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Contribution to the Theory of Disordered Alloys*

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A simple model of a disordered substitutional alloy, similar in some respects to transition-metal alloys, is studied in several approximations. A formalism is presented in which the Green's function for the alloy is represented in the form of an infinite perturbation series, the lowest term of which is the coherent-potential approximation introduced earlier. The average density of states for several model alloys is investigated, and it is found that corrections to the rigid-band model can be significant even in situations in which the constitutents are not very dissimilar. Study of certain terms in the perturbation series suggests that the coherent-potential approximation is adequate in many situations. The density of states localized about a particular type of atom is shown to bear little resemblance to the average density of states. It can be a strong function of the environment, but if an average environment is taken, the coherent-potential scheme gives good results. The variation of average and local state densities as a function of concentration is studied for a particular model.

I. INTRODUCTION

THIS paper presents the results of an analysis of some of the electronic properties of a simple model of a disordered substitutional alloy. The fundamental difficulty in such an analysis is that no exact solution of the Schrödinger equation for a disordered system is obtainable, a situation which strongly discriminates studies of ordered and disordered systems. One of the objects of the present work is, therefore, to study the techniques used in the analysis, with the aim of minimizing the occurrence of uncontrolled approximations. An analysis of the model becomes meaningful only after the limits of the approximations are established.

A considerable body of theoretical literature exists in this field. Early work involved the so-called rigid-band assumption,[1] in which it is posited that the density of electronic states is an alloy of two elements is the same as the density of states in either of the pure materials. This assumption is frequently invoked in analyses of experimental work. We shall attempt to see if it is a reasonable one. Similar in some cases to the rigid-band assumption is the virtual-crystal approximation. This assumes that the electrons in an alloy behave identically to the electrons in a hypothetical ordered material in which the crystalline potential is the average of the potentials of the pure materials. The virtual-crystal approximation represents the lowest-order term in a perturbation series and may be extended by including more terms. However, as has been discussed by Stern,[2] the usefulness of low-order perturbation theory is very limited.

More sophisticated techniques based on the multiple-scattering formalism of Lax[3] and others have also been introduced. Korringa[4] and, independently, Beeby[5] have suggested an approximation in which one reduces the crystalline potential to a sum of localized potentials and assumes that the electrons in an alloy behave as though they were moving in a particular ordered system of localized potentials, the scattering matrix of which is the average of the scattering matrices of the localized potential corresponding to each constituent. This approximation has been considered by Soven,[6,7] who found that it is not a reasonable one for the case where the localized potentials have a strength approaching that found in transition metals. The approximation reduces to the virtual-crystal one in the case where the potentials are weak. A formal perturbation-theory analysis leading to, among other things, an expression for the alloy density of states has been presented by Yonezawa and Matsubara.[8] The approximation to be considered below may be reached via their formalism,[9] although they have carried out no analysis of it.

The approximation scheme studied in this paper was introduced by Soven[7] under the name of "the coherent-potential method." In Ref. 7 application was made to the case of one-dimensional alloys, where the method appeared to be reasonable for many situations. Onodera and Toyozawa[10] independently arrived at the same approximation and applied it, in a somewhat different context, to a simple three-dimensional system. Velický *et al.* have carried out a detailed analysis of all of the approximations discussed above and, in particular, of the coherent-potential method. Their work is complementary to ours, overlapping in certain aspects, but in general analyzing the approximation in a different

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[1] See, for example, N. F. Mott and H. R. Jones, *The Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1959).

[2] E. A. Stern, Physics **1**, 255 (1965); Phys. Rev. **144**, 545 (1966).

[3] M. Lax, Rev. Mod. Phys. **23**, 237 (1951).

[4] J. Korringa, J. Phys. Chem. Solids **7**, 252 (1958).

[5] J. L. Beeby, Proc. Phys. Soc. (London) **A279**, 82 (1964); Phys. Rev. **135**, A130 (1964).

[6] Paul Soven, Phys. Rev. **151**, 539 (1966).

[7] Paul Soven, Phys. Rev. **156**, 809 (1967).

[8] F. Yonezawa, Progr. Theoret. Phys. (Kyoto) **31**, 357 (1964); F. Yonezawa and T. Matsubara, *ibid.* **35**, 357 (1966); **35**, 759 (1966).

[9] T. Matsubara and F. Yonezawa, Progr. Theoret. Phys. (Kyoto) **37**, 1346 (1967).

[10] Y. Onodera and J. Toyozawa, J. Phys. Soc. Japan **24**, 1341 (1968).

manner. Their conclusions about the ultimate usefulness of the coherent-potential approximation are consistent with ours.

Our presentation will be divided into several parts. The particulars of the model and the formalism used to analyze it are discussed in Sec. II. In Sec. III we calculate the electronic density of states and demonstrate that our calculation is an accurate one, while in Sec. IV we study the density of states localized about a particular lattice site. In Sec. V we very briefly discuss the representation of the alloy wave functions in terms of elementary Bloch waves. Section VI is concerned with the application of some of our results to a very elementary example. A brief summary and our conclusions is presented in Sec. VII.

II. DEFINITION OF THE MODEL

The model alloy studied in this paper is formed by randomly placing atoms of type A and B on the lattice sites of a simple cubic lattice. The concentrations of the constituents are denoted by c_A and $c_B=1-c_A$, respectively. We postulate that each atom has only a single eigenvalue in the energy range of interest, the eigenfunction of which is so compact that the electronic structure of the alloy may be conveniently studied in the tight-binding formalism. We further postulate that the atomic-wave functions for atoms A and B are essentially identical and that the matrix element of the alloy Hamiltonian between orbitals centered on different lattice sites is independent of the types of atoms occupying those sites. The atomic eigenvalues (the diagonal matrix elements of the Hamiltonian) are E_A and E_B, respectively. The model represents a disordered system only because $E_A \neq E_B$.

The most fruitful method of obtaining information about the electronic spectrum of the model is by studying the Green's function $\mathcal{G}$, which is defined by the operator equation

$$(E+is-\mathcal{H})\mathcal{G}=1\,, \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian, E is the energy, and s is a positive infinitesimal. It is important to note that this equation is deceptively simple in appearance; $\mathcal{H}$ is actually a random operator and so, therefore, is $\mathcal{G}$. A solution of Eq. (1) for the disordered system involves an inversion of the operator $E+is-\mathcal{H}$ for an arbitrary configuration of atoms followed by an ensemble average of the inverse. The remainder of this paper is devoted to surmounting this problem.

It is necessary to further define the model and to introduce some notation before proceeding with an analysis of the Green's-function equation. We work in two representations, a Wannier one defined by the functions $\varphi_l(\mathbf{x})$, where φ_l is the common atomic orbital centered on lattice site l, and the Bloch representation defined by the tight-binding functions

$$\psi_k(\mathbf{x})=N^{-1/2}\sum_l \exp(ik\cdot l)\varphi_l(\mathbf{x})\,.$$

The wave vectors of the ψ_k range over the first Brillouin zone of the simple cubic lattice.

In Wannier representation

$$\langle l|E-\mathcal{H}|l'\rangle=\delta_{ll'}(E-E_l)-(1-\delta_{ll'})W(l-l')\,, \tag{2}$$

where $W(l-l')$ is the matrix element of the Hamiltonian between orbitals centered on l and l', and E_l is E_A or E_B, as the case may be. In Bloch representation

$$\langle k|E-\mathcal{H}|k'\rangle=N^{-1}\sum_l (E-E_l)\times\exp[il\cdot(k-k')]-\delta_{kk'}W(k)\,, \tag{3}$$

where

$$W(k)=\sum_{l\neq 0}\exp(ik\cdot l)W(l)\,.$$

From Eqs. (1) and (3)

$$\langle k'|\mathcal{G}^{-1}|k\rangle=N^{-1}\sum_l (E-E_l)\times\exp[il\cdot(k-k')]-\delta_{kk'}W(k)\,. \tag{4}$$

The essence of the coherent-potential method, as applied to the present problem, is to expand $\mathcal{G}$ in a perturbation series based on a self-consistently determined Green's function G. We define G by replacing every E_l in Eq. (4) by an unknown parameter E_0. The quantity E_0 will be chosen to yield a good convergence rate for the perturbation series which one obtains when the exact Green's function $\mathcal{G}$ is expressed in terms of the coherent Green's function G. G itself satisfies the equation

$$\langle k'|G^{-1}|k\rangle=\delta_{kk'}[E+is-E_0-W(k)] \tag{5}$$

and is formally the band Green's function for an ordered system of atoms, each of which possesses atomic eigenvalue E_0.

Manipulation of Eqs. (4) and (5) leads to

$$\mathcal{G}=G+GV\mathcal{G}\,, \tag{6}$$

where

$$\langle k|V|k'\rangle=N^{-1}\sum_l \exp[il\cdot(k-k')](E_l-E_0)\,.$$

Provided that the resulting series converges, Eq. (6) may be solved in the usual iterative fashion to yield

$$\mathcal{G}=G+GVG+\cdots\,, \tag{7}$$

which in Wannier representation takes the form

$$\mathcal{G}_{ll'}=G_{ll'}+\sum_{l''}G_{ll''}v_{l''}G_{l''l'}+\cdots\,, \tag{8}$$

in which

$$G_{ll'}=N^{-1}\sum_k \frac{\exp[ik\cdot(l-l')]}{E-E_0+W(k)}\,.$$

The "perturbing potentials" v_l are defined by $v_A = E_A - E_0$ or $v_B = E_B - E_0$. The series may be partially summed by collecting together all terms in which the same site occurs successively. This leads to a perturbation series in terms of t matrices, which are defined in the present case by the equation

$$t_l = v_l + v_l G_{ll} v_l + \cdots = v_l / (1 - g_0 v_l) \tag{9}$$

in which we have introduced the notation $G_{ll}(E) = g_0(E)$. In terms of the t_l,

$$\mathcal{G}_{ll'} = G_{ll'} + \sum_{l''} G_{ll''} t_{l''} G_{l''l'} + \sum_{l'' \neq l'''} G_{ll''} t_{l''} G_{l''l'''} t_{l'''} G_{l'''l'} + \cdots . \tag{10}$$

This equation will form the basis for most of the subsequent discussion.

The utility of Eqs. (8) and (10) for studying the electronic spectrum depends upon the definition of E_0. If we were to choose $E_0 = c_A E_A + c_B E_B$ as a definition, the lowest-order term in Eqs. (8) and (10) would represent the virtual-crystal approximation but the higher-order terms would not be small. Instead, we chose E_0 by requiring that at every energy the average of the t matrices vanish.[7] In symbols,

$$c_A t_A + c_B t_B = 0 . \tag{11}$$

Substitution of Eq. (9) into (11) leads to the equation

$$(c_A E_A + c_B E_B) - E_0 = (E_A - E_0)(E_B - E_0) g_0(E - E_0) . \tag{12}$$

The essential, but awkward, feature of this equation is the dependence of the "unperturbed" Green's function on E_0. We base the perturbation series on a system in which the major effect of the atomic potentials is automatically included. In order to do this it is necessary that the scattering operators be defined in terms of the system itself. E_0 then becomes energy-dependent, as is obvious from Eq. (12).

It is convenient to introduce a dimensionless notation of the following type. Let the lattice constant of the simple cubic lattice be denoted by a. Then, for the case where only nearest-neighbor interactions are important,

$$W(k) = -W_0[\cos(ak_x) + \cos(ak_y) + \cos(ak_z)] ,$$

where W_0 is the common value of the overlap integral. We express all energies in terms of W_0 by the relations

$$E_A = W_0 \Delta , \quad E_B = -W_0 \Delta , \quad E = \epsilon W_0 , \quad E_0 = \epsilon_0 W_0$$

and assume, henceforth, that by $\mathcal{G}$ and G we mean W_0 times the actual Green's functions. Since $G_{ll'}$ is a function of the difference $l - l'$ (and the energy), we shall often denote it by $G(l - l')$. The values of $G_{ll'}$ used below were computed numerically, using techniques extensively discussed in the literature.[11]

In the new notation the defining equation for ϵ_0 becomes

$$\epsilon_0 = (c_A - c_B)\Delta + (\Delta^2 - \epsilon_0^2) g_0(\epsilon - \epsilon_0) .$$

The properties of this equation have been discussed extensively by Velický *et al.*[12] They show that for Δ sufficiently small $E_0(E)$ is real for all E outside of a finite interval and is complex for energies within that interval. For Δ greater than a certain critical value there are two separated energy intervals in which E_0 is complex. The significance of these properties lies in the fact that in the coherent-potential approximation,[7] in which one approximates the alloy Green's function by G, the density of states is nonzero only when E_0 is complex. Values of Δ smaller than the critical one thus correspond to a regime in which the energy eigenvalues are confined to a band that is more or less similar to that of the pure materials. This is presumably the situation that prevails in many systems, and is the one that will occupy our attention throughout this paper.

The series in Eqs. (8) and (10) involve the coherent Green's function for arbitrary spatial arguments. It is known[13] that for real E_0 the Green's function falls off inversely with the distance, an effect which leads to very slowly convergent sums in conventional perturbation theory. For complex E_0 an exponentially decaying factor is added, which greatly facilitates sums over lattice sites.

III. DENSITY OF STATES

We now turn to the calculation of the average density of states for an alloy of atoms A and B. We will be concerned exclusively with gaining an over-all picture of the density-of-states function and not, for example, with studying the change in the Fermi-level density of states as a function of the concentrations. Study of the latter quantity requires knowledge of the separation of the atomic-energy levels for each concentration and will be considered briefly below.

We compute the state density from the Green's function for the system. The average density of states is given by the standard formula

$$\rho(\epsilon) = -\mathrm{Im}\,\mathrm{Tr}\langle \mathcal{G} \rangle / \pi , \tag{13}$$

where $\mathrm{Im}(\cdots)$ is the imaginary part of $(\cdots)$, Tr denotes a trace over any complete set,[14] and $\langle \mathcal{G} \rangle$ is the ensemble average of $\mathcal{G}$. In Wannier representation

$$\rho(\epsilon) = -\sum_l \frac{\mathrm{Im}\langle \mathcal{G}_{ll} \rangle}{\pi} . \tag{14}$$

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[11] See, e.g., D. Hone, H. Callen, and L. R. Walker, Phys. Rev. 144, 283 (1966).

[12] B. Velický, S. Kirkpatrick, and H. Ehrenreich, Bull. Am. Phys. Soc. 13, 643 (1966); and (to be published).

[13] Joseph Callaway, J. Math. Phys. 5, 783 (1964).

[14] In the current model, the trace is over the set φ_l or any linearly independent combination of them.

Since $\langle \mathcal{G}_{ll} \rangle$ is independent of l, it follows that the average state density per atom is simply

$$\rho_0(\epsilon) = -\mathrm{Im}g/\pi , \qquad (15)$$

where $g = \langle \mathcal{G}_{ll} \rangle$. Exact evaluation of $\langle \mathcal{G} \rangle$ is out of the question. In the coherent potential approximation[7] we discard all but the first term appearing in Eq. (10) and write $g \simeq g_0$. An indication that this might be reasonable is provided by the observation that in calculating $\langle \mathcal{G} \rangle$ we average over the occupancy of every site, and that by definition of ϵ_0 and G the average of t_A and t_B is zero. This implies that every term of Eq. (10) in which a given site occurs only once vanishes on averaging. Because of the summation restrictions in Eq. (10) the series for $\langle \mathcal{G} \rangle$ begins with a term involving two sites and four t matrices.

If the approximation $g \simeq g_0$ is at all reasonable it must at least reproduce the correct total number of states per atom. Since $\mathrm{Im}\epsilon_0$ vanishes simultaneously with $\mathrm{Im}g_0$, the band edges are defined by the condition $\mathrm{Im}\epsilon_0 \rightarrow 0$. It may be shown that with the band edges defined in this manner the integral of $-\mathrm{Im}g_0/\pi$ from one edge to the other is indeed unity.[11,15]

Examples of the $\rho_0(\epsilon)$ curves following from this approximation are shown in Figs. 1 and 2. Both cases involve alloys of 60% of type A and 40% of type B. The example illustrated in Fig. 1 involves a case where the constituents differ only slightly, the separation between the atomic levels being only one-sixth of the unperturbed band width. In the second case the constituents differ considerably, the corresponding ratio being one-third. The virtual-crystal-state densities are shown for comparison. If the simple model considered here were taken to represent the d band of a transition metal, the second case would correspond to elements separated by two or three columns in the Periodic Table. Since the overlap matrix was taken to be identical for both atoms, the model applies only schematically to alloys of elements in different rows of the Periodic Table.

The two curves have common features. They illustrate that the band width in the alloy is always greater than the virtual-crystal model predicts and hence always greater than that occurring in either of the pure constituents. On the average, therefore, the density of states is smaller than that given by the virtual-crystal model although in the wings of the distribution it is larger (in the $\Delta = 1.0$ case, considerably larger) than one would have guessed from a knowledge of the pure materials. While the over-all shape of the curve for $\Delta = 0.5$ bears a close resemblance to the virtual-crystal curve, that for $\Delta = 1.0$ is entirely different. In both cases the van Hove singularities characteristic of the pure material are visible only in the form of a slight change in slope. The pronounced dip in the middle of the curve for $\Delta = 1$ may be characterized as an incipient band gap. For sufficiently big Δ a true gap appears in the spectrum.[12]

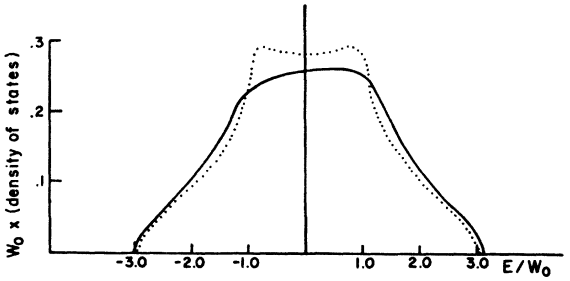

FIG. 1. Average density of states as calculated in the coherent-potential (solid line) and the virtual-crystal (dotted line) approximations for a 0.60–0.40 alloy in which $\Delta = 0.5$.

We turn to the question of whether the curves of Figs. 1 and 2 actually represent the averaged density of states for the model alloys. In order to gain some idea of the validity of the approximation leading to them we examine some of the higher-order terms in the perturbation series. The class of terms in Eq. (10) that appear to yield the largest correction to $\langle \mathcal{G}_{ll} \rangle - g_0$ are those involving multiple scattering between two sites l' and $l'+h$. Here l' and $l'+h$ represent any two different sites, one of which may be equal to l. As mentioned above, the lowest-order terms vanish on averaging. If we denote the contribution of these terms to $\langle \mathcal{G}_{ll} \rangle$ by g_{pair}, then the analytical expression corresponding to the pair terms is

$$g_{\mathrm{pair}} = \sum_{l'} \sum_{h \neq 0} G_{ll'} G_{l'+h,l} \langle t_{l'} t_{l'+h} G(h) / (1 - t_{l'} t_{l'+h} G^2(h)) \rangle$$
$$+ \sum_{l'} \sum_{h \neq 0} G_{ll'}{}^2 \langle t_{l'}{}^2 G^2(h) t_{l'+h} / (1 - t_{l'} t_{l'+h} G^2(h)) \rangle . \qquad (16)$$

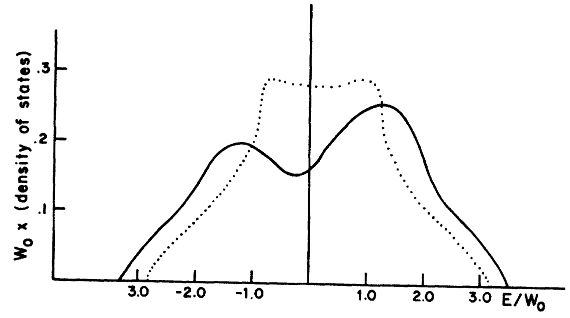

FIG. 2. Average density of states as calculated in the coherent-potential (solid line) and the virtual-crystal (dotted line) approximations for a 0.60–0.40 alloy in which $\Delta = 1.0$.

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[15] It is obvious that the complete spectrum of the random Hamiltonian is bounded by the extreme of the set of band edges of the pure materials states outside of the band edges predicted by the current approximation presumably correspond to poles in the higher-order terms of Eq. (10). As discussed in Ref. 16, the existence and nature of such states vary from case to case, and cannot be discussed in any simple and universal manner. All that we can say is that they apparently have very little weight, since the higher-order terms have only a small effect on the state density within the band as defined in the text.

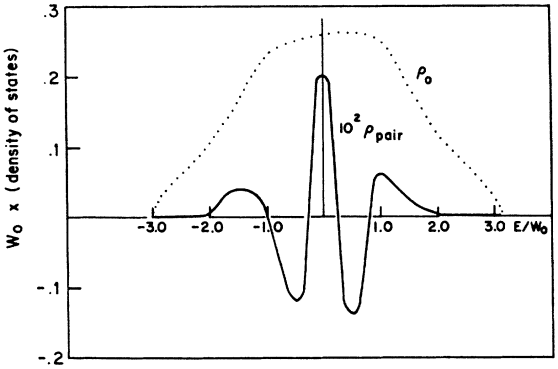

FIG. 3. Pair contribution to the average density of states in a 0.60–0.40 alloy in which $\Delta=0.5$. ρ_0 is shown for comparison. Note the factor of 100 multiplying $\rho_{\rm pair}$.

It is easily shown that

$$\sum_l G(l)G(l+h)=-\frac{\partial G(h)}{\partial\epsilon}, \qquad (17)$$

where the partial derivative indicates differentiation with respect to the explicit energy variable while ignoring the energy dependence of ϵ_0. Since the averages appearing in Eq. (16) are actually independent of l', we may combine Eqs. (16) and (17) to find

$$g_{\rm pair}=-\sum_{h\neq0}\frac{\partial G(h)}{\partial\epsilon}\langle tt'G(h)/(1-tt'G^2(h))\rangle$$
$$-\frac{\partial G(0)}{\partial\epsilon}\sum_{h\neq0}\langle t^2t'G^2(h)/(1-tt'G^2(h))\rangle, \qquad (18)$$

where t and t' are to be averaged independently.

We have evaluated this expression for the alloys considered previously. The lattice sums were carried out over all lattice vectors contributing significantly to the sum. Because of the exponential damping of $G_{ll'}$ the sum is very rapidly convergent, with the overwhelming contribution usually coming from the smallest lattice vector. The results are shown in Figs. 3 and 4, where we have plotted $\rho_{\rm pair}=-{\rm Im}g_{\rm pair}/\pi$. We call attention to the scale factors multiplying $\rho_{\rm pair}$. It is seen that the contribution of these terms to the average density of states is essentially negligible. The smallness of these terms is not due to the smallness of the terms within the angular brackets of Eq. (16). Indeed, for the shorter lattice vectors the quantities within the brackets are only slightly smaller than g_0 itself. Only the average is small, which is due to the vanishing of the average of the first few terms of the implied geometric series.

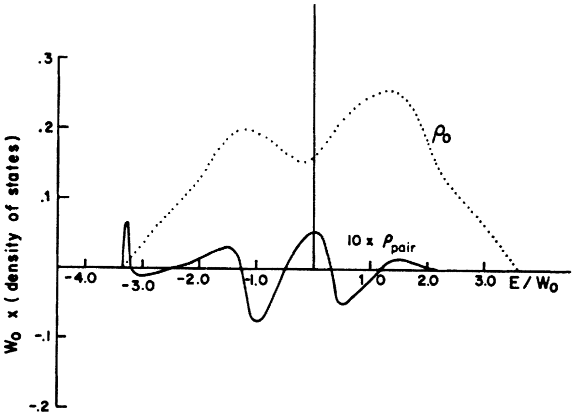

FIG. 4. Pair contribution to the average density of states in a 0.60–0.40 alloy in which $\Delta=1.0$. ρ_0 is shown for comparison. Note the factor of 10 multiplying $\rho_{\rm pair}$.

The structure of $\rho_{\rm pair}$ is easily understood. $\rho_{\rm pair}$ partially represents the effect of two degenerate systems interacting. When identical systems interact, spectral density is removed from energy regions surrounding the levels of the isolated systems (hence the negative portions of $\rho_{\rm pair}$) and transferred to other energy regions.

The low-energy side of the plot shown in Fig. 4 exhibits a slight bump. It is clear that this kind of behavior is to be expected in general. Since the band edges are defined by the condition that ${\rm Im}\epsilon_0\rightarrow0$, the damping of $G_{ll'}$ decreases as the band edge is approached and hence more and more terms contribute to Eq. (13). The accuracy of the approximation cannot, therefore, be judged solely by studying this expression. Instead we make recourse to our previous study of the one-dimensional alloy.[7] In that case, for which exact results are obtainable, we found that an approximation essentially identical to the one under discussion gave good results in the energy region in which it predicts the band edges to lie. While the energies defined by the condition ${\rm Im}\epsilon_0\rightarrow0$ are not the true band edges of the spectrum,[15,16] the state density is apparently so small outside of the region spanned by these points that it is of no consequence in metallic systems. Presumably the same phenomenon occurs in the three-dimensional case. On the basis of these results we would conclude that the lowest-order approximation gives an adequate representation of the complete series.

IV. LOCAL-STATE DENSITY

The average density of states discussed in Sec. III tells us the number of eigenstates having eigenvalues in a given energy range, but it conveys no information about the wave functions of those states. It is, of course, not possible to speak of wave functions without specifying the exact configuration of atoms in the particular system under consideration, and the concept of an averaged wave function is meaningless. We gain knowledge of the average modulus of the wave functions by studying various restricted averages of the Green's function. For example, we will calculate a quantity $\langle\mathcal{G}_{ll}\rangle_l$, where the subscript outside of the bracket indi-

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[16] I. M. Lifshits, Usp. Fiz. Nauk 83, 617 (1964) [English transl.: Soviet Phys.—Usp. 7, 549 (1965)].

cates that we average over the occupancy of all sites other than l. In a tight-binding formalism the imaginary part of this expression is proportional to the average state density localized around a particular *type* of atom. The numerical value of this quantity depends only upon whether an A or B atom is present at the site in question and is independent of the position of that site in the crystal. A further average of $\langle \mathcal{G}_{ll} \rangle_l$ over the occupancy of l yields the quantity $\langle \mathcal{G}_{ll} \rangle$ discussed earlier. We will refer to the quantity $-\mathrm{Im}\langle \mathcal{G}_{ll} \rangle_l/\pi$ as the local-state density. It is also interesting to study the magnitude of probable fluctuations in the local-state density as compared to its average value. To this end we will study an approximation to the quantity $\langle \mathcal{G}_{ll} \rangle_{l,l'}$, an average in which the occupancy of both l and l' are held fixed.

The lowest-order nontrivial approximation to $\langle \mathcal{G}_{ll} \rangle_l$ is obtained by neglecting all but the zeroth and first-order terms in Eq. (10). Since the average $\langle t_{l'} \rangle_l$ vanishes if $l \neq l'$, we have

$$\langle \mathcal{G}_{ll} \rangle_l \simeq G_{ll} + G_{ll} t_l G_{ll}. \tag{19}$$

This approximation amounts to calculating $\langle \mathcal{G}_{ll} \rangle_l$ by simply considering the atom at site l to be an isolated impurity atom with atomic level ϵ_l imbedded in a matrix of atoms formally having eigenvalue ϵ_0. Due to the complex nature of ϵ_0, this interpretation is only a formal one. Using Eq. (15) and the notation of Sec. II, the local-state density at an atom of type A is

$$\rho_A(\epsilon) = -\mathrm{Im}[g_0(1+g_0 t_A)]/\pi, \tag{20}$$

with a similar expression holding for type-B atoms.

In Figs. 5 and 6 we show plots of ρ_A, ρ_B, and ρ_0 for the alloys considered previously. These cases show quite dramatically that there are substantial differences between the average and local-state densities. It is obvious that states in the upper part of the band will tend to have the larger amplitude around the atom having the higher atomic level, but the magnitude of the difference (as given in the current approximation) is perhaps surprising.

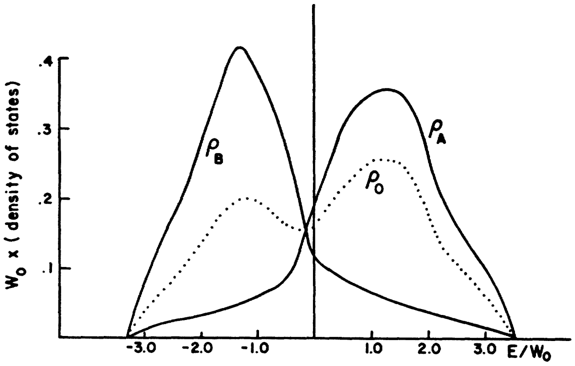

FIG. 5. Local density of states for a 0.60–0.40 alloy for which $\Delta=0.5$. The average density of states is shown for comparison.

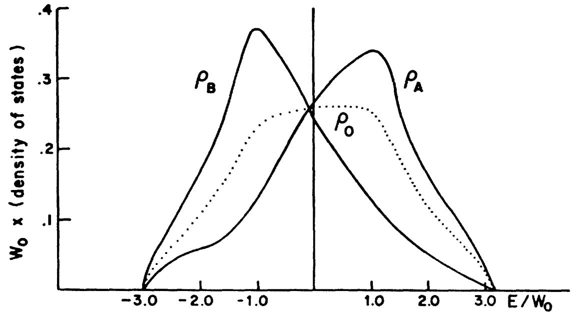

FIG. 6. Local density of states for a 0.60–0.40 alloy for which $\Delta=1.0$. The average density of states is shown for comparison.

A measure of the extent of fluctuations in the local density and of the validity of using the lowest approximation for the environmentally average local density may be gained by studying the effect of the next most important class of terms in the perturbation series. These include the effect of multiple scattering between the site l under consideration and another site denoted by l'.[17] The analytical expression for the contribution of these terms to $\mathcal{G}_{ll}$ is

$$(1+g_0 t_l)^2 G^2(h) t_{l'} / [1 - t_l t_{l'} G^2(h)], \tag{21}$$

where

$$h = l' - l.$$

We use this expression in two ways. First, we average over the occupation of site l' and sum over all values of h. Again the most important contribution is provided by the first- and occasionally the second-nearest-neighbor site. We do not show plots of the results because they are identical in character to those of Figs. 3 and 4. The corrections for the $\Delta=0.5$ alloy are of the order of a hundredth of the value of Eq. (20), while that for the $\Delta=1.0$ alloy are less than a tenth of the contribution of the lowest-order term.

The situation is entirely different when we employ expression (21) to estimate $\langle \mathcal{G}_{ll} \rangle_{l,l'}$ rather than $\langle \mathcal{G}_{ll} \rangle_l$. To do this we simply evaluate the above formula for, say, the nearest-neighbor distance and insert the actual t matrices corresponding to whatever combination of A and B atoms we chose to place on the two sites.

The results of such a calculation for the $\Delta=0.5$ alloy are shown in Fig. 7. The results for $\Delta=1.0$ are qualitatively similar but numerically more extreme. The figure shows the ρ_A discussed above together with ρ_A plus six times the contribution of expression (17). The factor of 6 represents the number of nearest neighbors in a simple cubic lattice; the curves, therefore, show the effect of a very extreme fluctuation. We emphasize that we have obtained only an estimate of the effect of such fluctuations, since many terms, in particular terms in-

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[17] The terms included are only a subset of those used for calculating ρ_{pair} in Sec. III, which actually included more than just the pair terms, in the sense in which the word is used here.

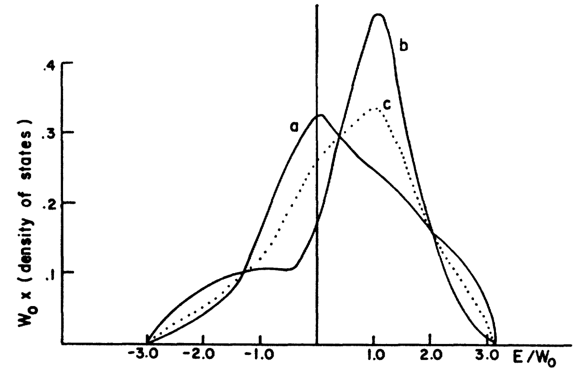

FIG. 7. Effect on the local density of extreme fluctuations in environment. The curves refer to a 0.60–0.40 alloy in which $\Delta=0.5$. Curve a is the local density on a type-A atom when it is surrounded by six other A atoms; b is the local density on a type-A atom when it is surrounded by six B atoms; c is the average local density already illustrated in Fig. 6.

volving multiple scattering among the neighbors, have been omitted. Also, the curves are plotted for highly improbable situations. The probability of finding six neighbors of type A or B is $c_A{}^6$ or $c_B{}^6$, respectively, which work out, for the alloys illustrated, to be 0.047 and 0.004. The figures do nonetheless indicate that the electron density existing at a site in a particular environment may be very different from that found when the atom is in the most probable environment.

V. SPECTRAL DENSITY

Discussions of the electronic structure of ordered systems usually exhibit plots of energy against reduced momentum. Since the energy eigenfunctions in an aperiodic system are not eigenfunctions of reduced momentum (the wave vector is not a "good" quantum number) no such plots can be made in the present case. Information about the momentum of the wave functions may be obtained by studying the spectral density

$$\rho(\epsilon,k)=-\operatorname{Im}\langle\mathcal{G}_{kk}\rangle/\pi .$$

The spectral density and the density of states are connected by the relation

$$\rho(\epsilon)=\sum_k \rho(\epsilon,k),$$

where the sum is over allowed wave vectors in the first Brillouin zone. The quantity $\rho(\epsilon,k)$ is not a spectral density in the way the term is usually used, because it does not refer to a decomposition into plane waves, but rather into the functions ψ_k, which are defined for only a limited number of wave vectors. The plane-wave decomposition depends upon the fourier transforms of the localized functions $\varphi_l(\mathbf{x})$. It is of no particular relevance in the present case.

In the case of an ordered system $\rho(\epsilon,k)$ takes the form of a δ function, there being only one energy eigenstate corresponding to each wave vector. In the disordered situation the δ function expands into a function of finite width, indicating that an energy eigenfunction corresponds to a whole spectrum of wave vectors. Viewed as a function of k for fixed ϵ, the function $\rho(\epsilon,k)$ has the general shape of a Lorentzian, the maxima occurring at a particular set of k vectors, and the half-width indicating the mean free path or spatial extent of typical eigenfunctions at that energy.

We use G_k as an estimate of $\langle\mathcal{G}_{kk}\rangle$. The cancellation that occurs in finding the average state density occurs here as well, and this approximation should be adequate for gaining an understanding of the spectral density. An expression for $\rho(\epsilon,k)$ may be derived by combining Eqs. (5) and the expression for $W(k)$ given in Sec. II to yield

$$\rho(\epsilon,k)=-(1/\pi)\operatorname{Im}[\epsilon-\epsilon_0-\cos(ak_x) -\cos(ak)_y-\cos(ak_z)]^{-1}.$$

In Figs. 8 and 9 we show plots of the position of the peak in the spectral density for k vectors in the [111] direction. The curves delimiting the shaded region are the loci of the wave vectors at which the spectral density has fallen to half the value obtained at the peak. The actual value obtained at the peak varies inversely with the width of the shaded region at constant energy. The dotted line is the usual $\epsilon(k)$ curve of an ordered system, obtained in the virtual crystal approximation. For the $\Delta=0.5$ alloy the shaded region is quite narrow (compared to, say, the distance to the zone corner) and k is a "fairly good" quantum number. The same statement may be made for the $\Delta=1.0$ alloy for energies in the extremities of the band. It is clear, however, that the eigenfunctions corresponding to

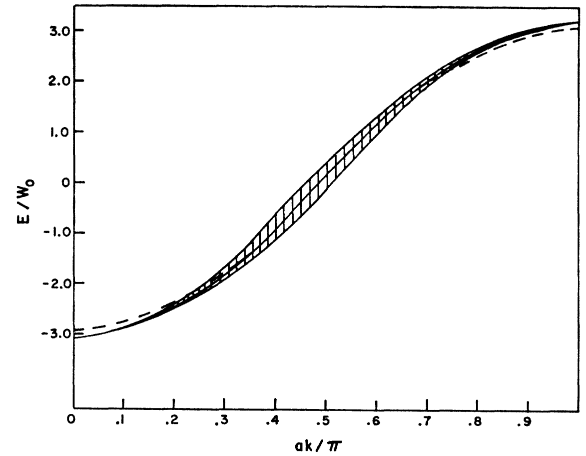

FIG. 8. Locus of the maximum of the spectral density for a 0.60-0.40 alloy in which $\Delta=0.5$. The boundaries of the shaded region define the momentum values at which the spectral density has a value one-half of that attained at the peak. The curve is plotted for wave vectors of the form $k(1,1,1)$. a is the lattice constant. The dotted line refers to the $\epsilon(\mathbf{k})$ relation in the virtual-crystal approximation.

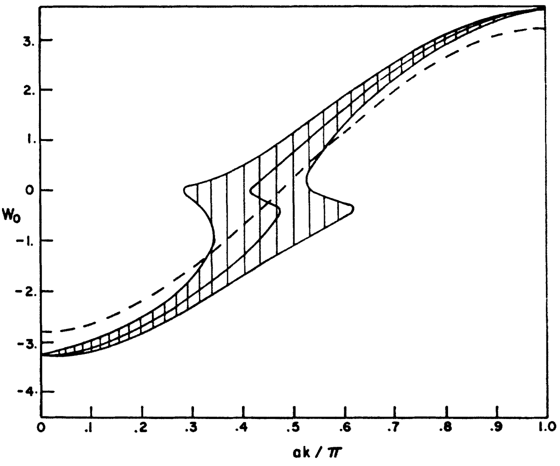

FIG. 9. Locus of the maximum of the spectral density for a 0.60–0.40 alloy in which $\Delta=1.0$. The boundaries of the shaded region define the momentum values at which the spectral density has a value one-half of that attained at the peak. The curve is plotted for wave vectors of the form $k(1,1,1)$. a is the lattice constant. The dotted line refers to the $\epsilon(\mathbf{k})$ relation in the virtual-crystal approximation.

energies in the middle of the band depart very seriously from simple Bloch waves. This is basically due to the stationary character of the trigonometric part of $W(k)$ for wave vectors about half way to the zone edge. The same phenomenon also produces the maximum in the density of states for a pure material. The Fermi surface would appear to be a concept of very limited utility for Fermi energies in this region of the band.

VI. SIMPLE EXAMPLE

We have emphasized in the Introduction that the bulk of this paper would be concerned with the study of the properties of a disordered alloy in which the position of the atomic eigenvalues were somehow fixed in advance. The connection between this kind of model and a real system is tenuous unless there is a prescription based on the properties of the constituents for fixing the position of these levels with respect to some Fermi energy.[18] In a metal, each atomic cell must have approximately zero net charge and the position of the levels will be internally adjusted to ensure that this is so. This fact is of no immediate use in applying our model to, say, the d band of a transition metal, since charge neutrality only fixes the total number of electrons in each unit cell and not necessarily the number of electrons in d-like states. However, it has been suggested[19] that the number of d electrons is itself fixed, but inspection of spectroscopic data indicates that this cannot be exactly true, since the difference between the ground-state energy and the lowest eigenvalue of atomic configurations in which the number of d electrons differs by one from that in the ground-state configuration tends to be smaller than typical band-widths. Nevertheless, this idea should serve as an approximate guide to the position of these levels, and it is of interest to examine this kind of assumption in the light of the results obtained above.

The quantity most accessible to experiment is the density of states at the Fermi level. To study the effect of alloying on this quantity we will repeat some of the calculations discussed above, but this time introducing a Fermi energy ϵ_f and adjusting Δ in order to fix the number of electrons at each site at a predetermined value. This requires that ϵ_f and Δ be functions of the concentrations. For ease of computation we use a model[10,11] in which the density of states in the pure system has the simple analytic form

$$\rho(\epsilon)=\frac{2}{\pi}(1-\epsilon^2)^{1/2}.$$

The relevant Green's function may be calculated with the aid of the relation[10,11]

$$g(z)=\frac{1}{\pi}\int_{-1}^{1}\frac{\rho(x)dx}{z-x}$$

and the local density, the integral of which determines the number of electrons at each site, with Eq. (20). We completely ignore the fluctuations in local density discussed in Sec. IV.

The type of results obtained for $\rho(\epsilon_f)$ is illustrated in Fig. 10, which shows the average density of states at

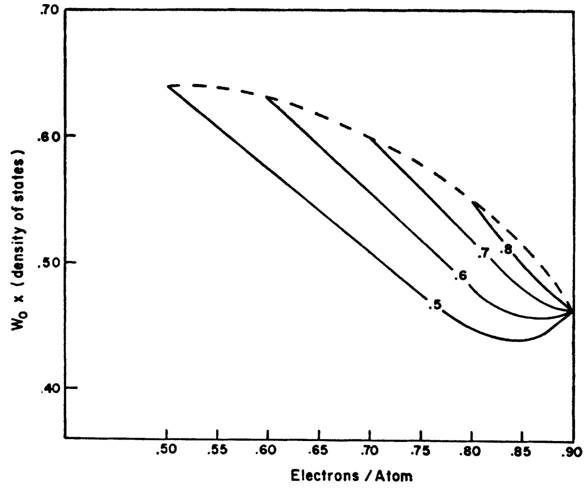

FIG. 10. The average density of states at the Fermi energy versus the average electron concentration for a series of alloys in which A has 0.9 electrons localized about it while B has the number indicated in the figure. The dotted line is the same quantity in the virtual-crystal approximation.

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[18] The phrase "atomic-energy level" should be understood as referring to the position of the d-wave resonance in the atomic scattering amplitude. See, e.g., V. Heine, Phys. Rev. **153**, 673 (1967).

[19] A complete discussion is given by Conyers Herring, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1966), Vol. IV.

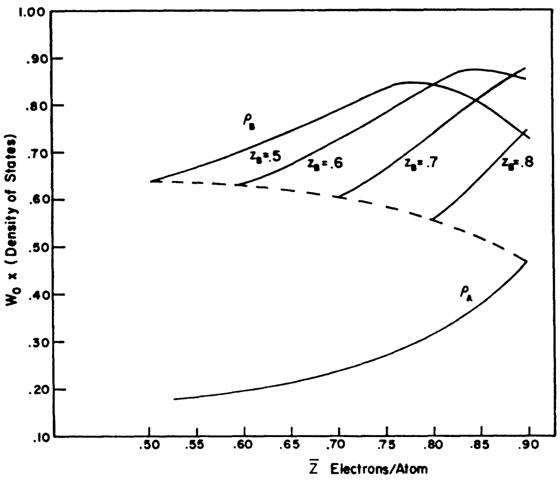

FIG. 11. The local density of states at the Fermi energy versus the average electron concentration for a series of alloys in which component A has 0.9 electrons localized about it while B has the number indicated in the figure. ρ_A is plotted for the alloy system in which B has 0.5 electrons.

the Fermi level for a series of alloys in which constituent A is assumed to have 0.9 electrons (in a nondegenerate level) while constituent B varies from one with 0.5 to 0.8 electrons. The absence of a universal relationship between Fermi-level density of states and average electron concentration is obvious, although the departure from one is not very great. The last observation must be tempered by noting that the assumed pure-material state density and consequently the Green's functions are very smooth functions, in contrast to what one finds in a transition metal. The immediate erosion of the van Hove edges discussed in Sec. III may have a large effect in real systems.

The variation of the local density of states at the Fermi level is also of interest. We show this in Fig. 11. The points corresponding to pure materials were obtained by a conventional impurity calculation. While there is no published literature dealing with the effect of many-body correlations on the magnetic susceptibility of alloys in which the amplitude of the wave function is different on different sites, it is probable that the relevant parameters are the product of the local-state density and a screened Coulomb interaction for each atom. In view of the strong dependence of local-state density on concentration that is illustrated in Fig. 11, it would appear that considerable caution must be exercised in the interpretation of susceptibility measurements in transition-metal alloys.

VII. SUMMARY AND CONCLUSION

Our aim in the present work has been twofold: to evaluate the usefulness of a particular technique for calculating the one-electron spectrum in a disordered alloy and to gain some idea of the spectrum in actual systems. To this end we have made a detailed study of the simple model which possesses some but not all of the features of a transition-metal alloy.

It appears that the techniques employed give an adequate description of the one-electron spectrum in the disordered system. The perturbation series for the average density of states was investigated by studying both the lowest-order (coherent-potential) approximation and what appear to be the largest class of correction terms. The effect of the correction terms was found to be very small. The density of states given by the lowest-order term can differ significantly from the predicted by the virtual crystal approximation. For alloys of not too dissimilar elements the difference does not appear to be very great, although this conclusion may not be valid if considerable structure appears in the pure material state density. The very rapid erosion of the van Hove singularities that was found even in the simple case lends strength to this stipulation.

We found that the local density of states is also adequately described by the lowest approximation, if an ensemble average over the environment is included in the definition of this quantity. The effect of fluctuations in the environment on the local density was found to be considerable. This fact raises interesting questions, which have not been considered in this paper. For instance, if the principle that the number of d electrons on each atom is fixed is approximately valid, then the position of the atomic energy level[18] on each atom may be a strong function of the environment of that atom, in which case one is in effect dealing with an alloy of a large number of constituents. Another of many unexplored phenomenon deals with ternary alloys, in which the third component is present in very small concentrations. Our results suggest that properties of the dilute component (e.g., whether it bears a magnetic moment) may depend more upon the environment of the element than upon the gross properties of the alloy.