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Second-Order Phase Transition in a Model Random Alloy

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We investigate the existence and stability of long-range order in a simple model of a binary alloy. We find that for electron concentrations in the vicinity of one per atom, in bipartite lattices, long-range order of the atoms exists at low temperatures, and we find that the system undergoes a second-order phase transition. We use a generalized form of the coherent-potential approximation (CPA) of Soven and find that this CPA reproduces exactly at least eight moments of the density of states. We derive an exact expression for the critical temperature when the alternating potential is much larger than the bandwidth.

I. INTRODUCTION

The electronic theory of disordered binary alloys has been widely studied in the last few years by means of a simple model which assumes that the two types of atoms differ only in their local pseudo-potentials. For this model the coherent-potential approximation (CPA)[1] has proved successful over all ranges of concentration at least as far as the single-particle properties, e.g., density of states, are concerned. In this paper we examine the possibility of electronically induced long-range order (LRO) of the atoms within this model. This is a problem which has been previously broached, in one dimension, by Foo and Amar,[2] who used the CPA and has been subsequently studied by us.[3] Using a transfer-matrix formulation, we showed that, in one dimension, LRO is always unstable and that the short-range-order parameter is a smooth func-

tion of temperature. In the present work we employ a modification of the CPA to find the electronic density of states in three dimensions. We compare the moments of the CPA density of states with the moments of the exact density of states and find that for any value of the potential and LRO parameter, CPA reproduces at least the first eight moments of the density of states. This indicates that CPA is a useful calculational tool even if the alloy is not totally disordered. Moreover, at large values of the on-site potential the thermodynamics is governed, for one electron per atom, entirely by the first moment of the lower subband of the density of states, as will be shown in Sec. IV. CPA yields this moment exactly to $O(1/V^3)$ and thus the exact asymptotic form of the critical temperature. CPA is known[4] to be exact at small values of the on-site potential. We may, therefore, expect our results to be reliable over the whole range of pa-

rameters.

To find the temperature dependence of the LRO parameter we compute the free energy of the system, composed of electronic free energy and lattice entropy and minimize it with respect to the LRO parameter. We find a second-order phase transition from the ordered to the disordered state.

II. MODEL AND GENERALIZED CPA

We consider the Hamiltonian

$$\mathcal{H} = \sum_{k,\sigma} \epsilon(k) C_{k\sigma}^{\dagger} C_{k\sigma} + \sum_{n,\sigma} V_n C_{n\sigma}^{\dagger} C_{n\sigma} , \qquad (1)$$

where $C_{k\sigma}^{\dagger}$, $C_{k\sigma}$ are the creation and annihilation operators for an electron of spin σ in a Bloch state $|k\rangle$; $C_{n\sigma}^{\dagger}$, $C_{n\sigma}$ are the creation and annihilation operators for an electron of spin σ in a Wannier state $|n\rangle$ with energy V_n. We assume a bipartite lattice structure, one which can be divided into A and B sublattices such that there exists a vector $\vec{Q}$: $\exp(i\vec{Q} \cdot \vec{R}_n) = +1, -1$ if $n \in A, B$, respectively, and where $\epsilon(\vec{K} + \vec{Q}) = -\epsilon(\vec{K})$. These assumptions hold for the simple cubic and body-centered-cubic lattices with tightly bound electrons.

Long-range order is introduced in the following way: at every site j, V_j is a random variable which takes the values $+V$, $-V$ with probabilities $P_+(j)$, $P_-(j)$, respectively. We assume an equal number of A and B atoms:

$$P_+(j) = \tfrac{1}{2}(1 + \eta \, e^{i\vec{Q} \cdot \vec{R}_j}) ,$$
$$P_-(j) = \tfrac{1}{2}(1 - \eta \, e^{i\vec{Q} \cdot \vec{R}_j}) , \qquad (2)$$

where $\eta (0 \le \eta \le 1)$ is the long-range-order parameter. For $\eta = 0$ the model reduces to the disordered binary alloy already treated by Soven et al.[1] and by Velický, Kirkpatrick, and Ehrenreich[4] in the CPA. Our theory reduces to this at and above the critical temperature T_c, as $\eta \to 0$.

To motivate our method of using the CPA, consider an effective Hamiltonian $\mathcal{H}_0$ where

$$\mathcal{H}_0 = \sum_k \epsilon(k) C_k^{\dagger} C_k + U_1(\omega) \sum_n C_n^{\dagger} C_n + U_2(\omega)$$
$$\times \sum_k e^{i\vec{Q} \cdot \vec{R}_n} C_n^{\dagger} C_n . \qquad (3)$$

The same $\mathcal{H}_0$ is used for both spin species as there are no electron-electron interactions. Henceforth, we drop the spin label. $U_j(\omega)$ are complex functions of ω with the property $U_{1,2}^*(\omega^*) = U_{1,2}(\omega)$. Real ω will always be taken to mean $\omega + iO$. We diagonalize $\mathcal{H}_0$ by the transformation

$$C_k = A_k(\omega) b_k + B_k(\omega) b_{\vec{k}+\vec{Q}} ,$$
$$C_k^{\dagger} = A_k(\omega) b_k^{\dagger} + B_k(\omega) b_{\vec{k}+\vec{Q}}^{\dagger} , \qquad (4)$$
$$A_{\vec{k}+\vec{Q}} = A_k , \quad B_{\vec{k}+\vec{Q}} = -B_k ,$$

$$\mathcal{H}_0 = \sum_k \left(\frac{\epsilon_k}{|\epsilon_k|} [\epsilon_k^2 + U_2^2(\omega)]^{1/2} + U_1(\omega) \right) b_k^{\dagger} b_k . \qquad (5)$$

The potentials $U_1(\omega)$, $U_2(\omega)$ are determined by the condition[1,4] that the average scattering vanish at each site:

$$\langle T_n(\omega) \rangle = 0 , \qquad n \in A, B , \qquad (6)$$

where T_n is the T matrix at site n and the angular brackets indicate averaging over lattice configurations. T_n may be written

$$T_n = (V_n - U_1 - U_2 e^{i\vec{Q} \cdot \vec{R}_n})$$
$$\times [1 - (V_n - U_1 - U_2 e^{i\vec{Q} \cdot \vec{R}_n}) F_n]^{-1} , \qquad (7)$$

where

$$F_n = (\omega - U_1 + U_2 e^{i\vec{Q} \cdot \vec{R}_n})(1/N)$$
$$\times \sum_k [(\omega - U_1)^2 - U_2^2 - \epsilon_k^2]^{-1} . \qquad (8)$$

Averaging over configurations for $n \in A, B$ by Eq. (2), we obtain the two complex equations

$$U_1 - \tfrac{1}{2}(V^2 - U_2^2)(F_A + F_B) + U_1 U_2 (F_A - F_B) = 0 ,$$
$$U_2 - \eta V - \tfrac{1}{2}(V^2 - U_1^2 - U_2^2)(F_A - F_B) \qquad (9)$$
$$+ U_1 U_2 (F_A + F_B) = 0 .$$

The configuration averaged density of electronic states is related to the functions F_A, F_B by

$$\rho_\sigma(\omega) = \rho_{-\sigma}(\omega) = -(1/\pi) \tfrac{1}{2}(F_A + F_B) \qquad (10)$$

$$\rho(\omega) = \rho_\uparrow(\omega) + \rho_\downarrow(\omega) . \qquad (11)$$

III. MOMENTS OF DENSITY OF STATES

The CPA developed in Sec. II differs in several important respects from conventional CPA.[1,4] To obtain the diagonal form of the effective Hamiltonian we had to make a complex transformation (4). This is in the spirit of CPA, but one might ask whether the results are as dependable in the ordered alloy as in the disordered alloy. A test of the theory are the moments of the density of states which one can calculate both exactly and in CPA. One defines the jth moment of $\rho(\omega)$ as

$$M_j = \int_{-\infty}^{\infty} d\omega \, \omega^j \rho(\omega) . \qquad (12)$$

It can be shown[4] that M_j may be written

$$M_j = (1/N) \, \text{Tr} \langle \mathcal{H}^j \rangle . \qquad (13)$$

In CPA these moments may be obtained from the high-frequency behavior of the function $-(1/\pi)$ $\times \tfrac{1}{2}(F_A + F_B)$. Outside the band, where both $U_1(\omega)$ and $U_2(\omega)$ are real we may expand them in the following series:

$$U_1(\omega) = \alpha_1/\omega + \alpha_2/\omega^3 + \alpha_3/\omega^5 + \cdots ,$$

$$U_2(\omega) = \beta_0 + \beta_1/\omega^2 + \beta_2/\omega^4 + \cdots . \qquad (14)$$

Using these in Eqs. (8) and (9), one obtains the moments of $\rho(\omega)$. In the symmetric case considered here $\sum_k \epsilon(k) = 0$ and $\pm V$ are present in equal concentrations. This implies that $\rho(\omega) = \rho(-\omega)$ and that all odd moments of the density of states are zero. The first few nonvanishing *exact* moments of the density of states are given by

$$M_0 = 1, \qquad M_2 = V^2 + M_2^{(0)},$$

$$M_4 = V^4 + 4V^2 M_2^{(0)} - 2\,\eta^2 V^2 M_2^{(0)},$$

$$M_6 = V^6 + 9V^4 M_2^{(0)} - 6\,\eta^2 V^4 M_2^{(0)} \qquad (15)$$

$$+ 3V^2 M_2^{(0)2}(1 - \eta^2) + 6V^2 M_4^{(0)}(1 - \tfrac{1}{2}\eta^2) + M_6^{(0)},$$

where

$$M_j^{(0)} = (1/N) \sum_k \epsilon_k^j .$$

CPA reproduces *at least* these moments exactly. Since $M_7 = 0$, both exactly and in CPA we have the first eight moments of the density of states given correctly by CPA.

When $V \gg W$, where $W = \max\epsilon(k) - \min\epsilon(k) \equiv 2$, the band is split into an upper and lower subband for all values of η. In this limit it is sensible to divide the density of states into two parts: $\rho_l(\omega)$, a function which is nonzero only over an interval W centered about $-V$, and $\rho_u(\omega)$ which is centered about $+V$. We can calculate the first few moments of these subbands about their respective centers at least to leading order in V^{-1} following a procedure of Velický, Kirkpatrick, and Ehrenreich.[4] We write $\rho(\omega) = \rho_l(\omega) + \rho_u(\omega)$,

$$M_j = \int_{-\infty}^{\infty} d\omega\,\omega^j\,\rho(\omega) = \int_{-\infty}^{\infty} d\omega\,(\omega + V - V)^j\,\rho_l(\omega)$$

$$+ \int_{-\infty}^{\infty} d\omega\,(\omega - V + V)^j\,\rho_u(\omega) \qquad (16)$$

$$= \sum_{n=0}^{j} \binom{j}{n} V^n [M_{j-n}^u + (-)^n M_{j-n}^l], \qquad (17)$$

where

$$M_k^{u,\,l} = \int d\omega\,(\omega \mp V)^k \rho_{u,\,l}(\omega). \qquad (18)$$

The symmetry of the density of states is for any value of

$$M_j^u = (-1)^j M_j^l, \qquad (19)$$

so that

$$M_j = \sum_{n=0}^{j} \binom{j}{n}(-)^n V^n [1 + (-)^j] M_{j-n}^l . \qquad (20)$$

All the subband moments are $O(W)$ so that one can use Eqs. (15) and (20) to obtain M_j^l to a given order in $1/V$. One finds

$$M_0^l = \tfrac{1}{2},$$

$$M_1^l = -\frac{M_2^{(0)}(1 + \eta^2)}{8V} + O\left(\frac{1}{V^3}\right), \qquad (21)$$

$$M_2^l = \tfrac{1}{4}[M_2^{(0)}(1 - \eta^2)] + O(1/V^2).$$

The moment M_1^l will be used to find the large-V behavior of the critical temperature.

IV. THERMODYNAMICS OF THE ORDER-DISORDER TRANSITION

Once the density of states as function of η is known, the temperature dependence of the order paramter $\eta(T)$ is obtained by minimizing the total free energy

$$F = F_{el}(\eta, T) - T S_{lat}(\eta, T), \qquad (22)$$

with respect to η. Here we use our formula[5] for the electronic free energy

$$F_{el}(\eta, T) = -N \int_{-\infty}^{\infty} d\omega\, f(\omega) \int_{-\infty}^{\omega} d\omega'\, \rho(\omega', \eta), \qquad (23)$$

where $f(\omega)$ is the Fermi function. For one electron per atom the chemical potential $\mu = 0$. The lattice entropy is given by

$$S_{lat} = -kN[\tfrac{1}{2}(1 + \eta)\ln\tfrac{1}{2}(1 + \eta) + \tfrac{1}{2}(1 - \eta)\ln\tfrac{1}{2}(1 - \eta)]. \qquad (24)$$

A phase transition is made possible by the fact that the electronic free energy $F_{el}(\eta, T)$ is a decreasing function of η, whereas the lattice entropy prefers $\eta = 0$.

Before discussing the numerical calculations we consider the limiting case $V \gg W$ in which exact results can be obtained. In this limit the band is split into subbands separated by a gap of $O(2V)$ in both the ordered and disordered case. At temperature $kT \ll V$ the lower subband is full and the upper subband empty. The electronic free energy then reduces to

$$F_{el} = 2N \int_{-\infty}^{\infty} d\omega\,\omega\rho_l(\omega) + O(e^{-2V/kT}) \qquad (25)$$

$$= -2VN M_0^l + 2M_1^l = -VN - N\frac{M_2^{(0)}(1 + \eta^2)}{4V} + O\frac{1}{V^3}, \qquad (26)$$

where we have used (21) for the subband moments. Expanding the lattice entropy in powers of η, we obtain

$$\frac{F}{N} = -V - \frac{M_2^{(0)}}{4V} - kT\ln 2 - \eta^2\left(\frac{M_2^{(0)}}{4V} - \frac{kT}{2}\right) + \frac{\eta^4}{12}kT. \qquad (27)$$

For $kT > M_2^{(0)}/2V$ the disordered state $(\eta = 0)$ has a lower free energy than the ordered state. At $kT_c \simeq M_2^{(0)}/2V$ the material undergoes a second-order phase transition to the ordered state. Corrections to this result are of $O(1/V^3)$ due to higher-order terms in the moment M_1^l and of $O[\exp(-4V^2/M_2^{(0)})]$ due to occupancy of the upper subband.

V. NUMERICAL CALCULATIONS

To facilitate the numerical calculations, we have used two distinct approximations to the unperturbed density of states of the simple cubic lattice, either
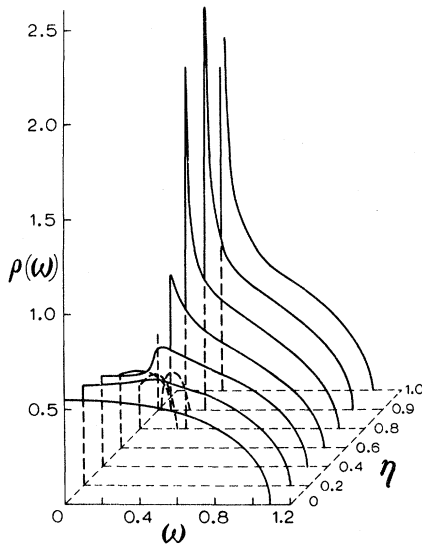
FIG. 1. Plot of the density of states $\rho(\omega)$ as function of ω for several values of η at $V = 0.25$. Since $\rho(\omega)$ is symmetric about $\omega = 0$ we show only the upper-half of the curve. An "impurity band" appears near each interval band edge when there is a slight deviation from perfect LRO.

$$\rho_0(\omega) = \tfrac{1}{2} \qquad \text{with } -1 \leq \omega \leq 1 \qquad (28)$$

or

$$\rho_0(\omega) = (2/\pi)(1 - \omega^2)^{1/2} \qquad \text{with } -1 \leq \omega \leq 1. \qquad (29)$$

The results, using either, came out essentially the same, and in Figs. 1–4 we quote results obtained with the semicircular density of states (29). We have solved Eqs. (9) for $V = 0.15$ and $V = 0.25$ as a function of ω over the whole range $0 \leq \eta \leq 1$. The density of states $\rho(\omega)$ of the alloy is plotted as a function of ω for several values of η for $V = 0.25$ in Fig. 1. We note that the density of states split first into three subbands at $\eta \simeq 0.6$. The middle subband itself splits into two subbands at $\eta \simeq 0.85$.
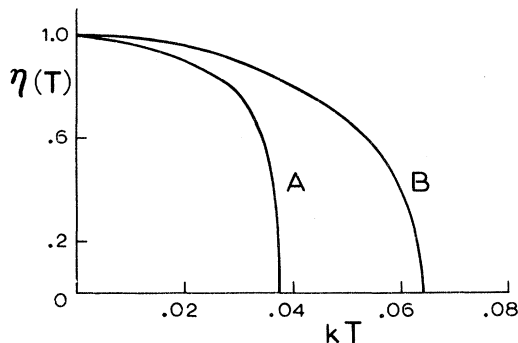

FIG. 2. Order parameter is plotted as function of temperature for (a) $V = 0.15$, (b) $V = 0.25$. In both cases $\eta(T)$ vanishes continuously as function of T.
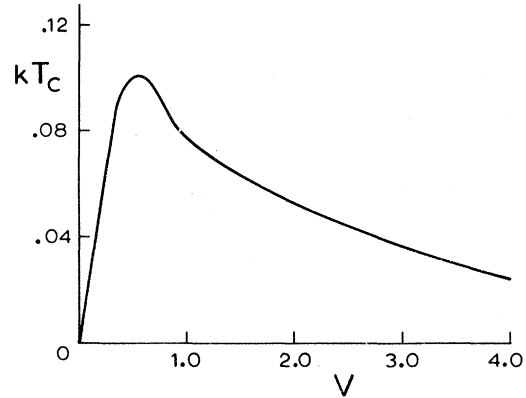

FIG. 3. Critical temperature kT_c is plotted as function of V. For large V, $kT_c \sim 1/V$.

These central bands become weaker and disappear at $\eta = 1$, the perfectly ordered case.

The temperature dependence of the LRO parameter $\eta(T)$ is shown in Fig. 2 for $V = 0.15$ and $V = 0.25$. In both cases $\eta(T)$ vanishes continuously as T approaches a critical temperature T_c. Since for every value of η the whole spectrum must be computed it is clear that η could not be varied continuously up from zero. However, we can rule out a first-order phase transition to the extent that any jump in $\eta(T)$ at T_c is less than 0.03 for both $V = 0.25$ and $V = 0.15$. Moreover, a second-order phase transition is most plausible, by analogy with the Bragg–Williams–Ising lattice-gas model, which has a second-order phase transition in two and three dimensions but none in one dimension. The analogy requires, however, temperature-dependent coupling constants as we have noted.[3]

We have roughly calculated the critical temperature of the alloy for V up to 4 by comparing the free energy of the system for $\eta = 0.1$ to that of $\eta = 0$. Since $\eta(T)$ drops quite steeply near T_c the temperature at which $F(0.1, T) = F(0, T)$ should be a good approximation to T_c. The results are shown in Fig. 3. $kT_c(V) \sim \tfrac{1}{4} V$ for small V and then reverses itself near $V = 0.5$. (The band splits at $\eta = 0$ for $V > 0.5$.) At $V = 2$ the asymptotic $1/V$ dependence can already be seen.

We also investigated the dependence of these results on *electron concentration*. At $V = 0.25$ the ordered ground state $\eta = 1$ is stable for $0.8 \lesssim n \lesssim 1.2$ where n is the number of electrons per atom. At $V = 1$ the ordered state is stable for $0.9 \lesssim n \leq 1.1$. Clearly, as $V \to \infty$, the region of stability will shrink to $n \equiv 1$, probably with an asymptotic $1/V$ dependence. Similarly, one can investigate the effect of changing the relative concentration of A and B atoms keeping $n = 1$ fixed. If an A atom is replaced by a B atom, at $\eta = 1$, two impurity states appear between the main subbands. In the
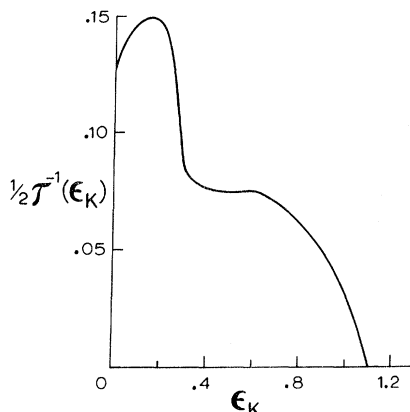
FIG. 4. Plot of the inverse lifetime $\frac{1}{2}\tau^{-1}(\epsilon)$ as function of ϵ for $\eta = 0.4$ and $V = 0.25$. For all η the $\tau^{-1}(\epsilon)$ function is similar to the function $\rho(\epsilon)$ except for the resonance peak near the inner band edge.

most disadvantageous case these two states could appear at $\omega = 0$, raising the energy of the electronic system by V for every impurity. At small V the ordered state lies an amount roughly $NkT_c \sim \frac{1}{4}VN$ below the disordered state so that a change in $A\text{-}B$ concentration of $O(25\%)$ is conceivable without in principle destroying the ordered state. Clearly, the effect is more subtle than this but it is clear that the ordered state is stable in a *finite* concentration range centered around the 50-50 alloy. Again one expects this range to decrease with increasing potential and to asymptotically approach zero as $1/V$.

Finally, we calculate the lifetime of the quasi-particles in the framework of our modified single-particle CPA.[6] We define (nonrigorously) a transport lifetime:

$$\frac{1}{2}\tau^{-1}(\epsilon) = \left| \, \mathrm{Im}\textstyle\sum (\omega, \, \epsilon_k, \, \omega = \epsilon_k) \, \right|$$

$$= \left| \, \mathrm{Im}\left(U_1(\omega) + \frac{\epsilon_k}{|\epsilon_k|} \, [\epsilon_k^2 + U_2^2(\omega)]^{1/2} \right)_{\omega = \epsilon_k} \right| . \quad (30)$$

$\tau^{-1}(\epsilon)$ is a symmetric function of ϵ and we plot it in Fig. 4 for $\epsilon > 0$ for $V = 0.25$ for $\eta = 0.4$. It will be seen that it is very similar to the density of states with a peak in the region of "localized" states.

VI. CONCLUSIONS

We have shown that in an alloy long-range order can be stabilized by the associated lowering of the electronic free energy. In this article we have investigated the type of lattice (e.g., simple cubic, body-centered cubic), which naturally divides into sublattices. Moreover, we have required that $\epsilon(\vec{K} + \vec{Q}) = -\epsilon(\vec{K})$, where $\vec{Q}$ is the vector specifying the pitch of the long-range order. Again this requirement is fulfilled in the case of tightly bound electrons in the above-mentioned lattices. These two assumptions make our LRO stable for arbitrarily small V. A second-order phase transition from the ordered to the disordered state takes place. In a future paper, we expect to discuss the stability of LRO in face-centered-cubic lattices in which one might expect the A and B atoms to order in alternating planes. In this case one would expect a critical V before ordering could stabilize and there is some hope for a first-order phase transition.

We note again, as in Ref. 3, the remarkable fact that the gaps in the density of states seem to have nothing to do with the order-disorder transition. By comparing Figs. 1 and 2 we see that the gap in $\rho(\omega)$ disappears at $\eta \approx 0.85$ at a temperature much below T_c. An insulator-metal transition, which can occur in this model for small enough V—we ignore the thorny question of localization of electronic states—would thus be independent of the structural transition.

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