

SURFACE CORE-LEVEL BINDING ENERGY SHIFTS IN ALLOYS

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A simple theory for the core-level binding energy shifts at the surfaces of binary alloys A_xB_{1-x} is presented. Results are given for the surface core-level shifts of Ni in Ni_xCu_{1-x} alloys and Pd in Pd_xAg_{1-x} alloys. It has been shown that the surface core-level shifts may depend sensitively on surface segregation.

RECENTLY there is a growing interest in the study of core-level binding energy shifts in metals and alloys. It is observed [1] that the core-level shifts depend sensitively on the chemical environment of the atom and the electronic structure of the valence electrons. Core-level shifts have been measured using photo electron spectroscopy for the surfaces of some transition metals [2] and for alloys [3] in bulk. Thus it is of considerable interest to study surface effects on core-level shifts. For alloys there is also surface segregation of impurities. It is the main purpose of this paper to illustrate that surface core-level shifts in alloys depend sensitively on surface segregation. Therefore, surface core-level shifts may be used to analyse surface segregation in alloys. So far this problem has not been studied experimentally.

In the following we calculate the surface core-level shifts in alloys by using the procedure of Johansson and Mårtensson [4]. In this approach one assumes a fully screened final state and the screening charge distribution around the core ionized site is approximated by that of a $(z + 1)$ atom where z is the atomic number in the initial state. Therefore this site can be treated as $(z + 1)$ impurity in the host. The bulk core-level binding energy of A component in a binary alloy A_xB_{1-x} can be written as

$$E_{c,F}^b(A, A_xB_{1-x}) = -E_{\text{coh}}^b(A^*) + E_{\text{coh}}^b(A, A_xB_{1-x}) + E_{c \rightarrow v}(A) + E_{A^*}^{\text{imp}}(A_xB_{1-x}) \quad (1)$$

$$\equiv -E_{\text{coh}}^b(A^*, A_xB_{1-x}) + E_{\text{coh}}^b(A, A_xB_{1-x}) + E_{c \rightarrow v}(A). \quad (2a)$$

A similar expression can be written for B ,

$$E_{c,F}^b(B, A_xB_{1-x}) = -E_{\text{coh}}^b(B^*, A_xB_{1-x}) + E_{\text{coh}}^b(B, A_xB_{1-x}) + E_{c \rightarrow v}(B) \quad (2b)$$

where

$$-E_{\text{coh}}^b(A^*, A_xB_{1-x}) = -E_{\text{coh}}^b(A^*) + E_{A^*}^{\text{imp}}(A_xB_{1-x}). \quad (3)$$

b and c denote respectively the bulk and the core. F denotes that the energies are measured with respect to the Fermi energy. A^* is the core ionized atom. $-E_{\text{coh}}^b(A^*, A_xB_{1-x})$ is the cohesive energy of A^* in the alloy and is equal to the sum of the cohesive energy $-E_{\text{coh}}^b(A^*)$ of pure A^* and the heat of solution $E_{A^*}^{\text{imp}}(A_xB_{1-x})$ of A^* in the alloy. $E_{c \rightarrow v}$ is the excitation energy of the core electron c into the valence electron v (for transition metals the d electrons). Now the rest of the terms are self explanatory. At the surface, the core-level binding energy can be written analogously:

$$E_{c,F}^s(A, A_{x_s}B_{1-x_s}) = -E_{\text{coh}}^s(A^*, A_{x_s}B_{1-x_s}) + E_{\text{coh}}^s(A, A_{x_s}B_{1-x_s}) + E_{c \rightarrow v}(A) \quad (4a)$$

and

$$E_{c,F}^s(B, A_{x_s}B_{1-x_s}) = -E_{\text{coh}}^s(B^*, A_{x_s}B_{1-x_s}) + E_{\text{coh}}^s(B, A_{x_s}B_{1-x_s}) + E_{c \rightarrow v}(B) \quad (4b)$$

Here s refers to the surface and it is assumed that the surface concentration is different from the bulk due to surface segregation. The surface core-level shift of A can therefore be written as

$$\Delta E_c^s(A) = E_{c,F}^s(A, A_{x_s}B_{1-x_s}) - E_{c,F}^b(A, A_xB_{1-x}) \quad (5)$$

$$= E_{\text{coh}}^b(A^*, A_xB_{1-x}) - E_{\text{coh}}^s(A^*, A_{x_s}B_{1-x_s}) + E_{\text{coh}}^s(A, A_{x_s}B_{1-x_s}) - E_{\text{coh}}^b(A, A_xB_{1-x}) \quad (6)$$

$$\equiv E^s(A^*, A_xB_{1-x}) - E^s(A, A_xB_{1-x}), \quad (7a)$$

where

$$E^s(A^*, A_xB_{1-x}) = E_{\text{coh}}^b(A^*, A_xB_{1-x}) - E_{\text{coh}}^s(A^*, A_{x_s}B_{1-x_s})$$

is the surface energy of A^* in the alloy. In other words, it is the work to be done if A^* in the alloy is removed from the bulk and put at the surface. Similarly for the surface core-level shift of B we can write

$$\Delta E_c^s(B) = E^s(B^*, A_xB_{1-x}) - E^s(B, A_xB_{1-x}). \quad (7b)$$

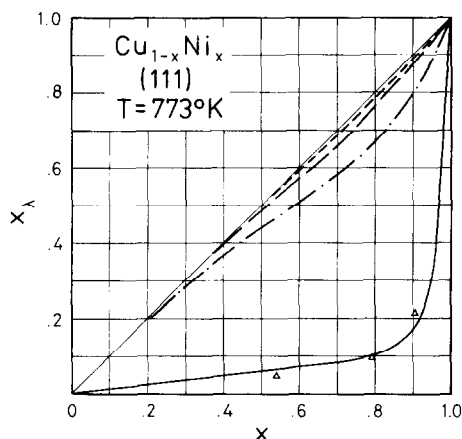


Fig. 1. Surface concentration x_λ for various layers $\lambda = 0, 1, 2, 3$, as a function of bulk nickel concentration in Cu–Ni alloys. $\lambda = 0$ represents the surface layer (—) whose concentration x_s (in the text) is measured experimentally. Δ shows the experimental results of [6]. (---), (- · - ·) and (- · · · ·) correspond respectively to $\lambda = 1, 2$ and 3 .

Equations (7a) and (7b) are the general expressions for the surface core-level shifts in alloys. Now if we assume that A and B are neighbouring elements in the periodic table and within the $(z + 1)$ approximation $A^* = B$, then

$$\Delta E_c^s(A) = E^s(B, A_x B_{1-x}) - E^s(A, A_x B_{1-x}). \quad (8)$$

It is easy to visualize that this represents the heat Q of surface segregation of B in the alloy. The first term is the work done in transferring one B atom from bulk to the surface whereas the second term represents the energy gain in transferring one A atom from surface to the bulk. Therefore if $\Delta E_c^s(A)$ is negative we expect surface enrichment of B and if $\Delta E_c^s(A)$ is positive, enrichment of A will occur at the surface. It is an important result as the surface core-level shifts can be used to determine the surface segregation in alloys of two neighbouring constituents. In binary alloys the surface concentration x_s of A can be written [5] as

$$\frac{x_s}{1-x_s} = \frac{x}{1-x} \exp(Q/kT). \quad (9)$$

For the special case of $z_x(z + 1)_{1-x}$ alloys we can write

$$\frac{x_s}{1-x_s} = \frac{x}{1-x} \exp(\Delta E_c^s(A)/kT). \quad (10)$$

As no experimental information is available for ΔE_c^s , we use the reverse procedure. The surface composition of several alloys has been measured in recent years. Out of these Cu–Ni alloys are the most studied and also appropriate to apply equation (10). Surface composition of Cu–Ni alloys has been measured by Brongersma *et al.* [6] using ion-scattering spectroscopy (ISS), which gives

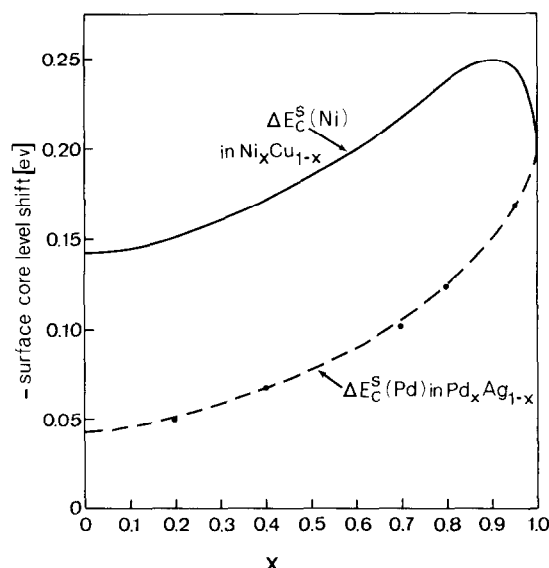


Fig. 2. Surface core-level shifts of Ni on the (111) surface of Cu–Ni alloys at 773 K and Pd in polycrystalline AgPd alloys at 975 K.

a very precise measurement of the surface concentration. We have calculated the surface composition in these alloys by using the surface energies of Cu and Ni in a regular solution model [5]. The variation of the regular solution parameter with concentration in the bulk and at the surface was also taken into account. Our results for the first four layers are shown in Fig. 1. The agreement with experimental results [6] is excellent. These values of surface concentration are then used to calculate $\Delta E_c^s(\text{Ni})$. The results are shown in Fig. 2. Also shown in the figure are the surface core-level shifts of Pd in $\text{Pd}_x\text{Ag}_{1-x}$ alloys. The surface composition of these alloys was taken from the measurement of Wood and Wise [8] using Auger electron spectroscopy (AES) at 975 K. As in these alloys, segregation of Cu and Ag occurs, the surface core-level shift is negative. A similar situation is expected in Pt–Au alloys. Further, the surface core-level shift of Pd increases smoothly as more and more Pd is added. However, in the case of Cu–Ni alloys it first increases until about 10% Cu is added and then it decreases. It should be noted that in Cu–Ni alloys, there is a strong segregation of Cu (Fig. 1) when a small amount of Cu is added to Ni. Therefore, a Ni atom at the surface with 10% Cu in the bulk sees completely different environment as compared to the bulk. When more Cu is added in the bulk, there is little change at the surface and so the core-level shift decreases. As these core-level shifts depend upon the chemical environment and the electronic configuration, it may help to understand some of the chemical reactions such as the increase of activity of nickel for dehydrogenation of cyclohexane when a few percent of Cu are added [9].

The variation of surface core-level shift with concentration is weaker as compared to the bulk. For Ag–Pd alloys, the bulk core-level shift [3] of Pd varies from 0.5 eV to 0 as one goes from pure Ag to pure Pd. At the surface, this difference is about 0.15 eV. Also the segregation is different on different crystal planes [7]. Accordingly, we expect $\Delta E_c^s(110) > \Delta E_c^s(100) > \Delta E_c^s(111)$ for face-centered cubic structure. In the case of no enrichment, this theory predicts no surface core-level shift of A . In the limit $x \rightarrow 1$, from equation (7), the surface core-level shifts of A reduce to the value of surface core-level shifts of pure A [10]:

$$\lim_{x \rightarrow 1} \Delta E_c^s(A) = E^s(B, A) - E^s(A). \quad (11)$$

Taking other limiting cases we obtain

$$\lim_{x \rightarrow 1} \Delta E_c^s(B) = E^s(B^*, A) - E^s(B, A), \quad (12)$$

$$\lim_{x \rightarrow 0} \Delta E_c^s(A) = E^s(B) - E^s(A, B), \quad (13)$$

$$\lim_{x \rightarrow 0} \Delta E_c^s(B) = E^s(B^*, B) - E^s(B). \quad (14)$$

It is interesting to note that the small contributions of the heat of solution of A in B or B in A , neglected in [2], are significant. Otherwise equations (11) and (13) will give the same result which is not true. Further from equations (11) and (13) the surface energy of B as an impurity in A or A as an impurity in B can be calculated if the surface energies of pure A and B are known. From equations (11), (12) and (14) surface energy of B^* as an impurity in A or B can be calculated. And therefore the heat of segregation of $(z + 2)$ impurity in $(z + 1)$ or (z) element, e.g. Zn in Ni or Fe in Cr can be calculated. For the latter experimental results of segregation are also known [11].

Adding equation (11) and (12) we obtain

$$\lim_{x \rightarrow 1} [\Delta E_c^s(A) + \Delta E_c^s(B)] = E^s(B^*, A) - E^s(A). \quad (15)$$

Now equations (11) and (15) can be used to calculate [12] the surface composition when B and B^* are dilute impurities in A . Equations (13) and (14) can be used to study surface segregation when A and B^* are impurities in B .

From the discussion of the last paragraph it is clear that the knowledge of surface core-level shifts can be used to supplement the surface techniques like ISS and AES to study the surface segregations in binary and ternary alloys – a problem of significant importance in catalysis and metallurgy.

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