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THE COHERENT POTENTIAL APPROXIMATION FOR A CLUSTER OF NON-OVERLAPPING SCATTERERS

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Abstract. — We argue that a reasonable way of extending earlier cluster calculations of the density of states for pure d-band metals to their alloys is to do a C. P. A. calculation for a cluster of non-overlapping muffin tin wells. We demonstrate the feasibility and the power of the method by explicit calculations on Ni-Cu and Cu-Zn systems.

1. Introduction. — As was first pointed out by Jones and Keller [1], for a close packed transition metal one can obtain a fairly realistic description of the d-band by considering the density of states due to a small cluster of potential wells representative of the crystal potential. The calculation entails the evaluation of Lloyd's expression [2] for the integrated density of states $N(E)$ due to a set of non-overlapping spherically symmetric scattering centres. Namely,

$$N(E) = N^0(E) - \frac{1}{\pi} \operatorname{Im} \ln \left| \sum_{L',L} i_{L'}^{-1} \delta_{L,L'} - G^{+}_{LL}(R_i - R_j) \right|,$$

where $N^0(E)$ is the integrated density of states for free electrons, $i_{L}(\hat{e})$ is the $L(=l,m)$ angular momentum component of the $t$-matrix on the energy shell describing the scattering properties of an individual well surrounded by a constant potential and $G^{+}_{LL}(R_i - R_j)$ is the structure constant which, in terms of the Gaunt numbers [3] $C_{LL'}^{L''}$, the spherical Hankel function $h_{L'}^+ (\sqrt{\hat{e}} | R |)$ and the spherical harmonics $Y_L(\hat{e})$, may be written as

$$G^{+}_{LL'}(R_i - R_j) = -4 \pi \sum_{L''} C_{LL'}^{L''} i^{L''} h_{L''}^+ (\sqrt{\hat{e}} | R_i - R_j |) Y_L(\hat{e}).$$

Note that the determinant in eq. (1) has to be taken with respect to the site indices $i$ and $j$ as well as the angular momentum $L$ and $L'$. The $t$-matrix components $t_L(\hat{e})$ are related to the scattering phase shifts $\delta_L(\hat{e})$ by the relation

$$t_L(\hat{e}) = \frac{-\sin \delta_L(\hat{e})}{\sqrt{\hat{e}}} e^{i \delta_L(\hat{e})}.$$

Hence, for a 13 scatterer cluster with $\delta_L = 0$ for $l \geq 3$ the determinant in eq. (1) is that of a 117 by 117 matrix and as such can be evaluated numerically with relative ease.

On figure 1 we show the density of states $n(\hat{e}) = d/d\hat{e} N(\hat{e})$ for a 13 well cluster representing a Cu atom and its nearest neighbour shell on a Cu lattice (f. c. c. with $a = 6.830$ Å). The phaseshifts were calculated from the usual muffin tin potential constructed according to the Mattheiss prescription [4] for a full Cu crystal. For comparison we also show the density of states obtained from a band structure calculation [5] for an infinite Cu crystal with the same muffin tin potential on every site as in the cluster calculation. The similarity
between the two density of states is encouraging and suggests that the simpler cluster calculation gives a fairly realistic account of the d-band of Cu.

Though other calculations [6] also support this view, as far as the density of states is concerned the cluster method is not particularly useful for pure metals since band structure calculations are almost as readily available. However, the case of random alloys is entirely different. There, one has no calculation with accuracy anywhere near to that of band theory and hence such a roughly hewn tool as the cluster method becomes very attractive indeed. In this paper we shall discuss ways of using the cluster method to calculate averaged density of states for random substitutional alloys.

2. The C. P. A. for a cluster. — Lloyd’s formula is still valid if the sites are occupied by different wells. One only needs to replace $t_i(e)$ by $t_{i,L}(e)$. For a binary alloy one would have $t_{i,L}(e) = t_{A,L}(e)$ or $t_{B,L}(e)$ depending on whether the site $i$ is occupied by an A or B atom. Thus for an arbitrary configuration eq. (1) can be just as easily evaluated as for a pure metal. However, even for such small clusters as 13 atoms the number of configurations is very large and hence an exact calculation of the configurationally averaged density of states $\bar{n}(e)$ is much too difficult. Therefore, we would like to suggest that the much more practicable C. P. A. programme should be used.

What this programme means for an infinite lattice of randomly distributed muffin tin potentials has been discussed elsewhere by Gyorffy and Stocks [7]. It is a trivial matter to rewrite their expressions in real space, replacing all Brillouin zone integrals by sums over the direct lattice. In that form all the relevant relations are directly applicable to a finite cluster. For instance, the effective scattering amplitude $t_{C,L}(e)$ which, when placed on every site in the cluster, gives rise to the averaged density of states has to satisfy the equation

\[
t_{C,L}(e) = ct_{A,L}^{-1} + (1 - c) t_{B,L}^{-1} + \left( t_{C,L}^{-1} - t_{A,L}^{-1} \right) S_{100}^{00}(e) \left( t_{C,L}^{-1} - t_{B,L}^{-1} \right)
\]

where $S_{100}^{00}(e)$ is the inverse of the matrix

\[
t_{C,L}^{-1} \delta_{1L} \cdot \delta_{1L} - G_{LL}^{+}(R_i - R_j) = (3^{-1})_{i,j,L,L'}
\]

at the centre of the cluster ($i = 0, j = 0$). Once eq. (4) has been solved for $t_{C,L}$ the averaged integrated density of states $\bar{N}(e)$ has to be calculated from the formula

\[
\bar{N}(e) = N_0(e) - \frac{1}{\pi} \text{Im} \ln \left\| t_{C,L}^{-1} \delta_{1L} \cdot \delta_{1L} - G_{LL}^{+}(R_i - R_j) \right\|
\]

where

\[
\left< t_{L}^{-1} \right> = c t_{A,L}^{-1} + (1 - c) t_{B,L}^{-1}
\]

Thus our programme is to solve eq. (4) and find the configurationally averaged integrated density of states from eq. (5). Though non trivial this is an entirely tractable calculation.

While we hope to present such calculations in the not too distant future, in this paper, as a preliminary effort, we shall discuss only a simplified version of it. As we argued elsewhere [6] under certain circumstances it is a good approximation to take the solution to eq. (4) to be $t_{C,L} = c t_{A,L} + (1 - c) t_{B,L}$. We called this using a simple averaged $t$-matrix as the effective $t$-matrix in eq. (5) the local C. P. A. In order to illustrate the power of the method we have outlined so far, we shall, in the next section, calculate the density of states for a CuNi alloy and an α-brass using this local C. P. A.

3. Calculating the density of states for a cluster in the local C. P. A. — In contrast to Ni when Zn is placed on a Cu lattice it gives rise to a muffin tin potential with a d-resonance which is below the Cu resonance. The $f = 2$ phase shifts for Cu, Ni are shown in figure 2 and for Cu, Zn in figure 3. Note that

![FIG. 2. - The d-phase shifts for the CuZn muffin tin potential wells. The potentials were constructed from the appropriate atomic charge densities placed on a Cu lattice.](image1)

![FIG. 3. - The d-phase shifts for the Cu, Ni muffin tin potential wells.](image2)
$E^Zn_d - E^Cu_d > E^Ni_d - E^Cu_d$ and that the Zn resonance is considerably sharper ($\Gamma^Cu = 0.1 \text{ Ry} \equiv \Gamma^Ni, \Gamma^Zn = 0.02 \text{ Ry}$) than the Cu and Ni resonances. Indeed, when we calculated the band structure for these phaseshifts on the copper lattice we found a zinc d-band width $w^Zn = 0.1 \text{ Ry}$ and a considerably wider Cu d-band $w^Cu = 0.2 \text{ Ry}$. Under these circumstances the usual multi-band tight binding C. P. A. scheme [5, 8], which worked so well for Cu-Ni and AgPd is not applicable because $W^Cu = \delta$ is too large and also, on account of $\Gamma^Zn < \Gamma^Cu$, the randomness of the hopping integrals is important. It is an indication of the power of our method that we can treat this difficult case with relative ease. Given the fact that the atomic d-functions are highly localised on both Cu and Zn atoms this system is ideally suited for a treatment by the cluster method.

The Argand plot of the effective scattering amplitude $f^{C,L}_{\infty} = -\sqrt{c_{\infty}^2} = c_{\infty}^2 + (1 - c) f^{L}_s$ for the Cu$_{0.90}$Zn$_{0.10}$ and Cu$_{0.90}$Ni$_{0.10}$ alloys are shown in figure 4. The plot for Cu$_{0.90}$Zn$_{0.10}$ should be read as follows: at the high energy side, the big loop near the unitarity circle represents an almost elastic Cu resonance and therefore, at these energies, we expect a slightly damped Cu d-band; at the low energy side, the small loop indicates a severely damped Zn resonance which will give rise to a very distorted d-band. Thus the Zn side band should be much sharper than the pure Zn band on the Cu lattice. An other interesting difference between Cu$_{0.90}$Zn$_{0.10}$ and Cu$_{0.90}$Ni$_{0.10}$ is that the damped impurity resonance, the small loop in figure 3, falls near $\eta = 0$ in the case of the former. As a consequence at the bottom and at the top of the impurity band the corresponding portion of the Argand plot falls near the unitarity circle. Therefore, we expect little damping and, however narrow, we expect the Zn band peak in the density of states to have most of the structure characteristic of the pure metal density of states. Clearly, this behaviour is very different from that found in the case of Cu rich Cu-Ni alloys, as is evident from figure 4 where the small loop is to be interpreted as a heavily damped resonance with considerable background scattering. Thus the Ni resonance is damped at all energies and the corresponding peak in the density of states is expected to be a smooth Lorentzian.

We have evaluated the formula

$$\bar{N}(\epsilon) = N^0(\epsilon) - \frac{1}{\pi} \text{Im} \ln \| \gamma_{L,L'} \delta_{L,L'} \delta_{i,j} - G_{L,L'}^{L,L'}(R_i - R_j) \| + \frac{1}{\pi} \text{Im} \ln \| \gamma_{L,L'}^L \| - \frac{c}{\pi} \text{Im} \ln \| \gamma_{L,L'}^L \| - \frac{1}{\pi} (1 - c) \text{Im} \ln \| \gamma_{L,L'}^{L,L'} \|$$

(6)

which follows from eq. (5) if we take $t_{c,L} = c_{A,L} + (1 - c) t_{B,L}$, for Cu$_{0.90}$Ni$_{0.10}$ and Cu$_{0.90}$Zn$_{0.10}$. The s and p phaseshifts were set equal to zero for simplicity and $t^s_{Cu,2}, t^s_{Zn,2}, t^p_{Ni,2}$ were calculated from the phaseshifts shown in figures 2 and 3. In figure 5 we show each contribution to $\bar{N}(\epsilon) = d\bar{N}/d\epsilon$ for Cu$_{0.90}$Ni$_{0.10}$ as they arise from the various terms in eq. (6). It is interesting to note that the Lloyd determinant (full line) gives a density of states which is not only split but goes negative at certain energies. This is the consequence of the fact that our inelastic scattering centers, described by $f_{C,L}$, not only deflect particles but also act as particle sinks.
Of course, the real alloy potential wells are not sinks, the inelasticity arises because we are describing a random potential by a single configuration of effective scatterers, hence \( n(\varepsilon) \) must be positive. As is evident from figure 5 this is ensured by the correction terms (dashed line) which can be shown [7] to be the consequences of the fact that \( f_{C,2} \cong f_2 \) must satisfy the self consistency requirement represented by eq. (4).

In figure 6 we show the total, averaged density of states \( \bar{n}(\varepsilon) \) for Cu-99Ni-10. As expected the Cu d-band hardly changed from what it was in pure Cu and we obtained a smoothly varying extra peak due to the Ni impurities. This peak is about 1.0 eV above the high energy edge of the Cu d-band and is about 0.7 eV wide in reasonable agreement with the tight-binding C. P. A. calculation of Stocks et al. [8]. The averaged density of states \( \bar{n}(\varepsilon) \) for Cu-99Zn-10 in the same approximation is given in figure 7. The sharp Zn band at the low energy side is clearly evident and it has enough weight at this concentration that it should be observable in a careful photoemission experiment. More detailed calculations showing the concentration dependence and the expected structure of the Zn side band will be published elsewhere.

References