

model used in these analyses, \mathbf{Q} has been assumed to remain aligned parallel to the field even as the field is lowered to zero. This assumption is certainly open to question. We suggest that a more definitive test of the SDW hypothesis might be possible if this experiment were repeated with a ql value of the order of 50 and a derivative technique used.

Some of the general features of the attenuation at oblique angles are worth emphasizing. As has been pointed out by Eckstein,¹ at high ql , the position of the Doppler-shifted cyclotron resonance edge gives a measure of $(m^*v_z)_{\max}$, where m^* is the cyclotron effective mass. An additional point emphasized by Eckstein,¹ applicable to materials in which v_s/v_F is an order of magnitude larger than in simple metals like potassium,

or in which ql is very large, is experimentally useful. This is the appearance of double edges. The observation of double edges facilitates the identification of the edge position, and allows both m^* and $(v_z)_{\max}$ to be determined independently. Finally, we note that although the geometric resonances associated with non-extremal orbits can, in principle, be used to map out the Fermi surface, in practice, it appears that this will be very difficult.

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Coherent-Potential Model of Substitutional Disordered Alloys

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We introduce a model of a substitutional alloy based on the concept of an effective or coherent potential which, when placed on every site of the alloy lattice, will simulate the electronic properties of the actual alloy. The coherent potential is necessarily a complex, energy-dependent quantity. We evaluate the model for the simple case of a one-dimensional alloy of δ -function potentials. In order to provide a basis for comparison, as well as to see if a simpler scheme will suffice, we also calculate the spectrum of the same alloy using the average t -matrix approximation introduced by Beeby. On the basis of these results, we conclude that the average t -matrix approximation is not adequate for the description of an actual transition-metal alloy, while the coherent-potential picture will provide a more reasonable facsimile of the density of states in such an alloy.

I. INTRODUCTION

THE work reported here was stimulated by an attempt to find a reasonably simple and numerically tractable formalism for calculating the electronic structure of a metallic alloy. We desired a scheme whereby the density of states and the position of the energy bands could be determined.

At present very little is known concerning the electronic spectra of real alloys. There is, however, a great deal of information on the spectra of hypothetical one-dimensional alloys,¹⁻⁴ most of which is quite discouraging to someone attempting to find tractable formulas for the density of states. In the simple case of a one-dimensional alloy of δ -function potentials the density of states is extremely irregular,⁴ possessing fine structure over energy intervals of the order of a few percent of

typical bandwidths. This is to be compared with the structureless density of states function for an ordered lattice of δ functions. It is not likely that simple formulas can be devised to yield the alloy spectrum in detail. Our aim, therefore, was to find expressions which, when applied to the one-dimensional case, would effectively average the exact density of states over energy intervals sufficiently small so that gross distortions were not introduced into the spectrum. From this point of view, the better the formula, the smaller the energy interval over which it yields an average of the exact density of states. In accordance with this view, we will compare the approximate calculations of the cumulative, rather than the differential, density of states with the results of exact calculations.

The exact results to which we refer are necessarily for a one-dimensional crystal. The problem of calculating the spectrum of such an alloy has been extensively treated in the literature²⁻⁵ and we will not dwell on it further except to say that the explicit numerical results for the cumulative density of states used for com-

¹ J. M. Luttinger, Phillips Res. Rept. **6**, 303 (1951).

² A. M. James and A. S. Ginzburg, J. Phys. Chem. **57**, 840 (1953).

³ R. Landauer and J. C. Helland, J. Chem. Phys. **22**, 1955 (1954).

⁴ R. L. Agacy and R. E. Borland, Proc. Phys. Soc. (London) **84**, 1017 (1964).

⁵ H. Schmidt, Phys. Rev. **105**, 425 (1957).

parisons in this paper have been calculated, using the distribution-function method of Schmidt,⁵ and are accurate to about 1%.

Aside from being able to yield a good average to the density of states of a one-dimensional alloy, we require that the formulas be tractable in three dimensions as well. The averaged t -matrix approximation introduced by Korringar^{5a} and Beeby⁶ has this property; and since it is an approximation of the same general character as the one introduced here, we will consider it in some detail below. A different approach to the problem has been taken by Yonezawa and Matsubara.⁷ They sum a selected class of terms in a perturbation series for the alloy Green's function. Their series of papers is not yet complete, and we will not consider their approach beyond saying that their work is a more systematic, as opposed to intuitive, attack on the alloy problem than the coherent-potential approximation to be presented below.

The paper is divided into several short parts. In Sec. II we briefly sketch the general properties of the spectrum of a one-dimensional alloy of δ -function potentials, in preparation for the following sections. The averaged t -matrix approximation is reviewed and evaluated for the one-dimensional case in Sec. III. In Sec. IV we introduce and in Sec. V we evaluate, again for the one-dimensional case, what we call the coherent-potential model of an alloy. Our conclusions are presented in Sec. VI.

II. CHARACTER OF THE SPECTRUM OF A ONE-DIMENSIONAL SUBSTITUTIONAL ALLOY

The spectrum of a one-dimensional substitutional δ -function alloy has been discussed at great length in many places.¹⁻⁴ Since we apply various approximate formulas to the one-dimensional case, it is useful to briefly summarize several results. Consider an alloy composed of two different types of atoms, denoted by A and B, and assume that pure crystals of A and B have

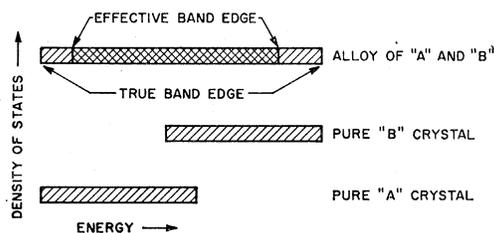


FIG. 1. A schematic representation of the lowest band of a one-dimensional alloy of δ -function potentials. The different types of atoms are denoted by "A" and "B."

^{5a} J. Korringar, *J. Phys. Chem. Solids* **7**, 252 (1958).

⁶ J. L. Beeby, *Phys. Rev.* **135**, A130 (1964).

⁷ F. Yonezawa, *Progr. Theoret. Phys. (Kyoto)* **31**, 357 (1964); F. Yonezawa and T. Matsubara, *ibid.* **35**, 357 (1966); **35**, 759 (1966).

bands which would overlap if superposed. This is illustrated schematically in Fig. 1. It has been shown by Luttinger¹ that an alloy of A and B can have no states in a region of energy simultaneously forbidden to pure crystals of either type. Furthermore, the fact that there is always a finite probability of finding a sufficiently long string of atoms of either type indicates that the alloy has states in any region of energy allowed to either or both crystals of the pure type. Thus, the alloy spectrum is as illustrated in Fig. 1.

The above arguments merely tell us where the density of states is nonzero; they say nothing about how large the state density is in any particular region of energy. Landauer and Helland³ have noted on the basis of numerical results that there are regions of energy where the state density, although strictly speaking nonzero, is nonetheless negligibly small. They characterize these as "almost forbidden" energy regions. It is clear that for finite concentration of both constituents there will always be an almost forbidden region sufficiently near the lower band edge of the lower-lying pure material band (the left-hand side of the pure-A band of Fig. 1) and also one near the upper band edge of the higher-lying band. In general, such regions can also exist within the middle of the band, producing nearly perfect band gaps where none would be expected on the basis of the simplest fluctuation argument. The existence of these almost forbidden regions of energy leads us to define an "effective band edge," which denotes the boundary between a region where the density of states is large and one in which it is sensibly, though not exactly, zero. It is clear that any formula useful for describing the spectrum of a real metallic alloy is only required to predict the effective band edges when it is applied to the one-dimensional case.

III. AVERAGED t -MATRIX APPROXIMATION

In this section we test the validity of the averaged t -matrix approximation.^{5a,6} It has already been shown by Beeby⁸ that the general formulas resulting from this approximation may be formally evaluated in three dimensions, while Soven⁹ has shown that with some further approximation numerical results may be obtained. All that we propose to do here is to determine the accuracy with which the model predicts the spectrum of a one-dimensional alloy.

A complete discussion of the approximation has been given by Beeby, and we will merely outline it here. We first define the notation used here and in Sec. IV. We denote the outgoing-wave free-election Green's function and the exact alloy Green's function by G_0 and G , respectively. The individual atomic potentials are denoted by v and the t -matrices corresponding to them by t . If either v or t is subscripted with a Latin letter or a numeral, a particular type of atom is denoted, while

⁸ J. L. Beeby, *Proc. Roy. Soc. (London)* **A279**, 82 (1964).

⁹ P. Soven, *Phys. Rev.* **151**, 539 (1966).

a Greek subscript denotes both a site index and the type of atom at the particular site. Thus, the atomic t -matrices are defined by the usual expression

$$t_i = v_i + v_i G_0 t_i, \quad (1)$$

and the Green's function G is given by

$$G = G_0 + \sum_{\alpha} G_0 t_{\alpha} G_0 + \sum_{\alpha} \sum_{\beta \neq \alpha} G_0 t_{\alpha} G_0 t_{\beta} G_0 + \dots \quad (2)$$

The density of states for the system is denoted by $\rho(E)$; it may be calculated by the general formula

$$\rho(E) = - (1/\pi) \text{Im Tr} \langle G \rangle, \quad (3)$$

where Tr denotes trace over any complete set, and the angular brackets indicate that an ensemble average is to be taken.

The approximation that is made is the replacement of the average of products of t -matrices by the products of the average t -matrix. One writes

$$\langle G \rangle \simeq G_0 + \sum_{\alpha} G_0 \langle t_{\alpha} \rangle G_0 + \sum_{\alpha} \sum_{\beta \neq \alpha} G_0 \langle t_{\alpha} \rangle G_0 \langle t_{\beta} \rangle G_0 + \dots \quad (4)$$

and then resums the series in the manner described by Beeby.

We have applied this approximation to the calculation of the spectra of a number of one-dimensional δ -function alloys. Here the potentials are given by $v_i \delta(x)$. The results for one of these alloys is shown in Fig. 2. For the reason emphasized in the Introduction, we have plotted the cumulative rather than the differential density of states. The most glaring discrepancy between the predictions of the model and the exact numerical results is the existence of a spurious band gap. This gap, the presence of which was noted by Beeby, is due to the fact that by averaging the atomic t -matrices one is generating an effective "atom" having two closely spaced orbitals. When "atoms" of this nature are combined into a crystal, the band formed by either orbital cannot overlap the band formed by the other. We note also that the model does not predict either the position or the shape of the effective band edges. In the region below the spurious band gap, model does provide a good fit to the numerical results, i.e., a relatively fine-grained average of the density of states. We will see in Sec. IV that this region of energy may be characterized as one of relatively long electron mean free paths. It is reasonable that the model will be accurate in its description of relatively spread-out eigenfunctions. The region of energy somewhat above the spurious gap will be shown below to be characterized by relatively short mean free paths, of the order of one interatomic spacing. The model was not intended to describe such states, which are better pictured in terms of a Slater-Koster¹⁰ isolated impurity model, and it is no reflection on the theory that it fails in this region.

¹⁰ G. F. Koster and J. C. Slater, Phys. Rev. **95**, 1167 (1954); G. F. Koster, *ibid.* **95**, 1436 (1954); G. F. Koster and J. C. Slater, *ibid.* **96**, 1208 (1954).

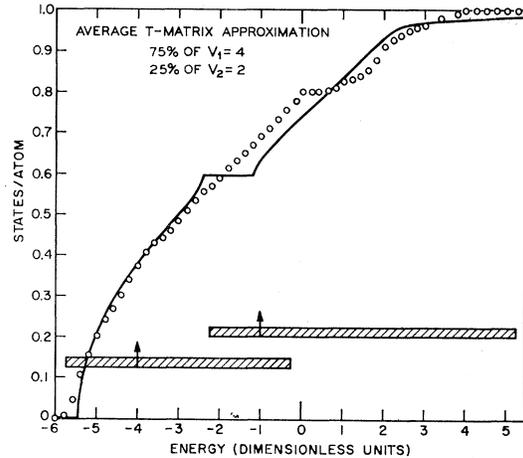


FIG. 2. The cumulative density of states for a particular one-dimensional alloy as calculated in the average t -matrix approximation (solid line) and numerically (circles). The energy is measured in units of the square of the inverse of the lattice constant and the amplitudes of the δ function in units of the inverse lattice constant. The reason for presenting the cumulative density of states is given in the text. The bands of pure crystals of the two potentials (at the same lattice spacing) are indicated by the bars, while the eigenvalues of the isolated potentials are given by the vertical arrows.

While it is extremely hazardous to discuss the validity of the model in the three-dimensional case on the basis of the one-dimensional alloy results, it is clear that the situation prevailing in the δ -function alloy considered here is quite analogous to that prevailing in a real transition-metal alloy. In both cases we have localized states (real in the one-dimensional case and virtual¹¹ in the three-dimensional one) spreading into bands of essentially tight binding character. We would conclude, therefore, that the model is not capable of describing real materials, even when the mean free path is relatively long, because of the introduction of a spurious band gap.¹²

IV. COHERENT-POTENTIAL MODEL

A method found useful in the calculation of the density of states in the impurity-band problem is the so-called modified propagator technique introduced by Lax.¹³ In this technique one approximately evaluates sums of the form of (2) using a modified free-electron

¹¹ J. Friedel, Advan. Phys. **3**, 446 (1954).

¹² As the strength of the stronger potential is increased, or its concentration diminished, a band gap (actually an almost forbidden region) does appear in the spectrum. Our point here is simply that the model inserts such gaps in the spectrum even when they are not actually present. It should be explained that for positive energies the model does not predict a true band gap. But, as argued by Beeby, the band gap present for negative energies will be changed into a region of extremely low state density for positive energies. It is one of the shortcomings of the δ -function model that such things as virtual bound states do not occur, and hence one cannot make a strict comparison with the situation prevailing in transition-metal alloys.

¹³ M. Lax, Rev. Mod. Phys. **23**, 287 (1951).

Green's function or propagator in place of the actual Green's function. Formally the replacement is

$$(E - k^2)^{-1} \rightarrow [E - k^2 - v_c(k, E)]^{-1}, \quad (5)$$

where $v_c(k, E)$, the coherent potential, is a complex quantity describing the average effects of the medium. One then introduces some criterion to determine v_c . The motivation for this procedure is that it is futile to attempt to describe the motion of an electron in a random system of potentials using free-electron Green's functions unless one is able to solve the problem exactly. If one takes into account only a subset of terms occurring in some expansion, then it is necessary to acknowledge at the start of the calculation that the electron is actually traveling through a medium, the presence of which modifies the dynamical properties of the particle.

This procedure is a useful one when treating a liquid; it is less useful in the substitutional alloy case, essentially because the off-diagonal components of the self-energy, of which v_c is approximately the diagonal part, are of the same order of magnitude as the diagonal terms. Physically, one may say that in a liquid one has, on the average, a uniform system, and hence as an approximate representation of the system a Green's function diagonal in momentum is a useful entity. However, in the alloy case on the average one has a periodic system, and it is more appropriate to modify the Green's function in such a manner that the new quantity has matrix elements between momentum vectors differing by the reciprocal lattice vectors of the average periodic system. We note that our calculation is similar to that of Yonezawa and Matsubara⁷ to the extent that they also maintain the off-diagonal terms of the self-energy.

Formally the scheme we introduce is quite simple; it proceeds as follows. At every site in the lattice we place an as yet unknown potential, which we denote by $v_0(\mathbf{x}-\mathbf{l})$ when it is at site \mathbf{l} . The true potentials at the site \mathbf{l} are either $v_1(\mathbf{x}-\mathbf{l})$ or $v_2(\mathbf{x}-\mathbf{l})$. Let \bar{G}_0 be the formal Green's function for the lattice of potentials v_0 :

$$\bar{G}_0 = G_0 + G_0 \left(\sum_{\mathbf{l}} v_0(\mathbf{x}-\mathbf{l}) \right) \bar{G}_0. \quad (6)$$

\bar{G}_0 determines the propagation through the as yet undetermined medium. Relative to the medium, the actual system consists of perturbing potentials $v_1 - v_0$ and $v_2 - v_0$. The t matrix describing the scattering of an electron which is propagating according to \bar{G}_0 when it encounters the perturbing potential $v_i - v_0$ is defined by

$$\bar{t}_i = (v_i - v_0) + (v_i - v_0) \bar{G}_0 \bar{t}_i. \quad (7)$$

These quantities may be combined into a formula of the form of Eq. (2) to yield an expression for the actual Green's function.

$$G = \bar{G}_0 + \sum_{\alpha} \bar{G}_0 \bar{t}_{\alpha} \bar{G}_0 + \sum_{\alpha} \sum_{\beta \neq \alpha} \bar{G}_0 \bar{t}_{\alpha} \bar{G}_0 \bar{t}_{\beta} \bar{G}_0 + \dots \quad (8)$$

Equation (8) is exact. Equations (6), (7), and (8) together constitute a formal rearrangement of Eq. (2), with v_0 being an arbitrary parameter. One way of defining v_0 is by the requirement that on the average there be no further scattering from the perturbing potentials, i.e., we require that

$$c_1 \bar{t}_1 + c_2 \bar{t}_2 = 0, \quad (9)$$

where c_i is the concentration of the i th constituent. With this definition, the average of Eq. (8) is given by

$$\langle G \rangle = \bar{G}_0 + \sum_{\alpha} \sum_{\beta \neq \alpha} \sum_{\gamma \neq \beta} \sum_{\delta \neq \gamma} \langle \bar{G}_0 \bar{t}_{\alpha} \bar{G}_0 \bar{t}_{\beta} \bar{G}_0 \bar{t}_{\gamma} \bar{G}_0 \bar{t}_{\delta} \bar{G}_0 \rangle + \dots \quad (10)$$

We note that the first correction to \bar{G}_0 is of the fourth order in the t matrices.

An equation for v_0 is easily derived by inserting (7) into (9). This yields

$$c_1 [1 - (v_1 - v_0) \bar{G}_0]^{-1} (v_1 - v_0) + c_2 [1 - (v_2 - v_0) \bar{G}_0]^{-1} (v_2 - v_0) = 0. \quad (11)$$

Making use of the operator identity

$$[1 - AB]^{-1} A = [(1 - AB)^{-1} - 1] B^{-1}, \quad (12)$$

Eq. (11) may be reduced to

$$u - v_0 = (v_1 - v_0) \bar{G}_0 (v_2 - v_0), \quad (13)$$

where u is the average potential $c_1 v_1 + c_2 v_2$.

The above is still an exact procedure. Noting again that the corrections to \bar{G}_0 in Eq. (10) for $\langle G \rangle$ are of fourth order in the t matrices and that the concept of an effective medium should be valid for sufficiently long mean free paths, we make the approximation

$$\langle G \rangle \simeq \bar{G}_0. \quad (14)$$

The validity of this approximation will be tested below. Before doing so, we note the following properties of the theory. It is symmetrical with respect to the two potentials. As noted by Yonezawa and Matsubara this is an essential requirement of any theory of nondilute alloys. We note further that the imaginary part of \bar{G}_0 is nonzero only when v_0 is complex. This implies that the states described by the model are always damped, contrary to the predictions of the averaged t -matrix approximation. Equation (13) for v_0 is quite complicated and, in general, its solution will not have the functional form of v_1 and v_2 . Equation (13) is, however, soluble for the simple case of one-dimensional alloys of δ -function potentials, and, as we shall show in a succeeding publication, for simple but realistic three-dimensional alloys as well.

V. COHERENT-POTENTIAL CALCULATIONS FOR A ONE-DIMENSIONAL ALLOY

In Fig. 3 we show the cumulative density of states as calculated in the coherent-potential model together with the numerical results for the same alloy used to

illustrate the averaged t -matrix approximation. In the same figure we show the coherence length, defined as the inverse of the imaginary part of the poles of the Green's function \bar{G}_0 in the complex momentum plane.¹⁴ The coherence length is of the same order of magnitude as the mean free path.

We note the following points. The over-all fit is superior to that provided by the averaged t -matrix approximation. Most obvious is the fact that the spurious gap in the middle of the band produced in that approximation is not present here. The position of the effective band edges of the alloy are correctly predicted by the model. Furthermore, the shape of the effective band edges (the slope of the curve) is well approximated. Except in the region around zero energy the scale of averaging, as defined in the Introduction, is relatively fine. It is obvious, however, that in the energy region around zero in Fig. 3, the model provides far too coarse an approximation for it to be useful. This is certainly due to the fact that the coherence length is extremely small, approaching one interatomic spacing. Clearly the concept of an effective medium breaks down in such a limit. But whenever the coherence length is greater than two or three lattice spacings, as it certainly is in the bulk of the band of a real material, the approximation provides a relatively fine-grained average to the actual density of states.

To see if the approximation might be improved, we examined the contribution to the density of states of the simplest class of terms omitted in the approximation. We note that, in the three-dimensional case, the inclusion of even this class of terms would be extraordinarily difficult, although it is feasible in the one-dimensional case. The additional terms are of the form

$$\langle \bar{G}_{0\beta\alpha} \bar{G}_{0\beta\beta} \bar{G}_{0\beta\alpha} \bar{G}_{0\beta\beta} \cdots \bar{G}_{0\beta\alpha} \bar{G}_{0\beta\beta} \rangle,$$

corresponding to an electron being scattered repeatedly by two atoms. Recall that the lowest-order terms contain four t matrices. We included terms of this character to all orders and for all pair separations. The results were as expected. In these regions of energy where the coherence length was greater than or approximately equal to three lattice spacings, the contribution of these terms to $\rho(E)$ was usually much less than 10% of the contribution of \bar{G}_0 itself. In the regions where the coherence length was significantly less than three lattice spacings, the contribution to $\rho(E)$ was of the

¹⁴ At any energy within the band the Green's function \bar{G}_0 has an infinite number of poles. These have real parts differing by a reciprocal lattice vector but identical imaginary parts.

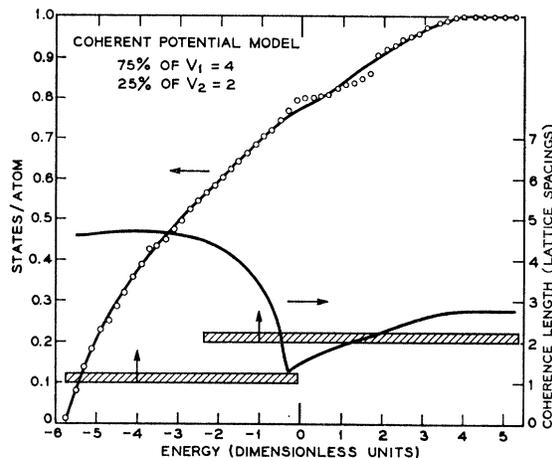


FIG. 3. The cumulative density of states for a particular one-dimensional alloy as calculated in the coherent potential model (solid line) and numerically (circles). The energy is measured in units of the square of the inverse of the lattice constant and the amplitudes of the δ function in units of the inverse of the lattice constant. The other curve shown is the coherence length in units of the lattice spacing. The reason for presenting the cumulative density of states is given in the text. The bands of pure crystals of the two potentials (at the same lattice spacing) are indicated by the bars, while the eigenvalues of the isolated potentials are given by the vertical arrows.

same order as that of \bar{G}_0 , confirming our conclusion that the approximation is invalid in regions of energy where highly damped states make the most significant contribution to the total density of states.

VI. SUMMARY

On the basis of the calculations presented here, we conclude that the procedure of simply averaging atomic t -matrices and then using the average quantities to describe a substitutional alloy will not yield reasonable results when applied to the case of a real transition-metal alloy. It appears that the coherent-potential model which modifies the electron Green's function and then determines the modified quantity in a self-consistent way is a more appropriate method to apply to the problem. In a later publication we will show that the procedure is practical for simple but realistic three-dimensional alloys.

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