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Dependence of configurational interactions on concentration in $\text{Ni}_{1-c}\text{Cu}_c$ alloys

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Abstract. Pair and triple configurational interactions in $\text{Ni}_{1-c}\text{Cu}_c$ alloys are calculated by the LMTO-ASA-CPA method. Strong dependence of these interactions on concentration connected with the crossing of the d-band edge by the Fermi level is revealed. General microscopic expressions for these interactions are discussed for the case when the electron–electron interaction terms are taken into account in the framework of the density functional method.

1. Introduction

To calculate phase diagrams of alloys and investigate the influence of short-range order effects in the environment of its constituents, phenomenological pairwise interactions V_{ij} are usually introduced. Recently a number of approaches permitting one to obtain values of these interactions from electronic structure calculations [1–3] were suggested. The analysis of microscopic expressions for these interactions revealed [1, 4, 5] that, in general, the magnitude of these interactions oscillates when the number of d-electrons in the alloy varies along the period of the Mendeleev table. Thus one can assume that when the number of d-electrons is changed by 1–2 electrons the interactions should vary from zero to their maximum value. But the analysis of experimental data on neutron scattering in $\text{Ni}_{1-c}\text{Cu}_c$ alloys for various concentrations c shows [6] that values of interactions vary by 2–3 times even at the much smaller interval $\Delta Z_d \sim c \sim 0.1$. It seemed to us desirable to carry out microscopic calculations that should bring about the understanding of such strong variations.

Various approaches to the calculation of pair- and n -particle configurational interactions were described and compared in [1]. We used the ‘cluster embedded in the CPA effective medium’ approach, extensively discussed in [1, 2]. All necessary expressions are summarized below, firstly to make certain our procedure, and secondly to discuss the influence of terms arising due to electron–electron interactions which were omitted in [1, 2] to estimate their contribution to configurational interactions. We also discuss the various possible approaches to the choice of the effective medium. The condition necessary for the embedding of the cluster in the reference medium in the case of the self-consistent density functional (DF) calculations in alloys is formulated. Calculations were carried out by the LMTO-ASA-CPA method. To verify the technique used we present results of $g(\varepsilon)$ calculations of these alloys for various c , which turn out to be in good agreement with the results of the full KKR-CPA calculations [7].

Calculated V_{ij} values are in good quantitative agreement with the experimental ones and reproduce qualitative effects correctly, i.e. strong variation of V_{ij} in the region $c \sim 0.6$, which turns out to be connected with the crossing of the d-band edge by the Fermi level.

2. Configurational interactions via density functional calculations

Main expressions of the method used are presented below. As it was pointed out in [8], the introduction of effective interactions between atoms for the binary substitutional alloy is, in essence, the exclusion of electron degrees of freedom in the total energy calculations for the system with the arbitrary distribution of a, b type atoms over the lattice sites:

$$V_0 + \sum_i V_i \hat{p}_i + \sum_{i < j} V_{ij} \hat{p}_i \hat{p}_j + \sum_{i < j < k} V_{ijk} \hat{p}_i \hat{p}_j \hat{p}_k + \dots \\ = -T \ln \text{Tr}_e \exp \left[-(\hat{H}_T + \hat{V}_{ei} + \hat{V}_{ee})/T \right] \quad (1)$$

where $\hat{p}_i = 1$ for a atoms and 0 for b atoms, \hat{H}_T is the electron kinetic energy operator, \hat{V}_{ei} and \hat{V}_{ee} are correspondingly electron-ion and electron-electron interactions. Tr_e denotes the summation over electronic subsystem phase space with the definite occupation of lattice sites i_1, \dots, i_n by a, b atoms. The right hand side of (1) is the full thermodynamic potential Ω of the electron subsystem in the external potential \hat{V}_{ei} , corresponding to this definite distribution of a, b atoms.

One of the main assumptions of the method used involves in neglecting the T dependence of the V_{ij} constants which are calculated at $T = 0$. In most cases the T corrections only arise due to variation in the electron distribution function and are really negligible ($\sim T/\epsilon_F$). In principle in some alloys the short-range order (SRO) can vary significantly with T , which in turn should influence the V_{ij} values. But even in this case the V_{ij} interactions can be self-consistently improved as one can determine them for the disordered alloy, calculate the SRO with them [6] and again recalculate constants taking into account correlations inside clusters [9]. Below we shall assume that in $\text{Ni}_{1-c}\text{Cu}_c$ alloys the SRO influence on V_{ij} is small.

In the density functional (DF) formalism one can divide Ω into double counting terms Ω_{ee} and terms Ω_e , corresponding to a one-electron movement in the full random potential $V = V_{ei} + V_{ee}$. Let us firstly discuss the one-electron potential Ω_e which at $T = 0$ is:

$$\Omega_e = -\frac{1}{\pi} \int_C \text{Tr} \ln(-G) dzdr \quad (2)$$

where the integration contour passes round the real axis and crosses it at the μ point. One of the possible ways of obtaining the unique partition of Ω_e in $V_{ij}, \dots, V_{i_1, \dots, i_n}$ terms consists in the cumulant expansion of the right hand side of the equation (1), subsequently taking into account groups of 1, 2, \dots, n atoms with the configurational averaging over all the other sites of the lattice. There are two obvious ways of writing down such an expansion. One is the standard diagram technique [10] of the expansion

in $\Delta V = V_a - V_b$ (figure 1(a)) with the resummation of these series [1]. The other is the cluster cumulant expansion for Ω with clusters occupying n sites i_1, \dots, i_n :

$$\Omega_c = \Omega_0 + \sum_i \Omega_i + \sum_{i < j} (\Omega_{ij} - \Omega_i - \Omega_j) + \sum_{i < j < k} (\Omega_{ijk} - \Omega_{ij} - \Omega_{ik} - \Omega_{jk} + \Omega_i + \Omega_j + \Omega_k) + \dots \tag{3}$$

where at $T = 0$

$$\Omega_0 = \frac{1}{\pi} \int_C \text{Tr} \ln(-\tilde{G}) dz \quad \Omega_{i_1, \dots, i_n} = -\frac{1}{\pi} \int_C \text{Tr} \ln \left(1 - \sum_{k=i_1, \dots, i_n} V_k \tilde{G} \right) dz \tag{4}$$

With $\tilde{G} = G_0$ (the Green function of the host lattice) we obtain virial expansion of Ω over c [11] and subsequent terms of this expansion are the values of the n -particle configurational interactions between atoms [1], which are independent of c in this case. This series probably has a slow convergence and the averaged Green functions should be included to improve it. The simplest correction involves the substitution of the CPA Green functions \tilde{G} in equation (4) which can be called the ‘cluster embedded in the CPA effective medium’ approach [1]. But as it is seen for example from the averaging of diagrams in figure 1(a), the terms corresponding to the diagram in figure 1(b) arise, which contain not only corrections to the the Green function self-energy, but also vertex corrections. One of the simplest vertices is shown in figure 1(c). It means that one-site effective medium approximation is inconsistent with the cumulant expansion and n -particle averaged Green functions should be included in the description of the reference medium if we intend to create the expansion which self-consistently reproduces partial energies of all the small clusters in the averaged medium. Nevertheless at the one-electron level such inner self-consistency of the approach is not in general necessary and various effective medium choices appear to result in slightly differing rates with which the obtained series converge.

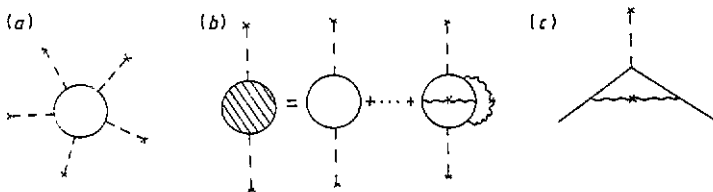


Figure 1. (a): Ω_c in the external field, (b): Ω_{eij} in the averaged medium with the external potentials in sites i and j , (c): vertex correction. The wavy line is the interaction arising after averaging.

We want to emphasize that the necessity of the reference medium and the embedded cluster consistency becomes much more urgent when the electron–electron interaction is taken into account. To discuss it, let us firstly write down the contribution from the electron–electron interaction to the configurational interactions in the framework of the DF method. With the fixed electron density $\rho(\mathbf{r})$ and a definite form for the electron–electron potential $V_{ee}[\rho]$ (in the local approximation for the exchange and correlation terms (LDA) $V_{ee}[\rho] = \int \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}' + \mu_{xc}(\rho(\mathbf{r}))$) Ω_{ee} can be found from the equation $\delta\Omega_{ee}/\delta\rho(\mathbf{r})|_{V_{ee}} = 0$:

$$\Omega = \Omega_e + \Omega_{ee} \quad \Omega_{ee} = \Phi_{ee}[\rho] - \int V_{ee}[\rho] \rho d\mathbf{r} \quad \delta\Phi_{ee}[\rho]/\delta\rho = V_{ee}[\rho] \tag{5}$$

and Ω_e is calculated from (2). In the LDA

$$\Phi_{ee}[\rho] = \frac{1}{2} \int \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'| d\mathbf{r}d\mathbf{r}' + \int \varepsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r}.$$

Making a cluster-cumulant expansion of Ω_{ee} with the arbitrary ρ_{i_1, \dots, i_n} -electron density, corresponding to the i_1, \dots, i_n site cluster, we get from (5) the contribution of this cluster to the thermodynamic potential. The proper value of ρ_{i_1, \dots, i_n} should be found in the process of the self-consistent calculations. For example, in the one-site CPA approximation we shall have after averaging the expression for the total energy derived in [12]. For the pairwise interaction we get

$$V_{ij} = \Omega_{ij}^{aa} + \Omega_{ij}^{bb} - 2\Omega_{ij}^{ab}$$

$$\Omega_{eeij}^{cd} = \frac{1}{2} \left[\frac{Z_i^c Z_j^d}{|\mathbf{R}_i - \mathbf{R}_j|} - \int \frac{\rho^{cd}(\mathbf{r} - \mathbf{R}_i)\rho^{cd}(\mathbf{r}' - \mathbf{R}_j)}{|\mathbf{r} - \mathbf{R}_i - \mathbf{r}' + \mathbf{R}_j|} d\mathbf{r} d\mathbf{r}' \right]$$

$$+ \int (\varepsilon_{xc} - \mu_{xc})\rho^{cd}(\mathbf{r} - \mathbf{R}_i) d\mathbf{r} + \int (\varepsilon_{xc} - \mu_{xc})\rho^{cd}(\mathbf{r} - \mathbf{R}_j) d\mathbf{r} \quad (6)$$

where ρ^{cd} is the electron density in the cluster when atoms of c and d types are in sites \mathbf{R}_i and \mathbf{R}_j . It is worth noting that though exchange-correlation terms are local in LDA, they nevertheless contribute to V_{ij} , as electron density $\rho_{ij}^{aa}(\mathbf{r})$ differs from that $\rho_{ij}^{ab}(\mathbf{r})$.

Of course $\rho_{ij}^{cd}(\mathbf{r})$ is not confined in the cluster cells i, j and the prime charge variation $\Delta Z_{\mathbf{R}}^{cd}$, on the background of the mean charge \bar{Z} in the \mathbf{R} cell, not coinciding with i or j cells, can be found in LMTO-ASA by multipole expansion:

$$\Delta Z_{\mathbf{R}}^{cd} = -\frac{2}{\pi} \text{Im Tr} \int \tilde{G}_{\mathbf{R}\mathbf{R}_i} T_{\mathbf{R}_i\mathbf{R}_j}^{cd} \tilde{G}_{\mathbf{R}_j\mathbf{R}} d\varepsilon \quad (7)$$

where T_{ij}^{cd} is the two-site scattering matrix, with the V^c and V^d potentials in \mathbf{R}_i and \mathbf{R}_j respectively.

The outer charge $\Delta Z_{\mathbf{R}}$ should vanish after averaging. Otherwise cluster of larger size should be involved in calculations of n -particle interactions, as happens in the problem of the single-site impurity [13]. We believe that this 'zero-charge' condition is very important for the self-consistency of calculations. From (7) it follows that for the pairwise interaction the condition is reduced to

$$\langle T_{ij} \rangle = 0. \quad (8)$$

Thus we see that the condition $\langle T_i \rangle = 0$, arising in the CPA approach, is insufficient for our purposes. The self-consistent calculations of the n -site interaction must in general include the effective medium which is in agreement with the n -particle cluster, though from the practical point of view equations (3), (4) and (5) can be a valuable approximation. For example, it is seen from equations (3), (4) and (6), that the Ω_{ee} contribution can be estimated in a non-self-consistent manner as

$$\Omega_{ee} = \frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} \frac{\delta Z_{\mathbf{R}}^c \delta Z_{\mathbf{R}'}^d}{|\mathbf{R} - \mathbf{R}'|} \quad (9)$$

$\delta Z_{\mathbf{R}}^d = -(Z^a - Z_0^a)\delta_{\mathbf{R}\mathbf{R}_i} + \Delta Z_{\mathbf{R}}^{cd}$, where Z_0 is the charge inside the 'impurity' cell and $\Delta Z_{\mathbf{R}}^{cd}$ is from (7) with $T_i^a \delta_{ij}$ instead of T_{ij}^{ab} . This $\delta Z_{\mathbf{R}}$ is small in a number of alloys and more refined self-consistent approaches would not significantly change the estimations obtained.

3. Results and discussion

In the case of $Ni_{1-c}Cu_c$ alloys the calculated charge transfer is approximately ~ 0.01 and from (9) we see that the Ω_{ee} contribution in V_{ij} is ~ 20 K even for the nearest neighbours. Besides, the density of states $g(\epsilon)$ in these alloys is practically independent of variation of Ni and Cu potentials under alloying, as follows from the full self-consistent KKR-CPA calculations [7]. For this reason we assumed these potentials in the alloy to be the same as in the pure metals Cu and Ni. Calculations were performed by the LMTO-ASA-CPA method in the two-centre approximation [14]. In this approximation all the expressions can be rewritten in the form simulating calculations with the tight-binding Hamiltonian [13] whose parameters can be taken from the first-principle calculations of Cu and Ni. Averaged values for LMTO parameters γ_l and Δ_l [13] corresponding to effective hopping parameters were taken [15]. Diagonal parameters C_l were the initial ones for the CPA calculations. Figure 2(a) represents the $g(\epsilon)$ on the ϵ curve for $c = 0.77$ when it appears to be deformed to a large degree in comparison with the pure metals' dependence. Results of the full KKR-CPA calculations [7] are also shown there. We believe that the close coincidence of the two curves indicates that at least for $Ni_{1-c}Cu_c$ alloys our technique is reliable.

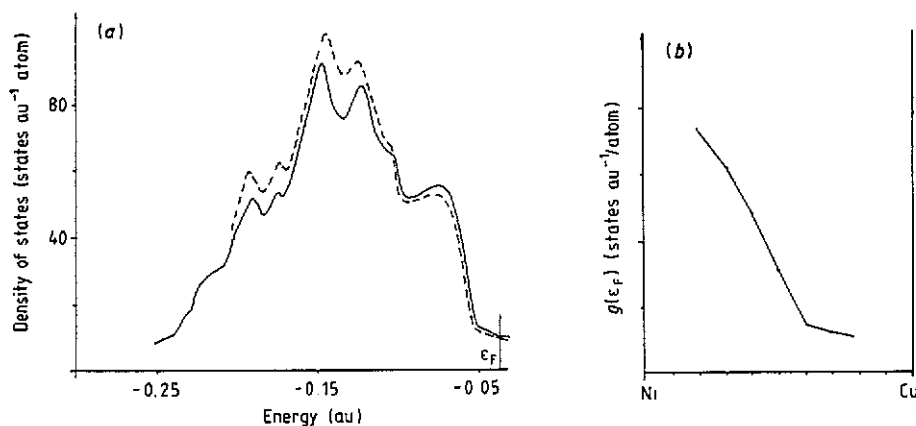


Figure 2. (a) Density of states for $c = 0.77$: full curve—present calculations, broken curve—from [7]. (b) Density of states at the Fermi level for $Ni_{1-c}Cu_c$ alloys.

Green functions \tilde{G} were calculated for every effective potential $\tilde{V}(z)$ with z on the integration contour in the complex plane by the tetrahedron integration method with the quadratic approximations of all functions between 102 points in the irreducible zone. Equation $\langle T_i \rangle = 0$ for $\tilde{V}(z)$ was solved by iteration.

The integration contour in (4) started at the lowest eigenvalue spectra point and passed parallel to the ϵ -axis at the distance of approximately 0.03 a.u. up to the Fermi energy value ϵ_F . The Fermi level was previously determined as the solution of the equation [16]:

$$N = \text{Im} \frac{2}{\pi} \left[\sum_{\mathbf{k}} \ln[\hat{H}_{\mathbf{k}} + \tilde{V}(\epsilon_F) - \epsilon_F] + \text{Sp} \langle \ln(1 - (V_i - \tilde{V})\tilde{G}) \rangle \right].$$

The integral over the Brillouin zone for $\ln(\epsilon_{\mathbf{k}} + \tilde{V}(\epsilon_F) - \epsilon_F)$ was calculated along with the $\tilde{G}(\mathbf{R} = 0)$ calculations.

Table 1. Calculated V^{theor} and experimental V^{exp} data in K. V^{exp} are extracted from experiments, carried out at 873 K. Uncertainty in V^{exp} is about 100 K.

c	V_1^{theor}	V_2^{theor}	V_3^{theor}	c	V_1^{exp}	V_2^{exp}	V_3^{exp}
0.19	-109	41	11	0.20	-292	262	-74
0.30	-189	102	-19	0.30	-270	209	-2
0.40	-253	277	-21	0.44	-277	151	-4
0.50	-580	318	12	0.52	-255	178	-97
0.60	-612	512	-81	0.60	-400	621	-139
0.70	-90	310	79	0.70	-371	531	-101

The concentration dependence of the nearest spheres pairwise interactions V_1, V_2, V_3 is shown in figure 3. V_{ij} values for several c are listed in table 1. The three-site interaction $V_3(0, \mathbf{R}_1, \mathbf{R}_2)$ value for $\mathbf{R}_1 = (0, 1, 1)$, $\mathbf{R}_2 = (1, 1, 0)$ was also calculated for $c = 0.19$ and was found to be small: $V_3 = -29$ K. Figure 2(b) represents the density of states at the Fermi-level $g(\epsilon_F)$ dependence on c in $\text{Ni}_{1-c}\text{Cu}_c$ alloys which closely correlates with the V_{ij} curves shown in figure 3. At $c \sim 0.6$ the Fermi level crosses the edge of the d-band, and the variation of the interactions is connected with the sharp density of states decrease in this region. The function $V_{ij}(\mu) = V_{aa}(\mu) + V_{bb}(\mu) - 2 * V_{ab}(\mu)$ can be roughly represented as the sum of integrals of cluster densities of states over ϵ . When ϵ_F gains the d-band edge the states near ϵ_F are mainly the Cu s-like states and the arising difference between partial densities on Cu and Ni immediately influence the V_{ij} values. Numerical analysis confirms this estimation. Points corresponding to V_{ij} values extracted from experimental data on neutron scattering in this alloy [6] are also shown in figure 3. We believe that experimental and theoretical dependences of V_{ij} on c are in good agreement not only qualitatively, but also quantitatively, in spite of uncertainties in both cases. Except for inaccuracies, mentioned above, microscopic calculations should include the contribution due to elastic forces, though our crude estimations show that these are about an order of magnitude less than electronic forces in this alloy. As for the experimental data used in [6], they are not complete enough to make their Fourier transformation totally reliable.

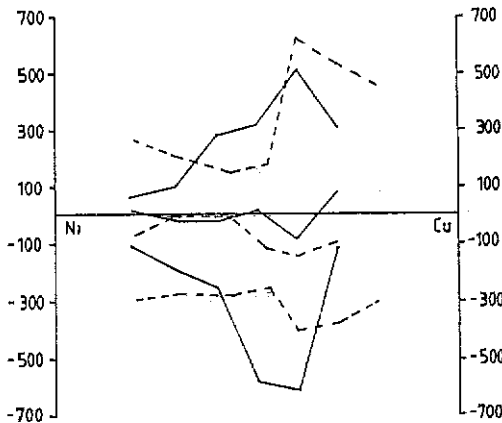


Figure 3. Calculated (full curve) and experimental (broken curve) V_{ij} values. Both lines are drawn to guide the eye.

Nevertheless, calculations confirm that the variations of the interactions under small $\Delta c \sim 0.1$ variations in the region $C \sim 0.5-0.6$ can be considerable and this effect may significantly influence the general structure of the phase diagram. This mechanism of considerable V_{ij} variations with c can be widely spread, especially in alloys, where the V_{ij} dependence on Z changes its sign. We intend to carry out an additional investigation of questions concerning the influence of the effective medium and cluster consistency on V_{ij} interactions.

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