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Electronic theory of binary alloys with face-centered-cubic crystal structure

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An electronic theory of binary alloys with face-centered-cubic crystal structure is presented. The close-packing effects of the fcc lattice are taken into account by calculating the local density of states in the Husimi model. It is shown that this formalism can be reduced to expressions similar to those in the Bethe-lattice method. By this method a much richer structure is obtained in the local density of states than that obtained by the Bethe-lattice method or in the coherent-potential approximation. Results for random alloys are presented.

I. INTRODUCTION

The cluster-Bethe-lattice method has been successfully applied to study properties of alloys with short- and long-range order.[1,2] This method consists of substituting the infinite periodic lattice for an infinite system of connected atoms, with the same coordination number z as the lattice under consideration, but without closed rings of bonds. This lattice has the property that the one-particle Green's functions at a given site can be expressed in terms of the Green's functions at the preceding site in the lattice.[3] In this way, it is possible to write analytical expressions for the Green's functions in terms of transfer functions.

The Bethe-lattice approximation is exact in one-dimensional systems, it is good in low-coordination three-dimensional lattices, and it is bad in closed-packed structures. For example, the threefold rings in fcc lattices originate pure antibonding states that in the Bethe lattice cannot exist.

A better approximation to treat fcc structures is the Husimi model.[4] It consists of an infinite system of connected tetrahedra (see Fig. 1), that describe the local topology in a more exact way. It has been shown[5] that in one-component systems, this approximation gives the exact position of the high-energy band edge and that its solution can be obtained by defining a single transfer function.

Studies of the order-disorder transformation in ordering alloys have shown that in order to obtain the observed first-order phase transition, it is necessary to treat the entropy in the tetrahedron approximation.[2,6,7] Lower approximations, like the Bethe or Bragg-Williams approximations, give a second-order phase transition in the ordering $A_{0.5}B_{0.5}$ alloy. Examples of this kind of alloys are (Ref. 8) CuAu, FeNi, etc. Thus, by calculating the electronic structure in the Husimi model, one would be able to obtain an expression for the free energy where the internal energy and the entropy are calculated within the same approximation.

Here we extend the Husimi model to study the electronic structure of binary alloys with fcc crystal structure. In Sec. II we outline our theory and in Sec. III we present and discuss our results.

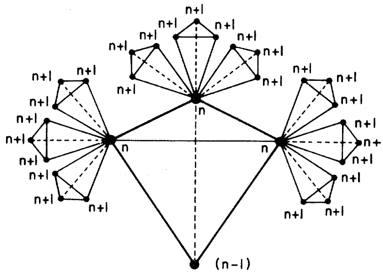


FIG. 1. Portion of the Husimi model, with tetrahedrons as units. The symbol n denotes the level in the hierarchy.

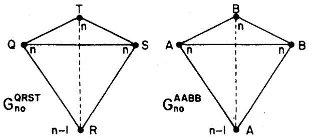


FIG. 2. Configuration showing the notation used in the Green's functions. A specific example is given.

II. THEORY

The binary alloy A_xB_y $(y=1-x)$ is represented by the tight-binding Hamiltonian

$$H=\sum_{i}\epsilon_i c_i^{\dagger} c_i+\sum_{j\neq i} t_{ij} c_i^{\dagger} c_j + \text{H.c.}, \tag{2.1}$$

where i and j denote lattice sites, ϵ_i and t_{ij} $(i,j=A,B)$ are the on-site and hopping matrix elements of the Hamiltonian, and $c_i^{\dagger}$ and c_i are the creation and annihilation operators.

The Dyson equation for this Hamiltonian is given by

$$(\omega-\epsilon_i)G_{ij}(\omega)=\delta_{ij}+\sum_{l\neq i} t_{il}G_{lj}(\omega)\ . \tag{2.2}$$

We define Green's functions for each site in the tetrahedron and for each type of atom. As it is illustrated in Fig. 2, each Green's function depends on its nearest neighbors and has four upper and two lower indices,

$$G_{n0}^{QRST}\ ,$$

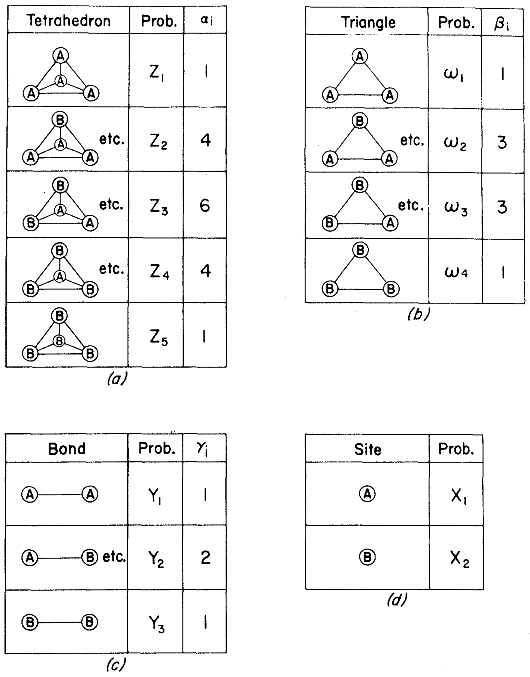
where Q denotes the type of atom (A or B) on the site under consideration on the nth level, R denotes the type of atom in which the studied tetrahedron is rooted, i.e., the parent atom in the $(n-1)$th level, and S and T denote the atoms at the same level of Q, i.e., nth level. To simplify our notation we omit upper indices S and T if they are of the same type of R. Illustrations are given in Fig. 2.

In general there are 5, 4, 3, and 2 different tetrahedron, triangle, pair, and site configurations,[9] respectively (Fig. 3). We denote by z_i, w_i, y_i, and x_i the corresponding probabilities and by α_i, β_i, and δ_i the multiplicity of the tetrahedron, triangle, and pair configurations. The probabilities are subject to the normalization conditions

$$\sum_{i=1}^{5}\alpha_i z_i=\sum_{i=1}^{4}\beta_i w_i=\sum_{i=1}^{3}\delta_i y_i=\sum_{i=1}^{2}x_i=1\ . \tag{2.3}$$

The probabilities w_i, y_i, and x_i can be written in terms of the z_i.

Now by using Eq. (2.2) we obtain for the Green's functions the expressions



Tetrahedron	Prob.	α_i
Ⓐ Ⓐ Ⓐ Ⓐ	Z_1	1
Ⓑ Ⓐ Ⓐ Ⓐ etc.	Z_2	4
Ⓑ Ⓐ Ⓑ Ⓐ etc.	Z_3	6
Ⓑ Ⓐ Ⓑ Ⓑ etc.	Z_4	4
Ⓑ Ⓑ Ⓑ Ⓑ	Z_5	1

(a)

Triangle	Prob.	β_i
Ⓐ Ⓐ Ⓐ	ω_1	1
Ⓑ Ⓐ Ⓐ etc.	ω_2	3
Ⓑ Ⓑ Ⓐ etc.	ω_3	3
Ⓑ Ⓑ Ⓑ	ω_4	1

(b)

Bond	Prob.	γ_i
Ⓐ—Ⓐ	Y_1	1
Ⓐ—Ⓑ etc.	Y_2	2
Ⓑ—Ⓑ	Y_3	1

(c)

Site	Prob.
Ⓐ	X_1
Ⓑ	X_2

(d)

FIG. 3. Different tetrahedron, triangle, pair, and single site configurations. The multiplicity is also shown.

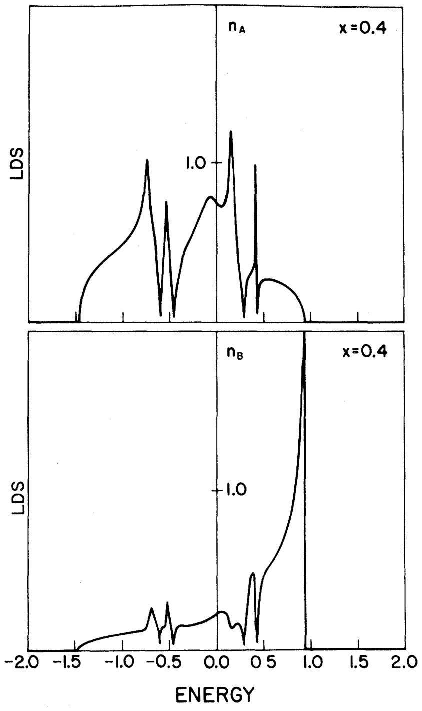


FIG. 4. Local density of electronic states n_A and n_B at A and B sites, respectively, for a random alloy with $x=0.4$ and $\epsilon_A-\epsilon_B=0.75$.

$$(\omega-\epsilon_A)G_{00}^{A}=1+12F(1)$$

and (2.4)

$$(\omega-\epsilon_B)G_{00}^{B}=1+12H(1)\ ,$$

depending if at the zeroth site there is an A or B atom and where the functions $F(n)$ and $H(n)$ are defined by

$$F(n)=t_1(w_1^1G_{n0}^{AA}+2w_2^1G_{n0}^{AAB}+w_3^1G_{n0}^{AABB})+t_2(w_2^1G_{n0}^{BA}+2w_3^1G_{n0}^{BAB}+w_4^1G_{n0}^{BABB}) \tag{2.5}$$

and

$$H(n)=t_2(w_2^2G_{n0}^{ABAA}+2w_3^2G_{n0}^{ABA}+w_4^2G_{n0}^{AB})+t_3(w_3^2G_{n0}^{BBAA}+2w_4^2G_{n0}^{BBA}+w_5^2G_{n0}^{BB})\ . \tag{2.6}$$

In Eqs. (2.5) and (2.6) $t_1=t_{AA}$, $t_2=t_{AB}$, $t_3=t_{BB}$, and w_i^j are the conditioned tetrahedron probabilities,

$$w_i^j\equiv\frac{z_i}{x_j}\ . \tag{2.7}$$

At level n, and if the parent atom is an A atom, the Green's functions can be of the following six different types:

$$\begin{aligned}
(\omega-\epsilon_A)G_{n0}^{AA}&=t_1G_{n-1,0}^{A}+2t_1G_{n0}^{AA}+9F(n+1)\ ,\\
(\omega-\epsilon_A)G_{n0}^{AAB}&=t_1G_{n-1,0}^{A}+t_1G_{n0}^{AAB}\\
&\quad+t_2G_{n0}^{BA}+9F(n+1)\ ,\\
(\omega-\epsilon_A)G_{n0}^{AABB}&=t_1G_{n-1,0}^{A}+2t_2G_{n0}^{BAB}+9F(n+1)\ ,\\
(\omega-\epsilon_B)G_{n0}^{BA}&=t_2G_{n-1,0}^{A}+2t_2G_{n,0}^{AAB}+9H(n+1)\ ,\\
(\omega-\epsilon_B)G_{n0}^{BAB}&=t_2G_{n-1,0}^{A}+t_3G_{n0}^{BAB}\\
&\quad+t_2G_{n0}^{AABB}+9H(n+1)\ ,\\
(\omega-\epsilon_B)G_{n0}^{BABB}&=t_2G_{n-1,0}^{A}+2t_3G_{n0}^{BABB}+9H(n+1)\ .
\end{aligned} \tag{2.8}$$

This set of equations can be written in terms of G_{n0}^{AA} and G_{n0}^{BABB},

$$\begin{aligned}
G_{n0}^{AAB}&=\frac{(\omega-\epsilon_A-2t_1)(\omega-\epsilon_B)}{(\omega-\epsilon_A-t_1)(\omega-\epsilon_B)-2t_2^2}G_{n0}^{AA}\\
&\quad+\frac{t_2(\omega-\epsilon_B-2t_3)}{(\omega-\epsilon_A-t_1)(\omega-\epsilon_B)-2t_2^2}G_{n0}^{BABB}\ ,\\
G_{n0}^{AABB}&=\frac{(\omega-\epsilon_A-2t_1)(\omega-\epsilon_B-t_3)}{(\omega-\epsilon_A)(\omega-\epsilon_B-t_3)-2t_2^2}G_{n0}^{AA}\\
&\quad+\frac{2t_2(\omega-\epsilon_B-2t_3)}{(\omega-\epsilon_A)(\omega-\epsilon_B-t_3)-2t_2^2}G_{n0}^{BABB}\ ,\\
G_{n0}^{BA}&=\frac{2t_2(\omega-\epsilon_A-2t_1)}{(\omega-\epsilon_A-t_1)(\omega-\epsilon_B)-2t_2^2}G_{n0}^{AA}\\
&\quad+\frac{(\omega-\epsilon_A-t_1)(\omega-\epsilon_B-2t_3)}{(\omega-\epsilon_A-t_1)(\omega-\epsilon_B)-2t_2^2}G_{n0}^{BABB}\ ,\\
G_{n0}^{BAB}&=\frac{t_2(\omega-\epsilon_A-2t_1)}{(\omega-\epsilon_A)(\omega-\epsilon_B-t_3)-2t_2^2}G_{n0}^{AA}\\
&\quad+\frac{(\omega-\epsilon_A)(\omega-\epsilon_B-2t_3)}{(\omega-\epsilon_A)(\omega-\epsilon_B-t_3)-2t_2^2}G_{n0}^{BABB}\ .
\end{aligned} \tag{2.9}$$

Similar expressions can be written for cases where the parent atom is of type B. In this case all the Green's functions can be written in terms of G_{n0}^{ABAA} and G_{n0}^{BB}. Then, we write Eqs. (2.4) in terms of the four independent Green's functions,

$$\begin{aligned}
(\omega-\epsilon_A)G_{00}^{A}&=1+12(g_{11}G_{10}^{AA}+g_{12}G_{10}^{BABB})\ ,\\
(\omega-\epsilon_B)G_{00}^{B}&=1+12(g_{21}G_{10}^{ABAA}+g_{22}G_{10}^{BB})\ ,
\end{aligned} \tag{2.10}$$

and

$$\begin{aligned}
(\omega-\epsilon_A-2t_1)G_{10}^{AA}&=t_1G_{00}^{A}+9(g_{11}G_{20}^{AA}+g_{12}G_{20}^{BABB})\ ,\\
(\omega-\epsilon_B-2t_3)G_{10}^{BABB}&=t_2G_{00}^{A}+9(g_{21}G_{20}^{ABAA}+g_{22}G_{20}^{BB})\ ,\\
(\omega-\epsilon_A-2t_1)G_{10}^{ABAA}&=t_2G_{00}^{B}+9(g_{11}G_{20}^{AA}+g_{12}G_{20}^{BABB})\ ,\\
(\omega-\epsilon_B-2t_3)G_{10}^{BB}&=t_3G_{00}^{B}+9(g_{21}G_{20}^{ABAA}+g_{22}G_{20}^{BB})\ .
\end{aligned} \tag{2.11}$$

In Eqs. (2.10) and (2.11),

$$\begin{aligned}
g_{11}&=w_1^1t_1+(A-2t_1)\left[\frac{2w_2^1}{D_1}(Bt_1+t_2^2)+\frac{w_3^1}{D_2}(Bt_1-t_1t_3+2t_2^2)\right]\ ,\\
g_{12}&=t_2\left[w_4^1+(B-2t_3)(A+t_1)\left[\frac{w_2^1}{D_1}+\frac{2w_3^1}{D_2}\right]\right]\ ,\\
g_{21}&=t_2\left[w_2^2+(A-2t_1)(B+t_3)\left[\frac{2w_3^2}{D_1}+\frac{w_4^2}{D_2}\right]\right]\ ,\\
g_{22}&=w_5^2t_3+(B-2t_3)\left[\frac{w_3^2}{D_1}(At_3-t_1t_3+2t_2^2)+\frac{2w_4^2}{D_2}(At_3+t_2^2)\right]\ ,
\end{aligned} \tag{2.12}$$

and

$$A=\omega-\epsilon_A,\quad B=\omega-\epsilon_B\ , \tag{2.13}$$
$$D_1=(A-t_1)B-2t_2^2,\quad D_2=(B-t_3)A-2t_2^2\ .$$

The set of equations (2.11) is similar to the equations contained in the Bethe-lattice method,[2] where now the coefficients g_{ij} depend on the probabilities, hopping terms, and energies. In analogy to that method we close the set of equations (2.11) by defining the four transfer functions

$$\gamma_1\equiv G^{AA}_{n+1,0}/G^{A}_{n0},\quad \gamma_2\equiv G^{ABAA}_{n+1,0}/G^{B}_{n,0}\ ,$$
$$\gamma_3\equiv G^{BABB}_{n+1,0}/G^{A}_{n,0},\quad \gamma_4\equiv G^{BB}_{n+1,0}/G^{B}_{n,0}\ . \tag{2.14}$$

We obtain then the set of coupled equations

$$9g_{11}\gamma_1^2+9g_{12}\gamma_1\gamma_3-(\omega-\epsilon_A-2t_1)\gamma_1+t_1=0\ ,$$
$$9g_{11}\gamma_1\gamma_2+9g_{12}\gamma_2\gamma_3-(\omega-\epsilon_A-2t_1)\gamma_2+t_2=0\ ,$$
$$9g_{21}\gamma_2\gamma_3+9g_{22}\gamma_3\gamma_4-(\omega-\epsilon_B-2t_3)\gamma_3+t_2=0\ ,$$
$$9g_{22}\gamma_4^2+9g_{21}\gamma_2\gamma_4-(\omega-\epsilon_B-2t_3)\gamma_4+t_3=0\ . \tag{2.15}$$

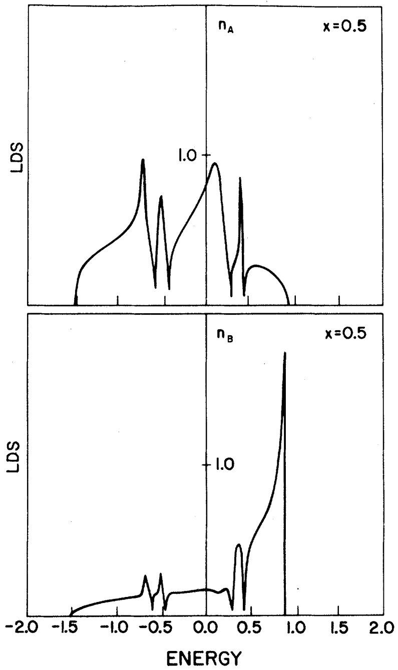


FIG. 5. Local density of electronic states n_A and n_B at A and B sites, respectively, for a random alloy with $x=0.5$ and $\epsilon_A-\epsilon_B=0.75$.

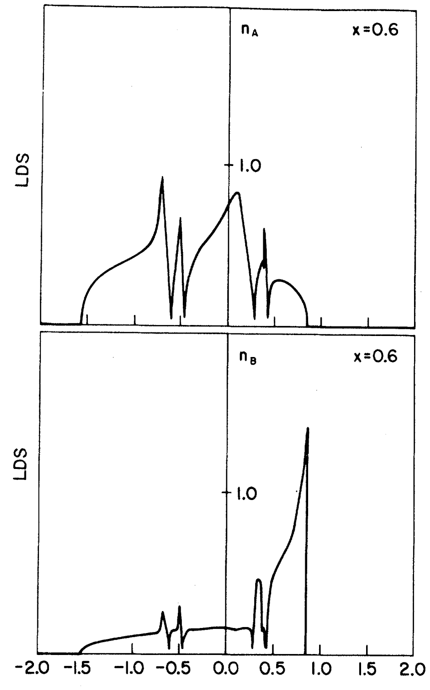


FIG. 6. Local density of electronic states n_A and n_B at A and B sites, respectively, for a random alloy with $x=0.6$ and $\epsilon_A-\epsilon_B=0.75$.

III. RESULTS AND DISCUSSION

In the completely disordered alloy, the probabilities w_i^j take the values

$$w_1^1=w_2^2=(x_1)^3,\quad w_2^1=w_3^2=(x_1)^2x_2\ ,$$
$$w_3^1=w_4^2=x_1(x_2)^2,\quad w_4^1=w_5^2=(x_2)^3\ , \tag{3.1}$$

where x_1 is the average concentration of element A and $x_2=1-x_1$. Under these circumstances and assuming only diagonal disorder, i.e., $t_1=t_2=t_3=t$, we obtain from Eqs. (2.15) that $\gamma_2=\gamma_1$ and $\gamma_3=\gamma_4$. The values for γ_1 and γ_4 are given by the solution of a third-order equation. The Green's functions (2.10) are then given in terms of γ_1 and γ_4 by

$$G^{A}_{00}=[\omega-\epsilon_A-12(g_{11}\gamma_1+g_{12}\gamma_4)]^{-1}\ ,$$
$$G^{B}_{00}=[\omega-\epsilon_B-12(g_{21}\gamma_1+g_{22}\gamma_4)]^{-1}\ . \tag{3.2}$$

In Figs. 4–6 we present the results for the local density of states (LDS)

$$n_i(\omega)=-\frac{1}{\pi}\mathrm{Im}G^{i}_{00}(\omega),\quad i=A,B \tag{3.3}$$

for concentrations $x=0.4$, 0.5, and 0.6. Here we took $\epsilon_B=-\epsilon_A=0.375$ and the energy is measured in units of half of the bandwidth of the pure elements ($t=\frac{1}{6}$).

As it is shown in these figures, the LDS are rich in structure, showing contributions coming from specific tetrahedron configurations like *AAAA*, *AAAB*, etc. We observe also that the discontinuity at high energies present in the pure *B* system does not disappear under alloying. This is not the case for the local density of states on atoms of type *A*. Here we have taken only diagonal disorder. The introduction of different hopping integrals would change only the bandwidths.

It is worth noting that short- and long-range order can be incorporated in a natural way. Thus this makes the theory most suitable to study order-disorder transformations. In conclusion, we have presented a theory for binary alloys with fcc crystal structure in which short- and long-range-order effects can be better accounted than in the previously used Bethe-lattice method.

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