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[22] These calculations were performed using the Hartree-Fock code of Dr. C. Froese. We would like to thank Dr. J. Tech of the National Bureau of Standards for performing this calculation and Dr. T. Carlson of the Oak Ridge National Laboratory for performing similar calculations on states of Ar III and K III which were useful in our analysis of the effects of Coster-Kronig processes and shakeoff on our results.

Order-Disorder Phase Transition in Binary Alloys–Coherent Potential Approximation*

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The electronic density of states of a one-dimensional *AB* model alloy with long-range order is calculated in the coherent potential approximation. Impurity states are found inside the energy gap and the energy gap disappears long before the alloy becomes completely disordered. The temperature-dependent long-range order exhibits a first-order order-disorder phase transition which causes a discontinuity in the electronic density of states at the middle of the energy gap at the critical temperature T_c.

Disordered systems and, more specially, disordered alloys constitute a central problem in modern statistical physics. While the electronic density of states (EDS)[1-7] and the atomic correlation function (ACF)[8,9] of alloys have been intensively studied in recent years by many authors, their relationship has received relatively little attention. The EDS has been calculated only where the ACF vanishes (completely disordered alloys).[1-6] Attempts to include a finite pair correlation have been so far unsatisfactory.[7] It is known, however, that the interatomic potential which determines the ACF depends on the overlap of electron distributions from the various sites and the EDS also depends on its environment (ACF). Since the ACF and the EDS are correlated, they should be determined in a self-consistent manner. In this paper, we use the powerful coherent potential approximation (CPA) of Soven[1] to calculate the EDS from a known ACF. Then the value of the ACF is so adjusted that the free energy of the alloys is a minimum, and the EDS and ACF are determined as functions of temperature T. For an alloy with a half-filled band, the EDS at the Fermi surface increases with T and has a discontinuity at a critical temperature T_c.

Soven's single-site CPA is modified for a partially ordered alloy with long-range order (LRO) η. The CPA is developed in the framework of multiple-scattering theory introduced by Lax.[10] In this approximation, the electron is regarded as propagating in an effective medium. The effective Hamiltonian retains the full crystal symmetry and has a coherent potential (CP) at each site. Here the CP is a complex quantity describing the average effect of the medium. The criterion to determine the CP is to require that a single scatterer embedded in this effective medium produce no further scattering on the average.

For a long-range ordered alloy consisting of two sublattices 1 and 2, the criteria are

$$\langle t_1\rangle = 0 \text{ and } \langle t_2\rangle = 0, \tag{1}$$

which can be rewritten as[1]

$$\epsilon_1 = \bar{\epsilon}_1 - (\epsilon_1 - \epsilon_A)(\epsilon_1 - \epsilon_B)G_{11}(\epsilon_1, \epsilon_2), \tag{2}$$

$$\epsilon_2 = \bar{\epsilon}_2 - (\epsilon_2 - \epsilon_A)(\epsilon_2 - \epsilon_B)G_{22}(\epsilon_1, \epsilon_2), \tag{2a}$$

where

$$\bar{\epsilon}_i = C_{iA}\epsilon_A + C_{iB}\epsilon_B; \quad i = 1,\ 2.$$

Here we assume that the atoms are randomly distributed within each sublattice. The quantity ϵ_i describes the CP of the ith sublattice, and ϵ_A and ϵ_B are the actual atomic potentials of A and B atoms, respectively. Their concentrations within the ith sublattice are denoted by C_{iA} and C_{iB} and are functions of the LRO η. For an AB-type binary alloy of equal concentration, we have[11]

$$C_{1A} = C_{2B} = 0.5(1+\eta),$$

and

$$C_{2A} = C_{1B} = 0.5(1-\eta). \tag{3}$$

The G_{ii} is the CP Green's function of the ith sublattice. The ϵ_i's can be determined by solving the coupled Eqs. (2) and (2a). The electronic density of states is given by

$$\rho(E) = -(1/2\pi)\,\mathrm{Im}(G_{11} + G_{22}). \tag{4}$$

In order to illustrate the modified CPA, we consider a simple one-dimensional nearest-neighbor interaction Hamiltonian for an AB-type binary alloy (50-50) which consists of two sublattices with the LRO parameter η:

$$H = \sum_n \epsilon_n |n\rangle\langle n| + (h/2)\sum_{n,\, m=n\pm 1} |n\rangle\langle m|, \tag{5}$$

where $|n\rangle$ represents a Wannier atomic orbital at site n with energy ϵ_n which may be ϵ_A and ϵ_B and h is the hopping integral (assumed to be composition independent). In the modified CPA we have to define two CP's ϵ_1 and ϵ_2 for two sublattices. The corresponding Green's functions are

$$G_{11} = (E - \epsilon_2)\Delta^{-1},$$

$$G_{22} = (E - \epsilon_1)\Delta^{-1},$$

where

$$\Delta = \{[(E-\epsilon_1)(E-\epsilon_2) - h^2/2]^2 - h^4/4\}^{1/2}. \tag{6}$$

The CP's ϵ_1 and ϵ_2 are determined by solving Eqs. (2) and (6), and the electronic density of states $\rho(\eta)$ can be obtained via Eq. (4). For convenience, we choose the zero of energy to be at $\frac{1}{2}(\epsilon_A + \epsilon_B)$, set $\epsilon_B - \epsilon_A = \delta$, and describe energies in units of the hopping integral h; then obviously

$$\epsilon_A = -\delta/2 \text{ and } \epsilon_B = \delta/2. \tag{7}$$

The electronic density of states is a symmetrical function of the electronic energy E with respect to $E=0$. Therefore, we need only to discuss the EDS in the region $E<0$. For $\eta=1$, all A atoms are in sublattice 1 and all B atoms are in sublattice 2. From Eq. (6) one can show that there is an energy gap of width δ centered at $E=0$. The EDS is extended from $-(\delta/2+h)$ to $-\delta/2$ and from $\delta/2$ to $\delta/2+h$.

In order to facilitate numerical computation, we have added a small imaginary part γ in the energy E. Because of finite γ a tail in the EDS which appears at the band edges should be ignored. The numerically calculated $\rho(E)$ for η ranging from 1 to 0 are shown in Fig. 1. In the CPA the energy gap disappears at $\eta \leq 0.6$, long before the alloy attains complete disorder. At the onset of disordering, new states appear inside the gap and gradually fill up the gap, in contrast to the narrowing of the energy gap occurring in the conventional virtual crystal approximation.[12]

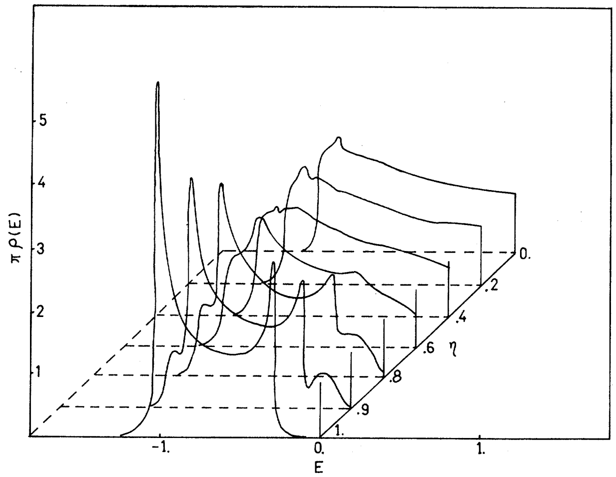

FIG. 1. The electronic densities of states of an AB alloy (50–50) calculated in the CPA are plotted for several LRO η. Since the EDS is symmetric with respect to $E=0$, we plot only the lower half of the EDS. Here $\delta=0.6$ and $\nu=0.02$.

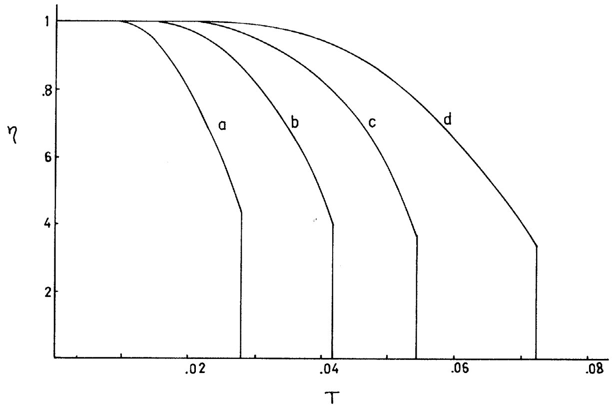

FIG. 2. The LRO η are plotted as functions of temperature T for the cases of $\delta = 0.3$ (line *a*), $\delta = 0.4$ (line *b*), $\delta = 0.5$ (line *c*), and $\delta = 0.6$ (line *d*).

As we have stated earlier, the ACF and the EDS are correlated and they should be mutually adjusted so that the configuration is most stable, or in other words, the total free energy $A(\eta)$ is a minimum. In the present case, the free energy is a sum of two contributions. One is the total electronic energy which is

$$E_e(\eta) = \int_{-\infty}^{E_F} E\rho(E)dE. \qquad (9)$$

Here E_F which is the Fermi energy is equal to zero for alloys with one electron per site. The second contribution is due to the lattice entropy which is[8]

$$S(\eta) = \tfrac{1}{2}(1+\eta)\ln[(1+\eta)/2] - \tfrac{1}{2}(1-\eta)\ln[(1-\eta)/2]. \qquad (10)$$

The free energy is then

$$A(\eta) = E_e(\eta) + TS(\eta). \qquad (11)$$

This system is unstable unless η is so chosen such that

$$\partial A(\eta)/\partial\eta = 0,$$

and

$$\partial^2 A(\eta)/\partial\eta^2 > 0. \qquad (12)$$

From conditions (12), one can determine numerically the LRO η as a function of temperature T, which is shown in Fig. 2. One observes a first-order order-disorder phase transition at the critical temperature T_c. Temperature T_c increases with δ.

Since $\rho(E_F)$ depends on η and η depends on T, therefore $\rho(E_F)$ is a function of T, which is shown in Fig. 3. One notices that there is discontinuity in $\rho(E_F)$ at the critical temperature T_c.[13] For $T < T_c$, the $\rho(E_F)$ increases with temperature and for $T > T_c$, the $\rho(E_F)$ remains essentially constant.

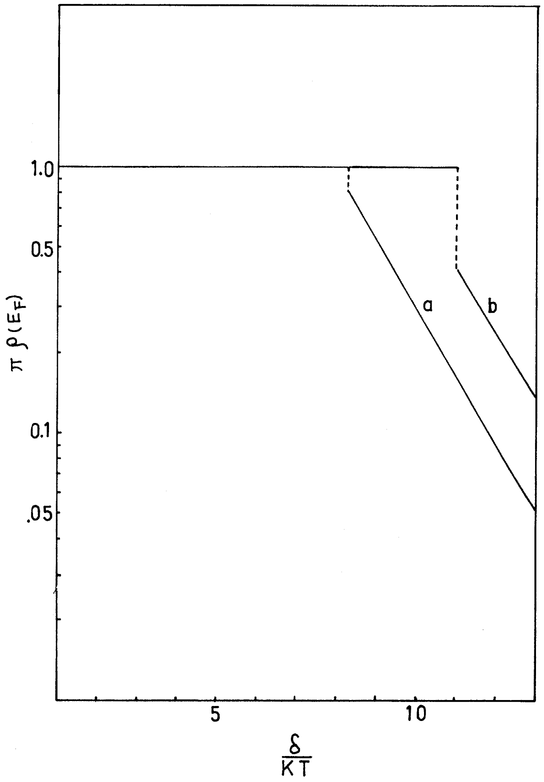

FIG. 3. The density of states at the Fermi surface is plotted as a function of δ/KT for the cases $\delta = 0.6$ (line *a*) and $\delta = 0.3$ (line *b*).

For $\delta > 1$, i.e., when the separation between the two atomic energy levels ϵ_A and ϵ_B is larger than the hopping integral, the energy gap persists even in the completely disordered phase ($\eta = 0$). Thus $\rho(E_F)$ vanishes for all values of η. For $\delta = 0$, the order and disorder phases are ill defined. Therefore our numerical calculations are limited to the region $0 < \delta < 1$, in which the discontinuity in $\rho(E_F)$ is expected to exist. We found that, for $0.3 < \delta < 0.6$, the ratio δ/kT_c increases as δ decreases and the first-order transition character is also enhanced. This phenomenon is expected to persist when the concentration deviates from 50-50.

The results of our method as applied to the one-dimensional alloy model are sufficiently promising to suggest the extension to three-dimensional alloys (for example, simple cubic) and the investigation of the localizability of states in the energy gap region. In this case, the existence of a mobility gap near $E = 0$ will imply a nonmetalto-metal transition.[14] It will be appropriate to extend Anderson's localization theory[15] to include the LRO.

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Correlated Small-Polaron Hopping Motion*

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Prior small-polaron hopping theories have tacitly assumed that the lattice relaxes rapidly enough after a jump to permit the treating of successive hops as independent. We conclude that the appropriate relaxation time is too long to permit consistent application of these theories to intermediate-mobility materials such as NiO and CoO. Furthermore, the activation energies associated with correlated hopping motion may be sufficiently small so that the mobility will not manifest an activated behavior.

As has been stressed in a number of review articles on polarons,[1-3] the electron-lattice interaction may be sufficiently strong in those polar materials which are characterized by rather low electronic mobilities to suggest that the carriers are to be viewed as small polarons. In particular, much effort (recently reviewed by Bosman and van Daal[5]) has been expended in order to ascertain whether the carrier drift mobility in a number of transition-metal oxides manifests the thermally activated temperature dependence predicted by both the adiabatic[6] and nonadiabatic[7] small-polaron hopping theories. In this Letter it is pointed out that these theories are only applicable to situations in which the mean time between small-polaron hops is substantially greater than the time characterizing the relaxation of the lattice following a small-polaron hop[4]; the present considerations indicate that the deduced values of the drift mobility[5] in NiO and CoO ($\sim 10^{-1}$-1 $\text{cm}^2/\text{V sec}$) correspond to sufficiently short hopping times so that comparison with the hopping theories of Refs. 6 and 7 is not appropriate. Furthermore, it is felt that for such "intermediate" mobilities a theory of small-polaron hopping is needed in which the probability of a hop depends on the prior experience of the carrier. Such a theory may find application to a number of intermediate mobility materials.

In addition, in this Letter it will be argued that in this intermediate regime, where successive small-polaron hops are correlated, the activation energy characterizing the drift mobility is reduced substantially from that of the uncorre-