z+1)$ atom or the B atom is now brought from infinity to the rest of the B

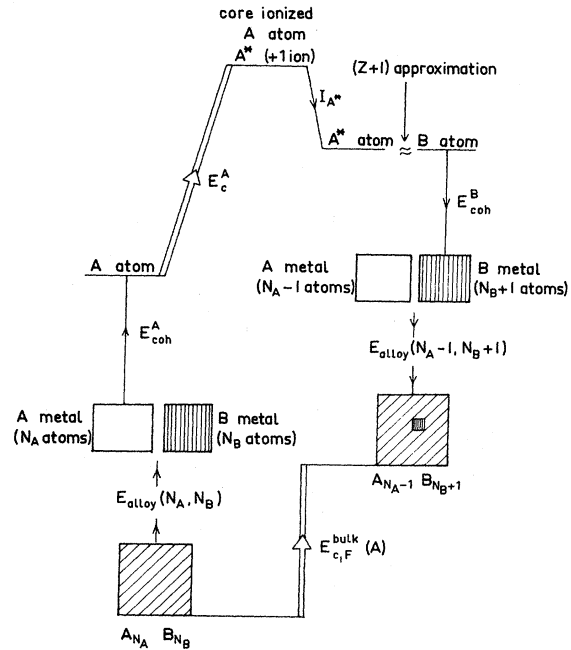


FIG. 1. Born-Haber cycle describing the core electron excitation process. In this process the original A atom is converted to a B atom [by means of the $(Z+1)$ approximation and the complete screening assumption].

atoms forming the B metal, the gain in energy of this process being the cohesive energy $E_{\text{coh}}(B)$. The two pieces containing A and B atoms, respectively, are now alloyed and thereby the energy $E_{\text{alloy}}(N_A-1, N_B+1)$ is gained. This state, illustrated in the lower right part of Fig. 1, is the final state of the photoionization process, more specifically for the bulk version of it. The processes in the Born-Haber cycle can therefore be summed up to give the excitation energy of the bulk core electron to the Fermi level $E_{c,F}^{\text{bulk } A}$ (compare Fig. 1) as follows:

$$E_{c,F}^{\text{bulk } A}(N_A, N_B) = E_{\text{alloy}}(N_A, N_B) + E_{\text{coh}}(A) + E_c^A - I_{A^*} - E_{\text{coh}}(B) - E_{\text{alloy}}(N_A-1, N_B+1). \quad (10)$$

The whole cycle, when repeated for atoms at surfaces, gives, with n_A and n_B being the numbers of surface layer A and B atoms, respectively, and $E_{c,F}^{\text{surf } A}$ being the binding energy of a surface core electron of the A atom relative to the Fermi energy,

$$E_{c,F}^{\text{surf } A}(n_A, n_B) = E_{\text{alloy}}^{\text{surf}}(n_A, n_B) + E_{\text{coh}}^{\text{surf}}(A) + E_c^A - I_{A^*} - E_{\text{coh}}^{\text{surf}}(B) - E_{\text{alloy}}^{\text{surf}}(n_A-1, n_B+1). \quad (11)$$

Here $E_{\text{coh}}^{\text{surf}}$ is the surface cohesive energy, i.e., the energy gained when a free atom is condensed

on the surface (while the surface area is increased by one atomic surface area unit). The term of $E_{\text{alloy}}^{\text{surf}}(n_A, n_B)$ is the energy cost of taking away the topmost layer of the segregated crystal, the layer containing n_A A atoms and n_B B atoms, and letting these A and B atoms form monolayers on top of pure crystals consisting of A atoms and B atoms, respectively (while increasing the surface area correspondingly). By subtracting Eq. (10) from Eq. (11) we obtain for the surface core-level shift $\Delta_c(A)$

$$\begin{aligned} \Delta_c(A) &= E_{c,F}^{\text{surf } A} - E_{c,F}^{\text{bulk } A} \\ &= E_s(B) - E_s(A) \\ &\quad - [E_{\text{alloy}}(N_A, N_B) - E_{\text{alloy}}(N_A - 1, N_B + 1)] \\ &\quad + [E_{\text{alloy}}^{\text{surf}}(n_A, n_B) - E_{\text{alloy}}^{\text{surf}}(n_A - 1, n_B + 1)], \end{aligned} \quad (12)$$

where $E_s(A)$ and $E_s(B)$ are the surface energies of the pure A and B metals, i.e.,

$$E_s(A) = E_{\text{coh}}(A) - E_{\text{coh}}^{\text{surf}}(A). \quad (13)$$

Considering the way the core-level shift is derived, taking the difference between the cycle described in Fig. 1 and its surface counterpart, it is clear that the entity $\Delta_c(A)$ is the energy cost of exchanging a B atom from the bulk with an A atom at the surface. Thus the surface core-level shift is just the heat of segregation $-\Delta H_0$ defined in the preceding section. This is further illustrated in Fig. 2. The core-level binding energy is the total energy difference between the final and the initial state. For the bulk excitation the final state is [according to the $(Z+1)$ approximation] a $(Z+1)$ bulk atom in the host, while for the surface excitation it is a $(Z+1)$ surface atom in the host (Fig. 2). By taking the difference, as is made in the lower part of Fig. 2, it is immediately clear that the surface core-level shift corresponds to the energy required to exchange a bulk $(Z+1)$ atom with a surface Z atom. For the sake of completeness we also show this explicitly within the NN bond model of the preceding section. If

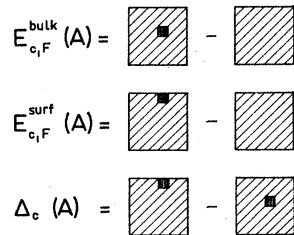


FIG. 2. Illustration of the correspondence between the surface core-level shift $\Delta_c(A)$ and the heat of segregation of a B atom [the $(Z+1)$ element relative to A].

one starts from Eq. (3) and includes the configuration-independent terms which were left out in the earlier treatment it turns out that by resummation, the configuration energy can be rewritten as

$$U = \sum_{\lambda=0} \Delta H^\lambda + H_\lambda^A + H_\lambda^B, \quad (14)$$

where

$$\Delta H^\lambda = N^\lambda \epsilon [Z_{LL} x_\lambda y_\lambda \alpha_\lambda + Z_{IL} (x_\lambda y_{\lambda+1} \beta_\lambda + x_{\lambda+1} y_\lambda \beta'_\lambda)], \quad (15)$$

$$H_\lambda^A = (Z_{LL} + 2Z_{IL} - Z_{IL} \delta_{\lambda 0})^{\frac{1}{2}} \epsilon_{AA} x_\lambda N^\lambda, \quad (16)$$

and

$$H_\lambda^B = (Z_{LL} + 2Z_{IL} - Z_{IL} \delta_{\lambda 0})^{\frac{1}{2}} \epsilon_{BB} y_\lambda N^\lambda. \quad (17)$$

That is, the configuration energy can be written as a sum layer by layer of the cohesive energies of the pure constituents and a layer heat of formation ΔH^λ . It is easily seen that this layer heat of formation for a bulk layer goes over to the conventional bulk heat of formation (as defined in the NN bond model). The term $E_{\text{alloy}}^{\text{surf}}(n_A, n_B)$, as defined above, will, accordingly, in the NN bond model correspond to $-\Delta H^0 = -\Delta H^0(x_0, x_1)$, where x_0 is the concentration of A atoms in the topmost layer. That is, Eq. (12), rewritten in the bond model, is

$$\begin{aligned} \Delta_c(A) &= -2BZ_{IL} - \epsilon [Z_{LL} \alpha_0 (y_0 - x_0) + Z_{IL} (\beta_0 y_1 - \beta'_0 x_1) \\ &\quad - Z \alpha_B (y_B - x_B)]. \end{aligned} \quad (18)$$

From Eq. (7) it is now immediately clear that $\Delta_c(A) = -\Delta H_0$. The thermodynamic interpretation of the second term of Eq. (7) is therefore just the difference between surface and bulk partial heat of formation.

For a general metallic alloy $Z_x Y_{1-x}$ it is still possible to give a thermodynamic interpretation of the surface core-level shift. For a dilute alloy, dilute in the Z component, the interpretation becomes particularly simple and here the surface shift corresponds to the difference in the heat of segregation between the Z and $(Z+1)$ atom in the host Y . By an analogous cycle the heat $-\Delta H_1$ defined in the preceding section can be shown to be equal to the shift in the core-level binding energy for an A atom sitting in layer one relative to a bulk A atom.

It is also of interest to study the chemical shift of the bulk core level in the alloy as compared with its position in the pure A metal. For the pure A metal the relation in Eq. (10) takes the form

$$E_{c,F}^{\text{bulk } A}(N, 0) = E_{\text{coh}}(A) + E_c^A - I_{A^*} - E_{\text{coh}}(B) - E_{\text{alloy}}(N-1, N_B=1). \quad (19)$$

The last term is the solution energy of a metallic B atom [the $(Z+1)$ atom] in the host metal A and it will in the following be denoted by $E_B^{\text{imp}}(A)$. From Eqs. (10) and (19) the bulk core-level shift (the chemical shift) between the alloy $A_{N_A} B_{N_B}$ and the pure metal becomes

$$\Delta_{\text{chem}}^{\text{bulk } A} = E_{\text{alloy}}(N_A, N_B) - E_{\text{alloy}}(N_A-1, N_B+1) + E_B^{\text{imp}}(A). \quad (20)$$

With $N_A + N_B = N$, where N is a constant, this may be rewritten as

$$\Delta_{\text{chem}}^{\text{bulk } A} = E_{\text{alloy}}(N_A, N - N_A) - E_{\text{alloy}}(N_A-1, N - (N_A-1)) + E_B^{\text{imp}}(A), \quad (21)$$

and for a macroscopic system the alloy terms might be expressed as a derivative, and we obtain

$$\Delta_{\text{chem}}^{\text{bulk } A} = \frac{d}{dN_A} [E_{\text{alloy}}(N_A, N_B)] + E_B^{\text{imp}}(A). \quad (22)$$

Introducing the concentration $x = N_A/N$ and $(1-x) = N_B/N$ as well as the heat of formation for the $A_x B_{1-x}$ alloy $-\Delta H(x) = E_{\text{alloy}}(N_A, N_B)/N$, Eq. (22) becomes

$$\Delta_{\text{chem}}^{\text{bulk } A}(A_x B_{1-x}) = \frac{d}{dx} [-\Delta H(x)] + E_B^{\text{imp}}(A). \quad (23)$$

Integration gives

$$-\Delta H(x) = \int_0^x \Delta_{\text{chem}}^{\text{bulk } A}(A_{x'} B_{1-x'}) dx' - E_B^{\text{imp}}(A)x, \quad (24)$$

where the boundary condition $\Delta H(0) = 0$ has been used. Thus from an experimental determination of the chemical shift of the core level of the bulk A atom as a function of concentration, it becomes possible to determine the heat of formation of the alloy $A_x B_{1-x}$, where B is the $(Z+1)$ element of A . The term $E_B^{\text{imp}}(A)$ is determined from the boundary condition $\Delta H(1) = 0$. The relation (24) has been used by Steiner and Hüfner¹⁹ to derive the heat of formation of the $\text{Pd}_x \text{Ag}_{1-x}$ alloy from the measured chemical shift of the $\text{Pd } 3d_{5/2}$ core level. Thereby they obtained a most satisfying agreement with the thermochemical data, suggesting that ESCA (electron spectroscopy for chemical analysis) calorimetry might become a very rapid and useful method for thermochemical investigations. However, it should be remembered that Eq. (24) only holds for a Z and $(Z+1)$ metallic alloy. For a general alloy, $Z_x Y_{1-x}$, ternary heat of solution terms enter, which renders the extraction of heat

of formation data from the chemical shifts much more difficult. Still the ternary solution terms might often be reasonably well approximated by (say) a linear function of the concentration x , thereby making a determination of the heat of formation for a more general alloy possible. This was recently applied to the $\text{Pd}_x \text{Cu}_{1-x}$ alloy²⁰ and the obtained agreement with thermochemical data was again most encouraging for further investigations of ESCA calorimetry also for more general alloys.

Returning to our Z and $(Z+1)$ alloy we can derive a similar equation like Eq. (24) for the surface. Thereby we obtain for the heat of formation of the topmost layer

$$-\Delta H^{\text{surf}}(x) = \int_0^x \Delta_{\text{chem}}^{\text{surf } A}(A_{x'} B_{1-x'}) dx' - E_B^{\text{surf, imp}}(A)x, \quad (25)$$

where x and x' denote surface concentrations and where the other notations should now be obvious. Thus the surface chemical shifts could be used to extract the energetics of the surface alloy. That would be particularly helpful since there are presently practically no thermochemical data at all available for this important alloy situation.

IV. DISCUSSION

In the given treatment the assumption of a fully screened final state is most important for our derivation of the relationship between the surface core-level shift and the heat of segregation. However, the validity of this assumption is corroborated by much experimental evidence, such as for example, the asymmetric line shapes of the core levels. Also, recent photoabsorption experiments,²¹ showing direct agreement between the absorption edge energy and the photoionization energy (relative to the Fermi energy), lend strong support to the validity of the view of a fully screened photoionized final state in a metallic system. Recently the complete screening picture and the $(Z+1)$ approximation have been used to accurately account for core-level binding-energy shifts between free and condensed metallic atoms,¹⁷ showing also the appropriateness of the $(Z+1)$ approximation. In the present case where we compare two different final-state situations in the condensed phase, the $(Z+1)$ approximation enters only in a differential way, which results in an improved accuracy. Further discussions on this can be found in Ref. 17. Somewhat more severe is the fact that the photoionization is a vertical process while we have treated it above as a thermal process (i.e., in principle we have allowed for relaxations of the positions of the nuclei surrounding the ionized atom). However,

since in general the atomic volume of the $(Z + 1)$ element does not differ very much from that of the Z element, our thermal approximation of the vertical process should be of sufficient accuracy, especially so since the thermal approximation also enters in a differential way in our present problem.

Except for the limitations just mentioned the surface core-level shift has in the present paper been shown to *exactly* correspond to the heat of segregation of a $(Z + 1)$ substitutional impurity. Facing this interpretation of the surface shift it is, of course, most important to know with what accuracy this shift can be determined experimentally. For the two best studied cases, tungsten¹⁴ and iridium,¹⁵ the claimed accuracy for the shift of the $4f_{7/2}$ level is about ± 0.02 eV. The shift itself has in general a magnitude of the order of 0.5 eV.¹⁸ Thus there is no doubt that measurements of surface core-level shifts are of immediate interest for segregation studies. Especially interesting is the expected surface plane dependence of the shift,^{16,17} which now also has been verified experimentally,¹⁵ whereby the anisotropy of the segregation can be fruitfully studied. Unfortunately, with the currently available techniques only surface shifts for the $5d$ metals can be studied with such a high accuracy (due to the fortunate situation of a low binding energy of the $4f$ core level). This means that at the moment an alloy system such as $\text{Ir}_x\text{Pt}_{1-x}$, an important catalyst in the production of high octane number gasoline, would be highly interesting and suitable as a case study. Furthermore, for this alloy system our thermal treatment of the vertical excitation should pose very little problem, due to the similarity of the atomic volumes of Ir and Pt.

Let us now return to the heat of segregation derived within the quasichemical approach. This contains the parameters B and ϵ . The first one is, as we have pointed out above, proportional to the difference in surface energy between the two pure constituents. Within the nearest-neighbor broken bond model this difference is proportional to the difference in heat of vaporization of the two metals, and this is how the parameter B is usually determined. However, it is known, for example, from the tight-binding calculation of Desjonquères and Cyrot-Lackmann,²² that this proportionality is a rather crude approximation. The second parameter ϵ is related to the heat of mixing and is both temperature and concentration dependent. The fact that the curves of heat of mixing versus mole fraction usually are not symmetric around the equiatomic concentration, indicating the existence of short-range order and thus motivating the

introduction of short-range order parameters, does not make it easier to extract this dependence.⁹ So within the quasichemical approach it is difficult to obtain the necessary parameters. Going beyond the treatment done so far, several attempts have been done to improve on it, such as, e.g., (a) including next-nearest neighbors in deriving the total configuration enthalpy, either by a direct summation or by introducing an effective number of neighbors^{7,23,24} and (b) introducing surface enthalpy relaxation either by assuming that only lateral bonds of the first layer are altered⁴ or that both lateral and vertical bonds are modified to the same fractional extent.^{6,7} The attempts made to improve on the simple NN treatment introduce new parameters to be determined. Fitting these parameters to experiment often gives rise to unrealistic values.^{4,6} *The great advantage of the measured core-level shift is that it immediately gives an accurate value for the heat of segregation.*

Finally we conclude by adding a few comments on the core-level shift to be measured. Firstly, the surface measurement should be made on a surface in thermal equilibrium, i.e., not on a surface immediately after cleaving the crystal. Still, of course, the latter situation would also provide important information. Secondly, the most useful and direct information is obtained for a $Z-(Z + 1)$ metallic alloy. If we are dealing with a nonregular solution, i.e., there is short-range order in the system, the photoionized atoms in the same layer could have rather different surroundings, although the statistical mean would be the same, leading to a broadening of the peaks to be observed. This effect is, of course, also present already for the case of a regular solution, but the effect should be more pronounced the more short-range order there is in the alloy. Due to the expected smallness and due to the broadening mechanism just mentioned, the shift in the second layer (corresponding to the heat $-\Delta H_1$) might be difficult to measure with presently available resolution.

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