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Electronic band structure of random binary alloys

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The Mott-Anderson band structure of a disordered system is modified in a random binary alloy due to the presence of a second kind of localized state $L2$. The physical nature of the extended states and the Mott-Anderson localized state $L1$ is clarified. The $L1$ states arising from quantum interference are located at the two ends of the band. The $L2$ states are strongly affected by the spatial distribution of disorder. They are found throughout the band. Transport properties based on this band structure are discussed. Results for the Anderson model are also described.

The Mott-Anderson band structure[1,2] of a disordered system is shown in Fig. 1(a). The two ends of the band are localized. Extended states occupy the central portion. The transitions from the localized-states regions into the extended-states region are marked by the critical values E_c and E_c'. Several substances have been found to behave as predicted by this band model, but there are others in which the existence of E_c and E_c' is less certain.[1]

Numerical calculations on systems like the Anderson Hamiltonian[3] and the binary random alloy[4] generally support this band structure. However, states with fairly localized wave functions are often found within E_c and E_c', the region occupied by extended states. Kirkpatrick and Eggarter[5] and Kohn and Olson[6] studied the spectrum of substitutional binary random alloys with $\epsilon_A = 0$ and $\epsilon_B \to \infty$. They found many sharp features in the density of states at nearly all concentrations. These peaks are found throughout the band, and have been identified to be associated with localized states. Recent studies on binary random alloys with finite ϵ_B by Srivastava and Weaire[7] and others[4,8] also reported similar observations.

After a detailed examination of many numerical calculations for several model Hamiltonians of disordered systems, and on further evidence from theoretical analyses, we come to the conclusion that there are two kinds of localized states, as first suggested by Kirkpatrick and Eggarter.[5] They are most clearly characterized in binary random alloys. We shall, therefore, restrict the main portion of our discussion to this model system. It is shown that these two kinds of localized states come from different physical origins and have different properties. A slight modification of the Mott-Anderson band structure for the binary random alloy is suggested. In each band there are two mobility edges, not as many as suggested previously.[5] A few observations on the Anderson Hamiltonian are given at the end of this paper.

The Hamiltonian of a substitutional binary random alloy with nearest-neighbor interaction in the tight-binding approximation is

$$H=\sum \epsilon_i \,|i\rangle\langle i| + V\sum |i\rangle\langle i\pm 1| , \qquad (1)$$

where $\epsilon_i = \epsilon_A$ or ϵ_B (with $\epsilon_B > \epsilon_A$) according to the occupancy at the ith site. The value $\delta = \epsilon_B - \epsilon_A$ is chosen to be greater than $2ZV$, where Z is the

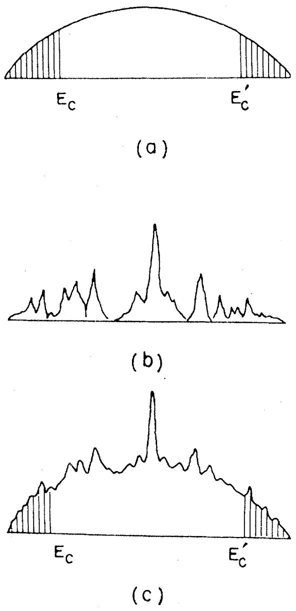

FIG. 1. (a) Mott-Anderson band structure of a disordered system. The localized states (shaded) at the two extremities of the band are called localized states of the first kind ($L1$) in this paper. (b) Localized states of the second kind ($L2$) and their distribution. (c) The modified band structure of one of the subbands in a binary random alloy. It is a combination of (a) and (b).

number of nearest neighbors, so that two split bands are formed. At energies in the *A* band (the lower band), it has been observed[4,9] that the electron wave functions have finite amplitudes only at the *A* sites. At energies in the *B* band, $|\psi|^2$ is large only at the *B* sites. This is clearly true in the limiting case $\delta \to \infty$. Numerical results definitely demonstrate this for finite δ, down to the limit that split bands are just formed. It is sufficient to see this by considering the case of a single impurity *B* atom in a lattice of *A*. In spite of the finite interaction of the impurity atom with the lattice atoms, if the impurity level E_I lies outside the *A* band, $\psi(E_I)$ is localized at the impurity site *B*. At energies in the *A* band, the eigenfunctions of the whole system, being orthogonal to $\psi(E_I)$, must have nearly zero amplitudes at the impurity site. Further arguments for this are presented in the Appendix. The analogous localized phonon state in the phonon spectrum of a single light impurity in a chain[10] also suggests this result.

This observation enables us to make use of the classical percolation idea.[11,12] Consider the case in which the concentration of *A* atoms is greater than the classical critical-percolation probability p_c for a given lattice. At such concentrations, connected routes of *A* sites are formed. Note that here we refer to the *A*-atom sites and not to the actual flow of electrons. In the following, the word "patches" will be used to mean large groups of *A* atoms joined by narrow channels of *A* atoms to form connected routes of *A* sites "percolating" throughout the system, and the word "island" is used to denote an isolated group of *A* atoms not directly joined to other *A* atoms except through sites occupied by *B* atoms. A typical example of a two-dimensional system at concentrations of *A* greater than p_c is shown in Fig. 2(a). We would like to emphasize that most of our studies are on three-dimensional systems. The reasoning and results stated below are for such systems. Only two-dimensional figures are used in graphical display for the sake of convenience.

We shall examine the detailed electronic structure of the *A* band. The behavior in the *B* band can be easily inferred using the quantum-percolation picture.[9] At energies in the *A* band under this split-band condition, the electron wave functions have finite amplitudes only at the A sites. The B sites have nearly zero amplitudes even for finite interaction between A sites and B sites. We can thus consider the isolated islands of A atoms and the connected routes of A atoms separately when we study their contributions to the A band. The spectrum in the A band of the A-B alloy is a superposition of spectra of the islands and those of the connected routes. This superposition is obviously exact in the limiting case $\delta \to \infty$, and is a good approximation, as argued above and illustrated by numerical results below, for finite δ even down to the split-band limit.

Let us first look at the electron states in the connected routes of A atoms formed of patches and channels. If the electrons behave like classical particles at the A sites, they would percolate through the system. Only extended states can exist in such connected routes. Quantum interference, however, may break the wave-function connections. In a typical connected route of A sites as shown on the right-hand side of Fig. 2(a), we see that, if quantum interference yields zero amplitudes at certain sites inside the patches, the wave function as a whole still extends across the whole system. It remains as extended. If, however, the effect of quantum interference is such that the amplitudes at the narrow-channel sites become zero, the connection of the wave function across the patches is broken. Quantum percolation stops. A localization of the first kind (*L*1) occurs. Such a localization is a result of quantum interference breaking the "weak" links in the channels of the connected routes.

Numerical evaluation of the wave amplitudes using several methods[9] related to the local Green's-function approach on various possible arrangements of the connected routes of A atoms shows that such a localization occurs only at energies close to the two ends of the A band. At all other energies in the central portion of the A band, the narrow-channel sites have finite wave amplitudes. Analytically we can roughly see why this is so. In the nearest-neighbor tight-binding interaction approximation the bandwidth of a cluster of atoms is about $2ZV$. Within the patches, each A atom has six neighbors of A atoms in a simple-cubic lattice and four neighbors in a square lattice. The bandwidth of the patches is about the same as that of the whole A band. It is centered around ϵ_A. The weak links connecting the patches are very likely linear chains of A atoms. The spectrum of linear chains (whether straight or crooked) occupies the central portion of the A band with a width of $4V$. A wave function extends over the whole system only if the channel sites have finite amplitudes. This means that in the A band of width $2ZV$, the extended states can exist only within a width of roughly $4V$ centered about ϵ_A. Beyond these limits, indicated by E_c and E_c', the links across the narrow channels are broken.

Thus we see that the spectrum in the connected routes of A atoms formed of patches and channels is exactly that described by Mott[1] [Fig. 1(a)]. The localized states *L*1 and the extended states cannot coexist. This is obvious because no channel states can exist beyond E_c and E_c', and within E_c and E_c' the channel states form a continuum.

Let us now consider the isolated islands of the A atoms. In the limit of $\epsilon_B \to \infty$, the wave function must be strictly localized on these sites. For isolated singlets of A atoms, the spectrum is a δ function at $\epsilon = \epsilon_A$. The channel states of the connected routes are extended at $\epsilon = \epsilon_A$. Thus the extended states and this kind of localized states can coexist. Similarly, spectra of islands of doublets, triplets, ... can coexist with the continuum of the connected channel states. Such states were first

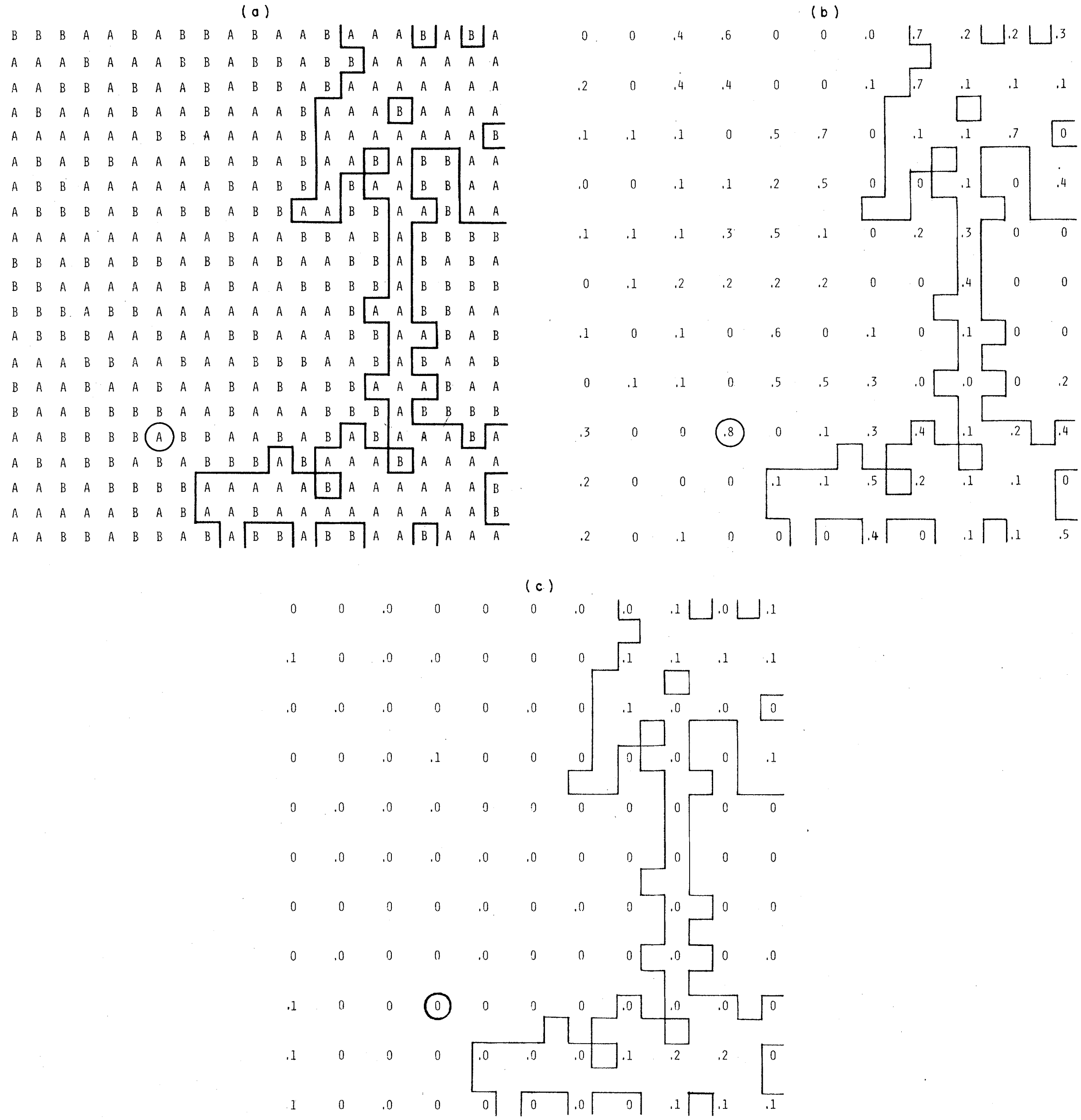

FIG. 2. (a) Central region of a (91 × 91) two-dimensional square random-binary-alloy lattice with 0.62 concentration of A atoms, showing a connected route of A sites (on the right-hand side) and an isolated singlet of A atom (circled). (b) Calculated $|\psi|^2$ at the center of the A band ($E = \epsilon_A = 0$) at each alternate site of the lattice shown in (a). $\delta = \epsilon_B - \epsilon_A$ is chosen to be $10V$ which is slightly larger than the split-band condition of $8V$. (c) Calculated $|\psi|^2$ at the tail part of the A band ($E = 3.25\,V$) at each alternate site of the lattice shown in (a). $\delta = 10\,V$. In (b) and (c), the number "0" indicates values less than 0.001, and the number ".0" indicates values lying between 0.001 and 0.05.

noted by Kirkpatrick and Eggarter,[5] and by Kohn and Olson.[6] At finite ϵ_B, a mixing of the wave functions occurs, but in the split-band regime this mixing is not sufficient to erase the sharp features in the density of states as observed in numerical computations.[4,5,7] Wave functions at isolated A sites are still mainly localized there. Even with small δ, we can always find isolated A sites and islands spatially far away from the connected routes so that their wave functions do not significantly mix with the patch states or with the channel states. These states coexist with the connected-route states. They are what we call localized states of the second kind ($L2$). Another possible name for these states is "resonances." It is important to note that the $L2$ states are dependent on the spatial position of the A sites. In the A-B random alloys, this means that $L2$ is a function of the concentration of A. At concentrations lower than the classical critical-percolation probability, all states are $L2$.

The $L2$ states are quantized differently on isolated islands of a great variety of sizes and shapes. They distribute throughout the whole A band. This we can easily see in the limit $\epsilon_B \rightarrow \infty$. Finite ϵ_B interaction shifts the positions slightly, broadens and splits the peaks. It is interesting to note that the singlets of A sites form a peak near ϵ_A; the doublet islands form two peaks nearly symmetric about ϵ_A; and the triplet A sites give roughly three peaks with the central peak near ϵ_A and the other two further away on both sides, and so on (see Fig. 4 of Ref. 4). Together they form a spectrum with many peaks like that shown in Fig. 1(b). Often we find that the sharp peak at the center ϵ_A is separated from the other $L2$ peaks on both sides by two dips in the total density of states [Fig. 1(c)]. The dips are most distinct at low concentrations of A, clearly related to the population of singlets and other smaller islands. Towards the ends of the band, the peaks of $L2$ states [Fig. 1(b)] become more and more spread out, forming a rather smooth density of states. Kirkpatrick and Eggarter[5] found that in their numerically computed spectrum the spike at ϵ_A sits in the center of a gap of zero density of states. We see from the above arguments that this cannot be true. In the $\epsilon_B \rightarrow \infty$ case, in which the gap was most clearly seen, $L2$ can coexist with the continuum channel states. The channel states and the patch states are never zero over a range of energies near E_A so as to form a gap. The reported gap size was not larger than the spacing of levels in a linear chain across the small cluster studied by them. As the cluster size increases, the gaps on the two sides of ϵ_A should become dips. In a recent numerical calculation on two-dimensional binary alloys by Yoshino and Okazaki,[8] this central spike was also observed. It is flanked by two dips, not gaps. These authors used periodic boundary conditions in one direction to remove the finite-cluster-size problem. Interaction of the isolated A sites or islands with the connected routes may break the continuum spectrum of a local connected route, but the *total* density of states cannot have gaps around ϵ_A or any other $L2$ states larger than the spacings of the quantum levels in a linear chain. In this sense, no new mobility edge is introduced by the presence of the $L2$ states.

Strictly speaking, states with large local amplitudes lying in a continuum are defined as resonance states in other fields. When the $L2$ states were first observed in random binary alloys, they had been referred to as localized states.[5,6] There are other reasons to retain this name.

In most systems in which resonances occur, the scattering sites are usually in the immediate neighborhood of sites which have a continuum spectrum. Examples are some surface or imbedded-impurity problems, atomic scattering, and α decay from the nucleus. The key point of interest in these problems is the tunneling from the resonance site into the continuum outside. Here in a random alloy, the situation is different. There are more isolated islands than percolating channels. Only a small percentage of these islands are in the neighborhood of the connected routes. The islands have different sizes and shapes. They have different resonance energies. At energies in the A band, the B sites appear as barriers. A resonance wave function at an A site decays exponentially through the barrier B sites. The analogous potential problem is schematically illustrated in Fig. 3. The tail of the resonance wave function at an isolated island far away from the connected route has to penetrate through many islands and barriers. Its amplitude cannot be significantly large on reaching the percolating channel. Hopping transfers among such isolated islands dominate over tunneling into the distant connected routes at finite temperatures. Although the transfer of electrons from an isolated island to the connected routes is resonance-like, transfer among the majority isolated islands not in the neighborhood of the connected routes behaves truly as would localized states.

As the concentration of A atoms falls below the classical critical probability, the continuum spectrum disappears. The $L2$ states are then localized in the sense that bound states of atoms in a cluster, or energy levels in colloids are localized. Whatever the preferred name for these $L2$ states, the significance of the localized state features in these states should be realized.

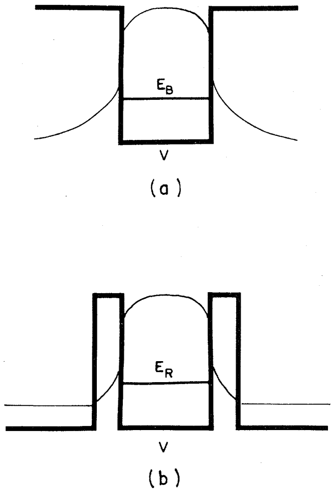

FIG. 3. $|\psi|^2$ of (a) a localized state in a potential well and (b) a resonance state E_R within potential barriers. In the latter case $|\psi|^2$ decays exponentially in the barrier regions and the leaked-out wave function is matched smoothly onto the oscillating wave of a free particle.

The above statements are fully supported by our numerical results. Although we studied many three-dimensional systems, for the convenience of presenting the data, only two-dimensional square-lattice results are shown here in Figs. 2(b) and 2(c). The numbers represent the relative magnitudes of the calculated $|\psi|^2$ at alternate sites of the particular sample of A-B alloy depicted in Fig. 2(a). Only the central portion of a much larger cluster (91×91) is shown here. Even in this example of a two-dimensional square lattice with $\delta = 10V$, which is only slightly larger than the split-band condition, $|\psi|^2$ is zero to three decimals at all B sites and at all energies in the A band. At $E = \epsilon_A = 0$, the channel sites are filled with electron wave functions, and the singlet A site (circled) is highly localized ($L2$ type). It is interesting to note that this particular site is only two steps away from another A atom. This means that an A atom hardly sees another A atom if there is a single B atom in between them, even at such small $\delta \sim 10V$. At $E = 3.25V$ [Fig. 2(c)], which is beyond E_c, the channel sites are not filled. The wave function in the connected route is broken into two pieces, each localized in one of the two patches ($L1$ type). A similar wave-function-amplitude contour map is obtained at $E = -3.25V$. In these calculations a broadening parameter η in $E + i\eta$ is introduced to pick up the localized states. This limits the numerical resolution mentioned above. A smaller η will enhance the contrast in the magnitude of $|\psi|^2$ between the extended and the localized states even further, but a smaller η decreases the number of localized states seen at a particular value of E.

The presence of $L2$ certainly complicates the calculation of transport properties. However, the overall picture is still fairly clear. Beyond E_c and E_c' localized states of the first kind dominate and only phonon-assisted hopping occurs. At finite temperatures, the dc conductivity ($\propto T^{-1/4}$) law of Mott is clearly valid. Within E_c and E_c', the extended-states contribution dominates. Because of the presence of hopping conductivity among isolated islands of various sizes and other local effects related to the $L2$ states, the dc conductivity of a system with a Fermi level lying within E_c and E_c' is no longer strictly temperature independent. A slight temperature effect ought to be observed. We still expect to see a change at E_c and E_c', but the discontinuity is less sharp owing to the presence of the $L2$ states on both sides of E_c and E_c'. In random alloys, this temperature effect coming from the $L2$ states changes with concentration. The positions of E_c and E_c' and $L1$ states are less sensitive to the concentration. They depend more on the atomic-interaction parameters V and $\epsilon_B - \epsilon_A$. In this way we can separate the $L2$ states from the $L1$ states. Of course, at very low concentrations of A, all states in the A band are $L2$, and E_c and E_c' no longer exist. In such cases, one is certain to find an extended-energy region in the B band. The conditions for the existence of extended states in the A band, in the B band, or in both hands simultaneously can be easily worked out from the quantum-percolation picture.[9] Tunneling is present within E_c and E_c', but its contribution is negligible in comparison to currents passing through the connected routes. Other transport properties can be inferred from the above modified band structure.

Many of the above conclusions remain valid in other disordered systems. A general disordered system can be pictured as a quantum-percolation problem. Ponds, lakes, and rivers are formed among mountains and valleys. The sizes and shapes of these change as the energy level is raised or lowered. The $L2$ states are localized on ponds or on the hill tops. They are dependent on the spatial distribution of the sites. The $L1$ states are caused by quantum interference.

In the Anderson model, ϵ_i in Eq. (1) can have any value within $\pm\frac{1}{2}W$. It is observed in this case that the two ends of the band are still occupied by localized states. Some of these localized states at the lower end of the band are found to be located in ponds (i.e., at low-value ϵ_i sites). Near the upper end of the band, localized states are often found on the hill tops (i.e., at the large value ϵ_i sites). These are the $L2$ states. The $L1$ type of localization can also be identified. The center of the band in the Anderson model does not corresond to the center of the A band in the binary alloy. It is more closely related to the center of both subbands. Numerical results indicate that, at large W, for example, $W = 10V$, all states in the band are localized, including those at the center of the band. For small values of W, for example, $W = 3V$, at energies close to the center of the band, all sites have more or less the same finite amplitudes. We observed this even in the two-dimensional square lattice. Although our numerical method is designed to study localized states, the uniformity of the amplitudes at all sites and for several different η leads us to believe that these states are extended at the center of the band. This conclusion is in agreement with previous numerical studies[8,13,14] of the Anderson model in two-dimensional systems.

A recent paper by Abrahams *et al.*[15] seems to show the absence of quantum diffusion in the two-dimensional Anderson model. Lee,[16] on the other hand, has reported the existence of extended states in the two-dimensional square lattice using renormalization group analysis. In the binary-random-alloy model, our argument based on quantum percolation definitely establishes the existence of extended states in the two-dimensional systems. If they are not found in the A band, they can be located in the B band. A similar theoretical argument fails to give conclusive results in the Anderson model because of state mixing and because $p_c \sim 0.5$ in the two-dimensional square lattice.

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APPENDIX

Our numerical results indicate that at $\delta > 2ZV$, in the split band regime, the wave functions have large amplitudes only at the A sites at energies in the A band, and the wave functions have large amplitudes only at the B sites at energies in the B band. Theoretical arguments will be given here to support this observation.

Consider a single impurity B in a crystal of A. We can rearrange the matrix elements of the tight binding Hamiltonian [Eq. (1)] in such a way that the upper-left element represents the impurity B. The matrix of H is of the form

$$\begin{bmatrix} \epsilon_B & X \\ Y & W \end{bmatrix}, \tag{A1}$$

where W, X, Y are the same matrix elements in the Hamiltonian of the pure crystal of A. The local Green's function at the impurity B site is just the upper-left element of the inverse matrix $(z - H)^{-1}$, where $z = E + i\eta$. If

$$M = \begin{bmatrix} A & B \\ C & D \end{bmatrix}$$

and

$$M^{-1} = \begin{bmatrix} \alpha & \beta \\ \gamma & \delta \end{bmatrix},$$

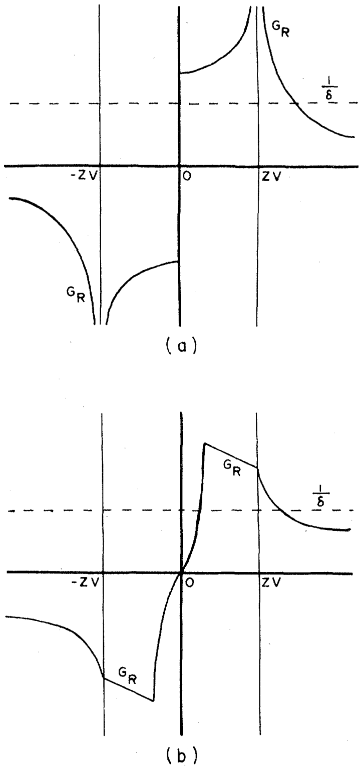

FIG. 4. (a) Real part of the lattice Green's function of a typical two-dimensional lattice. (b) Real part of the lattice Green's function of a typical three-dimensional crystal. The example here is an sc lattice in tight-binding model. The curves are schematic. The true numerical values can be found in Refs. 16 and 17.

one way of writing α is $(A - BD^{-1}C)^{-1}$. Thus the local Green's function at the impurity site is

$$\begin{aligned} G(i;E) &= 1/[z - \epsilon_B - X(ZI - W)^{-1}Y] \\ &= 1/\{[(z - \epsilon_A) - X(ZI - W)^{-1}Y] - (\epsilon_B - \epsilon_A)\} \\ &= 1/(G_0^{-1} - \delta) \\ &= G_0/(1 - \delta G_0)\,, \end{aligned} \tag{A2}$$

where G_0 is the local Green's function of the pure A crystal. G_0 is analytic everywhere except along a cut on the E axis from $-2ZV$ to $2ZV$. The impurity Green's function G has a pole at

$$G_0 = 1/\delta\,, \tag{A3}$$

where $\delta = \epsilon_B - \epsilon_A$ is real. The numerical plots of the real parts of G_0 for various crystal structure are known. A typical two-dimensional result, e.g. that of a square lattice,[17] is shown in Fig. 4(a). From the figure we see that we can always find a solution to (A3) in two-dimensional systems, at energies *outside* the A band no matter what the value δ may be. In a three-dimensional crystal, (A3) would have a solution at energies outside the band only for large enough δ. Fig. 4(b) gives the example of a sc crystal.[18] The split-band condition guarantees this. This solution out-side the band has no imaginary component in E. The wave function is localized at the B site, and its amplitude decays exponentially.

Consider now many impurity B sites clustering around a certain local region in the crystal of A atoms. We can always group the impurity matrix elements at the upper-left corner, and obtain a similar expression for G as in (A2). The quantity δ is now replaced by a diagonal matrix of real elements of 0's and δ's. In the split-band regime, the solutions must still give poles on the real axis outside the branch cut. At these poles of real energies, the wave functions have large amplitudes only at the B sites.

If the host Green's function G_0 is not suddenly changed as in the case of a phase transition, this argument can be extended to even higher concentrations in B until classical percolation routes of the B sites are formed. Then the $|\psi|^2$ at an energy in the B band after normalization is small but is still finite compared to that at an A site.

Similarly we can regard the A atoms as impurities in the crystal of B. Wave functions are large only at A atoms at energies of the impurity levels outside the B band.

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[1] N. F. Mott, Rev. Mod. Phys. 50, 203 (1978).
[2] P. W. Anderson, Rev. Mod. Phys. 50, 191 (1978).
[3] S. Yoshino and M. Okazaki, J. Phys. Soc. Jpn. 43, 415 (1977).
[4] B. Hede and B. Y. Tong, Solid State Commun. 25, 269 (1978).
[5] S. Kirkpatrick and T. P. Eggarter, Phys. Rev. B6, 3598 (1972).
[6] W. Kohn and J. Olson, J. Phys. (Paris) C3, 135 (1972); private communication.
[7] V. Srivastava and D. Weaire, Phys. Rev. B 18, 6635 (1978).
[8] S. Yoshino and M. Okazaki, Solid State Commun. 27, 557 (1978).
[9] M. M. Pant and B. Y. Tong, J. Phys. C (to be published).
[10] A. A. Maradudin, E. W. Montroll, and G. Y. Weiss, Solid State Phys. Suppl. 3, 160 (1963).
[11] V. K. S. Shante and S. Kirkpatrick, Adv. Phys. 20, 325 (1971).
[12] Morrel H. Cohen, Phys. Today 24(5), 26–32 (1971).
[13] S. Yoshino and M. Okazaki, J. Phys. Soc. Jpn. 43, 415 (1977).
[14] J. Stein and U. Krey, Solid State Commun. 27, 797 (1978).
[15] E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, Phys. Rev. Lett. 42, 673 (1979).
[16] P. A. Lee, Bull. Am. Phys. Soc. 24, 360 (1979); Phys. Rev. Lett. 42, 1492 (1979).
[17] S. Katsura, and S. Inawashiro, J. Math. Phys. (Cambridge, Mass.) 12, 1622 (1971).
[18] T. Morita and T. Horiguchi, J. Math. Phys. (Cambridge, Mass.) 12, 986 (1971).