

## Surface effects on the order-disorder phase transition of $A_3B$ alloys\*

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The order-disorder phase transition at the surface at  $A_3B$ -type alloys has been studied using the Bragg-Williams theory. A simple electronic theory for the order-disorder transition at the surface is also presented. In agreement with experiments for  $\text{Cu}_3\text{Au}$  one finds that the order parameter and in particular the discontinuity in the order parameter at the transition temperature  $T_c$  is strongly reduced for the first three atomic surface layers. We study also the effect of surface segregation on the order-disorder transition at the surface. One finds that due to segregation the order parameter can disappear at the surface at temperatures below  $T_c$ . Also, atomic ordering may suppress segregation.

### I. INTRODUCTION

As in the case of magnetism, superconductivity, melting, etc., one might expect that the order-disorder phase transitions are affected by the surface. One would like to know, for example, over which distance away from the surface the order parameter is affected by the surface, how the effect of the surface depends on the geometry of the surface, and how atomic segregation occurring at the surface affects the order-disorder transition.

In this paper we present a Bragg-Williams-type theory and also a simple electronic theory for the effect of the surface on order-disorder phenomena. The effect of surface segregation on atomic ordering is taken into account. It is shown that within the first few atomic layers at the surface the atomic ordering is strongly reduced due to the surface. This agrees with experimental results for  $\text{Cu}_3\text{Au}$ .<sup>1</sup> We show that the effect of the surface on the order-disorder transition is different for different surface geometry. Surface segregation has a strong effect on atomic ordering. As a result of surface segregation the order parameter in the vicinity of the surface can be strongly reduced and might even disappear at some temperature below the transition temperature.

In Sec. II we outline the Bragg-Williams-type theory for the effect of the surface on the order-disorder transition in alloys of type  $A_3B$  ( $\text{Cu}_3\text{Au}$ ,  $\text{Pt}_3\text{Sn}$ , etc.) with first-order phase transition in the bulk.<sup>2-4</sup> In Sec. III we present numerical results and a comparison with experiment. These results are discussed in Sec. IV. In Appendix A we give details of the determination of the internal energy using the Bragg-Williams approximation and outline in Appendix B a microscopic theory for order-disorder phenomena at the surface.

### II. THEORY

In the following we study atomic ordering at the surface of a fcc lattice for  $A_3B$ -type alloys. The lattice is decomposed into planes parallel to the surface. Then the atomic order parameter  $\eta_i$  for the  $i$ th plane away from the surface is defined by

$$\eta_i = p_{\alpha,i}^A - p_{\beta,i}^A, \quad (2.1)$$

where  $p_{\alpha,i}^A$  and  $p_{\beta,i}^A$  are the probabilities to find an  $A$  atom in the  $i$ th plane in the  $\alpha$  and  $\beta$  sublattice, respectively. Note, in the case of a fcc lattice and  $A_3B$  alloys the  $\alpha$  sublattice consists of all face-centered lattice sites and the  $\beta$  sublattice of all corner sites of the fcc lattice (Fig. 1). Noting that  $N_{\alpha,i}p_{\alpha,i}^A + N_{\beta,i}p_{\beta,i}^A = x_i N_i$ , where  $N_{\alpha,i}$  and  $N_{\beta,i}$  are the numbers of  $\alpha$  and  $\beta$  lattice sites in the  $i$ th layer with  $N_i$  atoms and concentration  $x_i$  of  $A$  atoms, one finds that

$$p_{\alpha,i}^A = \frac{\eta_i + (N_i/N_{\beta,i})x_i}{1 + N_{\alpha,i}/N_{\beta,i}}$$

and

$$p_{\beta,i}^A = \frac{N_i}{N_{\beta,i}} x_i - \frac{\eta_i + (N_i/N_{\beta,i})x_i}{1 + N_{\beta,i}/N_{\alpha,i}}.$$

Then,  $p_{\alpha,i}^B$  and  $p_{\beta,i}^B$  can be obtained from  $p_{\alpha,i}^A$ ,  $p_{\alpha,i}^B = 1 - p_{\alpha,i}^A$  and  $p_{\beta,i}^B = 1 - p_{\beta,i}^A$ . The equilibrium values for  $x_i$  and  $\eta_i$  are then determined by minimizing the free energy

$$F = U - TS, \quad (2.2)$$

with respect to  $x_i$  and  $\eta_i$ . This yields the equations

$$\frac{\partial F}{\partial \eta_i} = 0 \quad (2.3)$$

and

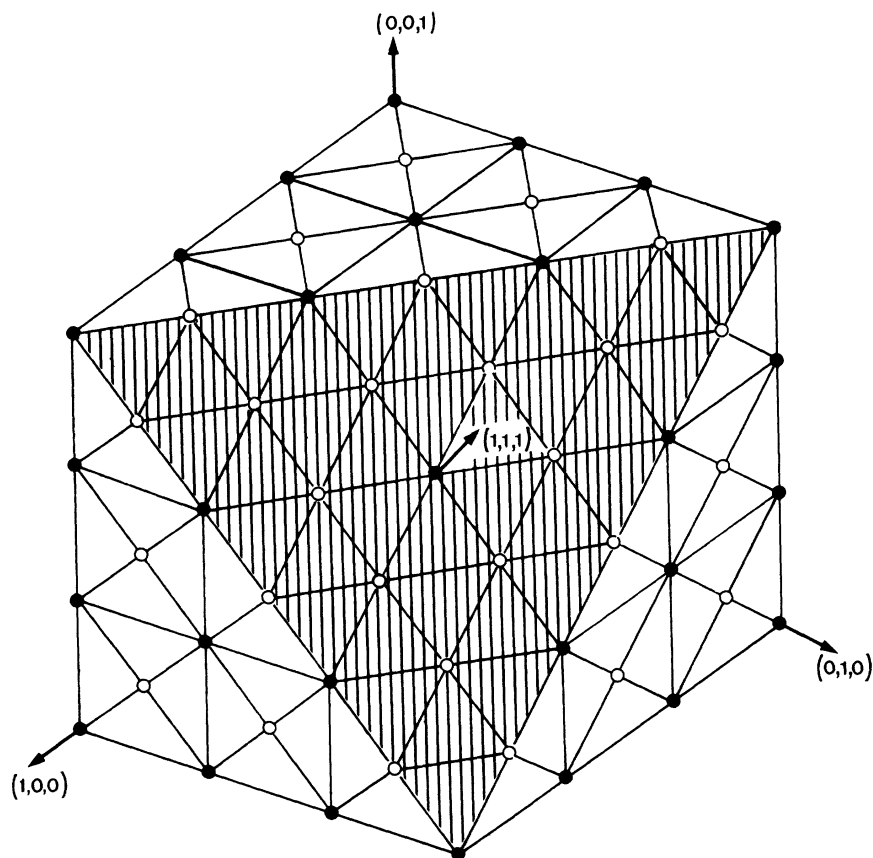


FIG. 1.  $\alpha$  and  $\beta$  sublattices of the considered fcc lattice.

- $\alpha$ -Site
- $\beta$ -Site

$$\frac{\partial F}{\partial x_i} = \frac{\partial F}{\partial x_b} \quad (2.4)$$

Here,  $x_b$  is the average concentration of A atoms in the bulk. The equations will be evaluated by using for the entropy  $S$  the expression  $S = \sum_i S_i$ , where  $S_i$  is the contribution due to the  $i$ th layer and is given by

$$S_i = k \ln \left( \frac{N_{\alpha,i}!}{N_{\alpha,i}^A! N_{\alpha,i}^B!} \right) \left( \frac{N_{\beta,i}!}{N_{\beta,i}^A! N_{\beta,i}^B!} \right).$$

Similarly, by using the Bragg-Williams approximation the internal energy  $U$  is written  $U = \sum_i (U_i^{(1)} + U_i^{(2)})$ , where  $U_i^{(1)}$  and  $U_i^{(2)}$  are the contributions due to the  $i$ th layer which result from nearest- and next-nearest-neighbor interactions. In the Appendix A these energies  $U_i^{(1)}$ ,  $U_i^{(2)}$  are determined explicitly.

#### A. (111) surface

In the following we evaluate Eqs. (2.3) and (2.4) for the case of a (111) surface plane. Then one finds

$$N_{\alpha,i} = \frac{3}{4}N_i \quad \text{and} \quad N_{\beta,i} = \frac{1}{4}N_i;$$

and

$$\begin{aligned} p_{\alpha,i}^A &= x_i + \frac{1}{4}\eta_i, \\ p_{\alpha,i}^B &= 1 - x_i - \frac{1}{4}\eta_i, \end{aligned} \quad (2.5)$$

$$p_{\beta,i}^A = x_i - \frac{3}{4}\eta_i,$$

and

$$p_{\beta,i}^B = 1 - x_i + \frac{3}{4}\eta_i.$$

Using now the explicit expressions for  $S_i$ ,  $U_i^{(1)}$ , and  $U_i^{(2)}$  one obtains from Eq. (2.3) the coupled set of equations

$$\frac{W^{(1)}}{kT}(\eta_1 + \frac{1}{2}\eta_2) - \frac{W^{(2)}}{kT}3\eta_2 = 3 \ln \frac{(x_1 + \frac{1}{4}\eta_1)(1 - x_1 + \frac{3}{4}\eta_1)}{(1 - x_1 - \frac{1}{4}\eta_1)(x_1 - \frac{3}{4}\eta_1)}, \quad (2.6)$$

$$\frac{W^{(1)}}{kT}(\eta_2 + \frac{1}{2}\eta_1 + \frac{1}{2}\eta_3) - \frac{W^{(2)}}{kT}3(\eta_1 + \eta_3) = 3 \ln \frac{(x_2 + \frac{1}{4}\eta_2)(1 - x_2 + \frac{3}{4}\eta_2)}{(1 - x_2 - \frac{1}{4}\eta_2)(x_2 - \frac{3}{4}\eta_2)},$$

⋮

and from Eq. (2.4) the coupled set of equations

$$\begin{aligned} \frac{W^{(1)}}{kT}(6x_1 + 3x_2 - 12x_b) + \frac{3}{2kT} [W^{(1)} - (U_{BB}^{(1)} - U_{AA}^{(1)})] + \frac{6W^{(2)}}{kT}(x_2 - 2x_b) &+ \frac{3}{kT} [W^{(2)} - (U_{BB}^{(2)} - U_{AA}^{(2)})] \\ &= \frac{3}{2} \ln \frac{(x_b + \frac{1}{4}\eta_b)^3(x_b - \frac{3}{4}\eta_b)(1 - x_1 - \frac{1}{4}\eta_1)^3(1 - x_1 + \frac{3}{4}\eta_1)}{(1 - x_b - \frac{1}{4}\eta_b)^3(1 - x_b + \frac{3}{4}\eta_b)(x_1 + \frac{1}{4}\eta_1)^3(x_1 - \frac{3}{4}\eta_1)}, \end{aligned} \quad (2.7)$$

$$\frac{W^{(1)}}{kT}(6x_2 + 3x_1 + 3x_3 - 12x_b) + \frac{6W^{(2)}}{kT}(x_1 + x_2 - 2x_b) = \frac{3}{2} \ln \frac{(x_b + \frac{1}{4}\eta_b)^3(x_b - \frac{3}{4}\eta_b)(1 - x_2 - \frac{1}{4}\eta_2)^3(1 - x_2 + \frac{3}{4}\eta_2)}{(1 - x_b - \frac{1}{4}\eta_b)^3(1 - x_b + \frac{3}{4}\eta_b)(x_2 + \frac{1}{4}\eta_2)^3(x_2 - \frac{3}{4}\eta_2)},$$

⋮

These equations determine  $x_i$  and  $\eta_i$ . The energies of unmixing  $W^{(1)}$  and  $W^{(2)}$  which refer to nearest- and next-nearest-neighbor bonds are given by  $W^{(i)} = 2U_{AB}^{(i)} - U_{AA}^{(i)} - U_{BB}^{(i)}$ ,  $i = 1, 2$ . Note that if segregation is absent or neglected then all  $x_i = x_b = 0.75$  and Eqs. (2.6) simplify to

$$\begin{aligned} \frac{W^{(1)}}{kT}(\eta_1 + \frac{1}{2}\eta_2) - \frac{W^{(2)}}{kT}3\eta_2 &= 3 \ln \left( 1 + \frac{16\eta_1}{3(1 - \eta_1)^2} \right), \\ \frac{W^{(1)}}{kT}(\eta_2 + \frac{1}{2}\eta_1 + \frac{1}{2}\eta_3) - \frac{3W^{(2)}}{kT}(\eta_1 + \eta_3) &= 3 \ln \left( 1 + \frac{16\eta_2}{3(1 - \eta_2)^2} \right), \end{aligned} \quad (2.8)$$

### B. (100) surface

In the [100] direction there are two types of different planes. There are planes of type 1 with equal number of  $\alpha$  and  $\beta$  sites, such that  $N_{\alpha,i} = N_{\beta,i} = \frac{1}{2}N_i$ . The other planes of type 2 contain only  $\alpha$  sites. Thus, one can define order parameters

$$\begin{aligned} p_{\alpha,i}^A &= x_i + \frac{1}{2}\eta_i, \quad p_{\beta,i}^A = x_i - \frac{1}{2}\eta_i, \\ p_{\alpha,i}^B &= 1 - x_i - \frac{1}{2}\eta_i, \quad \text{and} \quad p_{\beta,i}^B = 1 - x_i + \frac{1}{2}\eta_i \end{aligned} \quad (2.9)$$

for the planes of type 1. For the planes of type 2 one has

$$p_{\alpha,i\pm 1}^A = x_{i\pm 1} \quad \text{and} \quad p_{\alpha,i\pm 1}^B = 1 - x_{i\pm 1}.$$

If one now subdivides the lattice into these planes parallel to the (100) surface, one has to allow in-

terchange of atoms between adjacent planes in the way to properly describe the order. That is, the concentrations  $x_1^b, x_2^b$  referring to the two kinds of planes are functions of the temperature. In the complete ordered case the concentrations will be  $x_1^b = \frac{1}{2}$  and  $x_2^b = 1$ , respectively, and in the disordered situation the concentrations will be equal to 0.75 everywhere. To calculate for the bulk  $x_1^b, x_2^b$ , and  $\eta_b$  as a function of  $T$  we use the equations

$$\frac{\partial F}{\partial x_1^b} = \frac{\partial F}{\partial x_2^b} = \frac{\partial F}{\partial \eta_b} = 0,$$

with

$$x_1^b + x_2^b = 2x_b.$$

The solution of these equations are shown in Fig. 2. This gives a linear dependence of the concentrations on  $\eta_b$ :

$$x_1^b = \frac{3}{4} - \frac{1}{4}\eta_b \quad \text{and} \quad x_2^b = \frac{3}{4} + \frac{1}{4}\eta_b.$$

In the case that the surface plane is of type 1 the equations determining  $\eta_{2i-1}$  and  $x_i$  are

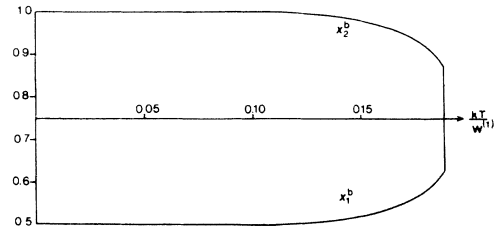


FIG. 2. Temperature dependence of the concentrations  $x_1^b$  and  $x_2^b$  referring to bulk (100) planes.  $W^{(1)}$  is the energy of unmixing due to nearest-neighbor bonds.

$$\begin{aligned}
\frac{4W^{(1)}}{kT} \eta_1 - \frac{2W^{(2)}}{kT} (4\eta_1 + \eta_3) &= \ln \frac{(\eta_1 + 2x_1)[2(1-x_1) + \eta_1]}{[2(1-x_1) - \eta_1](2x_1 - \eta_1)}, \\
\frac{4W^{(1)}}{kT} \eta_3 - \frac{2W^{(2)}}{kT} (4\eta_3 + \eta_1 + \eta_5) &= \ln \frac{(\eta_3 + 2x_3)[2(1-x_3) + \eta_3]}{[2(1-x_3) - \eta_3](2x_3 - \eta_3)}, \\
&\vdots \\
&\quad (2.10)
\end{aligned}$$

and

$$\begin{aligned}
\frac{8W^{(1)}}{kT} (x_1 + x_2 - x_1^b - 2x_2^b) + \frac{2W^{(2)}}{kT} (4x_1 + x_3 - 6x_1^b) \\
- \frac{4}{kT} (U_{BB}^{(1)} - U_{AA}^{(1)} - W^{(1)}) - \frac{1}{kT} (U_{BB}^{(2)} - U_{AA}^{(2)} - W^{(2)}) \\
= \ln \frac{4(x_1^b)^2 - \eta_b^2}{4(1-x_1^b)^2 - \eta_b^2} - \ln \frac{4x_1^2 - \eta_1}{4(1-x_1)^2 - \eta_1^2}, \\
\frac{8W^{(1)}}{kT} (x_2 + x_1 + x_3 - x_1^b - 2x_2^b) + \frac{2W^{(2)}}{kT} (4x_2 + x_4 - 6x_1^b) \\
- \frac{1}{kT} (U_{BB}^{(2)} - U_{AA}^{(2)} - W^{(2)}) \\
= \ln \frac{4(x_1^b)^2 - \eta_b^2}{4(1-x_1^b)^2 - \eta_b^2} - \ln \frac{x_2^2}{(1-x_2)^2}, \\
&\vdots \\
&\quad (2.11)
\end{aligned}$$

In the case where the surface plane is of type 2 the corresponding equations are

$$\begin{aligned}
\frac{4W^{(1)}}{kT} \eta_2 - \frac{2W^{(2)}}{kT} (4\eta_2 + \eta_4) &= \ln \frac{(\eta_2 + 2x_2)[2(1-x_2) + \eta_2]}{[2(1-x_2) - \eta_2](2x_2 - \eta_2)}, \\
\frac{4W^{(1)}}{kT} \eta_4 - \frac{2W^{(2)}}{kT} (4\eta_4 + \eta_2 + \eta_6) &= \ln \frac{(\eta_4 + 2x_4)[2(1-x_4) + \eta_4]}{[2(1-x_4) - \eta_4](2x_4 - \eta_4)}, \\
&\vdots \\
&\quad (2.12)
\end{aligned}$$

and

$$\begin{aligned}
\frac{8W^{(1)}}{kT} (x_1 + x_2 - x_1^b - 2x_2^b) + \frac{2W^{(2)}}{kT} (4x_1 + x_3 - 6x_1^b) \\
- \frac{4}{kT} (U_{BB}^{(1)} - U_{AA}^{(1)} - W^{(1)}) - \frac{1}{kT} (U_{BB}^{(2)} - U_{AA}^{(2)} - W^{(2)}) \\
= \ln \frac{4(x_1^b)^2 - \eta_b^2}{4(1-x_1^b)^2 - \eta_b^2} - \ln \frac{x_1^2}{(1-x_1)^2}, \\
\frac{8W^{(1)}}{kT} (x_2 + x_1 + x_3 - x_1^b - 2x_2^b) + \frac{2W^{(2)}}{kT} (4x_2 + x_4) \\
- \frac{1}{kT} (U_{BB}^{(2)} - U_{AA}^{(2)} - W^{(2)}) \\
= \ln \frac{4(x_1^b)^2 - \eta_b^2}{4(1-x_1^b)^2 - \eta_b^2} - \ln \frac{4x_2^2 - \eta_2^2}{4(1-x_2)^2 - \eta_2^2}, \\
&\vdots \\
&\quad (2.13)
\end{aligned}$$

### III. NUMERICAL RESULTS

In Fig. 3 we show for the bulk results for the order parameter  $\eta_b(T)$  in order to illustrate the

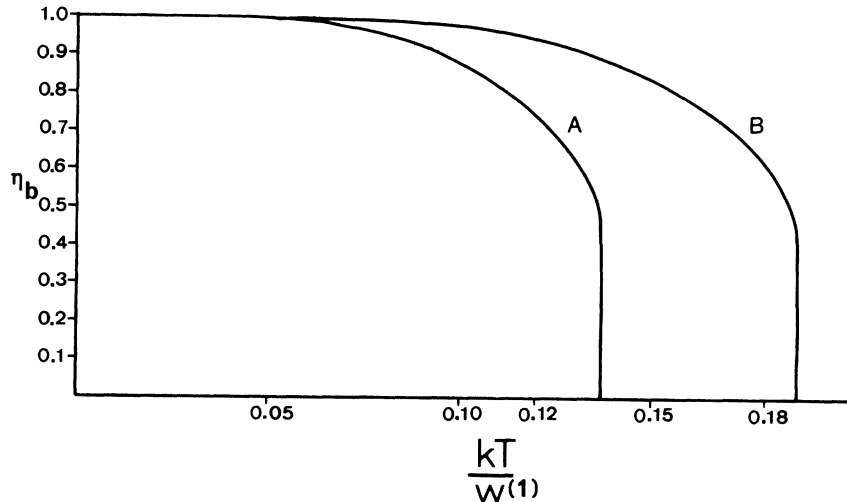


FIG. 3. Temperature dependence of the bulk order parameter. The curves A and B refer to  $W^{(2)} = 0$  and  $W^{(2)}/W^{(1)} = 0.125$ , respectively.

significance of taking into account next-nearest-neighbor bonds. Then, using Eqs. (2.6) and (2.7) we have calculated the temperature dependence of the order parameter in the vicinity of the (111)-surface. In Fig. 4 we show results obtained for the (111) surface for  $\eta_1$ ,  $\eta_2$ ,  $\eta_3$ , etc., in the absence of surface segregation. In order to study the effect of surface segregation on atomic ordering, we show in Fig. 5(a) results for  $\eta_i(T)$  obtained by taking into account the surface segregation shown in Fig. 5(b). Note, both surface segregation and atomic ordering have been calculated simultaneously from Eqs. (2.6) and (2.7). In order to study how the atomic ordering depends on the surface geometry, results are shown in Figs. 6 and 7 for the order parameter in the surface layers for the case of a (100) surface. The results refer to the different two possible surface configurations.

#### IV. DISCUSSION

In Fig. 7 the numerical results obtained for  $\eta_i(T)$  using the Bragg-Williams approximation are compared with experimental results<sup>1</sup> obtained for  $\text{Cu}_3\text{Au}$ . Note that from the experiment one obtains an average order parameter. In the experiment one observes an order parameter which is averaged with respect to different possible atomic configurations at the (100) surface and which is also averaged over the surface region which is proved by the experiment. Therefore, the results shown in Fig. 7 for the average order parameters  $\eta_{av}^{(2)} = \frac{1}{2}[\frac{1}{2}(\eta_1 + \eta_3) + \frac{1}{2}(\eta_2 + \eta_4)]$  and  $\eta_{av}^{(3)} = \frac{1}{2}[\frac{1}{3}(\eta_1 + \eta_3 + \eta_5) + \frac{1}{3}(\eta_2 + \eta_4 + \eta_6)]$  should be compared with the experimental results. It is interesting that  $\eta_{av}^{(3)}$  agrees better with the experiment than  $\eta_{av}^{(2)}$ . This might

indicate that the LEED experiment<sup>1</sup> probes a surface area which corresponds more to the spatial average yielding  $\eta_{av}^{(3)}$  than the one yielding  $\eta_{av}^{(2)}$ . As expected on physical grounds our numerical analysis yields that  $\eta_{av}^{(2)}$  and  $\eta_{av}^{(3)}$  increase for decreasing surface segregation. Therefore, the agreement with experimental results could be improved if values for the parameter ( $U_{AA} - U_{BB}$ ) are used which yield less segregation than was obtained in our calculation. Note, the previous Monte Carlo calculations of  $\eta_{av}^{(2)}$  assume no segregation. Also, it has been assumed in all our calculations that the bond energies do not change at the surface. It is of interest to study the validity of this assumption within a microscopic electronic theory. Clearly, if the bond energies are concentration dependent, then the surface will cause them to change. Finally, note that for an irregular surface one has to average the order parameter also over different surface configurations.

The theory presented could be easily extended by determining  $U$  within a microscopic electronic theory, for example, by using  $U = \sum_i U_i$  and  $U_i = \int_{-\infty}^{\infty} dE E N_i(E)$ , where  $N_i(E)$  is the electronic density of states referring to the  $i$ th layer parallel to the surface. However, as long as the unmixing energies  $W^{(1)}$  and  $W^{(2)}$  are only weakly concentration dependent, the Bragg-Williams approximation should be sufficient.

Note, we find that only the  $\eta_i$  for the first few atomic surface layers are strongly reduced. Comparing the results for  $\eta_i$  obtained at the (111) surface, see Figs. 4 and 5, with those at the (100) surface, see Figs. 6 and 7, one notes that the reduction of  $\eta_i(T)$  depends strongly on the surface geometry. The results shown in Figs. 5 and 6 indicate that surface segregation may have a strong

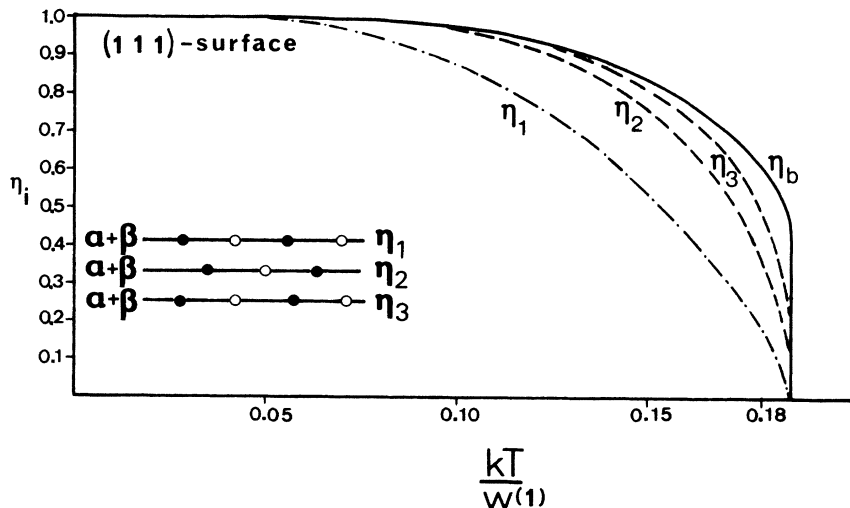


FIG. 4. Temperature dependence of the layer-dependent order parameters  $\eta_i$ , for the (111) surface. Surface segregation is neglected. As indicated by the inset, each plane parallel to the surface consists of  $\alpha$  and  $\beta$  sites and  $\eta_1$  refers to the surface plane,  $\eta_2$  to the second layer, etc., and  $\eta_b$  to the bulk.

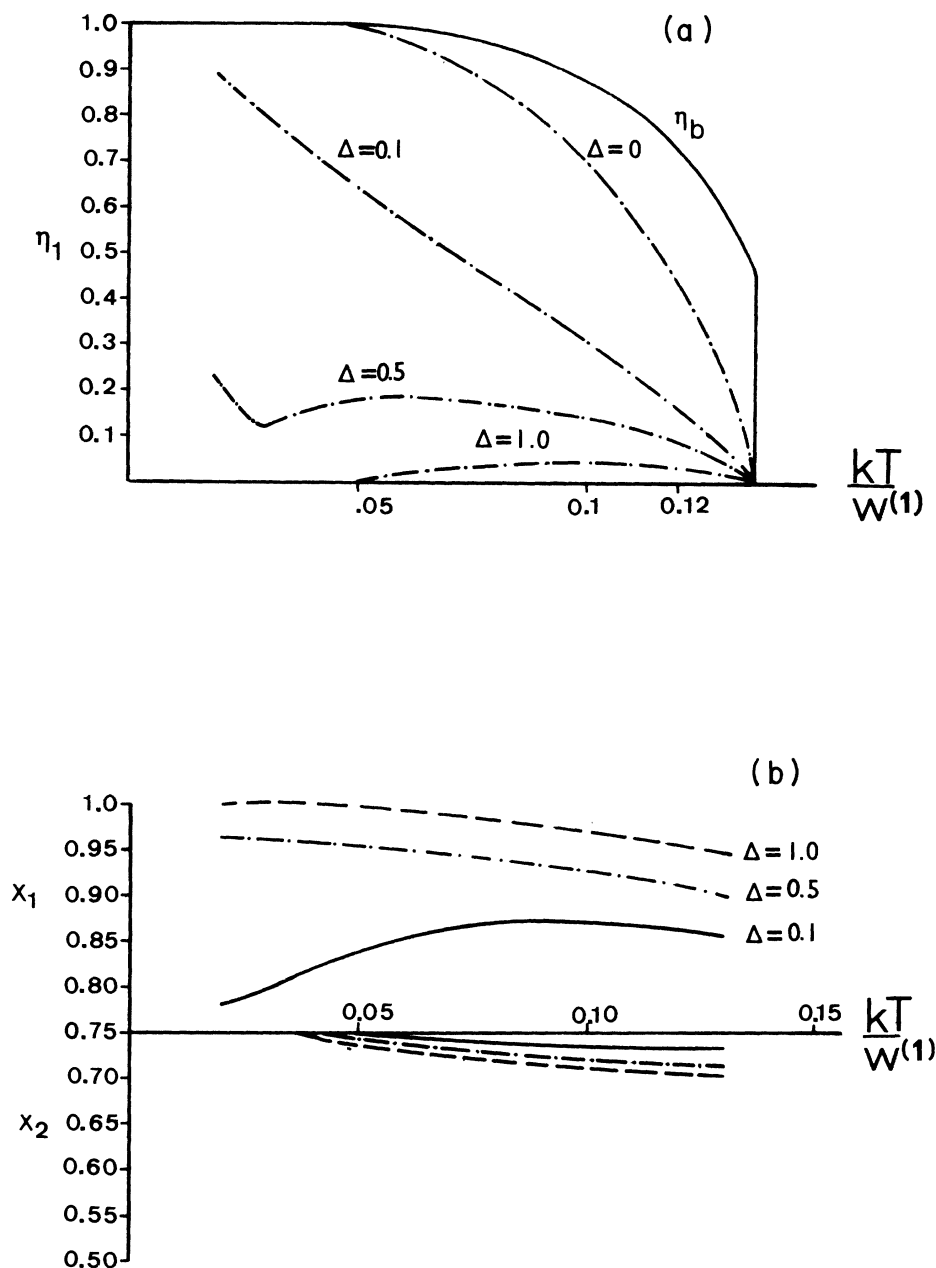


FIG. 5. (a) Temperature dependence of the order parameter  $\eta_1$  at the (111) surface, taking into account the segregation shown in (b) for different values  $\Delta \equiv (U_{BB}^{(1)} - U_{AA}^{(1)})/W^{(1)}$ . (b) Results for the temperature dependence of the surface segregation. The concentrations  $x_1$  and  $x_2$  refer to the first and second surface layer.

effect on atomic ordering. Note that at  $T_c$  all  $\eta_i$  disappear. In view of the fact that approximately  $T_c \propto x(1-x)$ , one might expect due to surface segregation ( $x_i \neq x_b$ ) that at the surface  $T_c \geq T_c^{\text{bulk}}$  depending on  $x \geq 0.5$ . However, if the surface segregation occurs over a distance  $d$  away from the surface, then for  $d < \xi_1(T)$  all  $\eta_i(T)$  disappear at the same temperature and hence  $T_c^{\text{surface}} = T_c^{\text{bulk}}$ .  $\xi_1(T)$  refers to the correlation length measuring atomic ordering in a direction perpendicular to

the surface. However, note for  $d \geq \xi_1(T)$  it seems possible that  $T_c^{\text{surface}} \neq T_c^{\text{bulk}}$ . This argument explains why due to surface segregation  $\eta_i(T) \rightarrow 0$  ( $i = 1, 2$ ) at temperatures below  $T_c$ , where  $\xi_1(T) \rightarrow 0$  (see the results shown in Fig. 5).

More local experiments would be desirable for a comparison with our numerical results for  $\eta_1(T)$ ,  $\eta_2(T)$ , etc., obtained for different surface geometries. In particular, it would be interesting to check experimentally our results

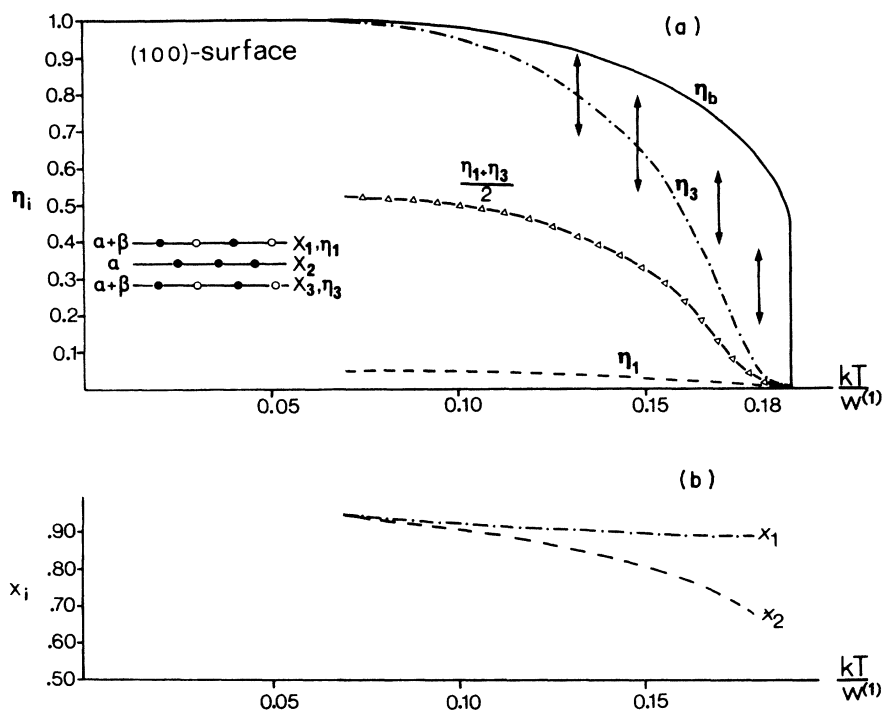


FIG. 6. (a) Temperature dependence of the order parameters  $\eta_1$ ,  $\eta_3$ , and  $\frac{1}{2}(\eta_1 + \eta_3)$  at the (100) surface. The inset schematically shows the surface configuration of type 1 which has been used (see text). The bars represent experimental results (Ref. 1). (b) Surface segregation vs temperature.

$$\eta_1(T) \xrightarrow{(T \rightarrow 0)} 0$$

(see Fig. 5) obtained in the presence of surface segregation. It would be interesting to study order-disorder transitions in alloys  $A_xB_{1-x}$  with  $x_b < 0.5$  and surface segregation such that at the surface  $x > x_b$ .

In the disordered case, the equations that determine the concentrations  $x_i$  reduce to the equations

for segregation in regular solutions.<sup>5,6</sup> Here we have assumed no surface relaxation, but since the effect of relaxation is to reduce the segregation, if the pair bonds at the surface are stronger,<sup>5</sup> we expect a less drastic reduction for the surface order parameters in that case.

Our results shown in Fig. 5 indicate that surface segregation and atomic ordering affect each other. We find that for  $A_3B$ -type alloys segregation always tries to destroy the atomic order, but also

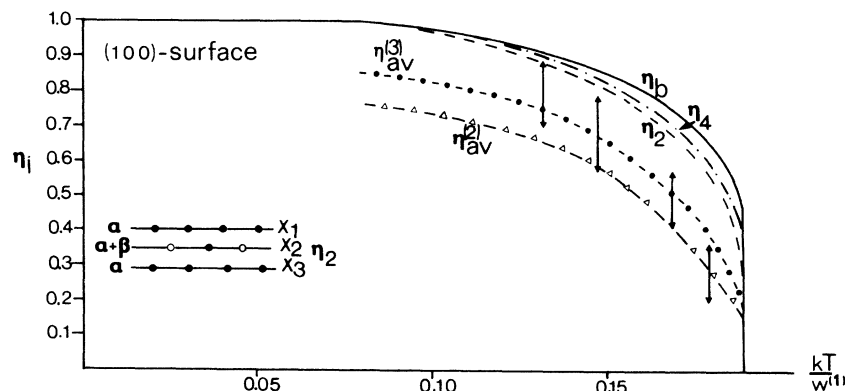


FIG. 7. Temperature dependence of the order parameters  $\eta_i$  at the (100) surface. As indicated by the inset, the surface configuration of type 2 has been assumed. Average order parameters

$$\eta_{av}^{(2)} = \frac{1}{2} \left[ \frac{1}{2}(\eta_1 + \eta_3) + \frac{1}{2}(\eta_2 + \eta_4) \right] \quad \text{and} \quad \eta_{av}^{(3)} = \frac{1}{2} \left[ \frac{1}{3}(\eta_1 + \eta_3 + \eta_5) + \frac{1}{3}(\eta_2 + \eta_4 + \eta_6) \right],$$

with respect to the two and three topmost  $\alpha + \beta$  layers for the two types of (100) surface configurations are shown. The experimental results (Ref. 1) are shown by bars.

that ordering can suppress segregation if the difference  $\Delta = (U_{BB}^{(1)} - U_{AA}^{(1)})/W^{(1)}$  is small (Fig. 5). Until now theories that describe surface enrichment in ordered alloys have assumed the same order at the surface and the bulk.<sup>7,8</sup>

Note, if  $x_i^s > x_b$  and if  $T_c(x)$  increases for increasing  $x$ , then  $\eta_i^{\text{surf}}(T) \geq \eta_b(T)$  at  $T < T_c$  may be possible.

It is of considerable interest to study the effect of the surface on the order-disorder transition by using a microscopic theory for the electronic structure at the surface. Thus, the dependence of order-disorder phenomena at the surface on the various electronic parameters, electron-charge transfer, chemisorbed atoms and molecules, etc., may be studied. In Appendix B we present such a microscopic theory for surface effects on order-disorder phenomena. In order to simplify the theory we consider a (100) surface of a simple cubic lattice.

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#### APPENDIX A: DETERMINATION OF THE INTERNAL ENERGY $U$

The internal energy is given by

$$U = \sum_{i=1}^N (U_i^{(1)} + U_i^{(2)}),$$

where

$$U_i^{(n)} = -(2/Z_n) [N_{AA}^{i,i(n)} U_{AA}^{i,i(n)} + \frac{1}{2} (N_{AA}^{i,i\pm 1(n)} U_{AA}^{i,i\pm 1(n)}) + N_{BB}^{i,i(n)} U_{BB}^{i,i(n)} + \frac{1}{2} (N_{BB}^{i,i\pm 1(n)} U_{BB}^{i,i\pm 1(n)}) + N_{AB}^{i,i(n)} U_{AB}^{i,i(n)} + \frac{1}{2} (N_{AB}^{i,i\pm 1(n)} U_{AB}^{i,i\pm 1(n)})].$$

Here,  $Z_1$  and  $Z_2$  are the number of nearest- and next-nearest neighbors,  $N_{AA}^{i,i(n)}$  are the number of A-A nearest- ( $n=1$ ) and next-nearest-neighbor atomic pairs ( $n=2$ ) in the  $i$ th layer with  $U_{AA}^{i,i(n)}$  bond energies. All the other quantities have a similar meaning.

Using Table I and the probabilities given in Eq. (2.5) we get for the (111) surface the expressions

$$N_{AA}^{1,1(1)} = \frac{3}{2} N_{\parallel} [(x_1 - \frac{3}{4}\eta_1)(x_1 + \frac{1}{4}\eta_1) + (x_1 + \frac{1}{4}\eta_1)^2],$$

$$N_{AA}^{1,2(1)} + N_{AA}^{2,1(1)} = \frac{3}{4} N_{\parallel} \{ (x_1 - \frac{3}{4}\eta_1)(x_2 + \frac{1}{4}\eta_2) + (x_1 + \frac{1}{4}\eta_1)[2(x_2 + \frac{1}{4}\eta_2) + (x_2 - \frac{3}{4}\eta_2)] \},$$

⋮

TABLE I. Number of nearest- and next-nearest neighbors for each  $\alpha$  and  $\beta$  site in the (111) planes. (a) Number of nearest-neighbor  $\alpha$  sites in the  $i$ th layer. (b) Number of nearest-neighbor  $\beta$  sites in the  $i$ th layer. (c) Number of nearest-neighbor  $\alpha$  sites in the  $(i \pm 1)$ th layer. (d) Number of nearest-neighbor  $\beta$  sites in the  $(i \pm 1)$ th layer. (e) Number of next-nearest-neighbor  $\alpha$  sites in the  $i$ th layer. (f) Number of next-nearest neighbor  $\beta$  sites in the  $i$ th layer. (g) Number of next-nearest-neighbor  $\alpha$  sites in the  $(i \pm 1)$ th layer. (h) Number of next-nearest-neighbor  $\beta$  sites in the  $(i \pm 1)$ th layer.

Site in the $i$ th layer	a	b	c	d	e	f	g	h
$\alpha$	4	2	2	1	0	0	3	0
$\beta$	6	0	3	0	0	0	0	3

$$N_{BB}^{1,1(1)} = \frac{3}{2} N_{\parallel} [(1 - x_1 + \frac{3}{4}\eta_1)(1 - x_1 - \frac{1}{4}\eta_1) + (1 - x_1 - \frac{1}{4}\eta_1)^2],$$

$$N_{BB}^{1,2(1)} + N_{BB}^{2,1(1)} = \frac{3}{4} N_{\parallel} \{ (1 - x_1 + \frac{3}{4}\eta_1)(1 - x_2 - \frac{1}{4}\eta_2) + (1 - x_1 - \frac{1}{4}\eta_1)[2(1 - x_2 - \frac{1}{4}\eta_2) + (1 - x_2 + \frac{3}{4}\eta_2)] \},$$

⋮

$$N_{AB}^{1,1(1)} = 3N_{\parallel} - N_{AA}^{1,1(1)} - N_{BB}^{1,1(1)},$$

$$N_{AB}^{1,2(1)} + N_{AB}^{2,1(1)} = \frac{3}{2} N_{\parallel} - (N_{AA}^{1,2(1)} + N_{AA}^{2,1(1)}) - (N_{BB}^{1,2(1)} + N_{BB}^{2,1(1)}),$$

⋮

and for next-nearest-neighbor atomic pairs,

$$N_{AA}^{1,1(2)} = 0,$$

$$N_{AA}^{1,2(2)} + N_{AA}^{2,1(2)} = \frac{3}{4} N_{\parallel} [(x_1 - \frac{3}{4}\eta_1)(x_2 - \frac{3}{4}\eta_2) + 3(x_1 + \frac{1}{4}\eta_1)(x_2 + \frac{1}{4}\eta_2)],$$

⋮

$$N_{BB}^{1,1(2)} = 0,$$

$$N_{BB}^{1,2(2)} + N_{BB}^{2,1(2)} = \frac{3}{4} N_{\parallel} [(1 - x_1 + \frac{3}{4}\eta_1)(1 - x_2 + \frac{3}{4}\eta_2) + 3(1 - x_1 - \frac{1}{4}\eta_1)(1 - x_2 - \frac{1}{4}\eta_2)],$$

⋮

$$N_{AB}^{1,1(2)} = 0,$$

$$N_{AB}^{1,2(2)} + N_{AB}^{2,1(2)} = \frac{3}{2} N_{\parallel} - (N_{AA}^{1,2(2)} + N_{AA}^{2,1(2)}) - (N_{BB}^{1,2(2)} + N_{BB}^{2,1(2)}),$$

⋮

In the (100) surface we obtain, using Table II and the Eqs. (2.9) for the surface configuration type



TABLE II. Number of nearest- and next-nearest neighbors for each  $\alpha$  and  $\beta$  site in the two types of (100) planes. Columns (a), (b), (c), (d), (e), and (f) have the same meaning as in Table I. (g) Number of next-nearest neighbor  $\alpha$  sites in the  $(i \pm 2)$ th layer. (h) Number of next-nearest-neighbor  $\beta$  sites in the  $(i \pm 2)$ th layer.

Site in the $i$ th layer	a	b	c	d	e	f	g	h
$\alpha$ type 1	0	4	4	0	4	0	1	0
$\alpha$ type 2	4	0	2	2	4	0	1	0
$\beta$	4	0	4	0	0	4	0	1

### 1, the expressions

$$N_{AA}^{1,1(1)} = 2N_{\parallel}(x_1 - \frac{1}{2}\eta_1)(x_1 + \frac{1}{2}\eta_1),$$

$$N_{AA}^{1,2(1)} + N_{AA}^{2,1(1)} = 4N_{\parallel}x_1x_2,$$

⋮

$$N_{BB}^{1,1(1)} = 2N_{\parallel}(1 - x_1 - \frac{1}{2}\eta_1)(1 - x_1 + \frac{1}{2}\eta_1),$$

$$N_{BB}^{1,2(1)} + N_{BB}^{2,1(1)} = 4N_{\parallel}(1 - x_1)(1 - x_2),$$

⋮

$$N_{AB}^{1,1(1)} = 2N_{\parallel} - N_{AA}^{1,1(1)} - N_{BB}^{1,1(1)},$$

$$N_{AB}^{1,2(1)} + N_{AB}^{2,1(1)} = 2N_{\parallel} - (N_{AA}^{1,2(1)} + N_{AA}^{2,1(1)}) - (N_{BB}^{1,2(1)} + N_{BB}^{2,1(1)}),$$

⋮

and for next-nearest-neighbor atomic pairs,

$$N_{AA}^{1,1(2)} = N_{\parallel}[(x_1 + \frac{1}{2}\eta_1)^2 + (x_1 - \frac{1}{2}\eta_1)^2],$$

$$N_{AA}^{1,3(2)} + N_{AA}^{3,1(2)} = \frac{1}{2}N_{\parallel}[(x_1 + \frac{1}{2}\eta_1)(x_3 + \frac{1}{2}\eta_3) + (x_1 - \frac{1}{2}\eta_1)(x_3 - \frac{1}{2}\eta_3)],$$

⋮

$$N_{BB}^{1,1(2)} = N_{\parallel}[(1 - x_1 + \frac{1}{2}\eta_1)^2 + (1 - x_1 - \frac{1}{2}\eta_1)^2],$$

$$N_{BB}^{1,3(2)} + N_{BB}^{3,1(2)} = \frac{1}{2}N_{\parallel}[(1 - x_1 + \frac{1}{2}\eta_1)(1 - x_3 + \frac{1}{2}\eta_3) + (1 - x_1 - \frac{1}{2}\eta_1)(1 - x_3 - \frac{1}{2}\eta_3)],$$

⋮

$$N_{AB}^{1,1(2)} = 2N_{\parallel} - N_{AA}^{1,1(2)} - N_{BB}^{1,1(2)},$$

$$N_{AB}^{1,3(2)} + N_{AB}^{3,1(2)} = \frac{1}{2}N_{\parallel} - (N_{AA}^{1,3(2)} + N_{AA}^{3,1(2)}) - (N_{BB}^{1,3(2)} + N_{BB}^{3,1(2)}),$$

⋮

It is easy to derive a similar set of expressions for the surface configuration of type 2.

### APPENDIX B: ELECTRONIC THEORY FOR THE ORDER-DISORDER TRANSITION AT THE SURFACE OF BINARY ALLOYS

Recently, several authors have described the order-disorder phase transition in the bulk medium using a band-model calculation. All these calculations have been done in the coherent-potential approximation.<sup>9-12</sup>

Here we present such a calculation for the order-disorder transition at the surface. A continued-fraction technique is used for determining the local electronic Green's functions on the surface of a semi-infinite crystal. We assume that only the first three layers near the surface are affected by the surface. We find that atomic ordering occurs at  $T_c$  in the bulk as well as at the surface.

Consider a binary alloy  $A_xB_{1-x}$  with  $N$  lattice points and assume that these lattice points can be subdivided into two sublattices  $\alpha$  and  $\beta$ , such that there are  $\frac{1}{2}N$  sites of type  $\alpha$  and  $\frac{1}{2}N$  sites of type  $\beta$ . Each site  $\alpha$  has  $z$  sites  $\beta$  as its nearest neighbors, and each site  $\beta$  has  $z$  sites  $\alpha$  as its nearest neighbors. We consider now the simple case of a simple cubic lattice and an alloy with concentration  $x = 0.5$ . If the number of  $A$  atoms on  $\alpha$  sites is denoted by  $\frac{1}{2}(1 + \eta)\frac{1}{2}N$ , then the order parameter  $\eta$  varies between 0 and 1. Since all atoms which are not on  $\alpha$  sites are on  $\beta$  sites and all sites are occupied by  $A$  or  $B$  atoms, we have the following distribution:

$$N_{\alpha}^A = \frac{1}{2}(1 + \eta)\frac{1}{2}N = N_{\beta}^B, \quad N_{\beta}^A = \frac{1}{2}(1 - \eta)\frac{1}{2}N = N_{\alpha}^B. \quad (B1)$$

If  $\eta = 1$  (the complete order case) all  $A$  atoms are on the  $\alpha$  sublattice and all  $B$  atoms are on the  $\beta$  sublattice. If  $\eta = 0$  (the complete disorder case), there are as many  $A$  atoms on  $\alpha$  sites as on  $\beta$  sites and the same holds for  $B$  atoms. Values of  $\eta$  between 0 and 1 correspond to intermediate degrees of order.

The electrons in the binary alloy are described by the tight-binding Hamiltonian

$$H = \sum_{\alpha} \epsilon_{\alpha} c_{\alpha}^{\dagger} c_{\alpha} + \sum_{\beta} \epsilon_{\beta} c_{\beta}^{\dagger} c_{\beta} + \sum_{\alpha \neq \beta} t c_{\alpha}^{\dagger} c_{\beta}. \quad (B2)$$

Here, the electronic energy levels of atoms sitting in the  $\alpha$  and  $\beta$  sublattices take the values  $\epsilon_A$  or  $\epsilon_B$  with probabilities

$$p_{\alpha}^A = \frac{1}{2}(1 + \eta), \quad p_{\beta}^B = \frac{1}{2}(1 - \eta)$$

and

$$(B3)$$

$$p_{\beta}^A = \frac{1}{2}(1 - \eta), \quad p_{\alpha}^B = \frac{1}{2}(1 + \eta),$$

respectively.  $c_{\alpha}^{\dagger}, c_{\beta}^{\dagger}, c_{\alpha}, c_{\beta}$  are the usual electron-

ic creation and annihilation operators referring to sites in the  $\alpha$  and  $\beta$  sublattices. The hopping integral  $t$  describes electronic transitions between sites in the  $\alpha$  and  $\beta$  sublattices. The average local electronic Green's function  $G_{\alpha\alpha}$  on sites in the  $\alpha$  sublattice is given by

$$G_{\alpha\alpha}(E, \eta) = p_{\alpha}^A / (E - \epsilon_A - \Delta_{\alpha}) + p_{\alpha}^B / (E - \epsilon_B - \Delta_{\alpha}) \quad (\text{B4})$$

Here,  $\Delta_{\alpha}$  is the electron self-energy resulting from the electron hopping processes starting and ending at the site  $i$  of the  $\alpha$  sublattice

$$\begin{aligned} \Delta_{\alpha} &= \sum_{\beta} \frac{t_{\alpha\beta} t_{\beta\alpha}}{E - \epsilon_{\beta} - \Delta_{\beta}^{\alpha}} + \dots \\ &= z t^2 \left( \frac{p_{\beta}^A}{E - \epsilon_A - \Delta_{\beta}^{\alpha}} + \frac{p_{\beta}^B}{E - \epsilon_B - \Delta_{\beta}^{\alpha}} \right) + \dots \end{aligned} \quad (\text{B5})$$

$$\begin{aligned} \Delta_{\beta}^{\alpha} &= (z-1)t^2 \left( \frac{p_{\alpha}^A}{E - \epsilon_A - (z-1)t^2 [p_{\beta}^A / (E - \epsilon_A - \Delta_{\beta}^{\alpha}) + p_{\beta}^B / (E - \epsilon_B - \Delta_{\beta}^{\alpha})]} \right. \\ &\quad \left. + \frac{p_{\alpha}^B}{E - \epsilon_B - (z-1)t^2 [p_{\beta}^A / (E - \epsilon_A - \Delta_{\beta}^{\alpha}) + p_{\beta}^B / (E - \epsilon_B - \Delta_{\beta}^{\alpha})]} \right). \end{aligned} \quad (\text{B8})$$

This equation can be rewritten as a fifth-order equation in  $\Delta_{\beta}^{\alpha}$  as a function of  $z$ ,  $\epsilon_A$ ,  $\epsilon_B$ ,  $\eta$ , and  $E$ .

The average local Green's function for the  $\beta$  sublattice is given by

$$G_{\beta\beta}(E, \eta) = \frac{p_{\beta}^A}{E - \epsilon_A - \Delta_{\beta}} + \frac{p_{\beta}^B}{E - \epsilon_B - \Delta_{\beta}}, \quad (\text{B9})$$

with

$$\Delta_{\beta} = z t^2 \left( \frac{p_{\alpha}^A}{E - \epsilon_A - \Delta_{\alpha}^{\beta}} + \frac{p_{\alpha}^B}{E - \epsilon_B - \Delta_{\alpha}^{\beta}} \right). \quad (\text{B10})$$

Then, the average local density of states is calculated from

$$N(E, \eta) = -(1/2\pi) \text{Im}[G_{\alpha\alpha}(E, \eta) + G_{\beta\beta}(E, \eta)]. \quad (\text{B11})$$

To calculate the order parameter  $\eta$  we minimize the free energy

$$F(\eta) = U(\eta) - TS(\eta), \quad (\text{B12})$$

with respect to  $\eta$ . Here the internal energy is given by

$$U(\eta) = \int_{-\infty}^{E_F} dE E N(E, \eta) \quad (\text{B13})$$

and the entropy is given by  $S(\eta) = S(0) + \Delta S$ ,

$$\Delta S = -k \left( \frac{1+\eta}{2} \ln \frac{1+\eta}{2} + \frac{1-\eta}{2} \ln \frac{1-\eta}{2} \right). \quad (\text{B14})$$

In order to apply this theory for studying surface effects, we assume that the surface affects only the first three layers near the surface. We intro-

In a similar way one finds approximately

$$\Delta_{\beta}^{\alpha} = (z-1)t^2 \left( \frac{p_{\alpha}^A}{E - \epsilon_A - \Delta_{\beta}^{\alpha}} + \frac{p_{\alpha}^B}{E - \epsilon_B - \Delta_{\beta}^{\alpha}} \right). \quad (\text{B6})$$

The continued fraction is approximated by

$$\Delta_{\alpha}^{\beta} = (z-1)t^2 \left( \frac{p_{\beta}^A}{E - \epsilon_A - \Delta_{\alpha}^{\beta}} + \frac{p_{\beta}^B}{E - \epsilon_B - \Delta_{\alpha}^{\beta}} \right). \quad (\text{B7})$$

Thus, we get for  $\Delta_{\beta}^{\alpha}$  the equation

duce then as before layer-dependent long-range order parameters  $\eta_i$  which describe the atomic order in the  $i$ th layer parallel to the surface.

The local Green's function depends then also on a layer index

$$G_{\alpha\alpha}^i(E) = \frac{p_A^{\alpha,i}}{E - \epsilon_{A_i} - \Delta_{\alpha}^{\alpha,i}} + \frac{p_B^{\alpha,i}}{E - \epsilon_{B_i} - \Delta_{\alpha}^{\alpha,i}},$$

where

$$\begin{aligned} \Delta_{\alpha}^{\alpha,i} &= z_0 t_{ii}^2 \left( \frac{p_A^{\beta i}}{E - \epsilon_{A_i} - \Delta_{\beta i}^{\alpha i}} + \frac{p_B^{\beta i}}{E - \epsilon_{B_i} - \Delta_{\beta i}^{\alpha i}} \right) \\ &\quad + \sum_{j=i\pm 1} t_{ij}^2 \left( \frac{p_A^{\beta j}}{E - \epsilon_{A_j} - \Delta_{\beta j}^{\alpha i}} + \frac{p_B^{\beta j}}{E - \epsilon_{B_j} - \Delta_{\beta j}^{\alpha i}} \right). \end{aligned} \quad (\text{B15})$$

Here,  $p_A^{\alpha i}$  and  $p_B^{\alpha i}$  are the probabilities to find an A or B atom in the  $i$ th layer of the  $\alpha$  sublattice, and are given by

$$p_A^{\alpha i} = \frac{1}{2}(1 + \eta_i), \quad p_B^{\alpha i} = \frac{1}{2}(1 - \eta_i). \quad (\text{B16})$$

$t_{ii}$  is the hopping integral between the atoms in the same layer and  $t_{i,i\pm 1}$  is the hopping integral between atoms in  $i$ th and  $(i\pm 1)$ th layers.  $z_0$  is the number of nearest-neighbor atoms in the  $i$ th layer and  $z_1$  is the number of nearest neighbors laying in the adjacent layer.  $\Delta_{\beta i}^{\alpha i}$  refers to the self-energy which results from electron hopping processes starting and ending in a site in the  $i$ th layer of the  $\beta$  sublattice and avoiding a site in the same layer of the  $\alpha$  sublattice.

Using the same technique as before, see Eqs.

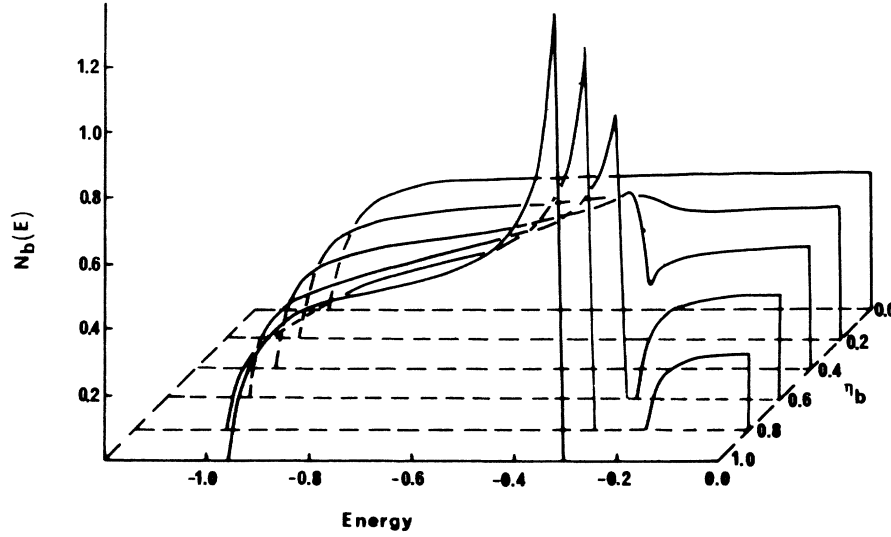


FIG. 8. Bulk local density of states  $N_b(E)$  for  $\delta = \epsilon_A - \epsilon_B = 0.6$  and for several values of  $\eta_b$ . We show only the lower-half of the band since  $N_b(E)$  is symmetric.

(B8), one obtains

$$\Delta_{B_i}^{\alpha i} = (z_0 - 1)t_{ii}^2 \left( \frac{\frac{1}{2}(1+\eta_i)}{E - \epsilon_{A_i} - \Delta_{\alpha i}^{B_i}} + \frac{\frac{1}{2}(1-\eta_i)}{E - \epsilon_{B_i} - \Delta_{\alpha i}^{B_i}} \right) + \sum_{j=i\pm 1} t_{ij}^2 \left( \frac{\frac{1}{2}(1+\eta_j)}{E - \epsilon_{A_j} - \Delta_{\alpha j}^{B_i}} + \frac{\frac{1}{2}(1-\eta_j)}{E - \epsilon_{B_j} - \Delta_{\alpha j}^{B_i}} \right), \quad (\text{B17})$$

$$\Delta_{B_{i+1}}^{\alpha i} = \dots,$$

$$\vdots \quad (\text{B18})$$

We may then proceed by writing

$$U = \sum_i U_i, \quad (\text{B19})$$

where  $U_i$  is given by the expression

$$U_i = \int_{-\infty}^{E_F} dE E N_i(E, \dots, \eta_{i-1}, \eta_i, \eta_{i+1}, \dots), \quad (\text{B20})$$

and where the electronic density of states  $N_i(E, \dots, \eta_{i-1}, \eta_i, \eta_{i+1}, \dots)$  referring to the  $i$ th layer is given by

$$N_i(E, \dots, \eta_{i-1}, \eta_i, \eta_{i+1}, \dots) = -(1/2\pi) \text{Im} [G_{\alpha\alpha}^i(E, \dots, \eta_{i-1}, \eta_i, \eta_{i+1}, \dots) + G_{\beta\beta}^i(E, \dots, \eta_{i-1}, \eta_i, \eta_{i+1}, \dots)].$$

Note, the energy  $U_i$  depends now approximately only on  $\eta_{i-1}$ ,  $\eta_i$ , and  $\eta_{i+1}$ . As before, the entropy is written in the form

$$\Delta S = \sum_i \Delta S_i,$$

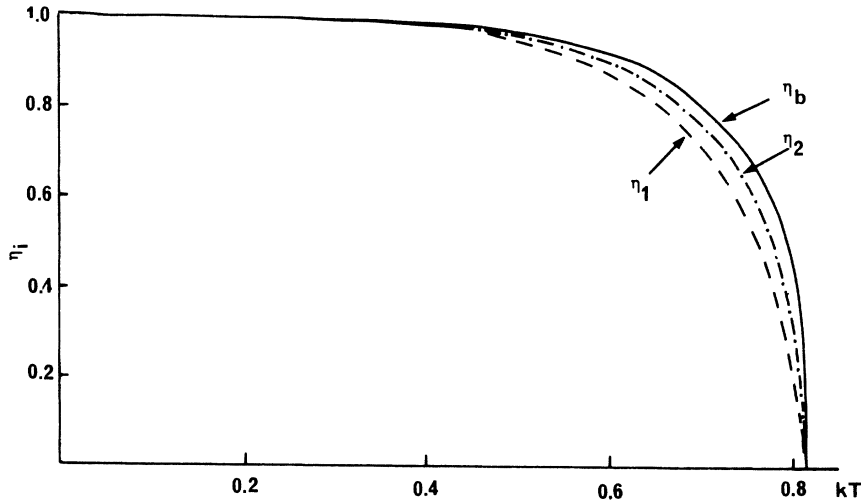


FIG. 9. Temperature dependence of the order parameters  $\eta_1$ ,  $\eta_2$ , and  $\eta_b$  using  $\delta = 0.6$  and for the hopping integrals  $t_{\text{surf}} = t_{\text{bulk}}$ .

where

$$\Delta S_i = -k \left( \frac{1+\eta_i}{2} \ln \frac{1+\eta_i}{2} + \frac{1-\eta_i}{2} \ln \frac{1-\eta_i}{2} \right).$$

In order to compare our simple theory with more elaborate theories,<sup>11</sup> we show in Fig. 8 results for the bulk local density of states as a function of the energy and the long-range order. Note, these results are in fair agreement with those shown by Plischke and Mattis<sup>11</sup> using a generalized form of the coherent-potential approximation. In Fig. 9 the results are shown for the order parameter  $\eta_i(T)$ . We see that the effect of the surface is not strong. However, this is only so because for a simple cubic lattice the coordination number is reduced only by one at the (100) surface. Also results for the average local densities of states in the first two layers are shown in Fig. 10.

It is of interest to expand the internal energy  $U_i$  and  $S_i$  near  $T_c$  as a function of the order parameters. One then obtains for the free energy the expression

$$\begin{aligned} F_i(E, \dots, \eta_{i-1}, \eta_i, \eta_{i+1}, \dots) \\ = F_i^0 + \frac{\partial F}{\partial \eta_i} \eta_i + \sum_{j=i\pm 1} \frac{\partial F}{\partial \eta_j} \eta_j \\ + \frac{\partial^2 F}{\partial \eta_i^2} \eta_i^2 + \sum_{j=i\pm 1} \frac{\partial^2 F}{\partial \eta_i \partial \eta_j} \eta_i \eta_j + \dots \end{aligned}$$

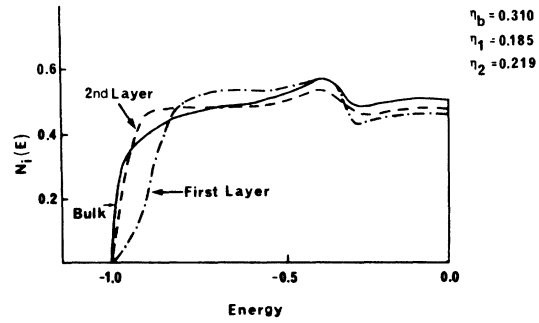


FIG. 10. Layer-dependent local density of states  $N_1(E)$ ,  $N_2(E)$ , and  $N_b(E)$  referring to the first, second, and bulk layer for the indicated set of  $\eta_1, \eta_2, \dots, \eta_b$  equilibrium values.

Note, the linear terms in  $\eta_i$  will disappear for  $i > 2$  ( $i = 2$  second layer) for symmetry reasons. However, for the two surface planes due to the broken symmetry these terms will remain and will try to reduce the order parameter to zero at the surface. From  $\partial F / \partial \eta_i = 0$  one finds thus a set of coupled Ginzburg-Landau-type equations determining  $\eta_1, \eta_2$ , etc.

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