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Surface segregation in alloys

Vijay Kumar
Department of Physics, D.B.S. College, Dehradun 248001, India

Deepak Kumar and S. K. Joshi
Department of Physics, University of Roorkee, Roorkee 247672, India

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We present a quasichemical theory to predict surface segregation in nonregular solutions. Surface concentration and surface short-range-order (SRO) parameters have been calculated for Ag-Au and Ag-Pd systems. Our results show segregation of Ag on the surface in both the systems. It is observed that the nonregular-solution model does not give results much different from the regular-solution model. However, the surface SRO parameters are significantly different from their bulk values. Surface concentrations averaged over the first few layers have also been calculated. Our results are in agreement with the results obtained from Auger electron spectroscopy.

I. INTRODUCTION

In recent years much interest has grown in the study of surfaces of solids in order to understand various chemical and physical processes at solid surfaces. Phenomena like catalysis, chemisorption, corrosion, etc. involve basically the properties at the surfaces of substances. Of particular interest are the alloys of several transition metals and noble metals which are used as catalysts in several chemical reactions. It has been observed that the chemical composition at the surfaces of alloys is in general different[1] from its bulk value and it varies with the temperature. Therefore, in order to study any physical property at the surfaces of alloys, it is important to study first the surface composition as a function of temperature and bulk concentration.

The best experimental probe to study the surface composition is the Auger electron spectroscopy[2] (AES). Quite a large number of systems like Cu-Ni,[3] Ag-Pd,[4] Pb-In,[5] Au-Ni,[6] Fe-Cr,[7] Fe-Ni,[8] Ag-Cu,[9] Cu-Au,[10] Ag-Au,[11] Au-Sn,[12] Pt-Sn,[13] Pt-Au,[14] Cu-Al,[15] Ni-Pd,[16] Cr-Au,[17] Au-Pd,[4,18] and dilute solid solutions[19] of Cr, Fe, and Ni in Pt have been studied using AES. Theoretical interpretations of these results have been given on the basis of two theories. According to one theory, known as quasichemical theory,[20-23] the constituent having the lower heat of vaporization segregates at the surface. In these studies the system is taken to be either an ideal solution in which case segregation occurs only in the top layer or the solution is assumed to be a regular solution in which case the composition is studied at the surface and in the layers parallel to the surface. The other theory, known as *strain theory*,[24] is based on the atomic size difference of the constituents. According to this theory the atoms having the larger size segregate at the surface in order to minimize the strain energy. These theories give a reasonably good description of the observed data in most cases. In few cases they fail seriously.[25] Burton and Machline[25] suggested a simple criterion for surface segregation. It is related to the equilibrium distribution of a solute in an alloy in its solid and liquid phases. According to their criterion, surface segregation of the solute should occur if and only if solid-liquid equilibrium is such that the liquid is richer in the solute. With this simple argument they noticed that most of the experimental results could be explained. But this type of criterion is not quantitative as it is not able to predict the amount of surface segregation. To develop a microscopic theory such as the electronic structure at the surfaces of alloys, one should know the chemical composition in various layers parallel to the surface. Further, the AES gives an average composition in the surface layers.[1] Recently measurements have been performed with various incident electron energies. Then, knowing the escape depth of the electrons one can calculate in principle the composition in various layers parallel to the surface. As yet there is some controversy about the results obtained in the various laboratories for various systems. But one expects that in future AES experiments will be amenable to more accurate interpretations.

One can now think of refining the regular solution theory or the strain theory to explain the experiments. One such attempt has recently been done by Wynblatt and Ku[26] who have modified the monolayer regular-solution theory to take into account the strain energy due to atomic size difference. However, the assumption that several alloys of interest can be regarded as regular solutions seems untenable in the light of the following evidence. The bulk phase diagrams of entropy and heat of mixing of various metallic solutions indicate that most solutions do not fall into the categories of either ideal or regular solution. There is generally an excess entropy and the heat of formation is nonzero.[27] In addition, the curves of heat of mixing versus mole fraction are often not symmetric at equiatomic concentration. This suggests that there is deviation from perfect randomness in the distribution of atoms in the system and that there exists some short-range order (SRO) in alloys. Therefore, the regular-solution theory should be modified in order to incorporate the SRO in bulk, i.e., to treat the nonregular solutions. A satisfactory incorporation of SRO in the theories of alloys can be made with the help of the Bethe-Peierls approximation (BPA). However, the application of BPA to an alloy with a surface requires one nontrivial modification. It should be noticed that unlike the case of treatment of bulk properties, we must introduce three SRO parameters. The basic reason is that the concentration of a constituent, say A, varies from layer to layer as we move down the surface. Now there can be two types of nearest-neighbor AA pairs: (i) ones in which both the atoms are in the same layer, and (ii) those in which the atoms are in successive layers. Since the concentration in successive layers is different, clearly the tendency for a given A atom to form AA pairs in its own layer is different from its tendency to form such pairs in the adjacent layer. The Bethe-Peierls approximation required for this purpose has already been developed for dealing with the problems of phase boundaries and surface tension within the Ising model.[28-30] These calculations can be easily transcribed to alloy language, and then our problem differs only in one boundary condition to be used at the surface.

The outline of the present paper is as follows. In Sec. II we present briefly the Bethe-Peierls treatment of solid solutions with a surface. This work[31] is an extension of our earlier publication[22] (hereafter to be referred to as I) where we have treated the regular solutions in the quasichemical approximation. A further improvement on the theory given in I is that we have considered the composition and temperature dependence of the interaction-energy parameter ϵ. Our treatment neglects the effects arising out of the size difference of the constituent atoms. This formalism has been applied to Ag-Au and Ag-Pd alloys in Sec. III. We have calculated the concentration and SRO parameters in the first three layers parallel to the surface. In addition we have also calculated compositions averaged over different number of layers, so that a detailed comparison with AES data can be made. Our conclusions are presented in Sec. IV.

II. FORMALISM

We consider a semi-infinite solid binary alloy in thermodynamic equilibrium. Here we shall treat clean surfaces which are assumed to be atomistically plane. A quasichemical approximation will be used for the configuration energy of the system. We assume that only the nearest-neighbor atom pairs interact. Therefore, the total configuration energy may be written as a sum of interaction energies of the nearest-neighbor atom pairs.

We divide the semi-infinite system into *layers* parallel to the planar surface and number the layers as $\lambda = 0, 1, 2, \ldots$; $\lambda = 0$ being the surface layer. Let N be the total number of atoms in the system and N^λ be the number of atoms in the λth layer. Let N_A^λ and N_B^λ denote the number of atoms of type A and B, respectively, in the λth layer, then $x_\lambda = N_A^\lambda / N^\lambda$ and $y_\lambda = N_B^\lambda / N^\lambda$ are the concentrations of A and B types of atoms in the λth layer $(x_\lambda + y_\lambda = 1)$. Let Z_λ denote the total number of nearest neighbors of an atom in the λth layer. Clearly,

$$\begin{aligned} Z_0 &= Z_{\mathrm{IL}} + Z_{\mathrm{LL}} , \\ Z_\lambda &= 2 Z_{\mathrm{IL}} + Z_{\mathrm{LL}} , \end{aligned} \tag{1}$$

where Z_{LL} denotes the number of nearest neighbors in a layer and Z_{IL} denotes the number of neighbors of a given atom in an adjacent layer. Now we introduce the following notations: $N^{\lambda\lambda}$ is the total number of nearest-neighbor pairs in the λth layer, $N^{\lambda\lambda+1}$ the total number of nearest-neighbor pairs between the two adjacent layers λ and $\lambda + 1$, $N_{AA(BB)}^{\lambda\lambda}$ the total number of nearest-neighbor AA (BB) pairs when both A (B) atoms lie in the λth layer, $N_{(AB)}^{\lambda\lambda}$ the total number of nearest-neighbor AB or BA pairs when both A and B atoms lie in the λth layer, $N_{AA(BB)}^{\lambda\mu}$ the total number of nearest-neighbor pairs of AA (BB) type when one A (B) atom lies in the λth layer and the other in the μth layer, $N_{AB}^{\lambda\mu}$ the total number of nearest-neighbor pairs of type AB when the A atom lies in the λth layer and the B atom lies in the μth layer, and $N_{BA}^{\lambda\mu}$ the total number of nearest-neighbor pairs of type BA when the B atom lies in the λth layer and the A atom lies in the μth layer. Then the total configuration energy of the system is given as

$$\begin{aligned} U = \sum_{\lambda=0}^{\xi} \epsilon_{AA}(N_{AA}^{\lambda\lambda} + N_{AA}^{\lambda\lambda+1}) + \epsilon_{AB}(N_{(AB)}^{\lambda\lambda} + N_{AB}^{\lambda\lambda+1} + N_{BA}^{\lambda\lambda+1}) \\ + \epsilon_{BB}(N_{BB}^{\lambda\lambda} + N_{BB}^{\lambda\lambda+1}) , \end{aligned} \tag{2}$$

where ϵ_{AA}, ϵ_{AB}, and ϵ_{BB} represent the bond enthalpies for $AA, AB, (BA)$, and BB nearest-neighbor pairs, respectively.

We now introduce the SRO parameters α_λ; $\lambda = 0, 1, 2, \ldots$, in the usual manner of solid solution theory. We write

$$N_{(AB)}^{\lambda\lambda} = 2x_\lambda y_\lambda \alpha_\lambda N^{\lambda\lambda}\,, \tag{3a}$$

$$N_{AA}^{\lambda\lambda} = x_\lambda(1-\alpha_\lambda y_\lambda)N^{\lambda\lambda}\,, \tag{3b}$$

$$N_{BB}^{\lambda\lambda} = y_\lambda(1-\alpha_\lambda x_\lambda)N^{\lambda\lambda}\,. \tag{3c}$$

α_λ is the SRO parameter for the λth layer and it varies from layer to layer. This variation will in most cases be confined to a few layers near the surface after which it acquires the bulk value α_b (the subscript b stands for bulk). Since the concentration is to vary with λ, we require two more SRO parameters β_λ and β'_λ to obtain similar expressions for interlayer pairs. We define

$$N_{AB}^{\lambda\lambda+1} = x_\lambda y_{\lambda+1}\beta_\lambda N^{\lambda\lambda+1}\,, \tag{4a}$$

$$N_{BA}^{\lambda\lambda+1} = y_\lambda x_{\lambda+1}\beta'_\lambda N^{\lambda\lambda+1}\,, \tag{4b}$$

$$N_{AA}^{\lambda\lambda+1} = x_\lambda(1-\beta_\lambda y_{\lambda+1})N^{\lambda\lambda+1}\,, \tag{4c}$$

$$N_{BB}^{\lambda\lambda+1} = y_\lambda(1-\beta'_\lambda x_{\lambda+1})N^{\lambda\lambda+1}\,. \tag{4d}$$

Here β_λ is the SRO parameter associated with the probability of finding a B atom in the $(\lambda+1)$th layer as the nearest neighbor to an A atom in the λth layer; whereas β'_λ is the SRO parameter associated with the probability of finding an A atom in the $(\lambda+1)$th layer as the nearest neighbor to a B atom in the λth layer. It is clearly seen from Eqs. (4a) and (4b) that $N_{AB}^{\lambda\lambda+1}$ and $N_{BA}^{\lambda\lambda+1}$ have different values in contrast to $N_{AB}^{\lambda\lambda}$ and $N_{BA}^{\lambda\lambda}$ which have the same value. Further even though the two SRO parameters β_λ and β'_λ have different values, they are not independent because of the following constraint:

$$N_{AA}^{\lambda\lambda+1} + N_{BA}^{\lambda\lambda+1} = Z_{\mathrm{IL}}N_A^{\lambda+1}\,. \tag{5}$$

Equation (5) can be simplified using the definitions in Eqs. (4a)–(4d) to obtain the following relation between β_λ and β'_λ

$$x_\lambda - x_{\lambda+1} = x_\lambda y_{\lambda+1}\beta_\lambda - x_{\lambda+1}y_\lambda\beta'_\lambda\,. \tag{6}$$

The expression (2) for the configuration energy of the system can be written in terms of $x_\lambda, \alpha_\lambda, \beta_\lambda$, and β'_λ by using definitions in Eqs. (3) and (4). Dropping the configuration-independent terms which can be eliminated by a suitable choice of the energy origin, the following form for U_N is obtained:

$$\begin{aligned}U_N(\{x_\lambda, \alpha_\lambda, \beta_\lambda\}) = \sum_{\lambda=0}^{\xi} N^\lambda\{\epsilon[Z_{\mathrm{LL}}x_\lambda y_\lambda\alpha_\lambda \\ + Z_{\mathrm{IL}}(x_\lambda y_{\lambda+1}\beta_\lambda + x_{\lambda+1}y_\lambda\beta'_\lambda)] \\ - 2B[Z_{\mathrm{LL}}x_\lambda + Z_{\mathrm{IL}}(x_\lambda + x_{\lambda+1})]\}\,,\end{aligned} \tag{7}$$

where ϵ, the interaction energy parameter, is given by

$$\epsilon = \epsilon_{AB} - (\epsilon_{AA} + \epsilon_{BB})/2 \tag{8}$$

and

$$B = \tfrac{1}{4}(\epsilon_{BB} - \epsilon_{AA})\,. \tag{9}$$

In BPA, the configurational entropy of the system is approximated as follows[28-30]:

$$S_N = k\ln(P_N) \tag{10}$$

and P_N is given as

$$P_N = \prod_{\lambda=0}^{\xi} \frac{N^{\lambda\lambda}!}{N_{AA}^{\lambda\lambda}!N_{AB}^{\lambda\lambda}!N_{BA}^{\lambda\lambda}!N_{BB}^{\lambda\lambda}!}\,\frac{N^{\lambda\lambda+1}!}{N_{AA}^{\lambda\lambda+1}!N_{AB}^{\lambda\lambda+1}!N_{BA}^{\lambda\lambda+1}!N_{BB}^{\lambda\lambda+1}!}\,(N_A^\lambda!N_B^\lambda!/N^\lambda!)^{Z_\lambda-1}\,. \tag{11}$$

Making use of Sterling's approximation for $N^\lambda!$, $N^{\lambda\lambda}!, N^{\lambda\lambda+1}!$, etc. and using Eqs. (3) and (4), we obtain the following expression for S_N:

$$\begin{aligned}S_N = k\sum_{\lambda=0}^{\xi} N^\lambda\Big((Z_\lambda - 1)(x_\lambda\ln x_\lambda + y_\lambda\ln y_\lambda) - \tfrac{1}{2}Z_{\mathrm{LL}}\{x_\lambda(1-\alpha_\lambda y_\lambda)\ln[x_\lambda(1-\alpha_\lambda y_\lambda)] \\ + 2x_\lambda y_\lambda\alpha_\lambda\ln(x_\lambda y_\lambda\alpha_\lambda) + y_\lambda(1-\alpha_\lambda x_\lambda)\ln[y_\lambda(1-\alpha_\lambda x_\lambda)]\} \\ - Z_{\mathrm{IL}}\{x_\lambda(1-\beta_\lambda y_{\lambda+1})\ln[x_\lambda(1-\beta_\lambda y_{\lambda+1})] + x_\lambda y_{\lambda+1}\beta_\lambda\ln(x_\lambda y_{\lambda+1}\beta_\lambda) \\ + y_\lambda x_{\lambda+1}\beta'_\lambda\ln(x_{\lambda+1}y_\lambda\beta'_\lambda) + y_\lambda(1-\beta'_\lambda x_{\lambda+1})\ln[y_\lambda(1-\beta'_\lambda x_{\lambda+1})]\}\Big)\end{aligned} \tag{12}$$

Our aim is to determine x_λ, α_λ, and β_λ (β'_λ being related to β_λ) with the knowledge of x_b and other bulk thermodynamic data. In order to do that we minimize the free energy per atom $F = U - TS$ ($U = U_N/N$ and S_N/N) with respect to x_λ, α_λ, and β_λ using the constraint that the overall concentration of various constituents in the alloys is fixed. Mathematically this constraint is

$$\sum_{\lambda=0}^{\xi} N^\lambda x_\lambda = N_A\,, \tag{13}$$

where N_A is the total number of A atoms in the solution. This minimization procedure leads to the following set of equations:

$$\frac{\epsilon}{kT}\{Z_{\mathrm{LL}}\alpha_\lambda(y_\lambda - x_\lambda) + Z_{\mathrm{IL}}(\beta_\lambda y_{\lambda+1} - \beta'_\lambda x_{\lambda+1} + y_{\lambda-1}\beta'_{\lambda-1} - x_{\lambda-1}\beta_{\lambda-1})\} - (2BZ_\lambda + \eta)/kT - (Z_\lambda - 1)\ln(x_\lambda/y_\lambda)$$
$$+\tfrac{1}{2}Z_{\mathrm{LL}}\{[1-\alpha_\lambda(y_\lambda - x_\lambda)]\ln[x_\lambda(1-\alpha_\lambda y_\lambda)] - [1+\alpha_\lambda(y_\lambda - x_\lambda)]\ln[y_\lambda(1-\alpha_\lambda x_\lambda)] + 2\alpha_\lambda(y_\lambda - x_\lambda)\ln(\alpha_\lambda x_\lambda y_\lambda)\}$$
$$+Z_{\mathrm{IL}}\left[\ln\left(\frac{x_\lambda(1-\beta_\lambda y_{\lambda+1})}{y_\lambda(1-\beta'_\lambda x_{\lambda+1})}\right) + y_{\lambda+1}\beta_\lambda \ln\left(\frac{\beta_\lambda y_{\lambda+1}}{1-\beta_\lambda y_{\lambda+1}}\right) - x_{\lambda+1}\beta'_\lambda \ln\left(\frac{\beta'_\lambda x_{\lambda+1}}{1-x_{\lambda+1}\beta'_\lambda}\right)\right.$$
$$\left. + y_{\lambda-1}\beta'_{\lambda-1}\ln\left(\frac{\beta'_{\lambda-1}x_\lambda}{1-\beta'_{\lambda-1}x_\lambda}\right) - \beta_{\lambda-1}x_{\lambda-1}\ln\left(\frac{\beta_{\lambda-1}y_\lambda}{1-\beta_{\lambda-1}y_\lambda}\right)\right] = 0 \quad (14a)$$

$$\frac{\epsilon}{kT} + \tfrac{1}{2}\ln\left(\frac{\alpha_\lambda^2 x_\lambda y_\lambda}{(1-\alpha_\lambda y_\lambda)(1-\alpha_\lambda x_\lambda)}\right) = 0, \quad (14b)$$

$$\frac{\epsilon}{kT} + \tfrac{1}{2}\ln\left(\frac{x_{\lambda+1}\beta'_\lambda y_{\lambda+1}\beta_\lambda}{(1-\beta_\lambda y_{\lambda+1})(1-\beta'_\lambda x_{\lambda+1})}\right) = 0. \quad (14c)$$

η is a Lagrangian multiplier and can be determined from

$$\frac{\epsilon}{kT} Z\,\alpha_b(y_b - x_b) - \frac{2BZ + \eta}{kT} - (Z-1)\ln(x_b/y_b)$$
$$+\tfrac{1}{2}Z\{[1-\alpha_b(y_b - x_b)]\ln[x_b(1-y_b\alpha_b)]$$
$$-[1+\alpha_b(y_b - x_b)]\ln y_b(1-x_b\alpha_b)$$
$$+2\alpha_b(y_b - x_b)\ln(\alpha_b x_b y_b)\} = 0. \quad (15)$$

Here Z is the number of nearest neighbors of an atom in the bulk. Equation (15) has been obtained from (14a) by replacing the surface variables by their corresponding bulk value. In the limit of perfectly random alloy ($\alpha_b = 1$), Eqs. (14) and (15) reduces to our previous results in I.

Now we have three unknowns x_λ, α_λ, and β_λ for each layer and three equations (14a), (14b), (14c) to determine these. In practice one usually considers first few layers near the surface in which the concentration is different from the bulk and after that it is assumed that the layers attain the bulk concentration. The bulk concentration is a known factor from the way in which the alloy is prepared. Further, depending upon the bulk concentration and temperature, the equilibrium lattice configuration is known. The other information we need is about ϵ, B, and α_b. These are determinable from the bulk thermodynamic data on alloys.[27] The parameter B is related to the difference in the heats of vaporization of two pure constituents.[32] ϵ is related to the heat of mixing of the solutions.[32,33] We have taken concentration and temperature dependence of ϵ and have followed the procedure of Averbach[32] to determine ϵ and α_b. We assume that the concentration and temperature dependence of ϵ are separable and we can define

$$\epsilon = u + j(x_b) + gT. \quad (16)$$

The values of $u + j(x_b)$, g, and α_b are then calculated[32] self-consistently with the knowledge of heat of mixing ΔH^m and the excess entropy ΔS_m^{ex}.

III. APPLICATION TO Ag-Au AND Ag-Pd ALLOYS

A. Ag-Au alloys

Silver is completely soluble in gold over the whole concentration range. The atomic sizes of silver and gold are almost identical and they have the same crystal structure, namely, fcc. Further, there is tendency of clustering of unlike atoms.[34] Therefore it forms a good system to apply our formulation. The bulk thermodynamic data for this system were taken from Hultgren *et al.*[27] at 800 °K. The values of various parameters are tabulated in Table I. We have studied (100), (110), and (111) surfaces of these alloys. It is assumed that the concentration is different only in the first three layers and after that the system acquires

TABLE I. Table of ϵ and α_b for Ag-Au alloys at 800 °K. Au is taken to be the A constituent.

x_b	H^m (cal/mol)	S_m^{ex} (cal/mol °K)	$N[u + j(x_b)]$ (cal/mol)	Ng (cal/mol °K)	$N\epsilon$ (cal/mol)	α_b
0.1	−430	−0.12	−384.4556	0.0867	−315.0956	1.0356
0.2	−750	−0.22	−368.0200	0.0779	−305.7035	1.0614
0.3	−970	−0.29	−356.7311	0.0713	−299.6911	1.0790
0.4	−1090	−0.33	−347.6946	0.0674	−293.7746	1.0885
0.5	−1110	−0.34	−339.4583	0.0660	−286.6583	1.0900
0.6	−1050	−0.33	−336.1584	0.0694	−280.6384	1.0846
0.7	−900	−0.29	−333.1505	0.0749	−273.2305	1.0720
0.8	−670	−0.22	−331.3079	0.0826	−265.2279	1.0533
0.9	−370	−0.12	−332.8094	0.0908	−260.1694	1.0294

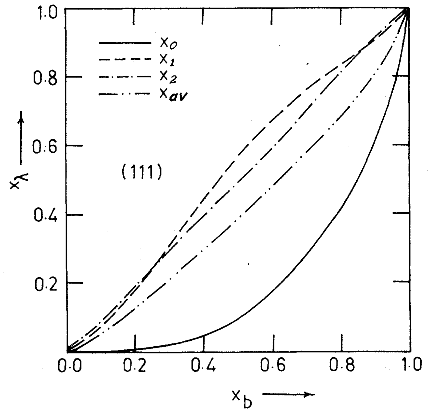

FIG. 1. Surface concentration of Au as a function of bulk Au concentration at the (111) surface of Ag-Au alloys. x_{av} shows averaged concentration over the first three layers.

bulk values. In Fig. 1 we have plotted the surface concentration of Au as a function of bulk concentration of Au for the (111) surface. It is noticed that segregation of Ag occurs at the surface, whereas Au is enriched in the second layer for $x_b \gtrsim 0.25$. In the third layer the concentration is almost close to the bulk value and thus validates our approximation that the concentration is different only in the first three layers. We have also plotted the averaged concentration of Au in the first three surface layers. This averaged concentration shows significantly less segregation of Ag. Since the usual experiments for surface studies like AES give averaged concentrations in the first few layers, one should compare the theoretical results of averaged concentration with the AES results. This system has been studied by Overbury and Somarjai[12] using AES. They observed enrichment of the surface with Ag but to an extent less than predicted by a monolayer regular-solution model. In Table II we have compared the results obtained from present theory and the regular solution model.[22] The results are almost identical. This shows that the SRO is not a

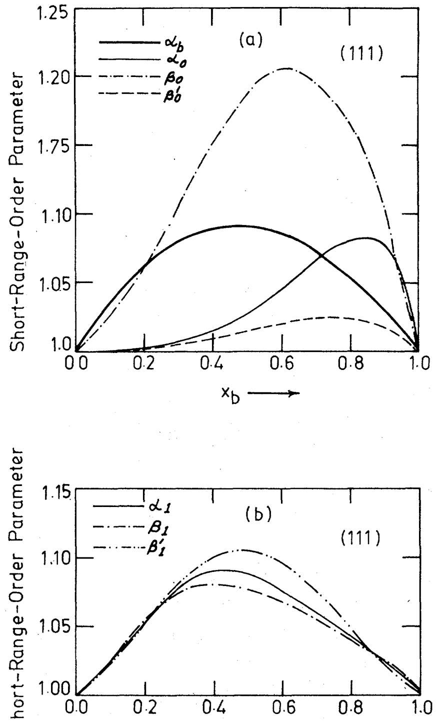

FIG. 2. Short-range-order parameters as a function of bulk Au concentration at the (111) surface of Ag-Au alloys. Thick line shows the bulk SRO parameter: (a) various SRO parameter for the top surface layer; (b) for second layer.

TABLE II. Comparison between surface concentrations at the (111) face as predicted by regular-solution and nonregular-solution theories for Ag-Au alloys at 800 °K.

x_b	Regular solution			Nonregular solution		
	x_0	x_1	x_2	x_0	x_1	x_2
0.1	0.003	0.110	0.099	0.002	0.074	0.077
0.2	0.011	0.231	0.195	0.008	0.182	0.187
0.3	0.027	0.354	0.290	0.020	0.310	0.295
0.4	0.055	0.473	0.385	0.046	0.443	0.393
0.5	0.102	0.585	0.483	0.095	0.567	0.490
0.6	0.175	0.686	0.583	0.172	0.672	0.591
0.7	0.277	0.777	0.686	0.278	0.759	0.699
0.8	0.413	0.856	0.791	0.415	0.834	0.810
0.9	0.598	0.927	0.897	0.603	0.909	0.915

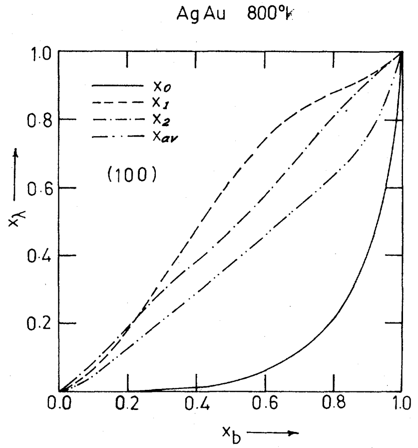

FIG. 3. Surface concentration of Au as a function of bulk Au concentration at the (100) surface of Ag-Au alloys.

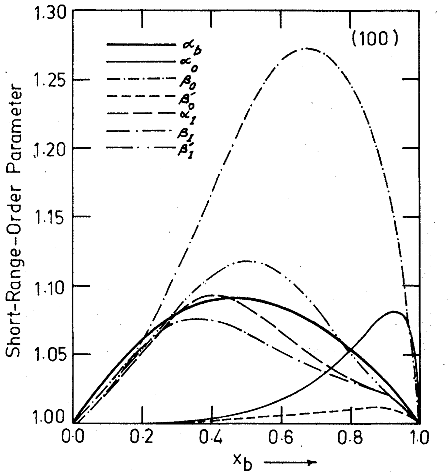

FIG. 4. SRO parameters as a function of bulk Au concentration at the (100) surface of Ag-Au alloys.

significant factor as far as segregation is concerned in this system. Our results show heavy segregation of Ag at the surface. But if we compare the averaged concentration x_{av} with the experimental results of Overbury and Somarjai[12] measured at 68 eV (which is expected to probe about three layers) for Au, then the agreement is fairly good. Nelson[12] has also studied this system using low-energy ion scattering spectroscopy. His results also show enrichment of surface with silver. The criteria of Burton and Machlin[25] also predicts segregation of Ag. Therefore, it appears that segregation of Ag should occur in clean samples of Ag-Au alloys in contrast to the observation of Bouwman *et al.*[12] who have found no segregation in this system. Here we draw the attention towards the fact[14] that segregation is significantly affected by the different methods of preparation of samples. Therefore much care should be exercised in comparing any theoretical result with the experimental results.

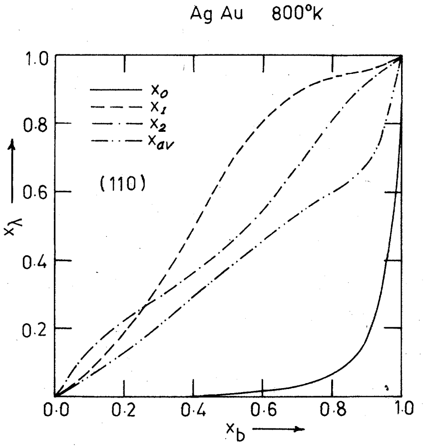

FIG. 5. Surface concentration of Au as a function of bulk Au concentration at the (110) surface of Ag-Au alloys.

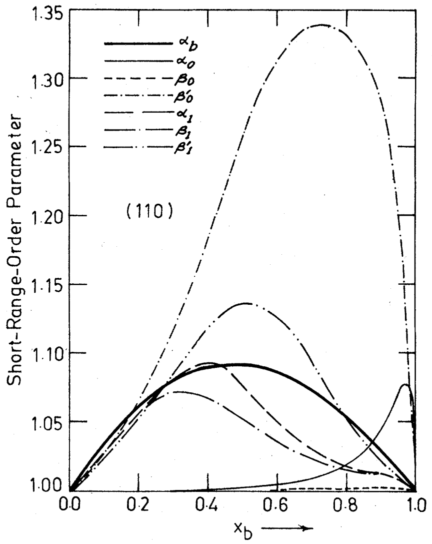

FIG. 6. SRO parameters on the (110) surface of Ag-Au alloys.

In Figs. 2(a) and 2(b) we have plotted the various SRO parameters for (111) surface. The thick line shows the bulk SRO parameter. It is seen that the surface SRO parameters α_0, β_0, and β'_0 are quite different from the bulk value and with each other. In the second layer the SRO parameters are close to the bulk value and in the third layer these are almost identical with the bulk value, hence not shown in the figure. Our experience with the bulk studies tells us that the SRO plays a significant role in governing the properties of elementary excitations. Therefore, while studying the elementary excitations at the surfaces of alloys these surface SRO parameters should be taken into account. To our knowledge no experimental results are available on surface SRO parameters on any system. We hope that in the near future, experiments like low-energy-electron diffraction (LEED) and AES will be sufficiently refined to obtain such information.

In Figs. 3 and 4 we have plotted, respectively, the surface concentrations and surface SRO parameters as a function of bulk concentration of Au for the (100) surface. It is seen that the enrichment is more significant in this case. The general trend is similar to the one observed for the (111) surface. The surface SRO parameters are quite different from the bulk value. The quite large value of β_0 and very small value of β'_0 should be expected because of heavy segregation of Ag at the surface (first layer) and the enrichment of second layer with Au. For the (110) surface our results are shown in Figs. 5 and 6. Here the seg-

TABLE III. Table of ϵ and α_b for Ag-Pd alloys at 1200 °K. Pd is taken to be the A constituent.

x_b	H^m (cal/mol)	S^{ex} (cal/mol °K)	$N(u+j(x_b))$ (cal/mol)	Ng (cal/mol °K)	$N\epsilon$ (cal/mol)	α_b
0.1	−664	−0.203	−596.8557	0.1650	−398.8562	1.0301
0.2	−1100	−0.305	−544.1494	0.1249	−394.3030	1.0529
0.3	−1317	−0.380	−491.8582	0.1136	−355.5798	1.0625
0.4	−1350	−0.438	−441.9707	0.1169	−301.7320	1.0660
0.5	−1200	−0.438	−380.8748	0.1171	−240.3948	1.0502
0.6	−1070	−0.489	−358.5022	0.1476	−181.4323	1.0363
0.7	−780	−0.405	−302.8062	0.1468	−126.6800	1.0222
0.8	−480	−0.279	−247.3083	0.1382	−81.5026	1.0110
0.9	−250	−0.167	−230.6820	0.1520	−48.2471	1.0035

regation is most prominent and even in the third layer the concentration is significantly different from bulk value. For this layer, Au gets segregated at the surface for Ag rich and Au rich alloys, while the segregation of Ag occurs in the intermediate concentration range. Other trends are similar to the one observed for the (111) surface. The surface SRO parameters in the second layer have significantly different values for $x_b > 0.3$ in this case. The reason for heaviest segregation on the (110) surface is that the number of broken bonds is largest ($Z_{IL} = 5$) for the (110) surface as compared to the (100) ($Z_{IL} = 4$) and (111) ($Z_{IL} = 3$) surfaces.

B. Ag-Pd alloys

The Ag-Pd system forms a continuous series of solid solutions over the entire composite-ion range, and like their constituents have the fcc crystal structure. The heat of mixing of these alloys is negative, thus a tendency of clustering of unlike atoms is expected. The atomic sizes of Ag and Pd are slightly different but in the present calculation this fact has not been taken into account explicitly. It is expected that to some extent the heat of mixing data includes contributions from any such physical effects. The bulk thermodynamic data for this system were taken from Hultgren *et al.*[27] at 1200 °K. The various values of parameters ϵ and α_b are listed in Table III. The surface energy of Pd is more as compared to Ag and hence segregation of silver is expected. Again we perform the calculation assuming that the concentration is different only in the first three layers. In Fig. 7 we have shown our results for the (111), (100), and (110) surfaces. It is seen that the segregation of Ag occurs at the surfaces in all three cases. Segregation is maximum at the (110) surface. In the second layer Pd is

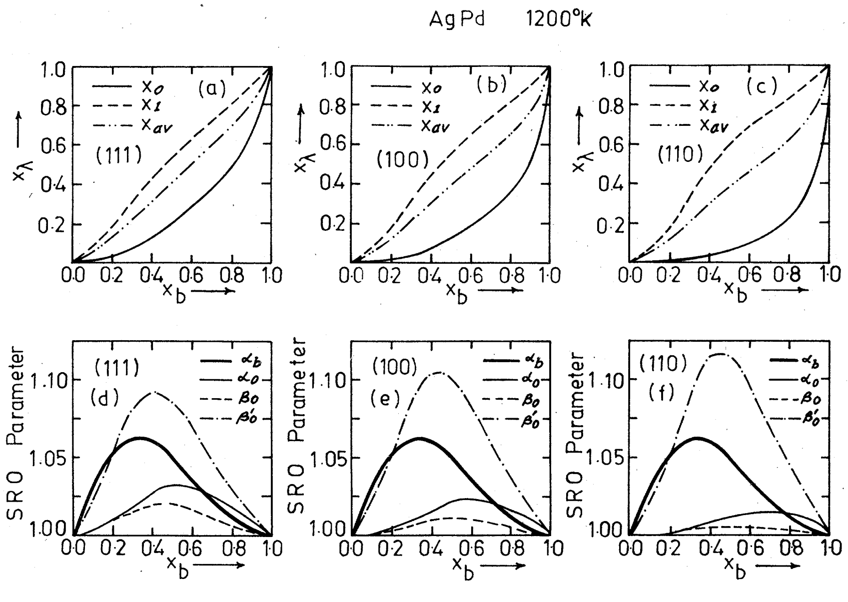

FIG. 7. Surface concentration and short-range-order parameters for Ag-Pd alloys at $T = 1200$ °K. (a) and (b) for the (111) surface; (b) and (e) for the (100) surface; and (c) and (f) for the (110) surface.

enriched; this is because ϵ has a negative value and hence AB bonding is stronger. In the third layer the concentration is almost similar to the bulk and hence not shown in the figure. x_{av} denotes the average concentration over the first three layers. Wood and Wise[4] have studied this system using AES. From their experimental details it is clear that they have probed first two or three layers. They showed that segregation of Ag occurs in this system. They have made studies at 975 °K. A glance at their results and our results shows that in our case the amount of segregation is less. This should be expected because we have done calculations at 1200 °K, and the amount of segregation should decrease with temperature.[22] The criterion of Burton and Machlin also predicts segregation of Ag at the surface. In this way we can conclude that our results are in good agreement with experiments.

The variation of surface SRO parameters has also been shown in Figs. 7(d)–7(f). The thick line shows the bulk SRO parameters. Only the parameters α_0, β_0, and β_0' are shown. They are quite different from the bulk and also with each other as was seen in the case of Ag-Au alloys. In the second and third layer their values are not very different from the bulk and hence not shown.

IV. CONCLUDING REMARKS

In conclusion, we would like to observe that the amount of segregation calculated in our refined theory is not appreciably different from the regular-solution theory. Though it must be stressed that the agreement of regular-solution theory with experiments and with the present theory is rather fortuitous, as there is considerable short-range order in the alloys which have been studied. Our theory shows rather interesting results in regard to short-range-order parameters. In the surface layers, these are found to be quite different from their bulk values. This factor is important for developing microscopic theories, say of electronic band structure at surfaces of alloys. Further, these considerations may find some significance in the study of phenomena like chemisorption, catalysis, etc.

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