

Electronic structure of disordered BCC alloys

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Abstract. This paper describes and analyses a self-consistent cluster coherent potential approximation calculation of the electron density of states of a random, binary alloy on a BCC lattice.

Keywords. Random alloy; augmented space; cluster coherent potential approximation; electronic structure; BCC alloys.

1. Introduction

In a preceding communication (Kumar *et al* 1982, hereafter referred to as I) the authors have developed a self-consistent cluster-coherent potential approximation (CCPA) including effect of off-diagonal disorder and short-range order (SRO) which retains the Herglotz property essential for physically valid density of states. The application was made to model Hamiltonians on diamond lattices. This was in view of subsequent application to III-V ternary semiconducting alloys, which provide four sp^3 -hybridised orbitals per site for bonding into a tetrahedral structure. The study of the model Hamiltonian was extremely instructive—as discussed in detail in I, it enabled us to identify the regimes where cluster and off-diagonal effects predominate and to analyse the cluster origin of the structures observed in the density of states in these regimes. This study is essential in deciding under what conditions such generalisations are useful. This would not have been possible if we started immediately with the more complicated ‘bond-orbital’ model for the III-V ternary alloys, although the generalisation from a single orbital to four orbitals per site is a straightforward one involving a generalisation with the recursion procedure known and documented for some time (Haydock *et al* 1972).

In this communication we turn our attention to BCC lattices. The aim is a subsequent study of BCC sd-metallic alloys like β -brass. These provide six sd^5 orbitals per site. To analyse the effect of clusters, off-diagonal disorder and SRO we shall begin by a bcc alloy with one orbital per site.

2. Formalism

The starting Hamiltonian is expressed in a suitably chosen tight-binding basis

$$\mathbf{H} = \sum_i \sum_n e_{in} \mathbf{P}_{in} + \sum_{i \neq j} \sum_n \sum_m V_{in \ jm} \mathbf{T}_{in \ jm}, \quad \mathbf{H} \in \mathcal{H}, \quad (1)$$

where \mathbf{P} and \mathbf{T} are projection operators and transfer operators in \mathcal{H} . The basis could be atomic orbitals, e.g. in the case of BCC, s - d metallic alloys, they could be six s - d hybridised orbitals per site. For covalent alloys one could use the bonding orbitals for the valence bands. The problem of non-orthogonality of the basis poses a problem. One could avoid the use of non-diagonal overlap matrix $\mathbf{S} = \langle in | jm \rangle$ by setting up the basis in the chemical pseudo-potential approach of Bullett (1975). The basis are now the pseudo-orbitals. Both the diagonal terms (e_{in}) and the off-diagonal terms ($V_{in, jm}$) form a set of random variables described by

$$\begin{aligned} e_{in} &= e_{in}^A N_i + e_{in}^B (1-N_i), \\ V_{in, jm} &= V_{nm}^{AA} N_i N_j + V_{nm}^{BB} (1-N_i) (1-N_j) \\ &+ V_{nm}^{AB} [N_i (1-N_j) + N_j (1-N_i)], \end{aligned} \quad (2a)$$

where N_i are a set of random "occupation" variables for the constituents A and B . In the absence of short range order the various N_i 's are independent random variables with probability densities

$$p(N_i) = c \delta(N_i-1) + (1-c) \delta(N_i). \quad (b2)$$

Using (2a) we may write (1) in a more useful form:

$$\begin{aligned} \mathbf{H} &= \mathbf{H}_B + \sum_i \sum_n e_n N_i \mathbf{P}_{in} + \sum_{i \neq j} \sum_n \sum_m V_{nm}^{(1)} N_i N_j \mathbf{T}_{in, jm} \\ &+ \sum_{i \neq j} \sum_n \sum_m V_{nm}^{(2)} (N_i + N_j) \mathbf{T}_{in, jm}, \end{aligned} \quad (3)$$

where \mathbf{H}_B is the Hamiltonian of the pure B constituent,

$$e_n = e_n^A - e_n^B, \quad V_{nm}^{(1)} = V_{nm}^{AA} + V_{nm}^{BB} - 2V_{nm}^{AB} \text{ and } V_{nm}^{(2)} = V_{nm}^{AB} - V_{nm}^{BB}$$

The Hamiltonian is now in a form appropriate for the augmented space formalism. The formalism has been discussed in great detail in I. Nevertheless, we briefly summarise the procedure here so that the subsequent discussion may be put in context. Corresponding to each N_i there is an operator $\mathbf{M}^{(i)}$ in a two-dimensional vector space $\phi^{(i)}$. A representation of $\mathbf{M}^{(i)}$, in a basis $\{|v_0^i\rangle, |v_1^i\rangle\}$ is (Mookerjee 1973)

$$\begin{pmatrix} c & \{c(1-c)\}^{1/2} \\ \{c(1-c)\}^{1/2} & 1-c \end{pmatrix}$$

where c is the concentration of the solute A . The augmented space Hamiltonian is

$$\begin{aligned}
 \tilde{\mathbf{H}} &= \mathbf{H}_B \otimes \mathbf{I} + \sum_n e_n \sum_i \mathbf{P}_{in} \otimes \mathbf{M}^{(i)} \otimes \mathbf{I}^{(i)} \\
 &+ \sum_{nm} V_{nm}^{(1)} \sum_{i \neq j} \mathbf{T}_{in, jm} \otimes \mathbf{M}^{(i)} \otimes \mathbf{M}^{(j)} \otimes \mathbf{I}^{(ij)} \\
 &+ \sum_{nm} V_{nm}^{(2)} \sum_{i \neq j} \mathbf{T}_{in, jm} \otimes (\mathbf{M}^{(i)} \otimes \mathbf{I}^{(i)} + \mathbf{M}^{(j)} \otimes \mathbf{I}^{(j)}) \\
 \tilde{\mathbf{H}} &\in \mathcal{H} \otimes \prod_i \phi^{(i)}. \tag{4}
 \end{aligned}$$

$\mathbf{I}^{(i)}$ and $\mathbf{I}^{(ij)}$ in the above equation indicate identity operators in all sub-spaces $\phi^{(k)}$ except those superscripted.

The configurationally-averaged Green's function is then given by

$$\langle G_{in, jm}(z) \rangle = \langle \mathbf{r}_i, n, t^0 | (z \tilde{\mathbf{I}} - \tilde{\mathbf{H}})^{-1} | \mathbf{r}_j, m, t^0 \rangle$$

$$\text{with } | t^0 \rangle = \prod_i | v_0 \rangle. \tag{5}$$

Note that to this stage the relations are all exact. The density of states then follows directly

$$\langle n(E) \rangle = -\frac{1}{\pi} \sum_n \text{Im} \langle \mathbf{G}_{in, in}(E + i\delta) \rangle_{\delta \rightarrow 0^+} \tag{6}$$

Short-range chemical ordering may be described in an elementary way by a Markovian type pair between neighbouring sites \mathbf{r}_i and \mathbf{r}_j .

$$\begin{aligned}
 p(N_j; N_i = 1) &= (1 - a(1 - c)) \delta(N_j - 1) + a(1 - c) \delta(N_j), \\
 p(N_j; N_i = 0) &= ac \delta(N_j - 1) + (1 - ac) \delta(N_j). \tag{7}
 \end{aligned}$$

The single parameter a then is a measure of short-range ordering. If $a = 1$ there is no short-range order and the alloy is purely random. If $1 < a < (1 - c)^{-1}$, then AB type of clustering is favoured. The maximum value corresponds to a situation when the alloy is not really random at all, but forms a super-lattice of A and B constituents. If $a < 1$, then AA or BB type of clustering is favoured.

Having formally performed the configuration averaging exactly we shall now proceed to generate the approximations methodically, keeping in mind the important Herglotz property which must not be violated at any stage. We shall adopt a graphical formulation. It is well-known that the calculation of Green's function on connected graphs using the nested path technique always produces Herglotz results (Haydock *et al* 1972). This methodology has been described in great detail by Bishop and Mookerjee (1974) and Kumar *et al* (1982). We have the result

$$\langle \mathbf{G}_{in, im}(z) \rangle = \sum_{L=0}^{\infty} \sum_{P_L \in C_L} k_{nm}(P_L), \tag{8}$$

where $k(P_L)$ is the contribution of P_L , a self avoiding path beginning and ending at the site r_i and of length L and C_L is the contribution of all such paths on a given lattice.

The approximation now involves ignoring paths. The relation of these polygonal paths to the CPA has been discussed by Bishop and Mookerjee (1974) and Mookerjee (1975b) has demonstrated their relation to the multiple scattering diagrams. The philosophy of approximation is as follows:

We consider exactly all paths that involve only the spatial part of the augmented space *i.e.* \mathcal{H} . Such paths are connected to the lattice structure and must not be approximated or delinked without destroying some of the features of the underlying lattice. In three or two dimensions the recursion method helps us to deal with this infinite set of paths.

If we want a CCPA ($r_1, r_2 \dots r_n$) within the cluster then all polygonal paths that do not completely lie in the subspace \mathcal{H} and involve these vertices and none others must also be exactly accounted for. These are related to multiple scattering within the cluster.

Larger polygonal paths which involve sites within and without the cluster but which do not completely lie in the subspace \mathcal{H} must be delinked.

According to this prescription, after delinking procedure, each n -site cluster in the original lattice has in augmented space ($n \times 2^n$) polygon decorating it. The polygon corresponding to a two-site cluster is shown in figure 1a and that corresponding to a 3-site is shown in figure 1d. The vertices of the polygon correspond to different configurations of the n -site cluster. Because of the cluster delinking no polygon belonging to a cluster has any connection to one another, corresponding to another cluster through an augmented space link. This exactly implements the idea that within this approximation correlated scattering from sites belonging to different clusters is ignored. The final effect is that each cluster is renormalized. Figure 1b and 1c show the renormalisation of a cluster of 2-sites. The n -cluster renormalisation procedure has been discussed in detail in I. Here we shall briefly summarize the main points of formulation.

The aim is to calculate self-energy \mathcal{S} self-consistently. The self-energy, hence the CCPA is cluster diagonal—a property essential to preserve Herglotz property (Butler 1973). The effective Hamiltonian is invariant with respect to cluster translations. However the exact effective Hamiltonian is translationally invariant. In contrast in the CCPA's, the self-energy at the cluster centre and cluster boundary are indeed different. Unless it is possible to construct clusters in which all the sites are equivalent (as in the 2-CPA) this distinction is unavoidable and inherent in any cluster approximation (Tsukada 1972).

The self energy is calculated self-consistently in iterative procedure describe in I. The starting point may be the 1-CPA self-energy or for the cluster-CPA the 2-CPA results.

The first equation for the self-consistent CCPA calculation is

$$\sigma = \mathbf{H}^{(1)} + \mathbf{H}^{(\text{int})} \mathbf{G}^{(2)} \mathbf{H}^{(\text{int})}, \quad (9)$$

where σ describes the renormalization of the cluster (the bond AE in case of 2-CPA) by the rest of the medium. Here $\mathbf{H}^{(1)}$ is the Hamiltonian corresponding to cluster

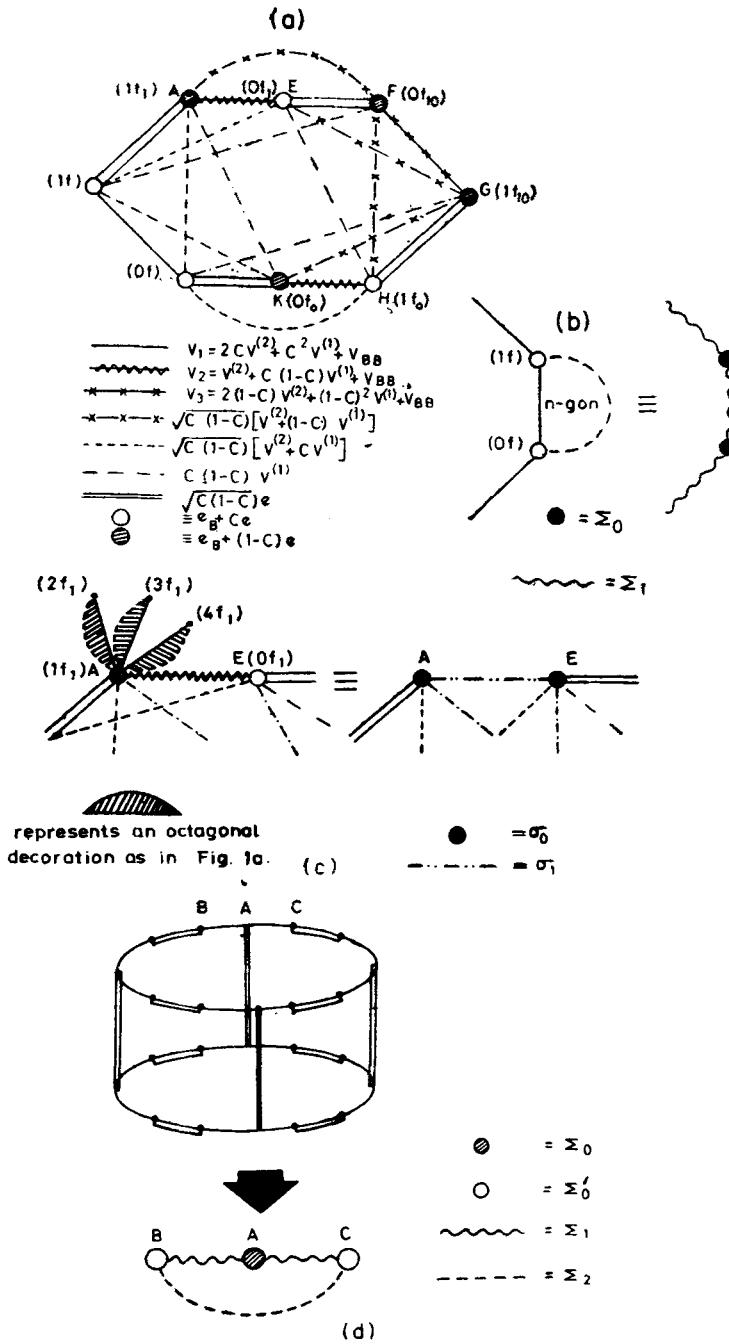


Figure 1. (a) The augmented space octagon decorating a bond. (b) Renormalization of the bonds by augmented space octagons. (c) Renormalization of the octagon by the medium. (d) The augmented space 24-gon for a 3-CPA calculation.

only and $\mathbf{H}^{(2)}$ is that of the original lattice minus the cluster (bond AE in case of 2-CPA) and in which all bonds and sites are renormalized by $\underline{\Sigma}$.

$\mathbf{H}^{(\text{int})}$ is the linking Hamiltonian which links the cluster to the rest of the medium.

Using the notation (as in I) \mathbf{X}^{-P}_y to denote the inverse of the operator \mathbf{X} in the subspace y we can write

$$\mathbf{G}^{(2)} = [z\mathbf{I} - \mathbf{H}^{(2)}]^{-P}_z. \quad (10)$$

The second equation is for $\underline{\Sigma}$, which describes the renormalization of the n -site cluster by the rest of the polygon. The equation is:

$$\underline{\Sigma} = \tilde{\mathbf{H}}^{\text{cl}} + \tilde{\mathbf{H}}^{\text{cl}, M} \mathbf{G}^M \tilde{\mathbf{H}}^{M, \text{cl}} \quad (11)$$

where $\tilde{\mathbf{H}}^{\text{cl}}$ is the Hamiltonian of the n -site cluster (a bond in case of 2-CPA) and $\tilde{\mathbf{H}}^M$ is the Hamiltonian of the rest of the polygon M . Here again $\tilde{\mathbf{H}}^{\text{cl}, M}$ is the linking Hamiltonian, which links the cluster to the rest of the polygon M . Also

$$\mathbf{G}^M = (z\tilde{\mathbf{I}} - \tilde{\mathbf{H}}^M)^{-P}_M.$$

The set of equations (9) and (11) involve a self-consistent iterative solution of $\underline{\Sigma}$. The various Green functions involved can be easily calculated using the recursion technique of Haydock *et al* (1972). If we are using energy-dependent effective Hamiltonians, the recursion has to be done separately for each value of energy.

The above method will be useful only if the procedure converges. The calculation has been carried out on a BCC lattice with off-diagonal disorder and the procedure converged rapidly.

3. Results and discussion

In this section we shall present results for the density of states for a single s -orbital per site model on a bcc lattice.

Figure 2 shows the 1-CPA, 2-CPA and CCPA density of states for a dilute 90-10 alloy with $W = 0.75$, the separation of well-depths of the constituents. In 1-CPA there is no separate impurity band but in 2-CPA and CCPA we observe a separate two peaked impurity band. Also there is an increase in the band-width from 1-CPA to 2-CPA and CCPA.

Figure 3(a) shows the 1-CPA and 2-CPA (without off-diagonal disorder) density of states for the dilute ($c = 0.1$) alloy but with larger separation in well-depths ($W = 1.0$). This is the "strong scattering" regime. Here even in 1-CPA we observe a separate impurity band. Figure 3b depicts the 2-CPA (with off-diagonal disorder) and CCPA density of states for the same alloy. Here again there is an increase in the band-width as compared to 1-CPA. The effect on majority band is very small and a single peak structure of the majority band is characteristic of the bcc lattice and not a feature of disorder. Both 2-CPA and CCPA show a two-peaked structure in the minority (impurity) band. In order to identify the structure in the impurity band,

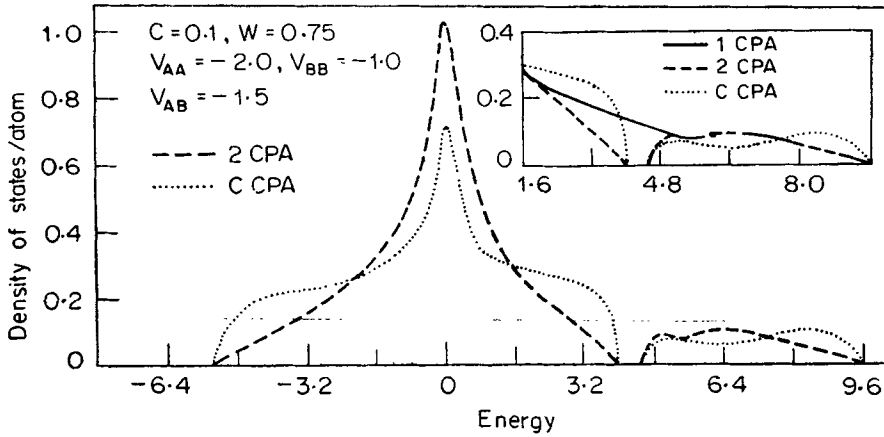
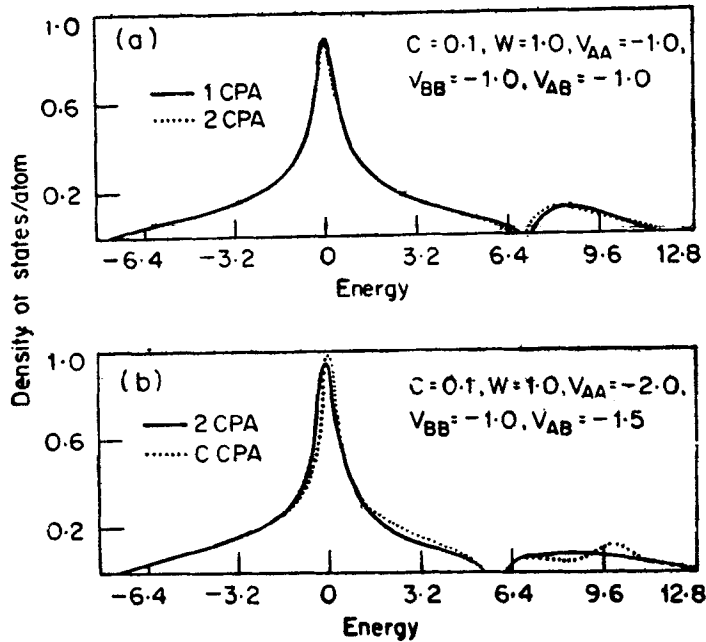


Figure 2. Density of states per site scaled by π (i.e. imaginary part of the diagonal Green's function) in 1-CPA, 2-CPA and CCPA. The separation $W = (|e_B - e_A| / |zV_{BB}|)$.



Figures 3a, b. (a) Density of states per site scaled by π full curve, 1-CPA; broken curve, 2-CPA (without off-diagonal disorder). (b) Density of states per site scaled by π full curve, 2-CPA; broken curve, CCPA.

the partial densities of states are shown in figures 3c and 3d. The peak around $E = 9.6$ is identified with an isolated impurity A in a B background (figure 3c) while the peak around $E = 8$ is identified with the cluster where AA interaction is dominant (figure 3d).

Figure 4 shows the effect of Markovian short-range order of the type described in the earlier section and characterised by a parameter α . $\alpha < 1$ enhances the probability of precipitation of A clusters in a B -background. This is clearly exhibited by the enhancement of the 1st peak in figure 3d. $\alpha > 1$ enhances AB type pairs which is exhibited by the enhancement of the second peak in figure 3c.

Figure 5 shows a concentrated 50-50 alloy with separation $W = 0.50$. Unlike the 1-CPA case of purely diagonal disorder here in 2-CPA and CCPA the density of states is not symmetric around the band centre. This is a feature of the Off-diagonal disorder and is due to the different band-widths of the host and impurity.

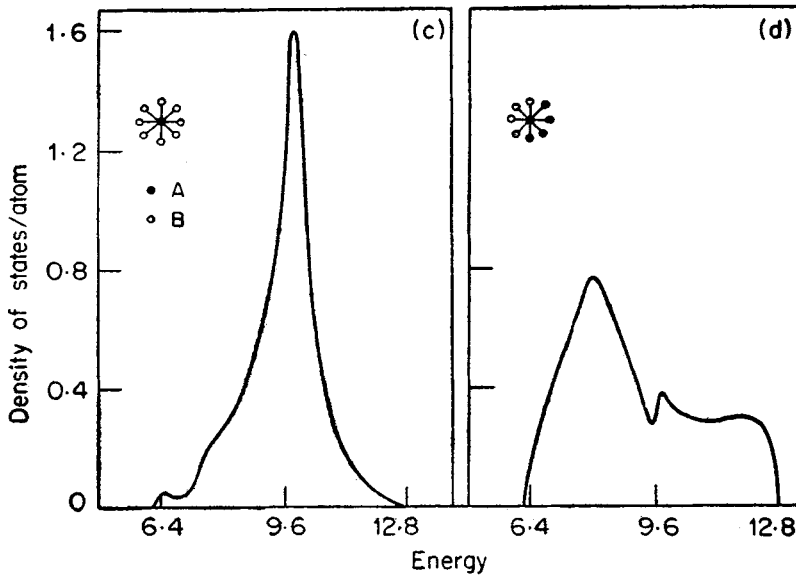


Figure 3c, d. Partial densities of states per site scaled by π for various configurations of the nearest neighbour cluster. Host atoms are indicated by open circles and impurity atoms by full circles. Here $c = 0.1$, $W = 1.0$, $V_{AA} = -2.0$, $V_{BB} = -1.0$, $V_{AB} = -1.5$.

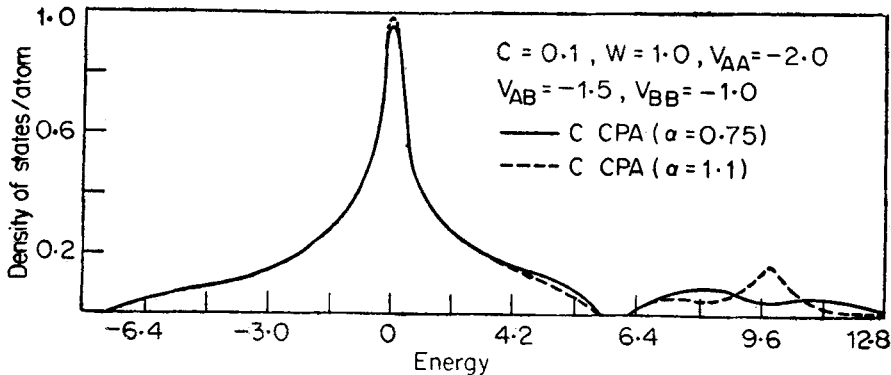


Figure 4. Densities of states per site scaled π with SRO, full curve, $\alpha = 0.75$; broken curve, $\alpha = 1.10$.

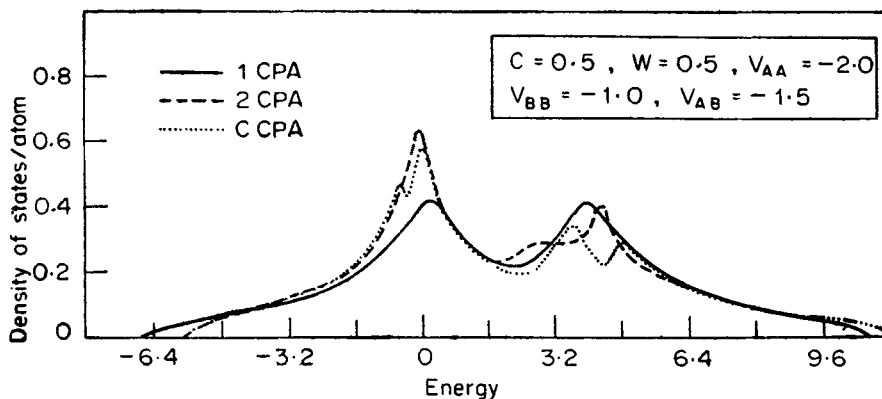


Figure 5. Densities of states per site scaled by π in 1-CPA, 2-CPA and CCPA.

These calculations establish that the augmented space formalism in conjunction to the real space recursion techniques is a practical and useful method of generating physically valid (Herglotz) self-consistent cluster generalisations for reasonably realistic models of alloys including off-diagonal disorder and short-range order. We have so far considered only one orbital per site. The generalisation to several orbitals per site is straightforward. This work provides us with a sufficient theoretical basis for application to the physically interesting cases of metallic alloys like beta-brass etc which have a BCC structure.

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References

- Butler W H 1973 *Phys. Rev.* **B8** 4499
- Bishop A R and Mookerjee A 1974 *J. Phys.* **C7** 2161
- Bullett D W 1975 *J. Phys.* **C8** 2695
- Haydock R, Heine V and Kelly M J 1972 *J. Phys.* **C5** 2845
- Kumar V, Mookerjee A and Srivastava V K 1980 ICTP, Trieste, Preprint IC/80/142
- Kumar V, Mookerjee A and Srivastava V K 1982 *J. Phys.* **C15**-1939
- Mookerjee A 1973 *J. Phys.* **C6** 1340
- Mookerjee A 1975a *J. Phys.* **C8** 1524
- Mookerjee A 1975b *J. Phys.* **C8** 29
- Tsukada M 1972 *J. Phys. Soc. Jpn.* **32** 1475