Electronic properties of an alloy with off-diagonal disorder

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Densities of states and spectral functions are computed for relatively large (~ 8000 atom) models of an alloy with off-diagonal disorder. A nearest-neighbor tight-binding electronic Hamiltonian is assumed. The numerical results are compared with those obtained from calculations based on the coherent-potential approximation (CPA) with the "additive limit." The overall agreement is quite satisfactory. In particular, the two approaches yield remarkably similar descriptions of the minority states in the case of purely off-diagonal scattering. As expected, the substructure in the electronic spectrum due to minority clusters is not reproduced by the CPA.

It has recently become possible to obtain exact results for the electronic and magnetic states of certain simple Hamiltonians representing three-dimensional models with a relatively large number of atoms.[1,2] These results are expected to reproduce the essential features of the spectra in infinite systems and can be used, therefore, to distinguish between various approximation schemes.

In the present paper, we consider the electronic properties of a single-band tight-binding model of a binary alloy. Two kinds of atoms, A and B, are arranged at random on the sites of a simple cubic lattice. Their relative concentrations are x and $y = (1 - x)$. A single orbital $|i\rangle$ is associated with the atom centered at the site i and the one electron Hamiltonian is written

$$H = \sum_i |i\rangle \epsilon_i \langle i| + \sum_{i \neq j}' |i\rangle t_{ij} \langle j|, \qquad (1)$$

where the prime indicates that only nearest-neighbor pairs are included in the summation. The local energy levels ϵ_i may assume either of the two values ϵ^A or ϵ^B, while the transfer integrals t_{ij} take the values t^{AA}, $t^{AB} = t^{BA}$, or t^{BB} depending on the configuration of the sites i and j. The disorder in the alloy is manifest in both the diagonal and off-diagonal matrix elements of H and the two effects must be treated on an equal footing.

The structure of Hamiltonian (1) is such that the disorder depends on the configuration of *pairs* of neighboring atoms. This complicates the formulation of a multiple-scattering theory because the various lattice sites do not contribute *independently* to the scattering of an incident electron. There is, however, a special relationship among the t_{ij}'s which simplifies the scattering formulation. This is the additive limit[3]: $t^{AB} = \frac{1}{2}(t^{AA} + t^{BB})$. In this case the disordered terms in Hamiltonian (1) can be written as a sum of independent finite-range scattering potentials, and the conventional methods of perturbation theory can be used to derive the appropriate generalization of the coherent-potential approximation[4] (CPA). (It is of interest to note that a similar simplification obtains in the random Heisenberg ferromagnet.[5]) Since it would appear that the additive limit does not exclude any physically interesting aspects of the problem, we shall adopt it in what follows.[6]

Having imposed the condition $t^{AB} = \frac{1}{2}(t^{AA} + t^{BB})$, the disorder in the model is characterized in terms of the impurity concentration x and the scattering parameters

$$\delta = (\epsilon^A - \epsilon^B), \quad \delta_1 = 6(t^{AB} - t^{BB}). \qquad (2)$$

For convenience we assume that $\epsilon^B = 0$ and $t^{BB} = \frac{1}{6}$.

In Figs. 1 and 2 the CPA is compared with computer calculations[7] of the density of states in four alloys, each of which has $x = 0.15$. In all four cases the machine computations were carried out for models with 5540 and 7680 sites (that is, cubic structures with dimensions $14 \times 18 \times 22$ and $16 \times 20 \times 24$). These models are large enough to provide a statistically significant number of different impurity configurations. Their dimensions have purposely been made asymmetrical to minimize the effects of degeneracies introduced by cubic symmetry. The densities of states shown in Figs. 1 and 2 are an average of the results obtained from the two calculations. Despite this averaging, some of the features are clearly statistical artifacts. For example, the fine scale wiggles along the majority band were different for the two individual calculations which went into the averages and are therefore identified as finite sample effects. By
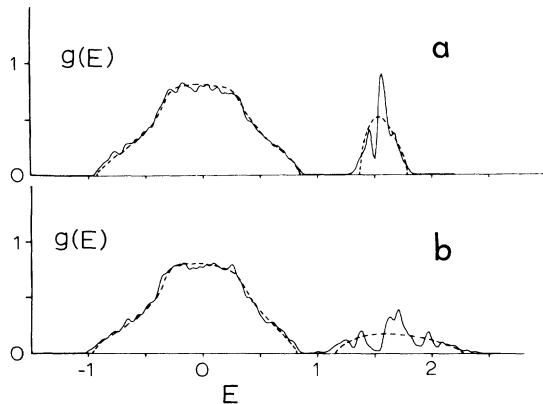
FIG. 1. Comparison of exact (solid) and CPA (dashed) densities of states: (a) $\delta = 1.5$, $\delta_1 = -0.2$; (b) $\delta = 1.5$, $\delta_1 = 0.4$. The exact results here and in all succeeding figures contain a Gaussian broadening with full width at half-height of 0.04 energy units.

contrast, the multipeaked structure of the minority band in Fig. 1 and the shoulders near $E = \pm 0.6$ in Fig. 2(b) were present in both individual results and are no doubt characteristic of an infinite alloy sample.

The results shown in Fig. 1 correspond to $\delta = 1.5$ and $\delta_1 = -0.2$ and 0.4. In these systems the effects of diagonal disorder are dominant and off-diagonal disorder may, in a sense, be viewed as a perturbation. Indeed, in both Figs. 1(a) and 1(b) the most significant feature of the spectrum is the appearance of a well defined subband centered around the impurity level $\epsilon^A = 1.5$. The main effect of the off-diagonal scattering is to rescale the shape of this minority band. A convenient way of characterizing this effect is in terms of a moment analysis of the
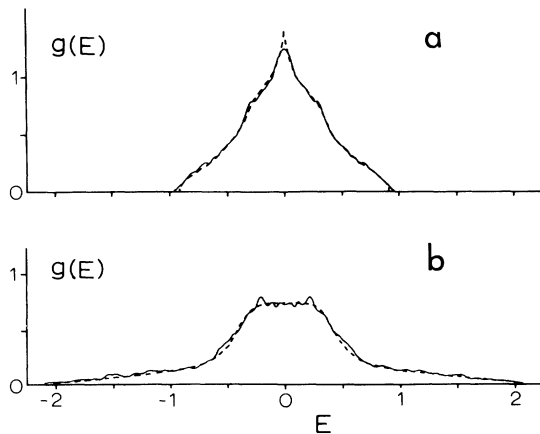

FIG. 2. Comparison of exact (solid) and CPA (dashed) densities of states: (a) $\delta = 0$, $\delta_1 = -0.5$; (b) $\delta = 0$, $\delta_1 = 1.5$.

average electronic spectrum.[3] In this context it can be shown that the heights $[h^{A(B)}]$ and widths $[w^{A(B)}]$ of the host and impurity subbands scale as

$$h^B = y^{1/2}/t^{BB}, \quad w^B = y^{1/2} t^{BB}, \tag{3a}$$

$$h^A = x^{1/2}/t^{AA}, \quad w^A = x^{1/2} t^{AA}. \tag{3b}$$

The comparison made in Fig. 1 indicates that the CPA accounts quite well for the general features of alloy spectrum. Two discrepancies, however, are worth noting. First is the fact that the exact spectrum is spread over a slightly larger range of energies than that predicted by the CPA; the states near the limits of the exact density of states being due to large single component clusters. Second, we note that the substructure within the minority band due to molecular clusters of A atoms is not present in the CPA results. Both discrepancies are associated with fluctuation effects and, as such, are expected in a comparison with a mean-field theory like the CPA.

In Figs. 2(a) and 2(b) we consider the effects of pure off-diagonal disorder. Here[8] the agreement between the exact calculations and the CPA is remarkably good. In the case $\delta_1 = 1.5$, the impurities produce broad wings above and below the central portion of the spectrum. Physically, these wings are due to an average distribution of the bonding and antibonding states associated with a single impurity. This interpretation is supported by the minority component density of states (plotted in Fig. 3) which is seen to peak in the vicinity of the bonding and antibonding levels. When the minority band width is narrower than that of the host (e.g., $\delta_1 = -0.5$) a peak in the center of the majority band is evident in both the CPA and exact results. The states in this peak are representative of those in the high narrow band of a pure A crystal, and are simply superimposed on the host spectrum.

Next we consider the separate contributions to the alloy density of states associated with each vector $\vec{k}$ of the Brillouin zone. These are given by the spectral functions $A(\vec{k}, E)$,
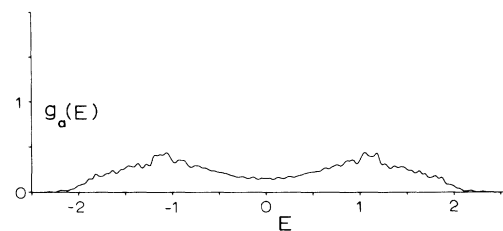
$$\rho(E) = N^{-1} \sum_{\vec{k}} A(\vec{k}, E), \tag{4}$$

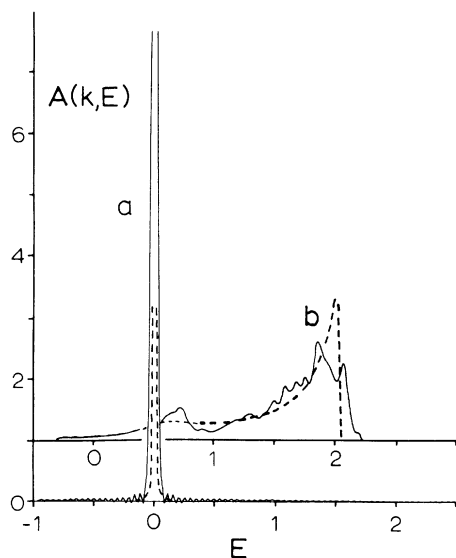FIG. 3. Exact result for the minority (A) component density of states in the case $\delta = 0$, $\delta_1 = 1.5$.

FIG. 4. Comparison of exact (solid) and CPA (dashed) spectral function for the case $\delta = 0$ and $\delta_1 = 1.5$: (a) $s(\vec{k}) = 0$; (b) $s(\vec{k}) = 1$.
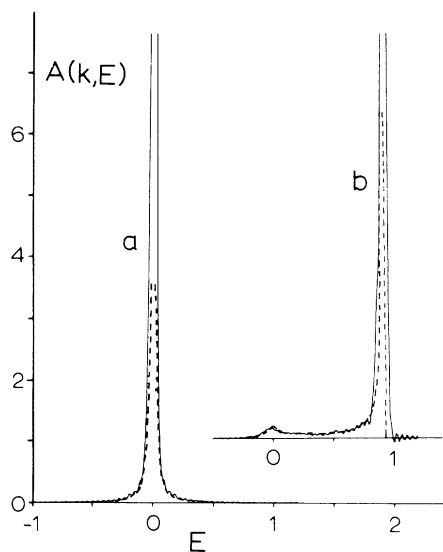

FIG. 5. Comparison of exact (solid) and CPA (dashed) spectral function for the case $\delta = 0$ and $\delta_1 = -0.5$: (a) $s(\vec{k}) = 0$; (b) $s(\vec{k}) = 1$.

where N is the total number of atoms in the model. In Figs. 4 and 5, machine calculations of $A(\vec{k}, E)$ for the two cases of purely off-diagonal disorder are compared with their CPA counterparts. (As mentioned above, the numerical results are averages of the results of computations carried out on 7680- and 5544-atom models.) The comparison is made at $\vec{k}$ points along the line Σ in the Brillouin zone. Within the CPA, $A(\vec{k}, E)$ depends on $\vec{k}$ only through the simple cubic energy-band function

$$s(\vec{k}) = \tfrac{1}{3}(\cos k_x a + \cos k_y a + \cos k_z a), \qquad (5)$$

where a is the lattice constant. The curves shown in Figs. 4 and 5 correspond to $s(\vec{k}) = 0$ and $s(\vec{k}) = 1$. $\{$In the case $\delta = 0$ it can be shown that both the coherent potential and exact results exhibit the symmetry $A[s(\vec{k}), E] = A[-s(\vec{k}), -E].\}$

The results for $\delta_1 = 1.5$ and $\delta_1 = -0.5$ have in common the feature that the spectral weight shifts from low to high energies as $s(\vec{k})$ increases from 0 to 1. Of course, this behavior is also characteristic of the perfect crystal. In the case $\delta_1 = 1.5$, contributions to the spectral functions for $s(\vec{k}) = 1$ may be divided into two parts. The contribution at larger values of $E (E \approx 1.80)$ is due primarily to the few highest-energy impurity states, and its multi-peaked structure is a finite-sample artifact. By contrast the smaller peaks near $E = 0.75$ represent majority states and are present in the numerical results for both alloy models. When $\delta_1 = -0.5$ the spectral functions for both $\vec{k}$ exhibit a sharp majority peak and a diffuse tail associated with the more localized minority states. In all of the cases considered here the agreement between the machine results and those of the CPA are quite satisfactory.

[1]R. Alben, M. Blume, H. Krakauer, and L. Schwartz, Phys. Rev. B 12, 4090 (1975).
[2]R. Alben and M. F. Thorpe, J. Phys. C 8, L275 (1975).
[3]H. Fukuyama, H. Krakauer, and L. Schwartz, Phys. Rev. B 10, 1173 (1974).
[4]A more general discussion of the off-diagonal disorder problem has been given by J. A. Blackman, D. M. Esterling, and N. F. Berk, Phys. Rev. B 4, 3350 (1971). In the additive limit the results of Blackman

et al. are equivalent to those derived in Ref. 3 (see Sec. IV of Ref. 3).
[5]See Appendix B of Ref. 3.
[6]In the numerical calculations, the additive limit provides no particular advantage. By contrast, the limit where $t^{AB} = (t^{AA} t^{BB})^{1/2}$, that is, the geometric mean, leads to great reductions in both the time and the storage requirement for the equation of motion method.
[7]The numerical method used here is essentially the same as that used in Ref. 1. The essential difference is that the time equation of motion for the Green's function involves pair-dependent off-diagonal terms. We have also changed the damping function which is

used to reduce "termination ripples." In Ref. 1 the damping function was an exponential. Somewhat more satisfactory results are obtained with a Gaussian damping function and this was employed here.

[8]When $\delta = 0$ it can be shown that the densities of states obtained from both the CPA and machine calculations must exhibit the symmetry $\rho(E) = \rho(-E)$.