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Electron correlations in narrow band alloys: Hubbard subbands and cohesive energies

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Abstract. The effect of strong electron–electron interactions (described by the single-band Hubbard Hamiltonian) on the electronic spectrum and cohesive energies of substitutionally disordered alloys has been studied. We use the Hubbard III solution to treat the correlations and coherent-potential approximation for configurational averaging. The use of the Lorentzian form of the host metal density of states enables us to obtain analytical expressions for various quantities of interest. Questions related to the problem of the calculations of cohesive energies in disordered systems with correlations are discussed and partially resolved.

1. Introduction

The electron–electron interactions play a particularly profound role in narrow-band materials. Theoretical attempts at description of the so-called correlated electrons in such systems have a long history and are connected with the names of Mott (1949, 1961), Hubbard (1963, 1964), Anderson (1959) and many others (for a review see Cyrot (1977)). Most of the work has been devoted to the study of clean systems, even though some interesting applications are concerned with disordered alloys (Spatek and Honig 1991). The problem of electron correlations in disordered alloys has been discussed previously (Wysokiński 1981) mainly in connection with the temperature dependence of conductivity in disordered transition-metal alloys.

Recently a renewed interest in the theory of strongly correlated electrons is observed, which is due to the fact that the parent compounds of the high-temperature superconductors La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_6$ are probably Mott insulators that undergo an insulator-to-metal transition after doping.

Doped materials are quite disordered, and some of them as, for example, $\text{La}_{2-x}\text{CuO}_4$, $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ or $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ are alloys. It might therefore be interesting to study the combined effect of correlation and disorder on their properties.

In this work we shall be dealing only with the normal state properties of A_xB_{1-x} alloys without referring to particular materials. We also limit our discussion to the paramagnetic phase leaving the problems of magnetic ordering for future studies.

In section 2 we shall describe the model and general scheme of treating disorder and electron–electron correlations on the same footing, which is the coherent-potential approximation (CPA). For the purposes of illustration we shall assume a Lorentzian density of states, which enables us to solve the resulting CPA equations exactly. Section

3 is devoted to the calculation of cohesive energies and the interplay between disorder and electron correlations. Some discussion connected with the difficult problem of the enthalpy of formation and the role of electron correlation is also given. We conclude the work in section 4.

2. Model and its solutions

We assume the alloy to be described by the Hubbard Hamiltonian

$$H = \sum_{i\sigma} \varepsilon_i n_{i\sigma} + \sum'_{ij\sigma} t_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{i\sigma} U_i n_{i\sigma} n_{i-\sigma} \quad (2.1)$$

where for an $A_x B_{1-x}$ alloy the parameters ε_i , U_i take on the values ε_A , U_A (ε_B , U_B) depending on whether the site i is occupied by an A(B)-type atom. The hopping integrals t_{ij} are assumed to be independent of the alloying and different from zero for nearest-neighbour sites only,

$$t_{ij} = \frac{1}{N} \sum_k \varepsilon_k \exp[ik(\bar{R}_i - \bar{R}_j)] \quad (2.2)$$

where N is number of sites in the crystal and ε_k is the energy spectrum of the electrons.

The density of states (DOS) of the 'host' metal (i.e. that with $\varepsilon_i = 0$, $U_i = 0$) D_0^g will be expressed through ε_k as

$$D_0^g(\omega) = \frac{1}{N} \sum_k \delta(\omega - \varepsilon_k). \quad (2.3)$$

As already mentioned for the purpose of this work we shall use the Lorentzian shape for $D_0^g(\omega)$

$$D_0^g(\omega) = \frac{1}{\pi} \frac{D}{\omega^2 + D^2} \quad (2.4)$$

where $2D$ is the band width of the host metal. This is not a very realistic DOS as it is unbounded and none of its moments, except for the zeroth one, exist. It is, however, theoretically very attractive as all the calculations can be done analytically, as we shall see. The model assumes the same band width for both A and B.

We are interested here in the strong disorder $|\varepsilon_A - \varepsilon_B| \approx D$ and also the strong correlations U_A/D , $U_B/D \geq 1$. To treat site-diagonal disorder we shall use the CPA (Soven 1967). The correlations will be studied in Hubbard's alloy analogy approximation in the version of the Hubbard III solution (Hubbard 1964). These two methods have been shown previously (Velicky *et al* 1968, see also Acquarone *et al* 1982) to be equivalent in their mathematical structure. They also have been already used to study the effect of correlations on the electrical conductivity of alloys in the two-band model by Elk *et al* (1979) and in a single-band model with off-diagonal and thermal disorder by Wysokiński (1981).

In an alloy an electron with spin σ propagating through the system scatters with the atoms. If the encountered atom is of type i and no electron is present on it the scattering potential is ε_i ; if on the other hand the atom already has $-\sigma$ electrons present then the

corresponding potential is $\varepsilon_i + U_i$. The system in this approximation looks like a four-component alloy with scattering potentials

$$V_\nu = (\varepsilon_A; \varepsilon_B; \varepsilon_A + U_A; \varepsilon_B + U_B) \tag{2.5}$$

and the corresponding probabilities of their occurrence

$$P_\nu^\sigma \equiv \{c_i, N_i^\sigma\} = (x(1 - n_{A-\sigma}); (1 - x)(1 - n_{B-\sigma}); xn_{A-\sigma}; (1 - x)n_{B-\sigma}) \tag{2.6}$$

where $c_i = \{x, 1 - x\}$, $N_i = \{1 - n_{i-\sigma}, n_{i-\sigma}\}$ for $i = A, B$.

Let the averaged system be described by the as yet unknown optical potential $\Sigma^\sigma(\omega)$. The CPA method to find this is to require the vanishing of the averaged single-site scattering matrix T_i^σ defined for the system with the potential V_i present at site i , with all other sites being described by $\Sigma^\sigma(\omega)$

$$\langle T_\nu^\sigma \rangle = \sum_\nu P_\nu^\sigma T_\nu^\sigma = \left\langle \frac{V_\nu - \Sigma^\sigma(\omega)}{1 - [V_\nu - \Sigma^\sigma(\omega)]G^\sigma(\omega)} \right\rangle = 0 \tag{2.7}$$

where

$$G^\sigma(\omega) = \frac{1}{N} \sum_N \frac{1}{\omega - \varepsilon_k - \Sigma^\sigma(\omega)} = \frac{1}{N} \sum_k G_k^\sigma(\omega) \tag{2.8}$$

is the single-site (Koster-Slater) Green function defined for the averaged medium. The single-site Green function G_ν^σ (averaged over 'sites' different from ν) is given by

$$G_\nu^\sigma = G^\sigma(\omega) / \{1 - [V_\nu - \Sigma^\sigma(\omega)]G^\sigma(\omega)\} \tag{2.9}$$

and the CPA condition (2.7) can be shown to be equivalent to

$$G^\sigma(\omega) = \langle G_\nu^\sigma(\omega) \rangle = \sum_{\nu=1}^4 P_\nu^\sigma G_\nu^\sigma(\omega). \tag{2.10}$$

Let us note that the number of 'effective' ν sites is double the number of real i sites, cf (2.5) and (2.6).

To proceed we use the host metal density of states (2.4) and obtain

$$G^\sigma(\omega) = \int d\varepsilon \frac{D^\sigma(\varepsilon)}{\omega - \Sigma^\sigma(\omega) - \varepsilon} = \frac{1}{\omega - \Sigma^\sigma(\omega) + iD \operatorname{sgn} \operatorname{Im} \omega} \tag{2.11}$$

and

$$G_\nu^\sigma(\omega) = 1/(\omega - V_\nu + iD \operatorname{sgn} \operatorname{Im} \omega). \tag{2.12}$$

From the last two expressions and (2.10) we find

$$\Sigma^\sigma(\omega) = \omega + iD \operatorname{sgn} \operatorname{Im} \omega - \left(\sum_{\nu=1}^4 P_\nu^\sigma G_\nu^\sigma \right)^{-1}. \tag{2.13}$$

To complete the solution of the problem we have to calculate the parameters $n_{A-\sigma}$ and

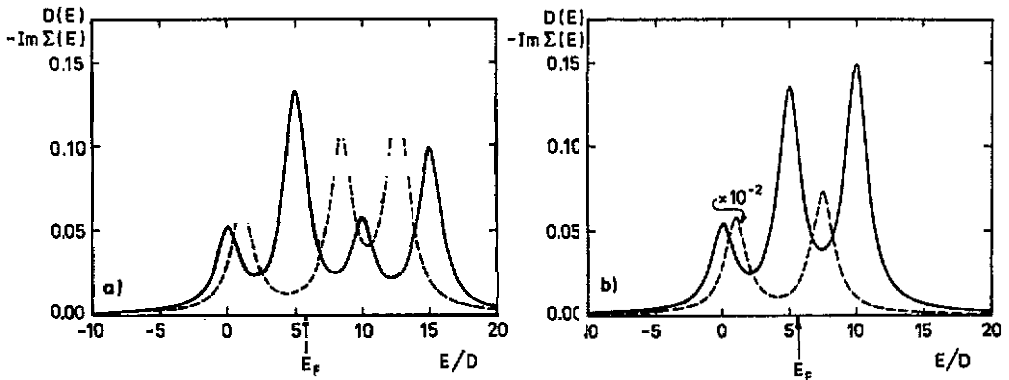


Figure 1. The alloy densities of states $D(E)$ (full curves) and the imaginary part of the self-energies $\text{Im } \Sigma(E)$ (broken curves) as functions of energy for $x = 0.3$, $\epsilon_A = 0$, $\epsilon_B = 5$, $U_A = 10$ with: (a), $U_B = 10$. (b) $U_B = 5$. E_F denotes the Fermi energy for $n = 0.9$. D denotes the half band width.

$n_{B-\sigma}$ entering the definition of the probabilities in (2.6). In the limit $T = 0$ K we are interested in, and in the paramagnetic phase $n_{A-\sigma} = n_{A\sigma} = n_A/2$, they are given by

$$n_i = \frac{2}{\pi} \int_{-\infty}^{E_F} d\omega \text{Im } \bar{G}_i(\omega + i0) \quad i = A, B. \tag{2.14}$$

The factor in (2) stems from the spin summation, and

$$\bar{G}_i(\omega) = (1 - n_i/2) / \{G^{-1}(\omega) - [\epsilon_i - \Sigma(\omega)]\} + (n_i/2) / \{G^{-1}(\omega) - [\epsilon_i - U_i - \Sigma(\omega)]\}. \tag{2.15}$$

The Fermi energy E_F is calculated from the total number of electrons, n , in the system, via

$$n = \frac{2}{\pi} \int_{-\infty}^{E_F} d\omega \text{Im } G(\omega + i0) \tag{2.16}$$

and obviously fulfils the requirement $n = xn_A + (1 - x)n_B$.

For the Lorentzian DOS we are using here the integrals in (2.14) and (2.16) can easily be performed analytically. We shall not give the results here. Equations (2.10), (2.14), (2.15) and (2.16), together with definitions (2.5) and (2.6), form a self-consistent set of equations. The density of states is given by

$$D(E) = -\frac{1}{\pi} \sum_{\sigma} \text{Im } G^{\sigma}(E + i0). \tag{2.17}$$

In figures 1(a, b) we show the densities of states calculated from (2.17) and the imaginary part of the self-energies (2.13). We have taken $x = 0.3$ and the following values of other parameters (in units of half the band width, $D = 1$): figure 1(a), $\epsilon_A = 0$, $\epsilon_B = 5$, $U_A = U_B = 10$; figure 1(b), ϵ_A , ϵ_B and U_A have the same values but $U_B = 5$. The last set of parameters is interesting as the resonance energies for double occupation $\epsilon_i + U_i$ are the same for the A and B atoms. Note that the inverse of $\text{Im } \Sigma(\omega)$ is proportional to the quasiparticle lifetime $\tau(\omega)$. It is seen that contrary to the clean case the Hubbard gap can be obtained for $n \neq 1$. This feature may be very important for the

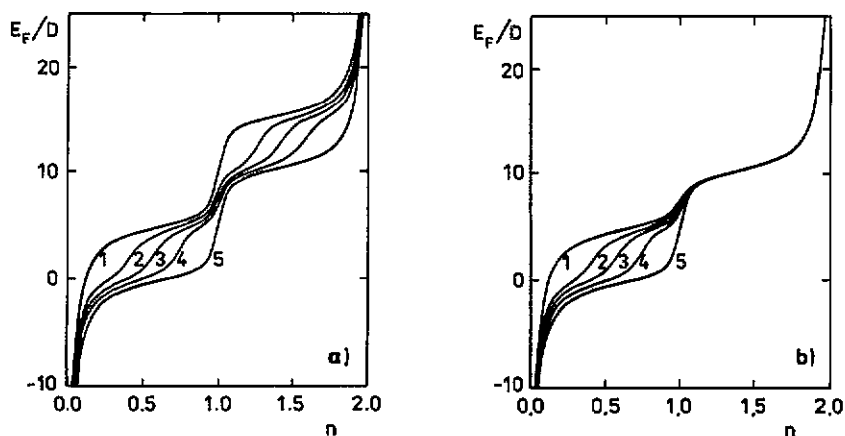


Figure 2. The Fermi energy E_F as a function of electron concentration for the same sets of parameters as in figures 1(a) and (b), respectively. The curves labelled 1 to 5 correspond to alloy concentrations of $x = 0.0, 0.3, 0.5, 0.7, 1.0$.

analysis of the energy spectrum in strongly correlated and disordered (with strong-disorder scattering) systems. The arrow shows the position of the Fermi energy calculated for the electron concentration $n = 0.9$.

Figure 2(a, b) shows the dependence of the position of the Fermi energy on the electron concentration for the same set of parameters as in figure 1(a, b), respectively, but for a number of values of x .

In our model there is no particle-hole symmetry, in general. For $U_A = U_B$, however, there is some generalized symmetry in respect of the simultaneous replacement $n \rightarrow 2 - n$ and $x \rightarrow 1 - x$. This also holds true for the behaviour of the cohesive energy as a function of electron concentration n to be studied in the next section.

3. Cohesive energy of an alloy

The calculation of the cohesive energies is one of the most difficult problems in the theory of solids. The number of questions connected with the problem has been explained by the French school with Friedel (1969), Cyrot and Cyrot-Lackmann (1976) and others (see, e.g., Sayers (1977), Kajzar and Mizia (1977)). Recently the cohesive energies of the 5d transition metals have been calculated from first principles (Fernando *et al* 1990).

For a (essentially free-electron) metal or alloy the cohesive energy is simply defined as the difference between the ground state energy of the solid and the energy of its constituent species. In the tight-binding scheme and for the one-band (d-band) model it can be written as

$$E_c = \int_{-\infty}^{E_F} (\omega - \varepsilon_d) D(\omega) d\omega \quad (3.1)$$

where ε_d is the position of the atomic d level and $D(\omega)$ is the total one-particle density of states function.

Equation (3.1) requires some modification if one is studying the effect of the electron-electron interaction on E_G . It has been found by Kjollerstrom *et al* (1966) that the correct expression for the ground state energy is

$$E_G^{\text{band}} = \frac{1}{\pi} \sum_{\sigma}^{\epsilon_F} d\omega \operatorname{Im}\{[\omega - \frac{1}{2}\Sigma^{\sigma}(\omega)] F_{\sigma}(\omega)\}. \quad (3.2)$$

Here $\Sigma^{\sigma}(\omega)$ is the proper Coulomb self-energy and $F_{\sigma}(\omega)$ is the on-site Green function.

The problem we are studying is more complicated as in the alloy the contributions to the self-energy from many-body interactions and impurity scattering are not in general additive and no simple generalizations to (3.1) or (3.2) are possible. To find the required expression we shall start with our Hamiltonian and find the ground state energy as its expectation value

$$E_G^b(\{i\}) = \langle H \rangle = \sum_{i\sigma} \epsilon_i \langle a_{i\sigma}^{\dagger} a_{i\sigma} \rangle + \sum_{ij\sigma} t_{ij} \langle a_{i\sigma}^{\dagger} a_{j\sigma} \rangle + \frac{1}{2} \sum_{i\sigma} U_i \langle n_{i-\sigma}^{\dagger} n_{i\sigma} \rangle \quad (3.3)$$

where the sign $\{i\}$ is used as an indication that the energy of the system is calculated for a given distribution of atoms in a solid, so it will be a subject of configurational averaging.

The correlators in (3.3) can be expressed in terms of the corresponding Green functions by means of the spectral representation. We find it convenient to work with thermodynamic two-time Green functions and at the end calculate the zero-temperature limit necessary in order to obtain the ground state energy. The two-particle correlation function can, as usual, be expressed in terms of the one-particle Green function

$$G_{ij}^{\sigma}(t) = \langle\langle a_{i\sigma}(t) | a_{j\sigma}^{\dagger}(0) \rangle\rangle.$$

From the equation of motion for $G_{ij}^{\sigma}(\omega)$ —the Fourier transform of $G_{ij}^{\sigma}(t)$ —one finds

$$\sum_{j'} [(\omega - \epsilon_i) \delta_{ij'} - t_{ij'}] G_{j'i}^{\sigma}(\omega) = \delta_{ij} + U_i \langle\langle a_{i\sigma} n_{i-\sigma} | a_{j\sigma}^{\dagger} \rangle\rangle_{\omega} \quad (3.4)$$

and from the spectral representation at $T = 0$ K (Zubarev 1960)

$$\langle n_{i\sigma} n_{i-\sigma} \rangle = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\omega \langle a_{i\sigma}^{\dagger} (a_{i\sigma} n_{i-\sigma}) \rangle_{\omega} = \frac{1}{\pi} \int_{-\infty}^{\epsilon_F} d\omega \operatorname{Im} \langle\langle a_{i\sigma} n_{i-\sigma} | a_{i\sigma}^{\dagger} \rangle\rangle_{\omega+i0} \quad (3.5)$$

and similarly

$$\langle a_{i\sigma}^{\dagger} a_{j\sigma} \rangle = \frac{1}{\pi} \int_{-\infty}^{\epsilon_F} d\omega \operatorname{Im} \langle\langle a_{j\sigma} | a_{i\sigma}^{\dagger} \rangle\rangle_{\omega+i0}. \quad (3.6)$$

Using (3.3) to (3.5) in (3.2) we find the ground state energy of a given configuration of atoms in an alloy as

$$E_G^{\text{band}}(\{i\}) = \sum_{ij\sigma} \left(-\frac{1}{2\pi} \right) \int_{-\infty}^{\epsilon_F} d\omega [(\omega + \epsilon_i) \delta_{ij} + t_{ij}] \operatorname{Im} G_{ji}^{\sigma}(\omega + i0). \quad (3.7)$$

For practical purposes and in the spirit of the CPA we average the equation (3.7) over various configurations and obtain the ground state energy per site

$$E_G = -\frac{1}{2\pi} \sum_{\sigma} \int_{-\infty}^{\epsilon_F} d\omega \left\{ \operatorname{Im} [\omega G_{\sigma}(\omega^+) + \overline{\epsilon_i G_i^{\sigma}(\omega^+)}] + \operatorname{Im} \left(\frac{1}{N} \sum_k \epsilon_k \bar{G}_k(\omega^+) \right) \right\}. \quad (3.8)$$

Using expression (3.8) for $\bar{G}_k(\omega)$ we obtain for the $A_x B_{1-x}$ alloy

$$E_G = -\frac{1}{\pi} \sum_{\sigma} \int_{-\infty}^{E_F} d\omega \operatorname{Im} \{ [\omega - \frac{1}{2}\Sigma^{\sigma}(\omega^+)] G_{\sigma}(\omega) + x\varepsilon_A \bar{G}_A^{\sigma}(\omega^+) + (1-x)\varepsilon_B \bar{G}_B^{\sigma}(\omega^+) \} \quad \omega^+ = \omega + i0 \tag{3.9}$$

where \bar{G}_i^{σ} is the Green function defined in (2.15).

Our expression (3.9) possesses the correct limiting behaviour for $x = 0, x = 1$ where it reduces to (3.2) and also for $U_A = U_B = 0$, where it reduces to (3.1) as it should.

To obtain the cohesive energy we have to subtract from (3.8) the energy of a collection of free atoms. They are described by the Hamiltonian

$$H = \sum_i (\varepsilon_i n_i + U_i n_{i\downarrow} n_{i\uparrow}) = \sum_i [\varepsilon_i n_i + U_i (n_i - n_{i\uparrow}) n_{i\uparrow}] \quad n_i = n_{i\uparrow} + n_{i\downarrow} \tag{3.10}$$

Calculation of the ground state energy in the atomic limit can be performed in the same way as has been done by Acquarone *et al* (1982). To this end let us note that the Fermi energy, which in general is not well defined for continuous values of n will stay at the level ε_A ($\varepsilon_A < \varepsilon_B$) until the level is fully occupied when the concentration of electrons n reaches the value $n = x$ and it then jumps to the next level at higher energy. For the parameters such that

$$\varepsilon_A < \varepsilon_B < \varepsilon_A + U_A < \varepsilon_B + U_B \tag{3.11}$$

the Fermi level jumps to ε_B and stays there until it is fully occupied with $1 - x$ electrons on it. At this moment all the sites in the system are singly occupied and for $n > 1$ the Fermi level jumps to $\varepsilon_A + U_A$ and then to $\varepsilon_B + U_B$. We thus obtain in the present case

$$E_G^{\text{at}} = n\varepsilon_A \quad n < x \tag{3.12a}$$

$$E_G^{\text{at}} = x\varepsilon_A + (n - x)\varepsilon_B \quad x < n < 1 \tag{3.12b}$$

$$E_G^{\text{at}} = x\varepsilon_A + (1 - x)\varepsilon_B + (\varepsilon_A + U_A)(n - 1) \quad 1 < n < 1 + x \tag{3.12c}$$

$$E_G^{\text{at}} = x\varepsilon_A + (1 - x)\varepsilon_B + x(\varepsilon_A + U_A) + (\varepsilon_B + U_B)(n - 1 - x) \quad 1 + x < n < 2 \tag{3.12d}$$

Similar expressions can be found in other non-trivial cases with a different ordering of the energy levels: $\varepsilon_A < \varepsilon_B < \varepsilon_B + U_B < \varepsilon_A + U_A$ and $\varepsilon_A < \varepsilon_A + U_A < \varepsilon_B < \varepsilon_B + U_B$.

The cohesive energy E_c is thus given by

$$E_c = E_G^{\text{band}} - E_G^{\text{at}} \tag{3.13}$$

Before we evaluate the cohesive energy of an alloy let us note that the expressions derived in this section can be used for a study of the enthalpy of formation of the alloy and the effect of electron interactions on it, with important extensions to the problems of phase stabilities.

The enthalpy of formation is usually defined (Cyrot and Cyrot-Lackmann 1976) as the difference between the cohesive energy (3.13) and the weighted energy of the pure metals forming the alloy

$$\Delta H = E_c - x \int_{-\infty}^{E_F^A} \omega D_A(\omega) d\omega - (1 - x) \int_{-\infty}^{E_F^B} \omega D_B(\omega) d\omega \tag{3.14}$$

Again this expression is valid for the free-electron alloy. (For a recent calculation of the mixing enthalpies of alloys see Wei *et al* (1990).)

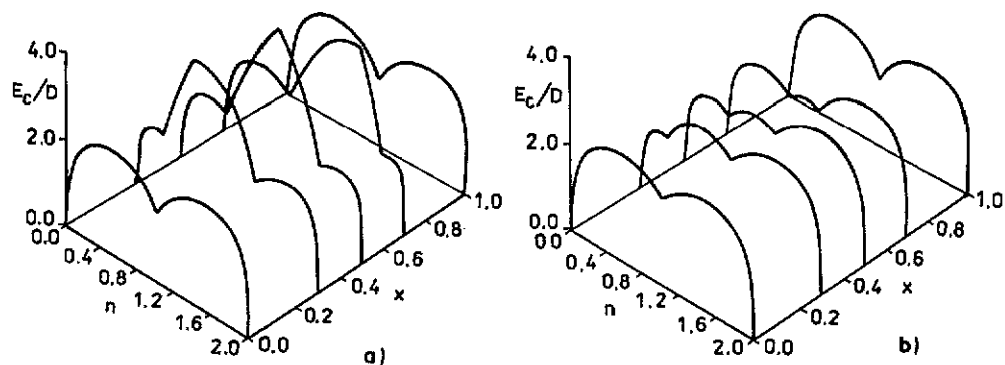


Figure 3. The cohesive energy E_c as a function of the electron concentration n for several alloy concentrations $x = 0.0, 0.3, 0.5, 0.7, 1.0$; the other parameters being the same as in figures 1(a) and (b), respectively.

In the correlated system ($U_A, U_B \neq 0$) the enthalpy of formation should be defined as the difference between E_c and the weighted sum of the cohesive energies of pure A and B metals, thus

$$\Delta H = E_c(\text{alloy}) - xE_c(A) - (1-x)E_c(B). \quad (3.15)$$

By expressing the total self-energy in our model as a sum

$$\Sigma = \Sigma_{\text{alloy}} + \Sigma_U + \Sigma_{\text{mix}} \quad (3.16)$$

where Σ_{alloy} is that part of Σ that is due to disorder, Σ_U is connected with the interactions U , and Σ_{mix} is the part due to the interplay between disorder and interactions; we see from (3.15) that to leading order ΔH does not depend on Σ_U .

This is one reason why we do not study in detail the enthalpy of formation of an alloy, another reason being the crudeness of our model, which does not take into account the different band widths of the constituent alloys—a feature that has previously been found (Cyrot and Cyrot-Lackmann 1976) to be of primary importance.

The cohesive energy of the strongly correlated alloy† is plotted in figures 3(a)–(b) as a function of electron density n and for different alloy concentrations x . Other parameters are the same as in the corresponding earlier figures. $E_c(n, x)$ is in general a complicated function of n , the shape of which depends strongly on the alloy parameters. We believe that the observed asymmetries in the cohesive energy and heat of formation can, to a large extent, be explained by the effects of alloying. In the limit of pure metals $x = 0$ or $x = 1$ our data reduce to those obtained by Acquarone *et al* (1982).

In figure 4 we have shown the enthalpy of formation as a function of the electron concentration n . The detailed shape of the function depends on the alloy parameters. The curve in this figure marked with open symbols strongly resembles the experimental data on Ni alloys as reproduced in Cyrot and Cyrot-Lackmann (1976).

The model we have studied possesses four parameters. These are the concentration x , the scattering potential $\delta = (\varepsilon_B - \varepsilon_A)/D$, and the correlations U_A/D and U_B/D . These can, in fact, be calculated from first principles nowadays.

† Note, that we have defined it to be positive for condensed system.

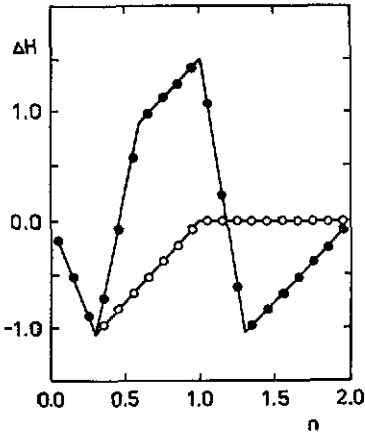


Figure 4. The alloy formation enthalpy ΔH as a function of electron concentration n . The open symbols are obtained for the alloy described by the parameters of figure 1(a) and full circles correspond to parameters of figure 1(b).

The analytical expressions for all the relevant quantities make it easy to study their behaviour as a function of the alloy parameters and the application to diverse systems.

4. Conclusions

We have studied the static properties of strongly correlated alloys by means of Hubbard-III and coherent-potential approximations. The use of the Lorentzian host metal density of states enabled us to find an analytical expression for the averaged density of states, the self-energy and the cohesive energy. This work can thus be viewed as an extension of the work of Acquarone *et al* (1982).

We have derived a formula for the cohesive energy of the alloy system. Our expression for E_c reduces to those used previously. It automatically takes care of the many-body and single-particle aspects of the problem. The expression (3.8) is thus very general and does not depend on the approximation used to treat disorder and electron interactions in the Hubbard model.

We believe that some of the discrepancies between theory and experiment discussed by Acquarone *et al* (1982) can be explained in our model. Our model does violate particle-hole symmetry, and the absence of this symmetry can be traced back to the alloying for $U_A = U_B$ and to the dependence of U on the type of atom occupying a given site. The experimental data on the cohesive energy of 4d and 5d alloys (see figures 12 and 13 in Fernando *et al* (1990)) do not in fact show particle-hole symmetry and this may be because of alloying or of different values of the U -parameters along the series.

Acknowledgment

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