Chemical compositions at alloy surfaces

Vijay Kumar

Institut für Theoretische Physik, Freie Universität Berlin, Arnimallee 3, 1 Berlin 33, Germany

(Received 9 April 1980; revised manuscript received 15 September 1980)

A quasichemical formulation for chemical composition at the surfaces of nonregular solid solutions is presented and applied to Ag-Au and Cu-Ni alloys. The results are compared with the existing experimental values. It is observed that the use of the surface-energy data instead of the heat of vaporization gives good agreement with the experiments. Surface relaxation effects have been taken into account. The free energy of segregation is calculated for several layers. The surface short-range order parameters are found to be quite different from the bulk values.

I. INTRODUCTION

A knowledge of chemical composition at alloy surfaces is essential to the understanding of several important phenomena of technological importance like catalysis,[1,2] corrosion and hydrogen storage in metals,[3] etc. Much advancement in this direction had been possible with the use of the Auger-electron spectroscopy (AES) and the ion-scattering spectroscopy (ISS). On the theoretical side[2,4,5] simple phenomenological models like the bond-breaking model[6,7] and the strain theory[8] have been successfully used to explain this behavior. Whereas it is possible with the ISS to get precise information of chemical composition in the surface layer, it is well known that the composition is different in a few layers in the vicinity of the surface. However, precise equilibrium in-depth information is still lacking. For example, in recent years there had been a lot of controversy about the in-depth surface composition in Cu-Ni alloys.[9-11] In the theoretical models the alloy is usually treated as an ideal[12] or a regular solution.[6,7] In the case of Cu-Ni alloys the regular solution model predicts a monotonic decrease of Cu segregation as one moves from the surface towards the bulk. However, in some experiments[9,10] an oscillatory behavior has been found. This discrepancy has been explained[10] taking surface relaxation effects into account in such a model. However, there is not always a random distribution of atoms in alloys as assumed in the regular solution models. In Cu-Ni alloys there is strong evidence[13] of clustering of like atoms. Further, from the thermodynamic data[14] on a large number of alloys the heat of mixing is not symmetric about equiatomic concentration, and in addition there is some excess of entropy. This means that most of the alloys are nonregular. Re-

cently Kumar et al.[15,16] presented a theory to treat nonregular solutions above the order-disorder transition temperature. A similar approach has been used independently also by Moran-Lopez and Falicov[17] for the whole temperature range. The aim of this paper is to rederive the formulation of Kumar et al.[15] in a more elegant way so that a calculation[16] of the free energy of segregation is possible. We have studied the Cu-Ni and the Ag-Au alloys because the atomic sizes of the constituents are quite similar and therefore the strain effects are negligible. Both the heat of vaporization and the surface energies have been used in the formulation. Effects of surface relaxation have been taken into account and its consequences have been discussed. The formulation has been presented in Sec. II. We have taken the first four layers to be different from the bulk. The results for the surface composition, the short-range-order (SRO) parameters, and the free energy of segregation are presented and discussed in Sec. III. We present our concluding remarks in Sec. IV.

II. FORMULATION

We consider a semi-infinite solid binary alloy $A_x B_y$, $(y = 1 - x)$ in thermodynamic equilibrium. In the quasichemical approach the total configurational energy of the system is written as the sum of the energies of various pairs. We consider only the nearest-neighbor interactions. A generalization to more neighbors is straightforward. We shall closely follow the notations of Kumar et al.[15] and so most of the details will be skipped here. The whole system is divided into layers parallel to the surface and the layers are numbered as $\lambda = 0, 1, 2, \ldots,$ $\lambda = 0$ being the surface layer. The total configurational energy of the system is written as

$$U = (N_{AA}^{00} + N_{AA}^{01})\epsilon_{AA}^{s} + (N_{(AB)}^{00} + N_{AB}^{01} + N_{BA}^{01})\epsilon_{AB}^{s} + (N_{BB}^{00} + N_{BB}^{01})\epsilon_{BB}^{s}$$

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

(1)

where $N_{ij}^{\lambda\mu}$ denote the number of pairs of ij type where an i ($i=A,B$) type of atom lies in the λth layer and a j ($j=A,B$) type of atom lies in the μth layer. $N_{(AB)}^{\lambda\lambda}$ denotes both the AB and the BA types of pairs in the λth layer. ϵ_{ij}^s and ϵ_{ij} represent the bond enthalpies for the ij-type nearest-neighbor pair in the surface[18] and in the bulk, respectively. The surface bond enthalpies can be expressed in terms of the bulk bond enthalpies using a relaxation parameter δ as follows:

$$\epsilon_{AA}^s = \epsilon_{AA}(1+\delta_A),$$

$$\epsilon_{BB}^s = \epsilon_{BB}(1+\delta_B), \tag{2}$$

$$\epsilon_{AB}^s = \epsilon_{AB}(1+\delta).$$

The number of pairs can be expressed in terms of the layer concentrations x_λ and the SRO parameters α_λ, β_λ, and β_λ' which are defined as

$$N_{AB}^{\lambda\lambda} = x_\lambda y_\lambda \alpha_\lambda N^{\lambda\lambda} = p_{AB}^{\lambda\lambda} N^{\lambda\lambda},$$

$$N_{AB}^{\lambda\lambda+1} = x_\lambda y_{\lambda+1}\beta_\lambda N^{\lambda\lambda+1} = p_{AB}^{\lambda\lambda+1} N^{\lambda\lambda+1}, \tag{3}$$

$$N_{BA}^{\lambda\lambda+1} = y_\lambda x_{\lambda+1}\beta_\lambda' N^{\lambda\lambda+1} = p_{BA}^{\lambda\lambda+1} N^{\lambda\lambda+1},$$

where $y_\lambda = 1 - x_\lambda$ and $N^{\lambda\lambda}$ and $N^{\lambda\lambda+1}$ denote the total number of nearest neighbors in the λth layer and between two adjacent layers λ and $\lambda+1$, respectively. p_{ij} denote the probability of an ij-type pair when i and j are, respectively, in the λth and μth layer. Dropping the configuration-independent term, one can now write the configurational energy as

$$U = N\epsilon^s\left[Z_0(x_0 y_0 \alpha_0 + \Delta^s x_0) + 2Z_1\left(x_0 y_1 \beta_0 + \frac{x_0}{2}(\Delta^s - 1) + \frac{x_1}{2}(\Delta^s + 1)\right)\right]$$

$$+ \sum_{\lambda=1}^{\infty} N\epsilon\{Z_0(x_\lambda y_\lambda \alpha_\lambda + \Delta x_\lambda) + 2Z_1[x_\lambda y_{\lambda+1}\beta_\lambda + \tfrac{1}{2}x_{\lambda+1}(\Delta + 1) + \tfrac{1}{2}x_\lambda(\Delta - 1)]\}, \tag{4}$$

where

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

$$\epsilon = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2, \tag{5}$$

and

$$\Delta^s = (\epsilon_{AA}^s - \epsilon_{BB}^s)/2\epsilon^s$$

$$\Delta = (\epsilon_{AA} - \epsilon_{BB})/2\epsilon. \tag{6}$$

Z_0 and Z_1 are the number of nearest neighbors of an atom in the same layer and in an adjacent layer, respectively. N is the total number of atoms in each layer. We consider only the configurational entropy contribution to the free energy. This can be written as

$$S = k\sum_{\lambda=0}^{\infty} N\left((Z^\lambda - 1)\sum_{i=A,B} p_i^\lambda \ln p_i^\lambda - \frac{1}{2}Z_0\sum_{ij} p_{ij}^{\lambda\lambda}\ln p_{ij}^{\lambda\lambda} - Z_1\sum_{ij} p_{ij}^{\lambda\lambda+1}\ln p_{ij}^{\lambda\lambda+1}\right), \tag{7}$$

where Z^λ denotes the total number of nearest neighbors of an atom in the λth layer. p_i^λ is the probability of finding an i type of atom in the λth layer. k is the Boltzmann constant. Minimizing[19] the free energy with respect to x^λ with the constraint that the total number of atoms of A and B types is fixed, one obtains the following expression:

$$\frac{x_\lambda}{1-x_\lambda} = \frac{x}{1-x}\exp(\Delta F_a^\lambda/kT), \tag{8}$$

where $\Delta F_a^\lambda = \Delta H_a^\lambda - T\Delta S_a^\lambda$ is the free energy of segregation in the λth layer. Here ΔH_a^λ and ΔS_a^λ are, respectively, the corresponding heat and entropy of segregation and are given by

$$\Delta H_a^0 = \epsilon Z\left[(y-x)\alpha + \Delta\right] - \epsilon^s\{Z_0[\Delta^s + (y_0 - x_0)\alpha_0] + 2Z_1[y_1\beta_0 + (\Delta^s - 1)/2]\}, \tag{9}$$

$$\Delta H_a^1 = \epsilon Z\left[(y-x)\alpha + \Delta\right] - 2Z_1\epsilon^s[(\Delta^s + 1)/2 - x_0\beta_0]$$

$$- \epsilon\{Z_0[\alpha_1(y_1 - x_1) + \Delta] + 2Z_1[(\Delta - 1)/2 + y_2\beta_1]\}, \tag{10}$$

$$\Delta H_a^\lambda = \epsilon\left[Z(y-x)\alpha - Z_0\alpha_\lambda(y_\lambda - x_\lambda) - 2Z_1(y_{\lambda+1}\beta_\lambda - x_{\lambda-1}\beta_{\lambda-1})\right], \quad \lambda \geqslant 2, \tag{11}$$

$$\Delta S_a^\lambda/k = Z \ln(x/y) - Z^\lambda \ln(x_\lambda/y_\lambda) - \frac{Z}{2}\left[\ln\left(\frac{p_{AA}}{p_{BB}}\right) + \alpha(y-x)\ln\left(\frac{p_{AB}p_{BA}}{p_{AA}p_{BB}}\right)\right]$$

$$+ \frac{1}{2}Z_0\left[\ln\left(\frac{p_{AA}^{\lambda\lambda}}{p_{BB}^{\lambda\lambda}}\right) + \alpha_\lambda(y_\lambda - x_\lambda)\ln\left(\frac{p_{AB}^{\lambda\lambda}p_{BA}^{\lambda\lambda}}{p_{AA}^{\lambda\lambda}p_{BB}^{\lambda\lambda}}\right)\right]$$

$$+ Z_1\left[\ln\left(\frac{p_{AA}^{\lambda\lambda+1}}{p_{BA}^{\lambda\lambda+1}}\right) + \beta_\lambda y_{\lambda+1}\ln\left(\frac{p_{AB}^{\lambda\lambda}p_{BA}^{\lambda\lambda}}{p_{AA}^{\lambda\lambda}p_{BB}^{\lambda\lambda}}\right) - \ln\left(\frac{p_{BB}^{\lambda-1\lambda}}{p_{BA}^{\lambda-1\lambda}}\right) - x_{\lambda-1}\beta_{\lambda-1}\ln\left(\frac{p_{AB}^{\lambda-1\lambda}p_{BA}^{\lambda-1\lambda}}{p_{AA}^{\lambda-1\lambda}p_{BB}^{\lambda-1\lambda}}\right)\right]. \qquad (12)$$

Here Z, α, and p_{ij} are, respectively, the coordination number, the SRO parameter, and the probability of an ij-type pair in the bulk. Minimization with respect to α_λ and β_λ leads to

$$\frac{\epsilon^s}{kT} + \frac{1}{2}\ln\left(\frac{p_{AB}^{00}p_{BA}^{00}}{p_{AA}^{00}p_{BB}^{00}}\right) = 0 ; \quad \frac{\epsilon^s}{kT} + \frac{1}{2}\ln\left(\frac{p_{AB}^{01}p_{BA}^{01}}{p_{AA}^{01}p_{BB}^{01}}\right) = 0 ,$$

$$(13)$$

and

$$\frac{\epsilon}{kT} + \frac{1}{2}\ln\left(\frac{p_{AB}^{\lambda\lambda}p_{BA}^{\lambda\lambda}}{p_{AA}^{\lambda\lambda}p_{BB}^{\lambda\lambda}}\right) = 0 ;$$

$$\frac{\epsilon}{kT} + \frac{1}{2}\ln\left(\frac{p_{AB}^{\lambda\lambda+1}p_{BA}^{\lambda\lambda+1}}{p_{AA}^{\lambda\lambda+1}p_{BB}^{\lambda\lambda+1}}\right) = 0 , \lambda \geq 1 . \qquad (14)$$

The quantities ϵ and Δ can be calculated from the heat-of-mixing and the heat-of-vaporization data of the constituents. If one uses the surface energy instead of the heat of vaporization for the surface bond enthalpies, one obtains

$$\Delta H_a^0 = (\sigma_B a_B - \sigma_A a_A) + \epsilon Z(y-x)\alpha$$

$$- \epsilon[Z_0(y_0 - x_0)\alpha_0 + 2Z_1(y_1\beta_0 - \tfrac{1}{2})] , \qquad (15)$$

where $\sigma_{A(B)}$ is the surface energy for pure $A(B)$ and $a_{A(B)}$ is the surface area per atom $A(B)$. For other layers the expression remains the same as in Eq. (11).

Further, β_λ' is related to α_λ, x_λ, and β_λ because of the constraint

$$N_{AA}^{\lambda\lambda+1} + N_{BA}^{\lambda\lambda+1} = Z_1 N_A^{\lambda+1} , \qquad (16)$$

where $N_A^{\lambda+1}$ is the total number of A atoms in the $(\lambda+1)$th layer. In the case of a completely disordered system $\alpha = 1$ and $\alpha_\lambda = \beta_\lambda = \beta_\lambda' = 1$. The entropy of segregation is zero and the expression for ΔH_a^λ reduces to that of Kumar et al.[6,20] If no relaxation is used, then above the order-disorder temperature where there is no long-range order, our results [Eqs. (9)–(14)] and those of Moran-Lopez and Falicov[17] are identical. (They have not derived explicit expressions for the heat and the entropy of segregation.) If some gas atoms C are chemisorbed at the surface, their effects can be included in our formulation. The only change is in Eq. (9) which now reads as

$$\Delta H_a^0 = Z\epsilon[(y-x)\alpha + \Delta] - \epsilon^s\{Z_0[\Delta^s + \alpha_0(y_0 - x_0)] + 2Z_1[(\Delta^s - 1)/2 + y_1\beta_0]\} - (\epsilon_{AC}Z_A - \epsilon_{BC}Z_B) , \qquad (17)$$

where Z_A and Z_B denote the number of links of an A or B atom, respectively with the chemisorbed atoms. ϵ_{AC} and ϵ_{BC} are the corresponding bond enthalpies.

III. RESULTS AND DISCUSSION

This formulation has been applied to (111) surface of $Ag_{1-x}Au_x$ and $Cu_{1-x}Ni_x$ alloys. In Ag-Au alloys there is evidence[21] of unlike atoms to be the nearest neighbors whereas in Cu-Ni alloys it is the reverse.[13] The bulk SRO parameters α and ϵ have been calculated from the bulk thermodynamic data[14] on the heat of mixing ΔH_m and the excess entropy ΔS^{ex} using the procedure of Averbach.[22] We have taken into account the concentration and temperature dependence of the parameter ϵ, which means to some extent inclusion of many-body interactions. For Cu-Ni alloys these values are summarized in Table I. For Ag-Au alloys, results were tabulated by Kumar et al.[15] at the temperature $T = 800$ K. We have chosen these

temperatures because the thermodynamic data at these temperatures are available.

For Ag-Au alloys our results for surface composition using surface energy data[4] are presented in Fig. 1. When expressed in terms of per mole the surface energies for Ag and Au are, respec-

TABLE I. Table of ϵ and α for Cu-Ni alloys at 973 K, Ni is taken to be the A component.

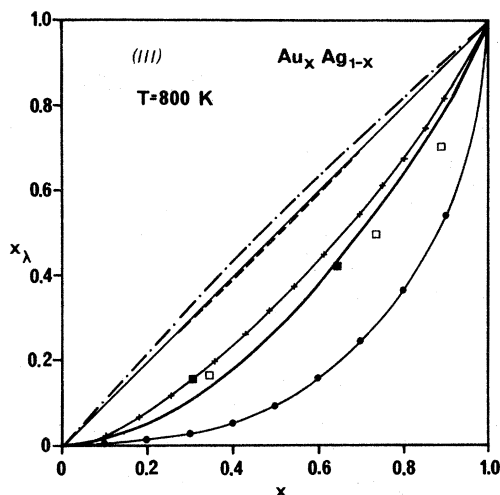| x	ΔH_m cal/mol	ΔS^{ex} cal/mol K	$N\epsilon$ cal/mol	α
0.1	74	−0.144	191.2940	0.9822
0.2	166	−0.230	193.0810	0.9680
0.3	265	−0.269	197.3899	0.9571
0.4	355	−0.274	203.2910	0.9495
0.5	425	−0.255	211.5060	0.9453
0.6	461	−0.221	222.0672	0.9449
0.7	449	−0.179	235.3573	0.9489
0.8	378	−0.124	249.2081	0.9588
0.9	232	−0.065	265.5519	0.9753

FIG. 1. Plots of surface versus bulk composition of Au in various layers using the surface-energy data. (—), (—·—), and (---) denote, respectively, the concentrations in $\lambda = 0$, 1, and 2 layers. (—) is the no-enrichment line. (—·—·—) denotes the surface composition obtained by using the heat-of-vaporization data. (-×-×-) denote the results of Ref. 31. ■ and □ represent, respectively, the experimental results of Nelson (Ref. 23) and Kelley $et\ al.$ (Ref. 24) obtained from ISS.

FIG. 2. Surface versus bulk concentration of Au in various layers using the heats of vaporization and taking surface relaxations into account. (—), (—···—), and (---) denote concentration in $\lambda = 0$, 1, and 2 layers, respectively. ■ and □ represent experimental points as in Fig. 1.

tively, 14.3 and 16.65 kcal. In this system there is an enrichment of Ag at the surface and our result is in very good agreement with the experiments.[23,24] In the second layer ($\lambda = 1$), however, Au segregates. In the third layer there is slight enrichment of Ag and in the fourth layer we get almost bulk composition. This result is consistent because for Ag-Au alloys the heat of mixing is negative and so also is ϵ negative. Segregation of Ag in the surface layer will cause Au to get segregated at the second layer.

It should be noted that Kumar $et\ al.$[15] obtained enrichment of Ag in $\lambda = 1$ layer (see Fig. 1 and Table II and also Figs. 3 and 5 of their paper) for $x \lesssim 0.25$ and a similar oscillatory curve for $\lambda = 2$ layer. This is because of their mistake in the minimization of the free energy. If one uses the heat of vaporization[14] (67.2 and 87.3 kcal/mole for Ag and Au, respectively) for the bond enthalpies with no surface relaxation, the amount of surface segregation of Ag is quite large and it is not in good agreement with the experimental results of Nelson[23] and Kelley $et\ al.$[24] obtained by using the ISS at 500 °C. Inclusion of a 15% surface relaxation in the bond enthalpies reduces Ag enrichment in the surface and is in quite good agreement with the experiments (Fig. 2). In the second layer, however, there is an increase in the Au concentration. This result can be understood from Eqs. (9) and (10). In the bond-breaking model, surface
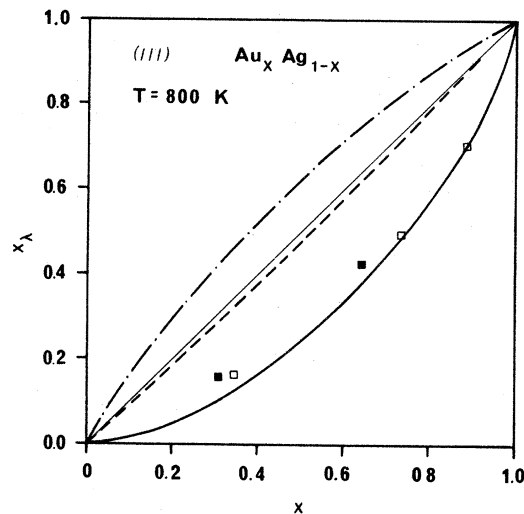
segregation depends upon the number of bonds broken at the surface. The smaller this number is, the smaller will be the segregation.[6] Inclusion of relaxation effectively modifies this number. If relaxation is taken to be the same for all the bonds, then leaving the term with ϵ, one has from Eq. (9),

$$\Delta H_a^0 = \frac{\epsilon_{AA} - \epsilon_{BB}}{2} \left[Z - (Z_0 + Z_1)(1 + \delta) \right]. \qquad (18)$$

$[Z - (Z_0 + Z_1)]$ is the number of bonds broken at the surface; if δ is positive this number and hence the segregation will be reduced. If δ is negative, this number and hence the segregation will be enhanced. In the $\lambda = 1$ layer, similarly, one can write

$$\Delta H_a^1 = -\frac{\epsilon_{AA} - \epsilon_{BB}}{2} Z_1 \delta + \epsilon F(x_\lambda, \alpha_\lambda, \beta_\lambda). \qquad (19)$$

If δ is positive and A segregates at the surface, then the first term is negative. If ϵ is also negative, then enrichment of B will be enhanced as in Ag-Au alloys. If ϵ is positive, enrichment of A in the $\lambda = 1$ layer will be reduced as will be discussed in the case of Cu-Ni alloys.

Surface relaxation of about 15% has been considered[10] to be quite large. Physically it can be thought to account for any change in bond enthalpies due to change in bond lengths at the surface; different local environments of atoms and a correction due to the use of the heat of vaporization for the surface bond enthalpies. Assuming the change in bond lengths to be negligible (i.e., alloys

of constituents having similar atomic radii and no surface contraction), a qualitative estimate of the relaxation parameter can be made. If one uses the surface tension of the pure constituents as a measure of the surface bond enthalpies,[25] then Overbury et al.[26] have shown empirically that the molar surface energies of pure solid metals correlate reasonably well with the heats of vaporization. Using the most recent compilation[14] of the heat of vaporization ΔH^{vap} Wynblatt and Ku[27] derived the relation

$$\sigma_i a_i = 0.174 \Delta H_i^{vap}, \quad i = A, B. \tag{20}$$

Now the bond enthalpies in Eq. (18) can be written in terms of ΔH^{vap}. Expressing the first term in Eq. (15) in terms of ΔH^{vap} using Eq. (20) and comparing with Eq. (18), one finds $\delta \approx 0.1$, using $Z_1 = 3$ for the (111) surface. Miedema[4] and Wynblatt and Ku[27] have used an average crystal plane where one-third of the bonds are missing corresponding to the (100) plane. Using this description one gets $\delta = 0.239$. It should be noted that in Eq. (20) the surface tension includes contribution from surface entropy. Crucq et al.[28] calculated this relaxation parameter for Cu and Ni from surface enthalpy (surface tension at zero temperature). They found $\delta = 0.131$ and 0.212 for Cu and $\delta = 0.086$ and 0.163 for Ni using $Z = 12$ and effective coordination $Z = 15$, respectively. In this calculation the surface entropy has not been considered. Donnelly and King[29] considered coordination dependence of bond enthalpies. At the (111) surface of Cu-Ni alloys their calculation shows about 20% relaxation in bond enthalpies. From this analysis it can be concluded that the use of heat of vaporization will in general predict more segregation and that a surface relaxation ($\sim 0.1 - 0.2$) will give a reasonable agreement with the experiments. It is interesting to note that $\delta \approx 0.15$ gives very good agreement with experiments on Cu-Ni,[10,30] Ag-Au, and Cu-Pt (Ref. 30) alloys. On the other hand, one expects reasonably good agreement with experiments using surface tension for the surface bond enthalpies as we see for Ag-Au alloys. A recent electronic theory[31] for surface segregation also predicts similar values of surface composition as we have obtained for Ag-Au alloys. The effect of inclusion of SRO on the surface concentration is to reduce slightly the enrichment of Ag. However, this difference is quite small. The surface SRO parameters are significantly different and are shown in Figs. 3 and 4. The calculated bulk SRO parameter is in good agreement with experimental results.[21] For the surface only those SRO parameters have been plotted which differ appreciably from the bulk. As one can see, use of different procedures can give slightly dif-
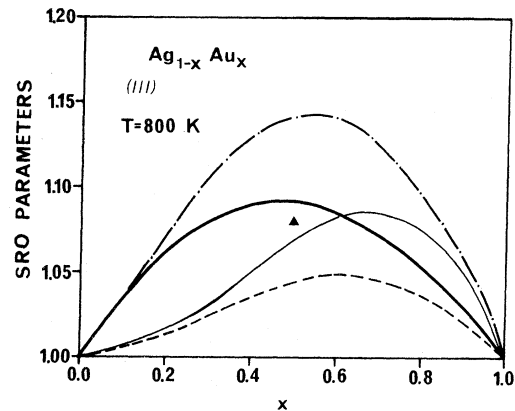

FIG. 3. SRO parameters as a function of bulk Au concentration. (—) represents the bulk SRO parameter. (—), (—·—), and (---) denote, respectively, γ_0, β_0, and β_0'. ▲ represents the experimental result for the bulk.

ferent results for the surface SRO. Since there exist no experimental results for the surface SRO parameters, no comparison can be made. The heat and the entropy of segregation in the $\lambda = 0$ and $\lambda = 1$ layers are tabulated in Table II for Ag-Au alloys using both the data. For the remaining layers these quantities are quite small as the segregation is small. The contribution of the entropy term to the free energy of segregation is quite small and therefore it does not affect the surface composition much.

For Cu-Ni alloys at $T = 973$ K our results for surface composition are presented in Figs. 5 and 6. It can be seen that there is a strong surface
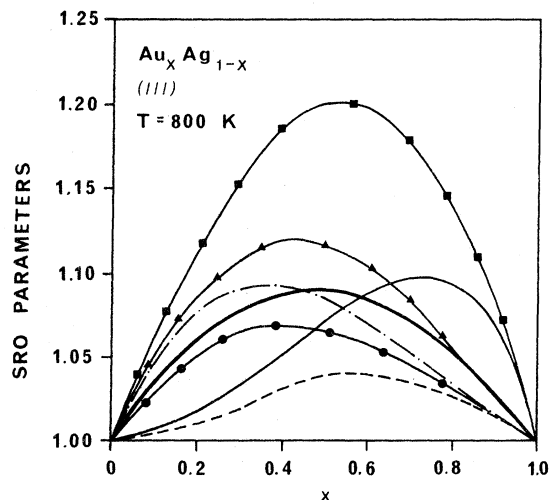

FIG. 4. SRO parameters for Ag-Au alloys corresponding to the surface compositions in Fig. 2. (—), (-■-), (---), (-·-), (-●-), and (-▲-) denote, respectively, α_0, β_0, β_0', α_1, β_1, and β_1'.

TABLE II. Heat and entropy of segregation of Ag-Au alloys at $T = 800$ K.

x	Using surface-energy data				Using heat of vaporization and relaxation			
	$\Delta H_a^0/kT$	$\Delta S_a^0/k$	$\Delta H_a^1/kT$	$\Delta S_a^1/k$	$\Delta H_a^1/kT$	$\Delta S_a^0/k$	$\Delta H_a^1/kT$	$\Delta S_a^1/k$
0.1	−1.7925	0.0240	0.0809	0.0178	−1.8430	0.0389	0.5313	0.0159
0.2	−1.5095	0.0384	0.1367	0.0251	−1.6053	0.0588	0.5143	0.0234
0.3	−1.2621	0.0468	0.1646	0.0252	−1.4185	0.0667	0.5071	0.0186
0.4	−1.0668	0.0492	0.1718	0.0190	−1.2239	0.0667	0.5109	0.0129
0.5	−0.9293	0.0465	0.1643	0.0092	−1.1212	0.0592	0.5014	−0.0003
0.6	−0.8442	0.0406	0.1492	−0.0008	−1.0445	0.0480	0.5030	−0.0127
0.7	−0.8057	0.0320	0.1320	−0.0009	−1.0289	0.0346	0.5058	−0.0230
0.8	−0.8099	0.0217	0.1109	−0.0133	−1.0695	0.0218	0.5064	−0.0283
0.9	−0.8592	0.0114	0.0770	−0.0123	−1.1774	0.0112	0.4931	−0.0257

segregation of Cu and it monotonically decreases to the bulk value (Fig. 5). Use of the surface energies give less segregation of Cu as compared to when ΔH^{vap} (with no surface relaxation) is used. Inclusion of clustering slightly enhances Cu segregation. We have compared our results with the available experimental results using the AES (Ref. 11) at 600 °C and the ISS (Ref. 30) at 500 °C on this system. It is found that in the surface, the segregation of Cu is greater than found experimentally. From a comparison of the in-depth analysis[11] of AES results, we find very good agreement for $\lambda = 1$ layer. However, in the surface layer there are large error bars and our results lie well within those bars. The change in Cu surface concentration is very small as the bulk

Cu concentration is varied from about 15% to pure Cu. From a large number of experimental data on Cu-Ni alloys, it is now well established that in this range there is quite strong segregation of Cu and the discrepancy between the experimental and the theoretical results is small. For low Cu concentration, however, there is some controversy. Recently Ng et al.[10] obtained an absolute composition depth profile of an Ni-Cu (5 atomic %) alloy at 550 °C using time-of-flight atom-probe field-ion microscope. They found Cu surface concentration to be $(54.1 \pm 4.7)\%$. In the second layer they found slight enrichment of Ni. Such behavior was also predicted by Ling et al.[9] using ultraviolet photoemission spectroscopy. A regular solution model predicts too high a surface Cu concentration for this bulk composition. Inclusion of 16% surface relaxation in the regular solution model gives very good agreement with the experimental
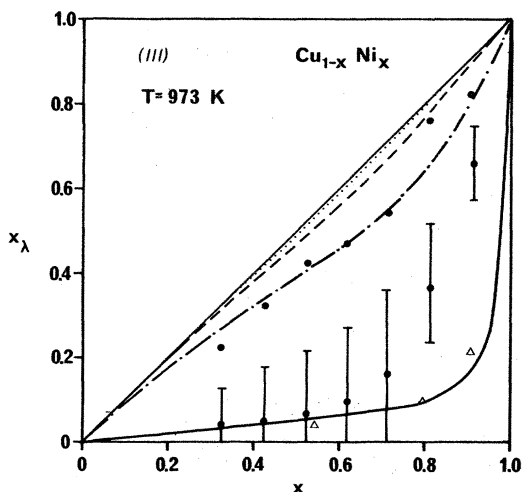

FIG. 5. Surface composition in Cu-Ni alloys obtained by using the surface energies. (—), (—·—), (---), and (·····) denote respectively, the Ni concentration in $\lambda = 0$, 1, 2, and 3 layers. $\blacklozenge$ and $\bullet$ denote the experimental results of Watanabe et al. (Ref. 11) in the $\lambda = 0$ and 1 layers, respectively. $\triangle$ represents the ISS results of Brongersma et al. at 500 °C.
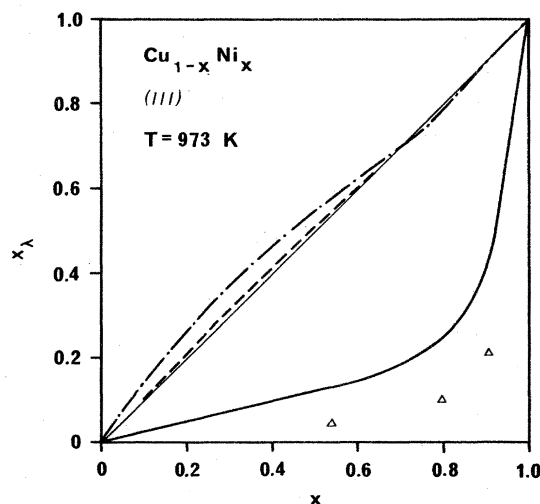

FIG. 6. Surface composition obtained by using the heats of vaporization and 15% surface relaxation. (—), (—·—), and (···) are the Ni concentration in $\lambda = 0$, 1, and 2 layers, respectively.

results.[10,30] If surface relaxation of 15% is taken into account in our formulation, then the surface concentration of Cu decreases (Fig. 6) and is comparable with experimental predictions.[30] In addition the new feature is that below $x = 0.7$ there is slight enrichment of Ni in the $\lambda = 1$ and 2 layers whereas for $x > 0.7$ there is slight enrichment of Cu in the $\lambda = 1$ and 2 layers. This result can be understood immediately from our previous discussion of the effects of surface relaxation parameter and from the fact that for concentrated Cu alloys the segregation of Cu in the $\lambda = 1$ layer is smaller as compared to Ni-rich alloys (Fig. 5). In the application of the regular solution model usually ϵ is taken to be constant over the whole composition range. However, in general this varies with the composition and temperature as considered here. For Cu-Ni alloys the variation in ϵ with x is quite significant and can be seen from the asymmetry of ΔH_m in Table I. The variation in $\lambda = 1, 2, \ldots$ layers comes because ϵ is nonzero. Therefore a proper choice of ϵ should be taken as far as in-depth variation of the surface composition is concerned.

Recently we[32] also considered variation of ϵ with surface composition and got closer agreement with experiments. It can be seen from Table I that if at the surface the value of ϵ is chosen so as to correspond to surface concentration, one would expect lower segregation of Cu. Furthermore in pure Cu (Ref. 33) and Ni (Ref. 34), the surface relaxation effects are known to be almost negligible. However, for Cu-Ni alloys the surface area changes[35] with bulk concentration. For 5 at. % Cu-Ni and 5 at% Ni-Cu there is a decrease in the surface area. For intermediate bulk concentration (30–60) at% Cu there is an increase in the surface area. This will correspondingly change bond energies or a_i and will affect surface composition. Though the oscillating behavior of surface composition is still doubted in this system, it may not be surprising for dilute alloys of Cu-Ni to find such an oscillatory behavior because of likely significant surface contraction. Further experimental work on surface relaxation and in-depth composition would be desirable for this system.

The SRO parameters are presented in Figs. 7 and 8 using, respectively, the surface energies and the heat of vaporization and relaxation. The values of the bulk SRO parameters are compared with the recent experimental results of Vrijen and Radelaar.[13] The agreement between the two is not good in the intermediate bulk concentration region. This may be because in Cu-Ni alloys it is known[13] that the clustering effects prolong up to several neighbors. We have considered only the nearest-
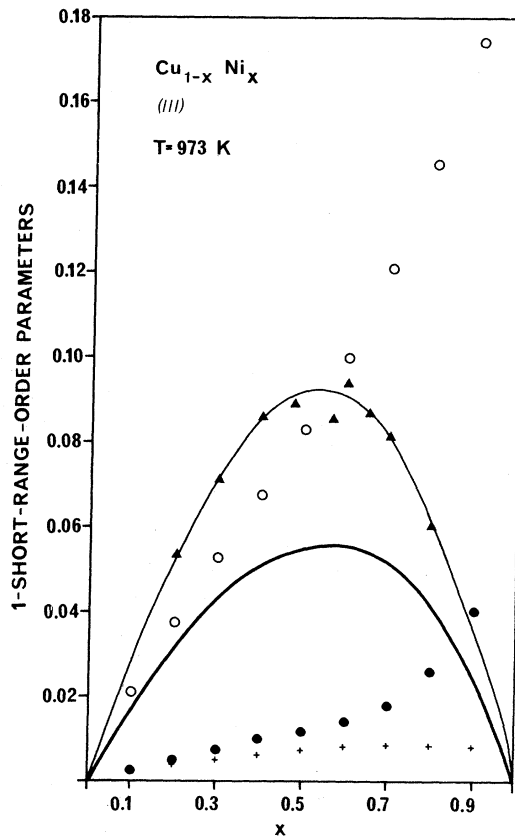

FIG. 7. SRO parameters in Cu-Ni alloys corresponding to the results in Fig. 5. ●, 0, and + represent, respectively, α_0, β_0, and β_0'. (—) is the bulk SRO parameter. ▲ denotes experimental results from Ref. 13.

neighbor interactions. Inclusion of more neighbor interactions will certainly give better agreement with the experiments. Our formulation can easily include second-, third- and so on neighbor interactions and the corresponding order parameters can be calculated. The surface SRO parameters are much different from the bulk values. Inclusion of relaxation predicts higher values of surface SRO parameters. The heat and the entropy of segregation are tabulated in Table III. In this system also, we find that the entropy of segregation is negligibly small. The heat of segregation is quite large and decreases with the inclusion of relaxation. For the $\lambda = 1$ layer the heat of segregation changes sign which should be expected as the segregation curve oscillates about the no-enrichment line.

IV. CONCLUSION

From our results it can be concluded that the component having the lower heat of vaporization or surface energy segregates at the surface. The use of the surface energies should be preferred

TABLE III. Heat and entropy of segregation of Cu-Ni alloys at 973 K.

x	Using surface-energy data				Using heat of vaporization and relaxation			
	$\Delta H^0_{a}/kT$	$\Delta S^0_{a}/k$	$\Delta H^1_{a}/kT$	$\Delta S^1_{a}/k$	$\Delta H^0_{a}/kT$	$\Delta S^0_{a}/k$	$\Delta H^1_{a}/kT$	$\Delta S^1_{a}/k$
0.1	−2.1362	0.0054	−0.0505	0.0049	−1.4392	0.0099	0.3731	0.0037
0.2	−2.3108	0.0089	−0.1275	0.0082	−1.5513	0.0159	0.3595	0.0062
0.3	−2.4891	0.0121	−0.2134	0.0110	−1.6763	0.0197	0.3284	0.0078
0.4	−2.6784	0.0149	−0.3132	0.0131	−1.8103	0.0220	0.2762	0.0081
0.5	−2.8849	0.0178	−0.4280	0.0147	−1.9769	0.0237	0.1988	0.0080
0.6	−3.1130	0.0206	−0.5555	0.0156	−2.1705	0.0251	0.0949	0.0070
0.7	−3.3609	0.0233	−0.6788	0.0148	−2.3733	0.0256	−0.0112	0.0035
0.8	−3.6101	0.0238	−0.7780	0.0102	−2.5260	0.0230	−0.0791	−0.0058
0.9	−3.8013	0.0184	−0.7787	−0.0026	−2.5527	0.0148	−0.0578	−0.0236

over the heat of vaporization for the surface bond enthalpies. Inclusion of short-range order does not change the surface composition much. However, these should be included and calculated at the surface where they are quite different and can play an important role in the study of elementary excitations at the surfaces of alloys. No experimental results are available so far on the surface

FIG. 8. SRO parameters corresponding to the results in Fig. 6. ●, 0, and + denote, respectively, α_0, β_0, and β'_0.

SRO parameters. We believe low-energy electron diffraction that the analysis will be done in the near future to study these parameters. As far as the in-depth analysis of surface composition is concerned, further careful experimental study should be done to get a depth profile of surface composition so that a precise comparison with theoretical results could be done. The heat of segregation should be measured for various systems because it can be calculated theoretically. For the systems studied, no such result is available. Regarding the surface relaxation, very little is known for alloy surfaces. For several noble metals and transition metals this is now known to be quite small. However, the situation may be different for their alloys as one can see from the surface-area measurements[35] on Cu-Ni alloys. An experimental study of surface relaxation will prove quite useful to interpret experimental results on surface segregation. With these data one can modify the surface bond energies while using the heat-of-vaporization data or use correct surface-area per atom with the surface energies.[4] The formulation presented here is simple as compared to the rigorous microscopic theories and the surface composition has been related to the experimentally assessable quantities like σ and ΔH_m. The additional features like the strain effect can also be incorporated in a manner done by Kumar[20] and also suggested by Miedema.[4] The effect of chemisorption is expected to be the same as obtained by Kumar et al.[6] and so no numerical results are presented. It may, however, change the order parameters at the surface, if the surface concentration changes.
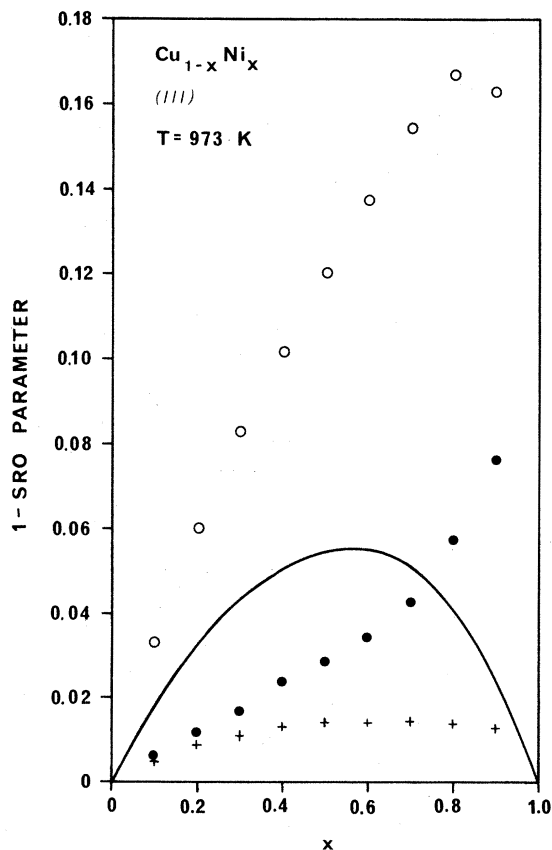
[1]V. Ponce, Surf. Sci. 80, 352 (1979).

[2]W. M. H. Sachtler and R. A. Van Santen, Appl. Surf. Sci. 3, 121 (1979).

[3]L. Schlapbach, A. Seiler, H. C. Siegmann, T. V. Waldkirch, and P. Zürcher, Int. J. Hydrogen Energy 4, 21 (1979).

[4]A. R. Miedema, Z. Metallk. 69, 455 (1978).

[5]M. Kelley, J. Catal. 57, 113 (1979).

[6]D. Kumar, A. Mookerjee, and V. Kumar, J. Phys. F 6, 725 (1976).

[7]F. L. Williams and D. Nason, Surf. Sci. 45, 377 (1974).

[8]D. McLean, Grain Boundaries in Metals (Oxford, London, 1957).

[9]D. T. Ling, J. N. Miller, I. Lindau, W. E. Spicer, and P. M. Stefan, Surf. Sci. 74, 612 (1978).

[10]Y. S. Ng, T. T. Tsong, and S. B. McLane, Jr., Phys. Rev. Lett. 42, 588 (1979).

[11]K. Watanabe, M. Hashiba, and T. Yamashina, Surf. Sci. 61, 483 (1976).

[12]S. Berglund and G. A. Somarjai, J. Chem. Phys. 59, 5537 (1973).

[13]J. Vrijen and S. Radelaar, Phys. Rev. B 17, 409 (1978) and references therein.

[14]R. Hultgren, P. D. Desai, D. T. Hawkins, M. Gleiser, and K. K. Kelley, Selected Values of Thermodynamic Properties of Binary Alloys (American Society for Metals, Metals Park, Ohio, 1973).

[15]V. Kumar, D. Kumar, and S. K. Joshi, Phys. Rev. B 19, 1954 (1979).

[16]V. Kumar, Solid State Commun. 32, 1159 (1979).

[17]J. L. Moran-Lopez and L. M. Falicov, Phys. Rev. B 18, 2542 (1978); 18, 2549 (1978).

[18]Bond enthalpies between atoms in the surface layer and the case when one atom lies in the surface layer ($\lambda = 0$) and an adjacent layer $\lambda = 1$, may in general be different. An extension to this general case is trivial.

[19]In Ref. 15 (also in Ref. 16) while minimizing the free energy both β_λ and β'_λ were by mistake treated as independent. Therefore their expression (14a) is not correct. However, in numerical values the difference is very little.

[20]V. Kumar, Surf. Sci. 84, L231 (1979).

[21]See M. Hansen and K. Anderko, Constitution of Binary Alloys (McGraw-Hill, New York, 1958).

[22]B. L. Averbach, in Energetics in Metallurgical Phenomena, edited by W. M. Mueller (Gordon and Breach, New York, 1965), Vol. II.

[23]G. C. Nelson, Surf. Sci. 59, 310 (1976).

[24]M. J. Kelley, D. G. Swartzfager, and V. S. Sundaram, J. Vac. Sci. Technol. 16, 664 (1979).

[25]Use of the surface tension for the surface bond enthalpies has been shown by Miedema (Ref. 4) and Wynblatt and Ku (Ref. 27) to be a better discription than the heat of vaporization as the latter overestimates the surface energies.

[26]S. H. Overbury, P. A. Bertrand, and G. A. Somorjai, Chem. Rev. 75, 547 (1975).

[27]P. Wynblatt and R. C. Ku, in Interfacial Segregation, edited by W. C. Johnson and J. M. Blakely (American Society for Metals, Metal Park, Ohio, 1977).

[28]A. Crucq, L. Degols, G. Lienard, and A. Frennet, Surf. Sci. 80, 78 (1979).

[29]R. G. Donnelly and T. S. King, Surf. Sci. 74, 89 (1978).

[30]S. H. M. Brongersma, M. J. Sparnaay, and T. M. Buck, Surf. Sci. 71, 657 (1978).

[31]C. A. Balseiro and J. L. Moran-Lopez, Phys. Rev. B 21, 349 (1980).

[32]V. Kumar and K. H. Bennemann, unpublished.

[33]S. K. S. Ma, F. W. De Wette, and G. P. Alldredge, Surf. Sci. 78, 598 (1978).

[34]W. C. Turkenburg and R. G. Smeenk, Surf. Sci. 74, 181 (1978).

[35]J. H. Sinfelt, J. L. Carter, and D. J. C. Yates, J. Catal. 24, 283 (1972).