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Approximate Calculation of Electronic Structure of Disordered Alloys—Application to Alpha Brass

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We have investigated the predictions of a model of a disordered binary alloy employing the averaged atomic t matrices as the effective scatterer. In order to facilitate the calculation we have introduced an energy-dependent model potential of δ-function character in place of the true atomic potentials. The energy dependence of the model potentials requires us to make an approximation other than the one invoked by the use of the averaged t matrix. On the other hand,the use of the model potentials allows us to do numerical calculations for a disordered alloy. Our calculations are done for α-brass. We have computed the spectral density for states of various symmetries. When considered as a function of wave vector, the width of the peaks in the spectral density corresponding to s-p–type states are of the order of 1% of a Brillouin-zone dimension, indicating that the wave functions are very nearly Bloch functions. The peaks corresponding to d-type states are considerably broader, the widths being of the order of 5% of a Brillouin-zone dimension.

I. INTRODUCTION

The quantum-mechanical study of disordered metallic alloys was begun nearly simultaneously with the study of ordered materials.[1] In recent years the latter area has progressed to the point where one can say that, as least as far as the one-electron picture is valid, the properties of pure metals and ordered intermetallic compounds may be calculated to a high degree of accuracy. To a great extent the theoretical work in this area has been stimulated by the availability of a huge body of microscopic experimental data. The overwhelming number of experimental techniques employed in the study of ordered materials are predicated upon the existence of long electron relaxation times and hence are completely inappropriate for the study of nondilute alloys. Nonetheless, in recent years data of a microscopic character, usually involving the optical properties of the alloy, has begun to appear in the literature and has stimulated theoretical work in this area.

Our work is based very heavily on a series of papers by Edwards and Beeby,[2–5] which treat the problem from the multiple-scattering point of view introduced by Lax[6] and others. Other work in the field includes that of Stern[7] who has performed an analysis of alloys in the tight-binding approximation and also considered the very delicate self-consistency problems involved in the determination of the potential field in an alloy. Somers, Amar, and Johnson[8] have made actual calculations of the electronic spectrum of several of the α-phase noble-metal alloys, using the "virtual-crystal" approximation in which the averaged potential of the constituents is used to calculate the energy bands of the alloy.

The great difficulty in doing numerical calculations of the one-electron energy levels in an alloy is that if the approximation employed is anything other than the "virtual crystal" one, then the lack of periodicity is indicated by the lack of a unique relationship between energy and (crystal) momentum. Since it is usually most convenient to carry out the formal analysis in momentum representation, in trying to calculate the density of states one is inevitably confronted with integrals ranging over all of momentum space, with the integrand having the interpretation of the density of states of a given momentum component. This integrand is in general a function of various atomic properties and therefore will be available, if at all, only in numerical form. The net effect of this is that straightforward computation in detail even approaching that currently achieved in band-structure calculations is difficult if not impossible.

In the present work our starting point is the averaged t-matrix approximation considered in great formal detail by Beeby.[4,5] The idea underlying the approximation is that the motion of an electron in a system of many potentials may be viewed as being the result of successive collisions with the individual potential fields. As a first approximation, therefore, in calculating the properties of a disordered binary alloy one can replace the two distinct atomic potentials by a single scatterer having the property that for a given incident wave it generates a scattered wave equal to the average of the scattered waves produced by the true potentials. Now the t matrix corresponding to a given potential is that quantity which operates linearly on an incident wave to produce the scattered wave. Hence, if we do our calculation with an effective t matrix equal to the average of the constituent t matrices we will have exactly averaged the waves scattered from individual atoms.

Our aim in the present work is not to improve on the

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

[2] S. F. Edwards, Phil. Mag. **6**, 617 (1961); Proc. Roy. Soc. (London) **A267**, 518 (1962).

[3] J. L. Beeby and S. F. Edwards, Proc. Roy. Soc. (London) **A274**, 395 (1962).

[4] J. L. Beeby, Proc. Roy. Soc. (London) **A279**, 82 (1964).

[5] J. L. Beeby, Phys. Rev. **135**, A130 (1964).

[6] M. Lax, Rev. Mod. Phys. **23**, 287 (1951).

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

[8] C. B. Sommers, H. Amar, and K. H. Johnson, Bull. Am. Phys. Soc. **11**, 73 (1966).

formal calculation performed by Beeby. Indeed, we will be forced to make approximations not introduced in his work. Rather, it is an attempt to cast it into a form where numerical calculations with it are only slightly more difficult than those required for a band-structure calculation, and then to do some exploratory numerical calculations for a particular alloy. Our choice for the numerical work is α-brass, simply because the one-electron spectrum of copper is well understood and because there appears to be more microscopic experimental data on it than on any other alloy. We emphasize at the start, however, that we do not seek complete agreement with experiment—our choice of potentials will be far too crude for that—but rather to simply understand the general nature of the results.

We have been guided in this work by the great success achieved in the study of pure metals by the introduction of a model potential,[9] i.e., of some potential, simpler in form that the original ionic potential, but still retaining enough of the true potential properties to allow one to calculate various things of interest. In particular, all that we will require of our model potentials is that, if properly manipulated, they reproduce the true density of states, although we shall argue that certain properties of the wave functions are approximately reproduced as well.

A word must be said concerning the type of system we are attempting to treat and the general nature of the results one expects. We consider only disordered substitutional binary alloys. Thus the atoms are arranged on a regular lattice, and we may define such things as reciprocal lattice vectors and Brillouin zones, although the usefulness of such concepts is not necessarily great in the disordered situation. Similarly, the concept of a crystal momentum has no fundamental significance—one cannot associate any particular momentum with a given eigenstate. The most that one can ask is what region of momentum space is associated with eigenstates of a particular energy. Thus, our equations will not be of the secular equation variety—designed to yield a definite answer to the question of whether an eigenstate exists at a given energy and momentum. They must instead be formulated from beginning in terms of densities—quantities designed to answer not the question of whether a state exists, but rather, what fraction of a state exists at the given energy and momentum.

The organization of the paper is the following: In Sec. II we will consider the nature of the true atomic potentials, the form of the model potentials to be substituted for them, and the t matrices corresponding to the particular model potential. We will also discuss the averaged t matrix and the best way to represent it. In Sec. III we analyze the relationship between systems of model potentials and real potentials and attempt to define quantities relevant to both. The formal calculations are carried out partially in Sec. IV and partially in the Appendix while in Sec. V we analyze the formalism and give the results of our numerical computations.

II. THE MODEL POTENTIALS

In this section we consider the sequence of steps leading from the true atomic potentials to an "effective alloy potential" that will enter into our final formulas. We assume that the atomic potentials are of the muffin-tin variety, i.e., spherically symmetric out to some distance R from the origin and constant for distances greater than R. The radius R is generally that of a sphere inscribed within the Wigner-Seitz cell. This is the type of potential that has been employed successfully in augmented-plane-wave[10] (APW) and Green's-function[11–13] band-structure calculations. The actual determination of the potential for each constituent is complicated and uncertain even for pure materials; in the alloy the nonuniform site environment and the different atomic properties of the constituents compound the uncertainty. Indeed, the very existence of a single potential for each constituent is dubious. The study[14] of the single-impurity problem has shown that the actual potential in the neighborhood of the impurity depends not only on the atomic properties of the impurity but also on the environment of the impurity site. In a real sense, therefore, the assumption that there exists a single potential for each constituent is equivalent to the neglect of fluctuations in the local, i.e., microscopic, distribution of constituents. In view of the fact that a similar, although much more severe neglect of fluctuations is made in the formal part of the calculation, we do not consider this further approximation about the nature of the potentials to be too serious.

For our numerical calculations we have chosen potentials that are expected to be approximately valid for α-brass. We have elected to use potentials independent of alloy concentration in order to ascertain the effects of alloying intrinsic in the model without the complicating effects of further concentration dependencies introduced via the potentials. For this reason we must keep in mind that certain effects of alloying have been omitted. On the copper sites we have placed a Hartree-Fock-Slater[15] atomic potential augmented by the (spherically averaged) tails of the potential of 12 Cu nearest neighbors, while on the Zn sites we have assumed a similar atomic Zn potential also overlapped with only Cu neighbors. These potentials are then

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[9] V. Heine and I. Abarenkov, Phil. Mag. 9, 451 (1964); I. Abarenkov and V. Heine, *ibid.* 12, 529 (1965).

[10] J. C. Slater, Phys. Rev. **51**, 846 (1937).

[11] P. M. Morse, Proc. Natl. Acad. Sci. U. S. 42, 276 (1956).

[12] J. Korringer, Physica **13**, 392 (1947).

[13] W. Kohn and N. Rostoker, Phys. Rev. **94**, 1111 (1954).

[14] P. A. Wolff, Phys. Rev. **124**, 1030 (1961); A. M. Clogston, *ibid.* **125**, 439 (1962); **136**, A138 (1964).

[15] For a discussion of this type of potential see, e.g., F. Herman and S. Skillman, *Atomic Structure Calculations* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1965).

truncated at the Cu inscribed-sphere radius. The difference in Cu and Zn potentials at the sphere radius was 0.1 Ry. When employed for the calculation of the bands of pure Cu, the potential yielded results agreeing with those of Burdick[16a] and Segall[16b] to within 0.01 Ry. We add in passing that we have also neglected the small change in lattice constant that occurs on alloying Zn into Cu.[17]

Our aim is to find approximate solutions to the Schrödinger equation of an electron under the influence of a collection of spherically symmetric nonoverlapping potentials. It may easily be shown that the property of the potentials determining whether at any given energy an eigenfunction for such a system exists is the set of logarithmic derivatives of the radial wave functions in each type of potential evaluated at the sphere radius of the potential. In the periodic case this may be seen explicitly in the formulas of Slater[10] for the APW method or of Morse[11] and Korringer-Kohn-Rostoker[12,13] (KKR) for the Green's function method. In the disordered case it may be proved by a simple extension of the formulas of Slater. This being so, all we need require of the model potentials is that they yield logarithmic derivatives identical with those generated by the real potentials.

Our choice for the model potentials is an energy- and angular-momentum-dependent δ-function potential. Explicitly, we introduce the following operator in place of the true atomic potentials.[18]

$$V^{(i)}(\mathbf{x},\mathbf{x}')=\sum_L Y_L(\mathbf{x})\frac{\delta(x-R)}{R^2}v_l^{(i)}\frac{\delta(x'-R)}{R^2}Y_L(\mathbf{x}')\,, \qquad (1)$$

where (i) indicates the type of atom to which the model potential corresponds, L denotes the angular-momentum quantum numbers (l,m), $Y_L(\mathbf{x})$ is the real spherical harmonic of the angles of $\mathbf{x}$, and $v_l^{(i)}$ is an appropriately chosen energy-dependent amplitude. A simple calculation shows that the $v_l^{(i)}$ are defined by the relation

$$v_l^{(i)}(E)=R^2[\gamma_l^{(i)}(E)-\kappa j_l'(\kappa R)/j_l(\kappa R)]\,,$$

where E is the energy, $\kappa^2=E$, j_l and j_l' the spherical Bessel function and its derivative, and $\gamma_l^{(i)}(E)$ is the exact logarithmic derivative of the radial wave function for angular momentum l and energy E evaluated at radius R. We shall refer to the $v_l^{(i)}$ as the atomic-potential amplitudes.

The t matrix corresponding to a potential of the form (1) may easily be determined.[19] In general the t matrix $T(\mathbf{x},\mathbf{x}')$ corresponding to a nonlocal potential $V(\mathbf{x},\mathbf{x}')$ is defined by the equation

$$T(\mathbf{x},\mathbf{x}')=V(\mathbf{x},\mathbf{x}')+\int V(\mathbf{x},\mathbf{y})G(\mathbf{y}-\mathbf{y}')T(\mathbf{y}',\mathbf{x}')d\mathbf{y}d\mathbf{y}'\,,$$

where $G(\mathbf{y}-\mathbf{y}')$ is the free-electron Green's function. If $V(\mathbf{x},\mathbf{x}')$ may be decomposed into angular-momentum components of the form

$$V(\mathbf{x},\mathbf{x}')=\sum_L Y_L(\mathbf{x})V_l(x,x')Y_L(\mathbf{x}')\,,$$

then $T(\mathbf{x},\mathbf{x}')$ may be similarly decomposed:

$$T(\mathbf{x},\mathbf{x}')=\sum_L Y_L(\mathbf{x})T_l(x,x')Y_L(\mathbf{x}')\,.$$

The $T_l(x,x')$ satisfy

$$T_l(x,x')=V_l(x,x')+\int V_l(x,y)G_l(y,y')T_l(y',x')y^2dyy'^2dy'\,. \qquad (2)$$

$G_l(x,x')$ is the lth component in the angular-momentum representation of $G(x-x')$,

$$G_l(x,x')=\kappa j_l(\kappa x_<)[n_l(\kappa x_>)-ij(\kappa x_>)]\,,$$

where $x_<$ is the lesser and $x_>$ the greater of x and x', and n_l is the spherical Neumann function. For a potential of the form (1) $T_l(x,x')$ may be written as

$$t_l[\delta(x-R)/R^2][\delta(x'-R)/R^2]\,. \qquad (3)$$

Substitution into Eq. (2) yields

$$t_l=v_l[1-v_lg_l]^{-1}\,, \qquad (4)$$

where $g_l=G_l(R,R)$.

The t matrix equal to the average of the atomic t matrices may also be written in the form (3). Formally one may use Eq. (4) to decompose the average t matrix and derive a set of complex amplitudes w_l

$$w_l[1-g_lw_l]^{-1}=c_1v_l^{(1)}[1-g_lv_l^{(1)}]^{-1}+c_2v_l^{(2)}[1-g_lv_l^{(2)}]^{-1}\,,$$

where c_1 and c_2 are the concentrations of the constituents. The most convenient representation of the w_l is in terms of real quantities u_l and Δ_l via the equation $w_l=u_l(1+i\Delta_l)^{-1}$. We shall refer to the model potential possessing amplitudes u_l as the effective alloy potential. The Δ_l will be seen to be of the nature of width parameters and determine the departure of the eigenfunctions from Bloch character. Denoting the real and imaginary parts of g_l by g_l' and g_l'', respectively, the expressions for u_l and Δ_l are

$$u_l=[(c_lv_l^{(1)}+c_2v_l^{(2)}-g'_lv_l^{(1)}v_l^{(2)})^2+(g''_lv_l^{(1)}v_l^{(2)})^2]/D_l\,, \qquad (5a)$$

$$\Delta_l=-c_1c_2g''_l(v_l^{(1)}-v_l^{(2)})^2/D_l\,, \qquad (5b)$$

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[16] (a) G. A. Burdick, Phys. Rev. **129**, 138 (1963). (b) B. Segall, *ibid.* **125**, 109 (1962) and private communication referred to in Ref. 16. The results quoted in Ref. 16 are for a calculation employing Burdick's potential, while the published results employ a slightly different potential. We note that Segall's calculations employ the Green's-function method and hence are more akin to the spirit of the present work than are Burdick's.

[17] E. A. Owen and E. W. Roberts, Phil. Mag. **27**, 294 (1939).

[18] The introduction of this type of potential in the ordered situation has been suggested independently by J. C. Slater, Phys. Rev. **145**, 599 (1966).

[19] J. L. Beeby, Phys. Rev. **137**, A933 (1965).

where D_l is given by

$$D_l=c_1v_l^{(1)}+c_2v_l^{(2)}-g_l'[c_1c_2(v_l^{(1)}-v_l^{(2)})^2+2v_l^{(1)}v_l(2)]$$
$$+|g_l|^2v_l^{(1)}v_l^{(2)}[c_2v_l^{(1)}+c_1v_l^{(2)}].$$

In the following we shall also employ the model potential possessing the average amplitudes $v_l=c_lv_l^{(1)}+c_2v_l^{(2)}$, and will refer to this potential simply as $V(\mathbf{x},\mathbf{x}')$.

III. VALIDITY OF THE MODEL POTENTIALS

In this section we will consider the extent to which the properties of a system of model potentials may be assumed to reflect the corresponding properties of the actual system. We are concerned here only with the predictions of a hypothetical exact calculation; in the following section we will consider the problems engendered by our doing only an approximate calculation for the model potentials themselves.

The model potentials are chosen to reproduce the energy spectrum of the alloy. It is obvious, however, that while the eigenvalues are the same for the two systems, the wave functions and all quantities depending explicitly on them are certainly different. One wave-function–dependent quantity of special interest is the spectral density, which is defined by the relation

$$\rho(E,\mathbf{k})=\textstyle\sum_n \delta(E-E_n)|\psi_n(\mathbf{k})|^2, \tag{6}$$

where $\psi_n(\mathbf{k})$ is the $\mathbf{k}$th Fourier component of the eigenfunction ψ_n, and E_n the corresponding eigenvalue. Assuming normalized eigenfunctions $\rho(E,\mathbf{k})$ satisfies

$$\rho(E)=\textstyle\sum_{\mathbf{k}} \rho(E,\mathbf{k}),$$

where $\rho(E)$ is the usual density of states and the sum is taken over all wave vectors permitted by boundary conditions. In the periodic case the spectral density takes the form

$$\rho(E,\mathbf{k})=\sum_{n,\mathbf{k}'} \delta(E-E_n(\mathbf{k}'))\sum_{\mathbf{K}}|\psi_{n\mathbf{k}'}(\mathbf{k}+\mathbf{K})|^2\delta(\mathbf{k}-\mathbf{k}'-\mathbf{K}),$$

where n now denotes the band index and $\mathbf{k}'$ the reduced wave vector of the eigenfunction, and $\mathbf{K}$ is a reciprocal-lattice vector. The form of this equation suggests that a more appropriate spectral density is the quantity

$$\tilde{\rho}(E,\mathbf{k})=\textstyle\sum_{\mathbf{K}} \rho(E,\mathbf{k}+\mathbf{K}), \tag{7}$$

where $\mathbf{k}$ is now confined to the first Brillouin zone (BZ). We shall refer to this quantity as the reduced spectral density. In the alloy case, of course, the Brillouin zone does not have the fundamental significance it possesses for the case of an ordered material. It is nonetheless clear that the quantity suitable for comparison with the energy-versus-momentum curves of an ordered system, which are defined only modulo a reciprocal lattice vector, is a spectral density modified in the above manner.

The reduced spectral density also has the advantage of being far less wave-function-dependent than the conventional spectral density from which it is derived. In the periodic case $\tilde{\rho}(E,\mathbf{k})$ is given by the simple expression

$$\sum_{n,\mathbf{k}'} \delta(E-E_n(\mathbf{k}'))\delta(\mathbf{k}-\mathbf{k}'),$$

and this is certainly independent of the wave function. In the alloy case the sum over reciprocal lattice vectors does not completely remove the wave function from the formula. Nonetheless, we assert that $\tilde{\rho}(E,\mathbf{k})$ is essentially identical for both systems. Our reasons are: (1) We apply our formulas only to alloys where the departure of the eigenfunction from Bloch-wave character is not too great (we do not consider local modes); (2)the reduced spectral density for both systems have identical normalizations when integrated over the finite BZ; (3) the wave functions for both systems are identical outside of the atomic spheres (typically 30% of the volume); (4) each angular momentum component of the corresponding wave functions has the same normalization within the interiors of the atomic spheres and the same amplitude at the sphere radius; and (5) by performing the sum over reciprocal-lattice vectors we have eliminated any gross differences in high-order momentum components of the corresponding wave functions. In spite of these arguments, it remains true that the modified spectral densities are not completely identical for the two systems. But the arguments given above indicate that there can be no gross differences between the two, and the simplicity and tractibility introduced into the formalism by the use of the model potentials more than compensates for any slight error in $\tilde{\rho}(E,\mathbf{k})$. And, of course, $\rho(E)$ is in any event given correctly.

IV. FORMALISM

The ultimate aim of the calculation is the determination of the density of states for a disordered alloy. If $\mathcal{G}$ is the (outgoing wave) Green's function, then the usual formula for the density of states is

$$\rho(E)=-(1/\pi)\mathrm{Im}\ \mathrm{Tr}\mathcal{G},$$

where Im indicates the imaginary part of the following expression and Tr means that a trace is to be taken over any complete set. This formula implicitly assumes that the potentials in the system are energy independent. The point is simply that in energy representation $\mathcal{G}$ is $[E+is-E_n]^{-1}$, where the E_n are the eigenvalues and s is a positive infinitesimal. Since $\mathrm{Im}[E+is-E_n]^{-1}=-\pi\delta(E-E_n)$ and $\rho(E)=\sum_n \delta(E-E_n)$, the above formula follows directly. But if one has energy-dependent potentials, $\mathcal{G}$ is actually $[E+is-E_n'(E)]^{-1}$, where $E_n'(E)$ is the formal eigenvalue of the energy-dependent Hamiltonian. Now our potentials are chosen to ensure that $E_n'(E_n)=E_n$, but due to the implicit energy dependence this is not sufficient to make the density of states come out correctly. Explicitly, we want the quantity $\sum_n \delta(E-E_n)$ while we actually calculate $\sum_n \delta(E-E_n'(E))$. But since $E_n'(E_n)=E_n$, there is the relation

$$\delta(E-E_n)=\delta(E-E_n'(E))[1-(dE_n'/dE)].$$

Hence, the density of states is given by

$$\rho(E)=-\frac{1}{\pi}\sum_n \ \mathrm{Im}[E+is-E_n'(E)]^{-1}\left(1-\frac{dE_n'}{dE}\right),$$

which may be written in a general representation as

$$\rho(E)=-\frac{1}{\pi}\mathrm{ImTr}\mathcal{G}\left(1-\frac{\partial\mathcal{V}}{\partial E}\right),$$

where $\mathcal{V}$ is the potential energy and the only energy-dependent term in the Hamiltonian of the system.

It has been noted by Lifshitz[20] that the alloy problem is a self-averaging one in the sense that the correct solution for, say, $\mathcal{G}$, is equal to an ensemble-averaged solution. Nonetheless, averaging simplifies the work, and we will be concerned with the calculation of

$$\rho(E)=-\frac{1}{\pi}\mathrm{TrIm}\left\langle \mathcal{G}\left(1-\frac{\partial\mathcal{V}}{\partial E}\right)\right\rangle, \tag{8}$$

where the angular brackets indicate that an average over an ensemble is taken.

The essence of the approximation is to calculate $\mathcal{G}$ under the assumption that on each site there is a potential giving rise to the average atomic t matrix. Formally the argument proceeds as follows. The Green's function may be expanded in a perturbation series of the form[3]

$$G+\sum_\alpha GT_\alpha{}^{(i)}G+\sum_\alpha\sum_{\beta\neq\alpha} GT_\alpha{}^{(i)}GT_\beta{}^{(j)}G+\cdots,$$

where α,β refer to the lattice point and i,j to the type of atom on the particular site. The approximation is the factorization

$$\langle GT_\alpha{}^{(i)}GT_\beta{}^{(j)}\cdots GT^{(m)}\rangle \rightarrow GT_\alpha GT_\beta\cdots GT_\delta, \tag{9}$$

where $T=c_1T^{(1)}+c_2T^{(2)}$.

Several comments may be made. By making the factorization (9) the random system has been reduced to a periodic one, thereby effecting enormous simplification in the formalism. This is not to say that the wave functions of the system are Bloch functions. We have seen in Sec. II that the "potential" corresponding to the averaged t matrix is complex: The imaginary part will produce the damping of waves expected in a random system. Nonetheless, it remains true that this model averages at a very early stage in the calculation. This will have serious consequences whenever the states under consideration arise from the resonance of an electron in a particular configuration of atoms. Consider a term in the perturbation series where the t matrix on a given site occurs N times. In a correct calculation the concentration dependence arising from averaging this particular term would be linear, whereas the present technique includes it with a c^N dependence.

The presence of the energy derivative of the potentials in Eq. (8) is a difficulty engendered by the introduction of the model potentials. It is not *a priori* clear what approximation to $\langle\mathcal{G}\partial\mathcal{V}/\partial E\rangle$ is consistent with the averaged t-matrix approximation. In Appendix B we show that it is reasonable to make the factorization

$$\langle\mathcal{G}\partial\mathcal{V}/\partial E\rangle \rightarrow \langle\mathcal{G}\rangle\partial/\partial E\langle\mathcal{V}\rangle,$$

where $\langle\mathcal{V}(\mathbf{x},\mathbf{x})\rangle=\sum_\alpha V(\mathbf{x}-\mathbf{r}_\alpha,\ \mathbf{x}'-\mathbf{r}_\alpha)$, in which $V(\mathbf{x},\mathbf{x}')$ is the averaged model potential defined in Sec. II.

A group of quantities appearing throughout the equations are the Green's function defined by Kohn and Rostoker.[13] These are defined by the expression

$$G_{\mathbf{k}}(\mathbf{x}-\mathbf{x}')=\frac{1}{\Omega_0}\sum_{\mathbf{k}}\frac{\exp[i(\mathbf{k}+\mathbf{K})\cdot(\mathbf{x}-\mathbf{x}')]}{E+is-(\mathbf{k}+\mathbf{K})^2},$$

where Ω_0 denotes the primative cell volume. These quantities are simply properly symmetrized free-electron Green's functions. Using these quantities we define a Green's matrix $\mathbf{G}_{\mathbf{k}}$ by

$$\langle L|\mathbf{G}_{\mathbf{k}}|L'\rangle=\int Y_L(\mathbf{x})\frac{\delta(x-R)}{R^2}\times G_k(\mathbf{x}-\mathbf{x})\frac{\delta(x'-R)}{R^2}Y_{L'}(\mathbf{x}')d\mathbf{x}d\mathbf{x}'.$$

The calculations leading to an explicit formula for $\rho(E)$ are involved and are given in detail in the Appendix A. The result is the following formula:

$$\rho(E)=\frac{1}{\pi}\sum_{\mathbf{k}}{}'\ \mathrm{ImTr}\left[\frac{\partial\mathbf{G}_{\mathbf{k}}}{\partial E}+\mathbf{G}_{\mathbf{k}}\frac{\partial\mathbf{V}}{\partial E}\mathbf{G}_{\mathbf{k}}\right]\mathbf{W}(1-\mathbf{W}\mathbf{G}_{\mathbf{k}})^{-1}, \tag{10a}$$

where $\mathbf{V}$ and $\mathbf{W}$ are diagonal matrices with components v_l and w_l, respectively, and the trace is over the angular-momentum indices. The momentum-space sum is confined to the first Brillouin zone. Hence, the reduced spectral density is given by

$$\tilde{\rho}(E,\mathbf{k})=\frac{1}{\pi}\mathrm{ImTr}\left(\frac{\partial\mathbf{G}_{\mathbf{k}}}{\partial E}+\mathbf{G}_{\mathbf{k}}\frac{\partial\mathbf{V}}{\partial E}\mathbf{G}_{\mathbf{k}}\right)\mathbf{W}(1-\mathbf{W}\mathbf{G}_{\mathbf{k}})^{-1}. \tag{10b}$$

Before proceeding to an analysis of the content of Eq. (10b) we make one slight change in notation. Ham and

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[20] I. M. Lifshitz, Usp. Fiz. Nauk **83**, 617 (1964) [English transl.: Soviet Phys.—Usp. **7**, 549 (1964)].

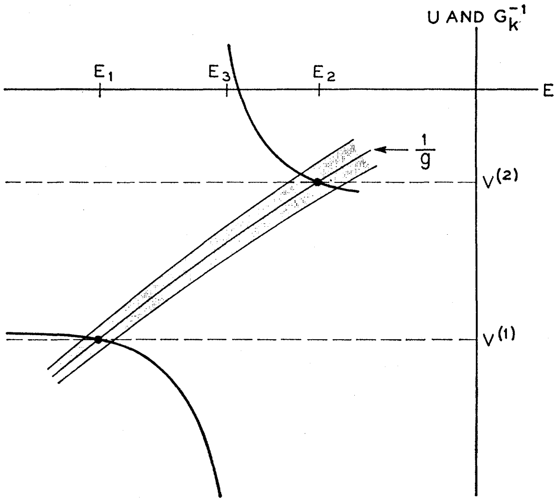

FIG. 1. Schematic drawing of the effective potential for negative energies and the case where the constituent amplitudes are energy-independent. The shaded region is the domain of the inverse of the KKR Green's function. E_1 and E_2 are the atomic bound-state energies.

Segall[21] show that the components of the matrix $\mathbf{G}_\mathbf{k}$ may be written in the form

$$\langle L|\mathbf{G}_\mathbf{k}|L'\rangle = i^{l-l'}(\text{real quantity}).$$

If we make the correspondence $\mathbf{G}_\mathbf{k} \to \mathbf{I}\mathbf{G}_\mathbf{k}\mathbf{I}^{-1}$, where $\mathbf{I}$ is the matrix with components $i^l\delta_{L,L'}$, and substitute this into Eq. (10), an expression of the same form results. This is convenient since it shows that we need only concern ourselves with the imaginary term arising from the complex nature of $\mathbf{W}$. The imaginary part may now easily be evaluated. Written in terms of the effective potential amplitudes u_l and the width parameters Δ_l, the expression for the reduced spectral density is

$$\tilde{\rho}(E,\mathbf{k}) = -\frac{1}{\pi}\mathrm{Tr}\left[\mathbf{U}\frac{\partial \mathbf{G}_\mathbf{k}}{\partial E} + \mathbf{U}\mathbf{G}_\mathbf{k}\frac{\partial \mathbf{V}}{\partial E}\mathbf{G}_\mathbf{k}\right] \times [\mathbf{\Delta} + (\mathbf{1} - \mathbf{U}\mathbf{G}_\mathbf{k})\mathbf{\Delta}^{-1}(\mathbf{1} - \mathbf{U}\mathbf{G}_\mathbf{k})]^{-1}, \quad (11)$$

where $\mathbf{U}$ and $\mathbf{\Delta}$ are diagonal matrices with components u_l and Δ_l, respectively. If $\mathbf{G}_k$ were diagonal, the inverse matrix would have components

$$\Delta_l[\Delta_l^2 + (1 - u_l(L|\mathbf{G}_k|L))^2]^{-1},$$

which illustrates the effect of the Δ_l in determining the width of the peaks in $\tilde{\rho}(E,k)$.

For negative energies, and of course for all energies in the limit of a pure material, the Δ_l vanish. In this case the inverse matrix must be treated with special care. A similar situation arose in the work of Beeby,[4] and we refer the reader to his article for the details of the limiting process. The result is that in the limit as all $\Delta_l \to 0$,

$$\tilde{\rho}(E,\mathbf{k}) = -\delta(\det(1 - \mathbf{U}\mathbf{G}_\mathbf{k}))\mathrm{Tr}\left[\mathbf{U}\frac{\partial \mathbf{G}_\mathbf{k}}{\partial E} + \mathbf{U}\mathbf{G}_\mathbf{k}\frac{\partial \mathbf{V}}{\partial E}\mathbf{G}_\mathbf{k}\right] \times \det(\mathbf{1} - \mathbf{U}\mathbf{G}_\mathbf{k})(\mathbf{1} - \mathbf{U}\mathbf{G}_\mathbf{k})^{-1}, \quad (12)$$

where the zero of the determinant cancels the infinity in the inverse matrix. The condition $\det(\mathbf{1} - \mathbf{V}^{(1)}\mathbf{G}_k) = 0$, which results as $c_2 \to 0$, may be shown to be equivalent to the Morse[11] and KKR[12,13] eigenvalue equation. If $\mathbf{G}_k$ is diagonal, Eq. (12) is a sum of terms of the form

$$-\delta(\mathbf{1} - u_l(L|\mathbf{G}_k|L)) \times \left[u_l\left(L\left|\frac{\partial \mathbf{G}_k}{\partial E}\right|L\right) + \frac{\partial v_l}{\partial E}(L|\mathbf{G}_k|L)\right]. \quad (13)$$

We note that as $c_2 \to 0$ expression (13) has the correct normalization when integrated as a function of energy over the position of the eigenvalue.

The formulas have now been reduced to a form suitable for calculation. Whether or not the calculation is feasible is dependent upon the order of the matrices entering Eq. (11). In principle, of course, the matrices are of infinite order; in practice one may easily show that they may be truncated at a low value of l. As a practical matter, it is known from our work and that of others that for pure copper accuracies of order 0.01 Ry are obtainable at nearly all points in the zone if the matrices are truncated at $l=2$. This leaves a 9×9 matrix, which may easily be handled on a computer.

The Green's matrix entering into (11) is an energy- and momentum-dependent quantity which must be calculated numerically. Ham and Segall[21] have given an exhaustive discussion of the properties and of the methods of calculating these functions. While in our numerical work we employed accurately calculated Green's functions, for the purposes of explication it will be useful to introduce approximate forms for these functions. For negative energies the matrix takes the form

$$(L|\mathbf{G}_\mathbf{k}|L') = g_l\delta_{LL'} + (L|\mathbf{\Gamma}_\mathbf{k}|L'), \quad (14)$$

where the components of $\mathbf{\Gamma}_\mathbf{k}$ may be written in terms of trigonometric functions of the type entering into tight-binding energy-band calculations. For positive energies a typical component of $\mathbf{G}_\mathbf{k}$ may be approximated as

$$A + B[|\mathbf{k} + \mathbf{K}_n|^2 - E]^{-1}, \quad (15)$$

where the $\mathbf{K}_n$ is that reciprocal-lattice vector for which the energy denominator is smallest, and A and B are functions of both energy and momentum. A is of the order of g_l' for the appropriate l.

V. ANALYSIS AND CALCULATIONS

We turn now to an analysis of the formulas. Although the energy bands of interest in metals occur for energies

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[21] F. S. Ham and B. Segall, Phys. Rev. 124, 1786 (1961).

above the muffin-tin zero, the formulas are simpler for negative energies and we will briefly consider this region. To a certain extent this has been done by Beeby. However, as we believe that our formulas are somewhat more transparent than his, we will to a limited degree repeat his work. In the negative energy region the Δ_l vanish (because the g_l are real) and Eq. (12) for $\bar{\rho}(E,\mathbf{k})$ is applicable. We will consider only diagonal matrices and omit the angular momentum subscripts on the Green's matrix elements.

Let us assume that the $v_l^{(i)}$ are constant in energy and satisfy the relations $v_l^{(1)}<v_l^{(2)}<0$. Using expression (14) for the diagonal components of the Green's matrix the eigenvalues of pure (i) material are given by the equation

$$1-v_l^{(i)}G_{\mathbf{k}}=1-v_l^{(i)}(g_l+\Gamma_{\mathbf{k}})=0.$$

The essential point is that if this equation has a solution then the $v_l^{(i)}$ must be of order g_l^{-1}. Indeed, the free-atom eigenvalues, E_i, are given by the equation $1-v_l^{(i)}g_l(E_i)=0$, and for the tight-binding situation being considered here this approximately defines the middle of the band. Examination of Eq. (5a) shows that its denominator vanishes for some energy between E_1 and E_2. We schematically represent the state of affairs in Fig. 1. In the sketch the shaded region represents the domain of the function $G_{\mathbf{k}}^{-1}$; there is a solution to the eigenvalue equation for every energy for which the value of u_l lies within the shaded region. We note that if $c_2=0$, $u_l=v_l^{(1)}$ and the curve becomes horizontal. The theory predicts that the bandwidth of the band arising from each constituent decreases as the concentration of the second constituent increases. The actual variation as a function of concentration is a complicated function depending upon the actual values of the potential and upon the energy dependence of the Green's functions.

The theory predicts that the infinity in u_l occurs even as the atomic energies E_1 and E_2 approach each other, and hence that there is a gap in the energy spectrum even when the bands of the separate pure materials would otherwise overlap. We view this result with scepticism. The gap appears to arise from an artificial intra-atomic matrix element introduced by averaging the atomic t matrices; the averaging process in effect puts the orbitals of both types of atoms on the same site thereby allowing them to interact strongly, whereas in the tight-binding situation being considered it is clear the major matrix elements are of interatomic character.

We will not discuss the case of energy-dependent potentials in the negative-energy region, as the states occurring there are of no interest in metallic alloys. The situation in the positive-energy region is considerably complicated by the finite values of the width parameters Δ_l. We shall find that the predictions are reasonable for states which in a pure material would consist of a few orthogonalized plane waves (OPW), but that there are ambiguities for states of $3d$ character.

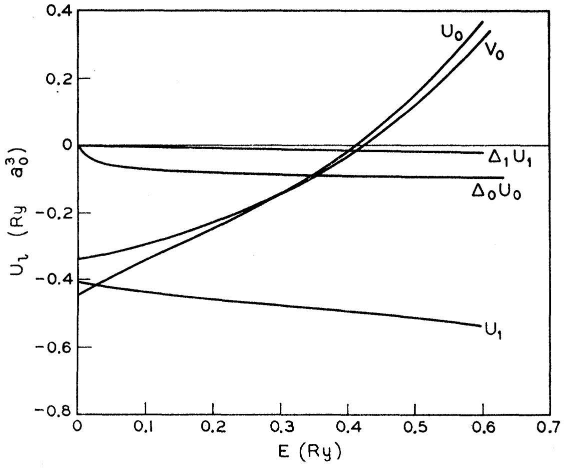

FIG. 2. The effective alloy amplitudes u_l and the quantities $\Delta_l u_l$, where the Δ_l are the width parameters, for an alloy of 75% Cu and 25% Zn. The curved marked V_0 is the average model potential amplitude for $l=0$.

The mathematical criterion distinguishing these situations may be given in many guises. For our purposes the following inequalities are most convenient:

$$u_l g_l' \ll 1 \quad \text{(few OPW behavior)}, \tag{16a}$$

$$u_l g_l' \simeq 1 \quad (3d \text{ behavior}), \tag{16b}$$

where the u_l represent the effective potential amplitudes for those l of greatest importance in determining the character of the state. The basis for this distinction is our observation that the Green's matrix is of the general nature given in Eq. (15). If condition (16a) is applicable, the eigenvalue can occur only resonably near the singularity of the Green's function, yielding nearly free-electron bands, while if (16b) applies the eigenvalues are far from the free electron $E=k^2$. We emphasize that, distorted as they may appear, for our purposes we include the copper s–p band in the free-electron category. It is true, of course, that this sharp dichotomy does not really exist in a material such as α-brass. It clearly breaks down whenever there is significant s-d hybridization.

The implication of condition (16a) is that a reasonable approximation to u_l is simply v_l, the averaged potential amplitude. If the Δ_l are neglected, then use of the averaged amplitude is approximately equivalent to the use of averaged logarithmic derivatives in an APW calculation. From the conventional pseudopotentials point of view, it is equivalent to averaging the pseudopotentials of the two materials. In Fig. 2 we show a plot of the effective s-wave amplitude for a 25% Zn alloy together with a plot of the averaged amplitude. For the cases that have been investigated the effects of the s- and p-width parameters are qualitatively small. It may be shown that the use of the approximate equation

$$\Delta_l=-c_1c_2g_l''[v_l^{(1)}-v_l^{(2)}]^2/v_l$$

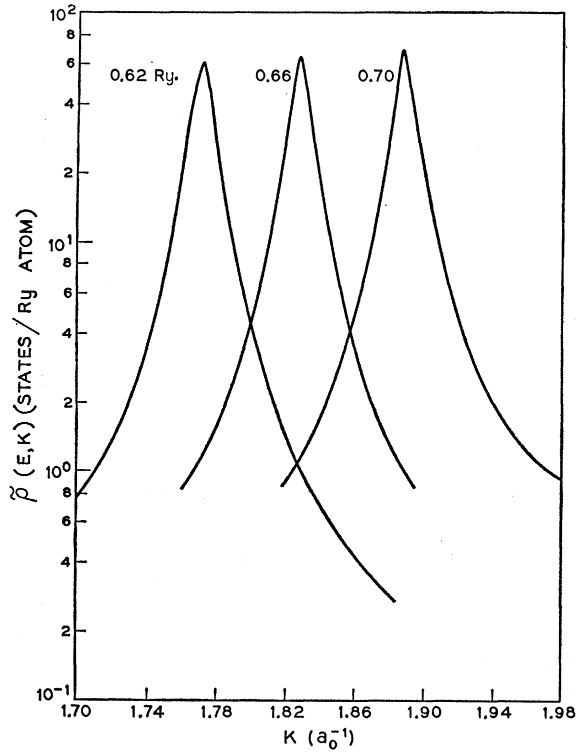

FIG. 3. The spectral density for Δ_1 states in α-brass for various energies, plotted as a function of k along the direction of the BZ. On the horizontal scale used here the ΓX Brillouin-zone dimension is 2.

together with Eq. (11) for the spectral density is essentially equivalent to calculating the momentum-space width of the eigenstate to the accuracy of the first Born approximation.

In Fig. 3 we plot the spectral density corresponding to the s-p Δ_1[22] band in fcc metals. The curves are for a 25% Zn concentration and are evaluated at energies sufficiently great that the d admixture may be neglected. We call attention to the fact that the half-width of these curves is approximately 1% of the ΓX BZ dimension. This simply means that the wave functions of these states may be characterized as being only small departures from true Bloch functions. This, however, is not surprising; the residual resistivity of α-brass has been measured[23] and one may employ simple formulas to obtain an estimate of the mean free path for Fermi-energy electrons. For the alloy for which the curves are calculated this turns out to be approximately 40 lattice spacings, indicating that the width of the states must be of the size quoted above.

The energies for which the curves of Fig. 3 are plotted are near the Fermi energy of the alloy. Hence, we can say that a Fermi surface may be defined up to an uncertainty of a percent or two. By way of comparison, one may note that if the thermal smearing present at helium temperatures is translated into momentum space, one finds an uncertainty in k_F of the order of 0.01%. Using any other standard, however, the smearing appears quite small, and in doing numerical calculations one may as well treat the states as though they were infinitely sharp. In this connection we note that the center of the peaks of the curves of Fig. 3 fall at the zeros of $\det(1-\mathbf{uG}_\mathbf{k})$.

We must emphasize that the s- and p-width parameters are not necessarily small compared to unity. In Fig. 2 we also plot $\Delta_0 u_0$ and $\Delta_1 u_1$ for the alloy concentration employed earlier. It may be seen that, particularly at the higher energies, $\Delta_0 u_0$ if of the order of u_0. In view of the fact that there is significant s-wave admixture in the states described by the curves of Fig. 3 one may ask why then do the curves come out looking so much like delta functions. Mathematically the reason is that for a given k the Green's function is changing so rapidly in the energy region where the states occur that it is only in a very narrow region that one can approach the resonance condition necessary for a peak in the density. Physically one may simply say that these states are basically free-electron-like to begin with and no reasonable tampering with the potential will significantly alter that.

We now consider the predictions of the model for the d bands in α-brass arising from the Cu atoms. We do

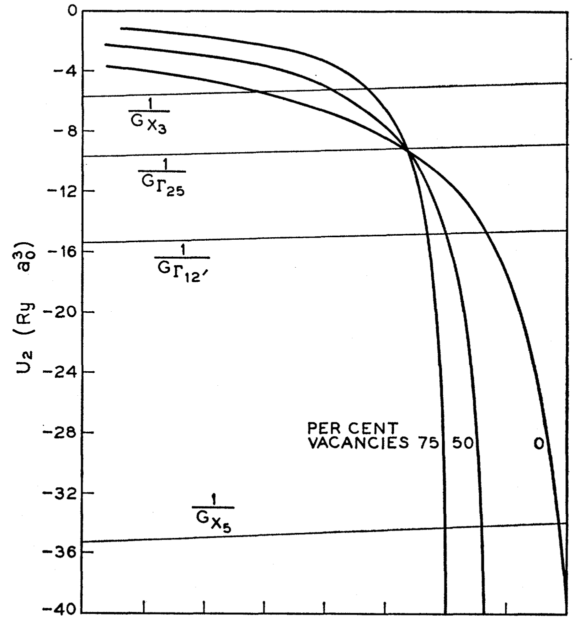

FIG. 4. Position of pure d-type states for a Cu lattice with vacancies. The maximum in the spectral density is given by the crossing of the inverse Green's-function curve with the curve marked with a percentage of vacancies. The latter curves are the effective alloy amplitudes u_2.

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[22] The use of Δ_l to denote the width parameters and of Δ_1 and Δ_5 to denote the symmetry of states should cause no confusion.

[23] W. R. G. Kemp *et al.*, Acta Met. **5**, 303 (1957).

not consider at all the *d* bands arising from the Zn atoms. It is clear that the model employed here can only be approximately valid when the states we are trying to describe are influenced by the combined effect of many potentials, while certainly in pure Zn and probably in α-brass the Zn *d* bands are highly atomic in nature and depend only upon the local environment. To a certain extent this is true for the Cu bands, as is evidenced by the fact that tight-binding formalisms employing only nearest-neighbor overlap integrals are able to satisfactorily account for the over-all shape of the *d* bands.[24]

We will treat in detail only points and lines in the BZ for which the singular part of the *d*-*d* submatrix [corresponding to the B of Eq. (15)] of the Green's matrix vanishes identically. Such states are representative of pure "*d*-band" behavior without the complicating effects of *s*-*d* hybridization. We also restrict ourselves to points in the zone for which the Green's matrix either exactly or to a good degree of approximation factors into diagonal submatrices. For such $\mathbf{k}$ vectors the eigenvalues in a pure material are given by the roots of the scalar equation $1-v_l^{(1)}G_{\mathrm{k}}=0$, where G_{k} represents the relevant component of $\mathbf{G}_{\mathrm{k}}$. In Fig. 4 we have plotted G_{k}^{-1} for several wave vectors together with the *d* amplitude for pure Cu. We note that the X_5 state defines the upper edge, and the X_3 state lies near the lower edge of the *d* band. We note also the near constancy in energy of the Green's function; this allows us to neglect the first term in the square bracket of Eq. (11). It also means that we are now dealing with a situation for which our model is not precisely equivalent to the averaged *t*-matrix one.

It is easiest to demonstrate the nature of the results and the difficulties of the calculation by considering the case where $v_2^{(2)}=0$ and $v_2^{(1)}$ is the Cu*d* amplitude. In this case the effective alloy amplitude is given by

$$u_2=c_1v_2^{(1)}[1-c_2g_2'v_2^{(1)}]^{-1}, \tag{17}$$

and the width parameter by

$$\Delta_2=-c_2g_2''v_2^{(1)}[1-c_2g_2'v_2^{(1)}]^{-1}.$$

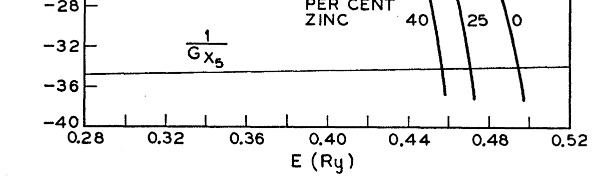

FIG. 5. Position of pure *d*-type states in α-brass. The maximum in the spectral density is given by the crossings of the inverse-Green's-function curves and the curves marked with the zinc percentage. The latter curves are the effective alloy amplitudes u_2.

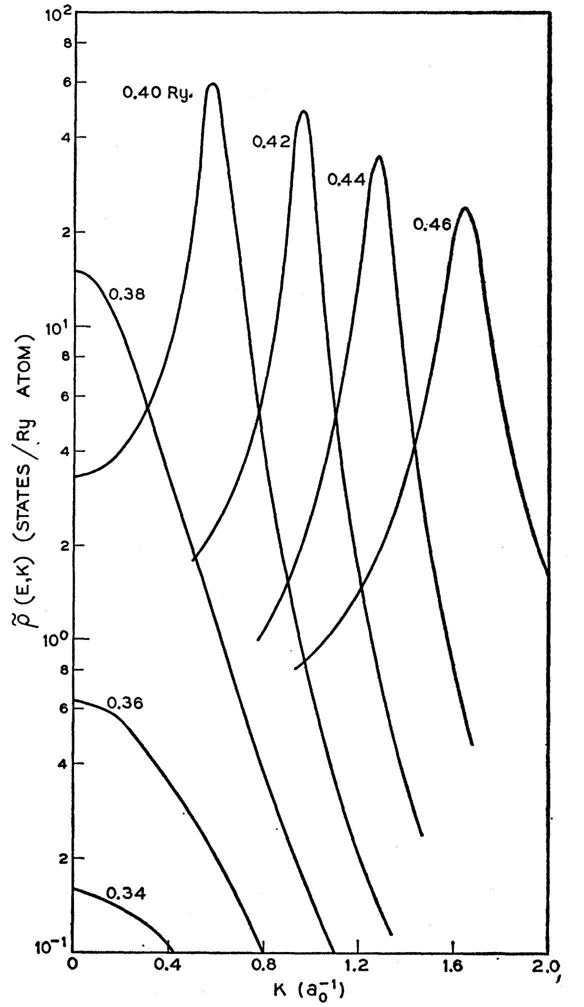

FIG. 6. The spectral density for Δ_5 states in α-brass for various energies plotted as a function of K along the ΓX direction in the BZ. The numbers next to each curve are the energy in Rydbergs above the muffin-tin zero.

Following the discussion in Sec. IV and Appendix B, we will consider only the physically interesting region of energy not too near the singularity in $v_2^{(1)}$.

To illustrate the nature of the results, in Fig. 4 we have plotted u_2 from Eq. (17) for several concentrations of vacancies. The peaks in the spectral density are given by the crossing of the curves of G_{k}^{-1} and the effective potential amplitude. The function u_2 always passes through the point where $1-g_l'v_l^{(1)}=0$, which may be shown to be the point where the conventional phase

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[24] F. M. Mueller, Phys. Rev. (to be published).

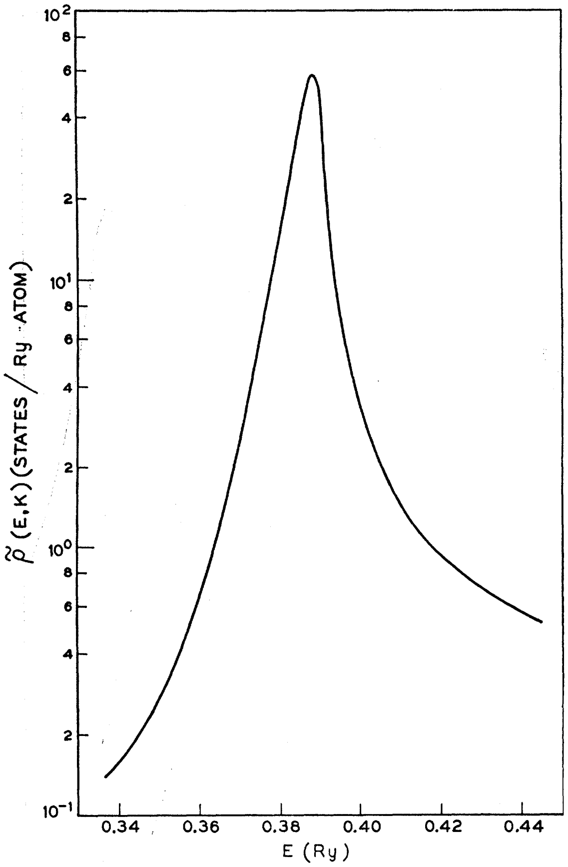

FIG. 7. The spectral density for Γ_{25} states in α-brass plotted as a function of energy.

shift equals $\pi/2$. However, as $c_1 \rightarrow 0$ it does so with ever increasing slope. For moderate concentrations of type (2) (vacancies) the curves show the expected band narrowing. But for large c_2 the band narrows to quite small widths. This is incorrect. It has been shown in many places[25] that an isolated d scatterer will yield a "band" of finite width. The reason for the discrepancy lies, of course, in our putting some small fraction of a t matrix on every site rather than a whole t matrix on a fraction of the sites. The point to be made here is the one made earlier: our approximations are valid only when the states under consideration are of a propagating nature.

Turning now to parameters appropriate to α-brass, we show in Fig. 5 the effective d amplitude for several Zn concentrations. For low Zn concentrations these curves are similar to those shown in Fig. 4 for Cu+vacancies. In Fig. 6 we have plotted the spectral density for states corresponding to those of Δ_5 symmetry in periodic fcc metals. The curves are for a 25% Zn alloy. They are similar to those plotted in Fig. 3 for the Δ_1 states, the major difference being that they are somewhat broader, possessing a half-width of order 5% of a BZ dimension. They are not, however, so broad that they cannot be satisfactorily defined by the position of the peak density. In Fig. 7 we show the spectral density as a function of energy for states of Γ_{25} symmetry for the same alloy composition.

At this point we have completed our discussion of the predictions of the model. We have not attempted to calculate a complete density of states for α-brass, feeling that such extensive calculation is not merited at this point because of the great uncertainty in the choice of potentials, the equally great ambiguity concerning the predictions of the model for the d bands, and the lack of really detailed experimental data with which to compare our results. By way of summary we have plotted in Fig. 8 the variation of the spectral-density peaks as a function of concentration for states of various symmetries. For orientation we have plotted in the same figure the approximate variation of the Fermi energy, calculated with the nearly constant specific-heat[26] density of states. We have compared our calcu-

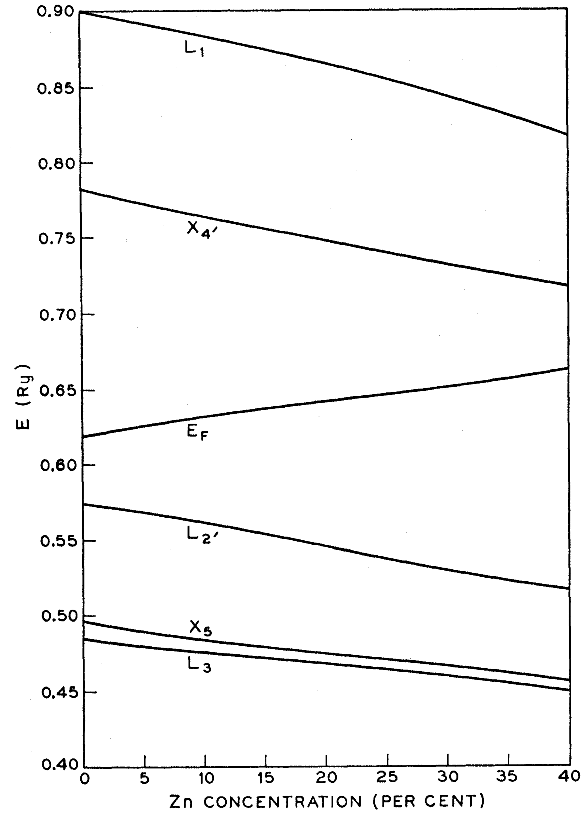

FIG. 8. The trajectories of several of the peaks in the spectral density in α-brass as a function of Zn concentration. The curve marked E_f is the Fermi energy calculated using the specific-heat density of states.

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[25] J. Friedel, Advan. Phys. 3, 446 (1954); P. W. Anderson and W. F. McMillan (to be published).

[26] J. A. Rayne, Phys. Rev. **108**, 22 (1957); B. W. Veal and J. A. Rayne, *ibid.* **130**, 2156 (1963); L. I. Isaacs and T. B. Massalski, *ibid.* **138**, A134 (1965).

lations with the results of optical-absorptivity measurements by Biondi and Rayne.[27] Making the common interpretation of the peaks in the optical absorbtivity as being due to direct electronic transitions[28] curves of Fig. 8 may be used to calculate the shift in the position of the absorbtivity peaks as a function of concentration. We have done this; and although the shifts we calculate are of the correct sense, they differ from the experimental ones by a factor of roughly 2. (We should add that in the case of the optical threshold we are talking about energy shifts of 0.1 eV, which is infinitesimal from the band-structure point of view.) It might be objected that because of the nonconservation of crystal momentum one cannot hope to predict the position of the absorbtivity peaks by considering only direct transitions. And it has recently been argued[29] that even in the case of pure Cu, indirect transitions are important. While we do not wish to discuss this question here, we simply point out that if direct transitions dominate in the pure material, then the 1% width of the *s*-*p* states and the 5% width of the *d* states indicate that the same transitions should dominate in the alloy also. We suspect, instead, that the discrepancy between the results of our calculation and the experiments of Biondi and Rayne lies either in the choice of potentials or in the manner in which the *d* bands were treated.

ACKNOWLEDGMENTS

We acknowledge helpful conversations with Dr. P. W. Anderson, Dr. W. L. McMillan, and Dr. D. W. Taylor. We wish to especially thank Dr. L. F. Mattheiss for the loan of several computer programs and for many interesting comments and Dr. M. Lax for much fruitful discussion on the nature of random systems.

APPENDIX A

In this Appendix we outline the calculations leading to Eq. (10a) for $\rho(E)$. The point is that once having made the averaged t-matrix approximation of Eq. (9) we can simply assume that we have a periodic system possessing the potential $W(\mathbf{x},\mathbf{x}')$ (the formal inversion of the average t matrix) on every lattice site.

We wish to calculate

$$\operatorname{Tr}\operatorname{Im}\mathcal{G}\left(1-\frac{\partial}{\partial E}\langle\mathcal{V}\rangle\right), \tag{A1}$$

where $\mathcal{G}$ is the Green's function and $\langle\mathcal{V}\rangle$ the average model potential. It is easily shown that $\mathcal{G}$ may be written

$$\mathcal{G}=\frac{1}{N}\sum\nolimits_{\mathbf{k}}{}'\,\mathcal{G}_{\mathbf{k}}, \tag{A2}$$

where N is the number of sites and the sum is confined to the first Brillouin zone. The function $\mathcal{G}_{\mathbf{k}}$ satisfies

$$\mathcal{G}_{\mathbf{k}}(\mathbf{x},\mathbf{x}')=G_{\mathbf{k}}(\mathbf{x},\mathbf{x}') +\int G_{\mathbf{k}}(\mathbf{x},\mathbf{y})W(\mathbf{y},\mathbf{y}')\mathcal{G}_{\mathbf{k}}(\mathbf{y}',\mathbf{x}')d\mathbf{y}d\mathbf{y}', \tag{A3}$$

where $\mathcal{G}_k$ is the KKR Green's function.[13] Equation (A3) may be solved to yield

$$\mathcal{G}_{\mathbf{k}}(\mathbf{x},\mathbf{x}')=G_{\mathbf{k}}(\mathbf{x},\mathbf{x}')+\sum_{L,L'}\langle\mathbf{x}|G_{\mathbf{k}}|L\rangle \times w_l\langle L|(1-\mathbf{W}\mathbf{G}_{\mathbf{k}})^{-1}|L'\rangle\langle L'|G_{\mathbf{k}}|\mathbf{x}'\rangle, \tag{A4}$$

where

$$\langle\mathbf{x}|G_{\mathbf{k}}|L\rangle=\int G_{\mathbf{k}}(\mathbf{x},\mathbf{x}')\frac{\delta(x'-R)}{R^2}Y_L(\mathbf{x}')d\mathbf{x}'$$

and the other symbols are defined in the text.

Following the work of Edwards, the imaginary part of the first term on the right-hand side of (A4) may be ignored. The trace in Eq. (A1) may then be evaluated using the relations

$$\int\langle\mathbf{x}|G_{\mathbf{k}}|L\rangle\langle L'|G_{\mathbf{k}}|\mathbf{x}\rangle d\mathbf{x}=-N\frac{\partial}{\partial E}\langle L|\mathbf{G}_{\mathbf{k}}|L'\rangle$$

and

$$\int\langle\mathbf{x}|G_{\mathbf{k}}|L\rangle\langle L'|G_{\mathbf{k}}|\mathbf{x}\rangle\frac{dV}{dE}d\mathbf{x} =N\sum_{L''}\langle L'|\mathbf{G}_{\mathbf{k}}|L''\rangle\frac{dV_l}{dE}\langle L''|\mathbf{G}_{\mathbf{k}}|L\rangle.$$

Combining these results with (A1), (A2), and (A3) immediately yields Eq. (10a) for the density of states.

APPENDIX B

In this Appendix we discuss the approximation

$$\left\langle\mathcal{G}\frac{\partial}{\partial E}\mathcal{V}\right\rangle\simeq\langle\mathcal{G}\rangle\frac{\partial}{\partial E}\langle\mathcal{V}\rangle \tag{B1}$$

which we have introduced in order to treat the energy dependence of the model potentials. A term involving $\partial\mathcal{V}/\partial E$ arises in the first place because in calculating the density of states of the actual system using the model potentials we have incorrectly treated the interior of the atomic spheres. Starting from the results of Ref. 25 it may be shown in a manner entirely independent of the method used in the text that the exact expression for the correction to the density of states within the atomic sphere of the ith atom is

$$\Delta\rho(E)=\frac{1}{\pi}\sum\nolimits_L\frac{dv_l^{(i)}}{dE}\operatorname{Im}\langle L|\mathcal{G}|L\rangle_i,$$

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[27] M. A. Biondi and J. A. Rayne, Phys. Rev. **115**, 1522 (1959).

[28] H. Ehrenreich and H. R. Phillip, Phys. Rev. **128**, 1622 (1962).

[29] C. N. Berglund and W. E. Spicer, Phys. Rev. **136**, A1030, (1964); **136**, A1044 (1964).

where $\mathcal{G}$ is the exact Green's function, and

$$\langle L|\mathcal{G}|L\rangle_i=\int\frac{\delta(x-R)}{R^2}Y_L(x)\mathcal{G}(\mathbf{x},\mathbf{x}')\times\frac{\delta(x'-R)}{R^2}Y_L(\mathbf{x}')d\mathbf{x}d\mathbf{x}',$$

where the integration is over the surface of the ith sphere and the notation is defined in the text.

Relation (B1) is therefore valid whenever the Green's function is essentially the same on all atomic spheres (such as for s-p type states) and is useful for semi-quantitative work whenever one type of atom completely dominates the average, such as occurs for the d-type state in α-brass. It is emphatically not valid near the region where the amplitude of one type of atom has a singularity (see Fig. 5). For near the singularity it may easily be shown that the imaginary part of the corresponding angular-momentum component of Green's function vanishes, yielding a finite $\Delta\rho(E)$, whereas our procedure yields a singularity in $\Delta\rho(E)$.

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Analysis of the Shubnikov–de Haas Effect in Bismuth*

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The Shubnikov–de Haas effect has been measured in single crystals of high-purity bismuth. Some of the observed oscillations have periods similar to those found by Lerner and attributed by him to heavy-holes and electrons. Some of these periods are shown to be the result of superposition of oscillations due to different parts of the Fermi surface of the two-carrier model of Smith, Baraff, and Rowell, and the others to be the result of frequency modulation due to oscillations in the Fermi energy.

INTRODUCTION

Recent measurements of the Shubnikov–de Haas effect,[1,2] the de Haas–van Alphen effect,[3] and cyclotron resonance[4] have revealed the presence of a group of holes in the band structure of bismuth, in addition to the electrons originally found by Shoenberg.[5] The differences between the estimates of the size and shape of the Fermi surface made by various authors are consistent with the differences in purity of the samples used in their experiments, and in each case a calculation of the electronic component of the low-temperature specific heat based on the band structure leads to a value an order of magnitude smaller than that measured.[6,7] This discrepancy may be explained by postulating another set of charge carriers in bismuth, with greater effective masses than those already observed. Lerner,[8,9] claims to have found Shubnikov–de Haas oscillations which are caused by these heavy carriers, and deduces from them the sizes and shapes of the corresponding pieces of Fermi surface. The measurements described here were made with the object of providing confirmatory evidence for Lerner's suggestions, whose validity has been doubted by several authors. It is found that a straightforward interpretation of our results is consistent with Lerner's observations, but that a more thorough analysis shows that all the results may be explained on the basis of the two-carrier model of the bismuth band structure.

EXPERIMENT

Zone-refined bismuth, purchased from the Consolidated Mining and Smelting Company of Canada Limited, and of a nominal purity of 99.9999% was subjected to further zone refining in Union Carbide grade AUC graphite boats *in vacuo*. Central sections, 15 cm long, cut from three 50-cm-long ingots which had each been passed through a zone-melting furnace at 4 cm/h 21 times, were placed end to end in another boat and repassed 13 times. Single crystals were grown from the central section of the resulting ingot by passing a molten zone along its, starting from a small

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[8] L. S. Lerner, Phys. Rev. **127**, 1480 (1962).

[9] L. S. Lerner, Phys. Rev. **130**, 605 (1963).