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Effect of Local Order on Energy Bands in Binary Alloys

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Equations are developed giving the dependence of the energy band shape on the state of local and long-range order in an alloy. The approximation used is the "empty-lattice virtual crystal" model, in which a free electron gas is perturbed by a fluctuating potential of zero average value. The energy correction is expressed in terms of the nearest-neighbor order parameter α and long-range parameter λ; this is done with the aid of a qualitative formula giving nonnearest-neighbor parameters as functions of α. The result is evaluated numerically, and it is shown how the band bottom gets squeezed out into a long tail as α proceeds from the perfect short-range order → random → clustered cases. The effect of long-range order is discussed and the conclusions are compared with those of a previous tight-binding calculation.

I. INTRODUCTION

THE change in energy band shape caused by variation in local order can have considerable influence on the physical properties of alloys. In a previous paper[1] the author discussed this problem in tight-binding approximation, in connection with the effect of order on paramagnetic susceptibility. The present work treats the opposite, weak-binding case, and uses a perturbation approach.

The earliest investigations of this question were confined to the random (zero local order) state. James and Ginzbarg[2] and Landauer and Helland[3] employed computers to obtain energy levels for a random one-dimensional alloy, while Parmenter[4] solved the random three-dimensional case by perturbation methods. The results showed that the effect of complete disorder was to produce a "tailing off" of energy levels into previously forbidden regions. Later, Flinn[5] demonstrated that certain second-order perturbation sums could be expressed in terms of the Cowley order parameters,[6] and thus obtained the total electronic energy of an alloy as a function of local order. Recently, Corciovei and Grecu[7,8] have considered the dependence of energy bands on long-range order, and, to a certain extent, the following discussion is complementary to their work.

Our calculation follows that of Flinn[5] up to the point where an expression is obtained for the correction to the single-particle energy levels at the bottom of the band, due to the state of order. At this stage, we introduce an "order function" which is evaluated by assuming a simple formula giving all distant Cowley parameters[6] in terms of α the nearest-neighbor parameter, and λ the long-range order parameter. This yields the energy $\epsilon(k)$, and the state density $g(\epsilon)$, as functions of α and λ. It is shown how increasing local disorder squeezes the band bottom out into a long rat-tail. The long-range order in the case considered has much less effect. The conclusions obtained are essentially a generalization of the results of Parmenter.[4]

II. HAMILTONIAN AND PERTURBATION

Since we are interested only in qualitative results, it will be adequate for our purposes to assume a simple cubic lattice, of edge length L, volume V, spacing d, density ρ, and containing N atoms. The fractions of A and B atoms are m_A, m_B, respectively, and we assume that the one-electron potentials on both types of atoms are proportional to the space function, $U(\mathbf{r})$. Then the one-electron Hamiltonian is

$$\mathcal{H}=\nabla^2+D\sum\nolimits_{\tau}U(\mathbf{r}-\boldsymbol{\tau})+\sum\nolimits_{\tau}C(\boldsymbol{\tau})U(\mathbf{r}-\boldsymbol{\tau}),\tag{1}$$

where

$$\begin{aligned}C(\boldsymbol{\tau})&=-m_B\quad\text{if}\quad \boldsymbol{\tau}\text{ at }A\text{-atom},\\&=+m_A\quad\text{if}\quad \boldsymbol{\tau}\text{ at }B\text{-atom},\end{aligned}\tag{2}$$

and the units are atomic. The term in D is an average potential and is perfectly periodic, while the last term is the fluctuating perturbation due to the disorder. The C's have been chosen so that

$$\sum\nolimits_{\tau}C(\boldsymbol{\tau})=0.\tag{3}$$

As Flinn[5] points out, if there is long-range order, then $C(\boldsymbol{\tau})$ has a periodic component, while for local order, $C(\boldsymbol{\tau})$ will have a nonrandom number of sign changes as $\boldsymbol{\tau}$ traverses the crystal.

We take $\mathcal{H}_0=\nabla^2$ as the unperturbed part of the Hamiltonian, with solutions

$$\epsilon^0(\mathbf{k})=k^2;\quad \psi_{\mathbf{k}}^0=V^{-\frac{1}{2}}e^{i\mathbf{k}\cdot\mathbf{r}}.\tag{4}$$

(Note: Hall[9] has shown that it is also feasible to take $\nabla^2+D\sum_{\tau}$ as the unperturbed Hamiltonian in such calculations.) Then, to second order,

$$\epsilon(\mathbf{k})=k^2+\langle\mathbf{k}|V_p+V_f|\mathbf{k}\rangle+\sum_{\mathbf{k}'\neq\mathbf{k}}\frac{|\langle\mathbf{k}|V_p+V_f|\mathbf{k}'\rangle|^2}{k^2-(k')^2},\tag{5}$$

where

$$V_p=D\sum\nolimits_{\tau}U(\mathbf{r}-\boldsymbol{\tau});\quad V_f=\sum\nolimits_{\tau}C(\boldsymbol{\tau})U(\mathbf{r}-\boldsymbol{\tau}).$$

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[1] R. D. Mattuck, J. Phys. Chem. Solids (to be published).

[2] H. M. James and A. S. Ginzbarg, J. Phys. Chem. **57**, 840 (1953).

[3] R. Landauer and J. C. Helland, J. Chem. Phys. **22**, 1655 (1954).

[4] R. H. Parmenter, Phys. Rev. **97**, 587 (1955).

[5] P. A. Flinn, Phys. Rev. **104**, 350 (1956).

[6] J. M. Cowley, Phys. Rev. **77**, 669 (1950).

[7] A. Corciovei and D. Grecu, Rev. phys. Acad. rep. populaire Roumaine **5**, 157 (1960).

[8] A. Corciovei and D. Grecu, Acta Phys. Polon. **20**, 197 (1961).

[9] G. L. Hall, Phys. Rev. **116**, 604 (1959).

The various terms may be evaluated using

$$\langle\mathbf{k}|V_p|\mathbf{k}'\rangle = DV^{-1}\sum_{\tau}\exp(i\mathbf{K}\cdot\boldsymbol{\tau})F(\mathbf{K}) = D\rho\delta_{\mathbf{K},\mathbf{K}_0}F(\mathbf{K}),$$

where

$$\rho = N/V, \quad \mathbf{K} = \mathbf{k}-\mathbf{k}', \quad \mathbf{K}_0 = 2\pi d^{-1}(n_x,n_y,n_z),$$

$$n_i = 0, \pm1, \cdots, \quad F(\mathbf{K}) = \int \exp(i\mathbf{K}\cdot\mathbf{r})U(\mathbf{r})d^3r, \quad (6)$$

and

$$\langle\mathbf{k}|V_f|\mathbf{k}'\rangle = V^{-1}\sum\nolimits_\tau C(\boldsymbol{\tau})\exp(i\mathbf{K}\cdot\boldsymbol{\tau})F(\mathbf{K}). \quad (7)$$

Substituting Eqs. (6) and (7) into Eq. (5), we find

$$\epsilon(\mathbf{k}) = k^2 + D^2\rho^2 \sum_{\mathbf{K}_0\neq0} \frac{|F(\mathbf{K}_0)|^2}{2\mathbf{k}\cdot\mathbf{K}_0 - K_0{}^2} + \frac{1}{V^2}\sum_{\mathbf{K}\neq0}\frac{|F(\mathbf{K})|^2}{2\mathbf{k}\cdot\mathbf{K}-K^2}$$
$$\times\{\sum_{\mu,\tau} C(\boldsymbol{\mu})C(\boldsymbol{\tau})\exp[i\mathbf{K}\cdot(\boldsymbol{\mu}-\boldsymbol{\tau})]\}. \quad (8)$$

We have dropped the first-order term since it is $\mathbf{k}$ independent and note that the cross-product terms like $\langle\mathbf{k}|V_p|\mathbf{k}'\rangle\langle\mathbf{k}'|V_f|\mathbf{k}\rangle$ have vanished because of the $\delta_{\mathbf{k},\mathbf{k}_0}$ factor in $\langle\mathbf{k}|V_p|\mathbf{k}'\rangle$ and the fact that $\sum_\tau C(\boldsymbol{\tau})=0$ [Eq. (3)]. Thus, the correction is broken into two parts: The D^2 term which is the standard result for a periodic lattice, with Brillouin zones given by $2\mathbf{k}\cdot\mathbf{K}_0 = \mathbf{K}_0{}^2$, and the last term which is the additional piece due to atomic disorder.

The D^2 term in Eq. (8) renders this equation invalid in the neighborhood of the Brillouin zone boundaries. To avoid this complication, we drop this term, thus obtaining the "empty lattice virtual crystal" approximation of Parmenter.[4] As he points out, since electrons at the bottom of higher bands behave as free electrons of altered effective mass, we may expect that our solution will give a qualitative picture of the influence of order on the band bottom in the more realistic filled-lattice case.

Finally, we introduce the "order function"

$$\begin{aligned} O(\mathbf{K}) &= \sum\nolimits_{\mu,\tau} C(\boldsymbol{\mu})C(\boldsymbol{\tau})\exp[i\mathbf{K}\cdot(\boldsymbol{\mu}-\boldsymbol{\tau})] \\ &= \sum\nolimits_\rho \exp(i\mathbf{K}\cdot\boldsymbol{\rho})[\sum\nolimits_\tau C(\boldsymbol{\rho}+\boldsymbol{\tau})C(\boldsymbol{\tau})], \end{aligned} \quad (9)$$

where

$$\boldsymbol{\rho} = \boldsymbol{\mu}-\boldsymbol{\tau},$$

and in the $\boldsymbol{\tau}$ summation, the limits of $\boldsymbol{\tau}$ depend on $\boldsymbol{\rho}$ as follows:

If $\rho_i>0$, then $0\leqslant\tau_i\leqslant(L-\rho_i)$;
if $\rho_i=0$, then $0\leqslant\tau_i\leqslant L$;
if $\rho_i<0$, then $|\rho_i|\leqslant\tau_i\leqslant L$, $i=x, y, z$. (9a)

We may then write $\epsilon(\mathbf{k})$ in the empty lattice model as

$$\epsilon(\mathbf{k}) = k^2 + \sum_{\mathbf{K}\neq0}\frac{|F(\mathbf{K})|^2}{2\mathbf{k}\cdot\mathbf{K}-K^2}O(\mathbf{K}). \quad (10)$$

[Note: The perturbation theory is invalid in the neighborhood of $\mathbf{K}$ such that $2\mathbf{k}\cdot\mathbf{K}-K^2=0$. However, as we shall see in Sec. IV, this singularity is only logarithmic, so the sum (integral) over $\mathbf{K}$ is convergent, and the qualitative properties of the solution are not disturbed. It should be mentioned, however, that the use of second-order perturbation theory in this sort of calculation has never been rigorously justified.]

III. THE ORDER FUNCTION

In the order function [Eq. (9)], the $\boldsymbol{\tau}$ sum may be rewritten in a form allowing introduction of the Cowley[6] order parameters. We first note that, assuming $\boldsymbol{\rho}$ is given, the number of terms in the $\boldsymbol{\tau}$ sum is

$$N(\boldsymbol{\rho}) = \prod_{i=x,y,z}(M-|n_i|), \quad (11)$$

where M = number of atoms on each crystal edge, $n_i=\rho_i d^{-1}$, and we have used Eq. (9a). Suppose $N_{AA}(\boldsymbol{\rho})$ of these $N(\boldsymbol{\rho})$ terms have an A atom on both $\boldsymbol{\tau}$ and $\boldsymbol{\tau}+\boldsymbol{\rho}$; then, using Eq. (2), the sum over just these will yield $N_{AA}(\boldsymbol{\rho})m_B{}^2$. Similarly, with $N_{AB}(\boldsymbol{\rho})$ cases of A on $\boldsymbol{\tau}$, B on $\boldsymbol{\tau}+\boldsymbol{\rho}$, etc., we find (assuming $N_{BA}=N_{AB}$) that

$$\begin{aligned} \sum\nolimits_\tau C(\boldsymbol{\rho}+\boldsymbol{\tau})C(\boldsymbol{\tau}) = N_{AA}(\boldsymbol{\rho})m_B{}^2 + N_{BB}(\boldsymbol{\rho})m_A{}^2 \\ -2N_{AB}(\boldsymbol{\rho})m_Am_B. \end{aligned} \quad (12)$$

The N_{XY}'s may be written in terms of $P(\boldsymbol{\tau};X)$, the probability of finding an X atom on site $\boldsymbol{\tau}$, and $P(\boldsymbol{\rho};X|Y)$, the probability that we will find an X on $\boldsymbol{\rho}+\boldsymbol{\tau}$, given a Y on $\boldsymbol{\tau}$, as follows:

$$\begin{aligned} N_{AA}(\boldsymbol{\rho}) &= N(\boldsymbol{\rho})P(\boldsymbol{\tau};A)P(\boldsymbol{\rho};A|A); \\ N_{AB}(\boldsymbol{\rho}) &= N(\boldsymbol{\rho})P(\boldsymbol{\tau};B)P(\boldsymbol{\tau};A|B), \end{aligned} \quad (13)$$

etc. The conditional probabilities are expressed directly in terms of the Cowley order parameters, $\alpha(\boldsymbol{\rho})$, defined by

$$P(\boldsymbol{\rho};A|B) = m_A[1-\alpha(\boldsymbol{\rho})]. \quad (14)$$

Thus

$$\begin{aligned} P(\boldsymbol{\rho};B|A) &= m_B[1-\alpha(\boldsymbol{\rho})], \\ P(\boldsymbol{\rho};A|A) &= 1-m_B[1-\alpha(\boldsymbol{\rho})], \\ P(\boldsymbol{\rho};B|B) &= 1-m_A[1-\alpha(\boldsymbol{\rho})], \\ P(\tau;A) = m_A&, \quad P(\tau;B)=m_B. \end{aligned} \quad (15)$$

Substituting Eqs. (15), (14), and (13) in Eq. (12) we find

$$\sum\nolimits_\tau C(\boldsymbol{\rho}+\boldsymbol{\tau})C(\boldsymbol{\tau}) = N(\boldsymbol{\rho})m_Am_B\alpha(\boldsymbol{\rho}), \quad (16)$$

which differs from Flinn's result[5] in that he has neglected the $\boldsymbol{\rho}$ dependence of N. Thus, the order function may be written

$$O(\mathbf{K},\cdots\alpha(\boldsymbol{\rho})\cdots) = m_Am_B \sum_{\substack{n_x,\,n_y,\,n_z\\=-M+1}}^{+M-1}\alpha(n_x,n_y,n_z)$$
$$\times\prod_{i=x,y,z}(M-|n_i|)e^{idK_in_i}. \quad (17)$$

To proceed further, we need an explicit expression for $\alpha(\mathbf{n})$. This will be determined by the nature of the interatomic forces and will be temperature dependent. Nevertheless, for qualitative purposes, we may choose a simple form for $\alpha(\mathbf{n})$ in the following fashion.

If there is no long-range order present, $\alpha(\mathbf{n}) \to 0$ as $|\mathbf{n}| \to \infty$, while, if there is long-range order, $\alpha(\mathbf{n}) \to \alpha_L$(finite) as $|\mathbf{n}| \to \infty$. Thus, $\alpha(\mathbf{n})$ may be broken up into

$$\alpha(\mathbf{n}) = \alpha'(\mathbf{n}) + \alpha_L,$$

where

$$\lim_{|\mathbf{n}|\to\infty} \alpha'(\mathbf{n}) = 0. \qquad (18)$$

We shall first obtain an expression for α_L in terms of the long-range parameter λ and then a crude formula for $\alpha'(\mathbf{n})$ in terms of the nearest-neighbor parameter α.

A. Long-Range Cowley Parameter

We take as a basis a two-sublattice crystal, with alternating a and b sites properly occupied by A and B atoms, respectively. Let r_a, r_b be the fraction of a, b sites actually occupied by A's, B's. Then the long-range order parameter λ is the average of λ for the two sublattices,

$$\lambda = \frac{1}{2}\left[\frac{r_a - m_A}{1 - m_A} + \frac{r_b - m_B}{1 - m_B}\right], \qquad (19)$$

from which

$$r_a = 2m_A m_B \lambda + m_A, \quad r_b = 2m_A m_B \lambda + m_B. \qquad (20)$$

Suppose $\boldsymbol{\rho}$ is such that $\boldsymbol{\tau}$, $\boldsymbol{\tau}+\boldsymbol{\rho}$ lie on the same sublattice (Cowley "even" case). Then we may have the given B in $P(\boldsymbol{\rho}; A|B)$ [see Eq. (14)] on an a site or a b site. In these two cases,

$$\begin{aligned} &P(A|B \text{ on } a) = P(A \text{ on } a) = r_a = m_A(1 + 2m_B\lambda), \\ &P(A|B \text{ on } b) = P(A \text{ on } b) = 1 - r_b = m_A(1 - 2m_B\lambda), \end{aligned} \qquad (21)$$

so that $\alpha_a = -2m_B\lambda$ and $\alpha_b = +2m_B\lambda$. The weighted average of α is

$$\alpha(\text{even}) = P(B \text{ on } a)\alpha_a + P(B \text{ on } b)\alpha_b = 4m_A m_B \lambda^2. \qquad (22)$$

Similarly,

$$\alpha(\text{odd}) = -4m_A m_B \lambda^2, \qquad (23)$$

where "odd" means $\boldsymbol{\tau}$, $\boldsymbol{\tau}+\boldsymbol{\rho}$ always lie on different sublattices. In general, we find the result

$$\alpha_L = 4m_A m_B \lambda^2 (-1)^{n_x + n_y + n_z}. \qquad (24)$$

[Note: Eq. (24) is not true for $\mathbf{n}=0$. In this case, Eqs. (14) and (18) demand that $\alpha_0 = \alpha_0' + \alpha_L = 1$. Since later in Eq. (29) we use $\alpha_0' = 1$, we may set $\alpha_L = 0$ for $\mathbf{n}=0$; this choice has no effect on any of the results to be obtained.]

B. Local Cowley Order Parameters

Consider the one-dimensional case first. Given a B atom at the origin 0 the probability of an A atom on site n is

$$\begin{aligned} P(A_n|B_0) &= P(A_n, B_0)P^{-1}(B_0) \\ &= P^{-1}(B_0)[P(A_n, A_{n-1}, B_0) + P(A_n, B_{n-1}, B_0)] \\ &= [P(A_n|A_{n-1}, B_0)P(A_{n-1}|B_0) \\ &\quad + P(A_n|B_{n-1}, B_0)P(B_{n-1}|B_0)], \end{aligned} \qquad (25)$$

from standard probability theory. We now assume that

$$P(A_n|X_{n-1}, B_0) \approx P(A_n|X_{n-1}), \qquad (26)$$

i.e., that, if we are given *both* a nearest-neighbor and an arbitrary configuration of more distant atoms, the nearest neighbor alone determines the probability. Thus,

$$\begin{aligned} P(A_n|B_0) &= P(A_n|A_{n-1})P(A_{n-1}|B_0) \\ &\quad + P(A_n|B_{n-1})P(B_{n-1}|B_0). \end{aligned} \qquad (27)$$

Using Eqs. (14), (15), and (27), we find

$$P(n; A|B) = P(A_n|B_0) = m_A[1 - (\alpha_1')(\alpha_{n-1}')], \qquad (28)$$

from which $\alpha_n' = \alpha_1' \alpha_{n-1}'$, so that

$$\alpha_n' = \alpha^{|n|}, \qquad (29)$$

where we write α for α_1' and $|n|$ since α_n' must be independent of the sign of n. Thus, in this simple case, all higher order Cowley parameters are determined by α the nearest-neighbor parameter. In turn, α itself is determined physically by nearest-neighbor interaction energy and temperature.

In the three-dimensional case, the above argument is not valid. There have been some calculations of higher order α's, notably those of Cowley,[6] who found α for the first five shells of neighbors in Cu_3Au, and Fosdick,[10] Flinn and McManus,[11] who did Monte Carlo calculations of α_1 and α_2. Since we are interested only in qualitative results, it will be sufficient if we simply choose a function for $\alpha'(\mathbf{n})$ which is mathematically tractable and physically not too unreasonable. An obvious choice is the generalization of Eq. (29):

$$\alpha'(n_x, n_y, n_z) = \alpha^{|n_x| + |n_y| + |n_z|}. \qquad (30)$$

Of course, in contrast to the true Cowley $\alpha(\mathbf{n})$, this function is anisotropic, being constant on the surface of a regular octahedron surrounding the origin. However, for qualitative purposes, we assume that Eq. (30) is adequate. [Note, using Eq. (14), that $\alpha > 0$, $\alpha < 0$ represent clustering order and short-range order, respectively.]

C. Expression for Order Function

Substituting the sum of Eqs. (30) and (24) into Eq. (17), we obtain

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[10] L. D. Fosdick, Phys. Rev. **116**, 565 (1959).

[11] P. A. Flinn and G. M. McManus, Phys. Rev. **124**, 54 (1961).

$$O(\mathbf{K},\alpha,\lambda)=4m_A{}^2m_B{}^2\lambda^2\prod_{i=x,y,z}\sum_{n_i=-M+1}^{+M-1}(M-|n_i|)\times(-1)^{|n_i|}e^{idK_in_i}+m_Am_B\times\prod_{i=x,y,z}\sum_{n_i=-M+1}^{+M-1}(M-|n_i|)\alpha^{|n_i|}e^{idK_in_i}. \quad (31)$$

The n_i sum involving α yields

$$\Phi(K_i,\alpha)=\sum_{n_i=-M+1}^{+M-1}(M-|n_i|)\alpha^{|n_i|}e^{iK_idn_i}=M+M\left[\frac{\beta-\beta^M}{1-\beta}+\text{c.c.}\right]-\left[\frac{\beta+(M-1)\beta^M-(M-1)\beta^{M-1}-\beta^M}{(1-\beta)^2}+\text{c.c.}\right],$$

where

$$\beta=\alpha e^{iK_id}. \quad (32)$$

The case for $\alpha=-1$ [first term in Eq. (31)] gives

$$\Phi(K_i,-1)=M^2\delta_{K_i,K_{ai}},$$

where

$$K_{ai}=\pi d^{-1}(2m_i+1),\quad m_i=0,\pm1,\cdots. \quad (33)$$

Thus, the complete order function may be written

$$O(\mathbf{K},\alpha,\lambda)=O_{\text{long-range}}(\mathbf{K},\lambda)+O_{\text{local}}(\mathbf{K},\alpha),$$

where

$$O_{\text{long-range}}(\mathbf{K},\lambda)=4m_A{}^2m_B{}^2\lambda^2N^2\prod_{i=x,y,z}\delta_{K_i,K_{ai}}, \quad (34)$$

$$O_{\text{local}}(\mathbf{K},\alpha)=m_Am_B\prod_{i=x,y,z}\Phi(K_i,\alpha) \quad (35)$$

[see Eq. (32).]

If α is not too close to ±1, Eq. (35) may be simplified. In Eq. (32), if we set $\beta=1-\Delta$ and if $\Delta\gg M^{-1}$, then it is easily shown that $M\beta/(1-\beta)+\text{c.c.}$ is much larger than the sum of the other terms. Under this condition we find

$$O_{\text{local}}(\mathbf{K},\alpha)=Nm_Am_B\prod_{i=x,y,z}\left[\frac{1-\alpha^2}{1+\alpha^2-2\alpha\cos(K_id)}\right] \quad (36)$$

if $(1-|\alpha|)\gg N^{-\frac{1}{3}}$.

IV. EFFECT OF ORDER ON ENERGY LEVELS AND DENSITY OF STATES

The general expression for the corrected energy levels in the $\alpha\neq\pm1$ case is obtained from Eqs. (35), (36), (9), and (10) and is

$$\epsilon(\mathbf{k})=k^2+4m_A{}^2m_B{}^2\lambda^2\rho^2\sum_{\mathbf{K}_a}\frac{|F(\mathbf{K}_a)|^2}{2\mathbf{k}\cdot\mathbf{K}_a-K_a{}^2}+\frac{N}{V^2}m_Am_B\sum_{\mathbf{K}}\frac{|F(\mathbf{K})|^2}{2\mathbf{k}\cdot\mathbf{K}-K^2}\times\prod_{i=x,y,z}\left[\frac{1-\alpha^2}{1+\alpha^2-2\alpha\cos(K_id)}\right], \quad (37)$$

with $\mathbf{K}_a$ defined as in Eq. (33).

We see immediately that the effect of the long-range term is to introduce Brillouin zone edges, hence energy gaps, at $\mathbf{k}$ values satisfying $2\mathbf{k}\cdot\mathbf{K}_a=K_a{}^2$. These zone edges are at values intermediate to those of the D^2 term in Eq. (8), and are the same as those for the well-known case of perfect long-range order. The new gaps vanish when $\lambda\rightarrow0$ in a manner which has been discussed by Corciovei and Grecu.[7,8] Here we shall only be interested in the behavior of this term for small $\mathbf{k}$.

In order to evaluate Eq. (37), we need an explicit expression for $F(\mathbf{K})$ as defined in Eq. (6). We make the usual assumption that $U(\mathbf{r})$ is given by the shielded Coulomb potential,

$$U(\mathbf{r})=Ar^{-1}e^{-ar}, \quad (38)$$

so that[5]

$$F(\mathbf{K})=A\int e^{i\mathbf{K}\cdot\mathbf{r}}e^{-ar}r^{-1}d^3r=4\pi A(a^2+K^2)^{-1}. \quad (39)$$

(Note that, in atomic units, $A=2Z$, where $Z=$ effective charge.)

For numerical estimates, we use the following, all in atomic units:

$$\begin{aligned}&d=4,\quad A=2,\quad m_A=1/2,\\&a=1,\quad P=1/d^3=1/64,\quad m_B=1/2.\end{aligned} \quad (40)$$

These values apply to a 50–50 Cu–Ni alloy. The a value was estimated roughly from Mott and Jones,[12] Eq. (85), applied to the holes in the Cu–Ni 3d band.

The λ^2 term in Eq. (37) may be crudely evaluated for low $\mathbf{k}$, by first restricting the sum to the first eight $\mathbf{K}_a$ values [because of the rapid drop-off of $F(\mathbf{K})$], and then expanding in powers of $\mathbf{k}\cdot\mathbf{K}_a$. This yields

$$\epsilon_{\text{long-range}}(k)=\frac{-512m_A{}^2m_B{}^2\lambda^2\rho^2\pi^2A^2}{(3\pi^2/d^2)(a^2+3\pi^2/d^2)^2}\left(1+\frac{4d^2k^2}{3\pi^2}\right)=-\lambda^2(2.05\times10^{-2})(1+2.16k^2). \quad (41)$$

We now consider the local order part of Eq. (37). Substituting Eq. (39) in Eq. (37), and converting from a sum to an integral, noting that there are $V(2\pi)^{-3}$ points per unit volume in $\mathbf{K}$-space, we find

$$\epsilon_{\text{local}}(k,\alpha)=2\rho m_Am_BA^2I(\mathbf{k},\alpha),$$

where

$$I(\mathbf{k},\alpha)=\frac{1}{\pi}\int d^3K\left\{\frac{1}{(a^2+K^2)^2(2\mathbf{k}\cdot\mathbf{K}-K^2)}\times\prod_{i=x,y,z}\left(\frac{1-\alpha^2}{1+\alpha^2-2\alpha\cos(K_id)}\right)\right\}. \quad (42)$$

We shall look at several special cases of Eq. (42), namely, (1) $\alpha=0$, (2) $0<\alpha<1$, (3) $\alpha<0$. In each case, the integral is evaluated numerically and substituted in

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[12] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Clarendon Press, Oxford, England, 1936), p. 87.

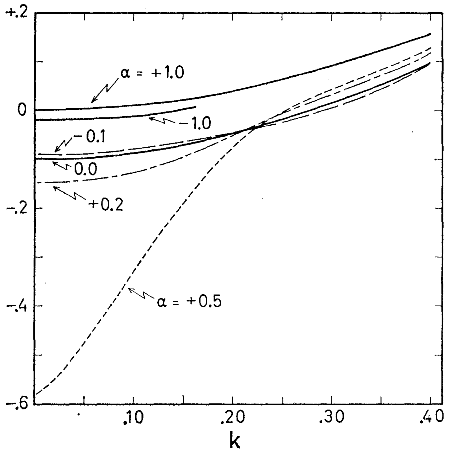

FIG. 1. Energy ϵ vs absolute value of momentum k for a free-electron gas perturbed by a fluctuating potential with specified local order parameter α. Units are atomic.

Eq. (37), assuming $\lambda=0$. The results, showing the local order corrections to $\epsilon(k)=k^2$, appear in Fig. 1. The cases $\alpha=\pm1$, also in Fig. 1, are considered separately.

Case 1. $\alpha=0$ (Complete Disorder)

Here, $I(\mathbf{k},\alpha)$ is

$$I(k,0)=\frac{1}{\pi}\int d^3K\left\{\frac{1}{(a^2+K^2)^2}\frac{1}{(2\mathbf{k}\cdot\mathbf{K}-K^2)}\right\} \tag{43}$$

$$=\frac{1}{k}\int_0^\infty dK\left\{\frac{K}{(a^2+K^2)^2}\ln\left|\frac{K-2k}{K+2k}\right|\right\}, \tag{44}$$

after integration over angle. This has been evaluated by Paramenter,[4] and we obtain the same final result as he does, i.e.,

$$\epsilon_{\text{local}}(k,\,\alpha=0)=-\left[2\pi\rho m_A m_B A^2/a(a^2+4k^2)\right]. \tag{45}$$

Case 2. $0<\alpha<1$ (Clustering)

Examination of $O(\mathbf{K},\alpha)$ in Eq. (36) for $\alpha>0$ shows that it has maxima of height $(1+\alpha)^3/(1-\alpha)^3$ located at the points $K_i=\pm2\pi n_i/d$, ($n_i=0,\ 1,\ 2\cdots$). If the $(a^2+K^2)^{-2}$ factor drops off rapidly enough, the maxima other than that at the origin will give negligible contribution; a rough criterion is

$$a<4\pi/d\sqrt{3}, \tag{46}$$

which means the first eight secondary maxima are reduced by a factor >10. Under these circumstances, the order function may be approximated by the spherically symmetric function

$$O_{\text{local}}(K,\alpha)\approx Nm_Am_B\frac{(1-\alpha^2)^3}{\left[1+\alpha^2-2\alpha\cos(Kd/\sqrt{3})\right]^3}\quad(\text{for } K\leqslant\pi\sqrt{3}/d),$$
$$\approx0\quad(\text{for } K>\pi\sqrt{3}/d). \tag{47}$$

[The value $\pi\sqrt{3}/d$ is where $O(K,\alpha)$ is minimum.] Thus we find

$$I(k,\,\alpha>0)$$
$$\approx\frac{1}{k}\int_0^{\pi\sqrt{3}/d}dK\left\{\frac{K(1-\alpha^2)^3}{\left[1+\alpha^2-2\alpha\cos(Kd/\sqrt{3})\right](a^2+K^2)^2}\times\ln\left|\frac{K-2k}{K+2k}\right|\right\}. \tag{48}$$

This approximation works best for $\alpha>0.2$.

We may determine the behavior of Eq. (48) in the limits where $\mathbf{k}$ is either much smaller or larger than the half width of the peak at the origin. This criterion is

$$\text{small } k:\quad k\ll\frac{1}{d}\cos^{-1}\left[2^{\frac{1}{3}}+\left(\frac{1+\alpha^2}{2\alpha}\right)(1-2^{\frac{1}{3}})\right],$$
$$\text{large } k:\quad k\gg\frac{1}{d}\cos^{-1}\left[2^{\frac{1}{3}}+\left(\frac{1+\alpha^2}{2\alpha}\right)(1-2^{\frac{1}{3}})\right]. \tag{49}$$

In these cases we may use

$$\ln\left[(K-2k/K+2k)\right]\approx-4k/K,\quad(\text{small } k), \tag{50}$$

$$\approx-K/k,\quad(\text{large } k), \tag{51}$$

from which we find

$$I(k,\,\alpha>0)=\text{constant},\quad(\text{small } k)$$
$$\propto k^{-2},\quad(\text{large } k) \tag{52}$$

showing that $\epsilon(k)\rightarrow k^2$ as $k\rightarrow\infty$. Note that the results in Eq. (52) are valid from the perturbation-theoretic standpoint, since the singularity in the integrand is no longer present.

Case 3. $-1<\alpha<0$ (Short-Range Order)

In this case, $O(\mathbf{K},\alpha)$ in Eq. (36) shows a *minimum* at the origin, surrounded by eight maxima at $K_i=\pm\pi/d$, etc. Thus, in general, we cannot replace $O(\mathbf{K},\alpha)$ by a spherically symmetric function. However, if α is not too negative, the maxima will not be highly pronounced, and will be flattened out by the $(a^2+K^2)^{-2}$ function. A rough estimate shows that Eq. (48) is usable down to $\alpha=-0.1$, provided we extend the integration to $K=2\sqrt{3}\pi/d$, the position of the secondary minimum.

Case 4. $\alpha\rightarrow1$ (Complete Clustering)

Equation (37) is not valid for this case, nor can we use Eq. (30), since, for complete clustering, the crystal is broken up into two parts, one with just A atoms, and the other with B's. It is easiest to work directly from Eq. (9) as follows:

$$O(\mathbf{K})=\sum\nolimits_\mu C(\boldsymbol{\mu})\exp(i\mathbf{K}\cdot\boldsymbol{\mu})\times\sum\nolimits_\tau C(\boldsymbol{\tau})\exp(-i\mathbf{K}\cdot\boldsymbol{\tau}). \tag{53}$$

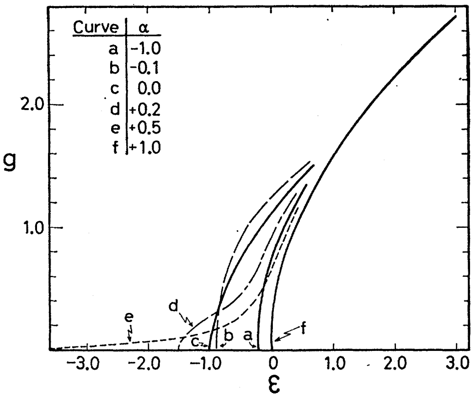

FIG. 2. Density of states g vs energy ϵ for a free electron gas perturbed by a fluctuating potential with specified local order parameter α. Units of g are arbitrary; of ϵ, atomic.

Breaking up the sum into its A and B components, we find

$$\begin{aligned}\sum_{\mu} C(\boldsymbol{\mu}) \exp(i\mathbf{K}\cdot\boldsymbol{\mu}) &= \sum^{A} C(\boldsymbol{\mu}) \exp(i\mathbf{K}\cdot\boldsymbol{\mu}) + \sum^{B} C(\boldsymbol{\mu}) \exp(i\mathbf{K}\cdot\boldsymbol{\mu}) \\ &= m_B \sum^{A} \exp(i\mathbf{K}\cdot\boldsymbol{\mu}) - m_A \sum^{B} \exp(i\mathbf{K}\cdot\boldsymbol{\mu}) \\ &= m_B N_A \delta_{\mathbf{K},\mathbf{K}_0} - m_A N_B \delta_{\mathbf{K},\mathbf{K}_0} \\ &= 0. \end{aligned} \tag{54}$$

Thus, for complete clustering, the second-order term in Eq. (10) vanishes.

Case 5. $\alpha=-1$ (Complete Short-Range Order)

The calculation here is exactly the same as that for perfect long-range order, and we obtain Eq. (41) with $\lambda=1$. The numerical results for all five cases are shown in Fig. 1.

The density of states, $g(\epsilon)$ may be found from

$$g(\epsilon)=\frac{dn}{d\epsilon}=\frac{dn}{dk}\bigg/\frac{d\epsilon}{dk}=\left(\frac{V}{2\pi^2}\right)k^2\bigg/\frac{d\epsilon}{dk}, \tag{55}$$

where $d\epsilon/dk$ is found from Fig. 1. The results are plotted in Fig. 2. Their significance is easily seen by starting with the curve for $\alpha=-1$ (perfect order). As the order begins to dissolve, moving toward the random ($\alpha=0$) case, the band gets pushed out and progressively flatter. In the clustering region, a rat-like tail forms, which becomes progressively thinner until $\alpha \rightarrow 1$ and the state density goes to that of a free electron gas. (It should be noted that the value of α for which the band shape becomes truly tail-like depends on a and A. As Parmenter[4] shows, for small enough a or large enough A we can find a tail even in the $\alpha=0$ case.)

The effect of long-range order on these curves is relatively small, as we can see by recognizing that the curve $\alpha=-1$ in Fig. 1 is just $\epsilon=k^2+\epsilon_{\text{long-range}}$, the second term being given by Eq. (41) when $\lambda=1$. [Of course, if we consider the new band gaps which appear, as mentioned just after Eq. (37), then the effect of long-range order is the dominant one, since it enters in first order.[7,8]]

These results may be briefly compared with those for the tight-binding case. If the $3d$ hole wave functions are sufficiently localized around just the A atoms in an AB alloy, it has been shown[1] that the energy expression has the form

$$\epsilon(k)=\epsilon_0-D(1+\alpha)f(k), \tag{56}$$

where $f(k)$ is a bounded function of k, α is the local order parameter for nearest neighbors, and ϵ_0, D are constants. Then, as α goes from $-1 \rightarrow +1$, the energy band broadens from zero to some finite value. Since the number of states in the band is conserved, this broadening implies a simultaneous decrease in band height. This result is in qualitative agreement with the conclusions for the weak binding case, as seen from Fig. 2.

Experimental detection of the change of band shape with order cannot be carried out by measurement of magnetic properties, since in this case the effect is dominated by variations due to exchange.[1] However, by choosing physical properties more directly related to band shape—like soft x-ray spectrum, Knight shift, or low-temperature specific heat,[13] for example—the phenomenon might be made observable.

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