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ELECTRONIC STRUCTURE OF BINARY SUBSTITUTIONAL ALLOYS (*)

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Since the contents of this talk will be published in several papers to appear elsewhere, an informal summary together with the relevant references should suffice for the present purposes. The multiple scattering approach, which has been very useful in dealing with electronic property of alloys, is summarized in the first part of this paper and applied to two simple three dimensional models in which the disorder is cell localized.

In order to make the calculations tractable the so-called single site approximation, which decouples the scattering from a single site from that due to the rest of the medium, is generally made. Within this framework the problem can be dealt with either self-consistently or non self-consistently. In the former case, one obtains the coherent potential approximation, or CPA, which corresponds to a mean field theory. The latter case, the so-called average *t*-matrix approximation (ATA) leads to a perturbation theoretic expansion of the multiple scattering series and requires the choice of a suitable unperturbed Hamiltonian. Since the implementation of self-consistent calculations is more difficult, it is of interest to compare the results obtained for these two single site approximations.

Such a comparison is made for two models. The first is the single site tight binding model first discussed extensively by Velicky, *et al.* [1]; the second is the *s*-*d* hybridization model introduced by Levin and Ehrenreich [2]. The latter, which simulates the situation encountered in transition metals, corresponds, for each alloy component, to a broad *s* band which intersects with a single narrow *d* band and hybridizes with it. In the alloy the *d* bands are treated either within the CPA or ATA while the conduction bands and hybridization effects are described within the virtual crystal approximation. Numerical comparisons of the CPA and ATA show good agreement particularly for the *s*-*d* hybridization model when the unperturbed Hamiltonian used in the ATA corresponds to that appropriate to the virtual crystal [3]. Indeed, the ATA may be regarded as the first step in an iteration procedure which results in the CPA when carried through to self-consistency.

The second major topic of this paper deals with the status of single site approximations. The CPA, for

example, interpolates between the virtual crystal and split band limits and thus is not clearly an approximation based on weak impurity scattering. It also leads to reasonable results for larger impurity concentrations than one might ordinarily suppose. The question then arises as to the nature of the small parameters in the CPA and the form of the leading corrections. Schwartz and Siggia [4] have formulated a systematic perturbation expansion of the self-energy using the functional derivative techniques of Martin and Schwinger and identified the diagrams contributing to the CPA for the simple cubic tight binding model. They have shown the CPA to contain all diagrams involving site diagonal matrix elements of the Green's function to all orders in the concentration and scattering strength. By contrast, the ATA only takes approximate account of the diagrams to lowest order in the concentration. Investigation of corrections to the CPA reveals the presence of another parameter, the number of nearest neighbors. The CPA, as expected for a mean field theory, is a better approximation if this number is large. Furthermore, it is the only one of the single site approximations to exhibit this property.

This approach or one based on multiple scattering theory can be used to generalize the CPA to include the effects of scattering from clusters of atoms [4], [5]. The effects of nearest neighbor pair clusters are considered in particular and the scattering from them is treated to all orders. Formally, the results can be expressed in terms of the two particle scattering matrix. Again, it is possible to construct an either non self-consistent or self-consistent theory. In the former case the two atom molecules are regarded as being embedded in a CPA medium. In the latter, the medium is determined self-consistently by requiring that the average of all two particle scattering matrices should vanish. This is the obvious generalization of the CPA condition which states that the scattering from a single site should vanish on the average. Numerical results for a reasonably large scattering strength and fairly small concentrations show the appearance of sharp levels (non self-consistent version) or narrow bands (self-consistent version) above and below the CPA type impurity bands. These levels may be interpreted respectively as antibonding and bonding states of the two atom molecules. This example emphasizes the difficulty encountered in obtaining band edge tails using this approach. Tails obviously consist of a

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convolution of such levels or bands resulting from many different kinds of clusters having varying sizes.

The final portion of the paper discusses some of the problems encountered in extending this type of approach to more realistic systems. The first such is the question of how to combine the machinery of band theory with the multiple scattering approaches. The muffin tin schemes are most suitable in this respect. Indeed, Soven [6] has already done such calculations within the ATA for CuZn. Perhaps most important, however, is the question of how to construct suitable alloy potentials. The renormalized atom picture, recently discussed by Watson, Ehrenreich, and Hodges [7], [8], may be particularly useful in this respect since the atoms are prepared as far as possible in the state with which they enter the crystal before they are actually placed together. In addition to providing quantitative insight with a minimum of computational effort concerning the relative positions

of conduction and d bands as well as d bandwidths for the 3d and 4d transition metals, this approach also shows promise in yielding a satisfactory description of the cohesive energies of the pure metals [9]. More importantly for the present purposes, the effects of charge transfer between alloy constituents can be taken into account more easily. This effect is of considerable importance even in isovalent alloys such as AgAu. For example, the concentration dependence of the fundamental interband transition in these alloys can be accounted for only if such effects are taken into account [2].

Problems of self-consistency in the band theory of alloys appear on two levels: first, in connection with the solution of the Hartree-Fock equations and secondly, with respect to the determination of the effective medium. If the ATA turns out to be a satisfactory approximation, this second level of self-consistency, whose implementation leads to considerable numerical complexity, is obviated.

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