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Coherent Potential Approximation of Short-Range Order in Cluster Models of Alloys

By

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In cluster approximation of coherent potential method the density of electron states of transitional element alloys with short-range order is obtained. On the base of these calculations the configurational part of the total energy is determined and the equilibrium value calculated of the short-range order parameter on the first co-ordination sphere. The obtained parameter of orderliness in most of the considered systems agrees by sign with the experimental data and qualitatively they depend on the concentration on the right way.

In der Clusternäherung der Methode des kohärenten Potentials wird die Elektronenzustandsdichte von Übergangsmetallegierungen mit Nahordnung berechnet. Auf der Grundlage dieser Rechnungen wird der Konfigurationsanteil der Gesamtenergie bestimmt und der Gleichgewichtswert des Nahordnungsparameters auf der ersten Koordinationssphäre berechnet. Der erhaltene Ordnungsparameter in den meisten der betrachteten Systeme stimmt im Vorzeichen mit den experimentellen Werten überein und hängt qualitativ in richtiger Weise von der Konzentration ab.

1. Introduction

In certain transition metals the character of atomic order can be described to a great extent by means of cluster effects. It could be demonstrated with the help of the diffuse scattering method [1] that in CuPt alloys the reduction of the platinum concentration will lead to a transition from short-range order of the type CuPt (Ll_1) to that of Cu_3Pt (Ll_1).

In the study of the phenomenon of order in these systems the cluster model of binary alloys was used which had been applied with success to non-ordered magnetic alloys [2, 3]. The main feature of this model is the dependence of the electron state of all atoms in the alloy upon the electron structure of Z_1 nearest neighbours. The detailed description of the method, which is essentially a variation of the molecular field approximation, can be found in our earlier communications [4, 5].

In the present work only the finally obtained equations are given which are compared to the results of calculations using the density of electron states.

2. Calculations

Let us consider the model of a one-band transition metal binary alloy whose state density is approximated by the density of the d-states. The composition of the alloy should be A_cB_{1-c} where c is the concentration of the component A. The system should be characterized by a Hamiltonian describing intense interaction and neglecting the

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states degenerated in d

$$H = \sum_n |n\rangle E_n \langle n| + \sum_n \sum_{m \neq n} |n\rangle h_{mn} \langle m| , \tag{1}$$

where E_n is the d-level energy of the atom n whose value can be either E_A or E_B, depending upon the occupation of the lattice site n by atom A or B, respectively. h_{mn} is the element m, n of the transition matrix which differs from zero only for the nearest neighbours and can thus have the values h_{AA}, h_{AB}, or h_{BB}, depending upon the occupation of the lattice sites by atoms A and A, A and B, or B and B. For the approximation of h_{AB} the following expression is accepted:

$$h_{AB} = (h_{AA} h_{BB})^{1/2} , \tag{2}$$

and it is further supposed that E_n depends upon the nearest neighbours as follows:

$$E_n = E_{n0} + U(n_n - n_{n0}) , \tag{3}$$

where E_{n0} is the d-level energy of the pure metal atom, n_n and n_{n0} are the numbers of electrons of the atoms in the alloy or metal, and U is the energy integral characteristic of the effective electron–electron interaction within the atom.

Table 1

Characteristic parameters of pure transition elements [2, 3]

i	$\varepsilon_i^0 - \varepsilon_{Pt}$ (eV)	$2w_i$ (eV)	n_{i0} (electron/atoms)
Ni	2	4.0	9.45
Cu	1	3.5	9.95
Pt	0	7.0	9.55

Let us now suppose that the different bandwidths of pure metals (Table 1)

$$w_A = Z_1 h_{AA} , \qquad w_B = Z_1 h_{BB} \tag{4}$$

cause the structure dependence of the off-diagonal elements of the Hamiltonian of the alloy.

A cluster consisting of a central atom n and of Z_1 nearest neighbours can be characterized by the type of the central atom and the number of neighbouring atoms of types A and B. The effective medium is determined by the one-electron approximation of the alloy. This medium can be calculated by means of the coherent electron scattering on the cluster within the medium. Determination of the effective medium leads to that of the coherent potential, Σ, or, in other words, to that of the off-diagonal disorder of the resolvent operator

$$h = (z - \Sigma)^{-1} . \tag{5}$$

The diagonal matrix elements G_n^* of the configurational cluster of the Green function in site representation depend both upon the type of the atom n in central position and upon the number of the neighbouring atoms A and B, that is upon n_A and n_B. Accordingly, G_{nn} depends upon the matrix elements of the Green function of the medium Λ_{nn}^k and this dependence is perturbed only by the first coordination sphere

$$G_{nn}^k = \frac{\gamma_n^2}{z - E_n} \left\{ 1 + \frac{\Lambda_{nn}^k \gamma_n^2}{[1 - (\gamma_n^2(z - E_n)^{-1} - h) \Lambda_{nn}^k] (z - E_n)} \right\} , \tag{6}$$

where

$$\Lambda_{nn}^k = U_0 + U^2(R) \langle T \rangle ;$$

$$\langle T \rangle = Z_1 \langle \tau \rangle (1 - Z_1 \langle \tau \rangle \Gamma)^{-1}, \qquad z = E + i0 , \tag{7}$$

and the average value of $\langle \tau \rangle$ is

$$\langle \tau \rangle = \frac{1}{Z_1} \left(\frac{n_A t_A}{1 + \Gamma t_A} + \frac{n_B t_B}{1 + \Gamma t_B} \right) \tag{8}$$

and

$$t_n = [\gamma_n^2 (z - E_n)^{-1} - h] \, [1 + (\gamma_n^2 (z - E_n)^{-1} - h) \, U_0]^{-1} . \tag{9}$$

In these expressions γ_n^2 is proportional to the bandwidth

$$h_{nm} = \gamma_n h \gamma_m , \tag{10}$$

where h is the structure-independent transition integral of the pure metal, while U_0, $U(R)$, and Γ can be expressed by the matrix elements of the Green function

$$G = \left(z - \sum_n |n\rangle \underline{\sum} \langle n| - \sum_n \sum_{m \neq n} |n\rangle h \langle m| \right)^{-1} ,$$

$$G_{nn} = \int \varrho_0(E) \, (h^{-1} - E)^{-1} \, dE ,$$

where $\varrho_0(E)$ is the density of state of the cubic metal crystal with a bandwidth $w = Z_1 h$ and

$$U_0 = h^{-2} G_{nn} - h^{-1} , \quad U(R) = h^{-1} U_0 , \quad \Gamma = [U(R) \, h^{-1} Z_1 - G_{nn} h^{-2}] \, (z_1 - 1)^{-1} .$$

If the density of electron states of a face-centred cubic (f.c.c.) lattice is $\varrho_0(E)$ which can be obtained from the calculation of the band structure [6], then this can be the analytical model of the density of states

$$\varrho_0(E) = \frac{2}{\pi} \sum_{i=1, 2} F_i^{-1} \sqrt{D_i - (E - \overline{E_i})^2} , \tag{11}$$

where the constants F_i, D_i, E_i determining $\varrho_0(E)$ correspond to the density of states shown in Fig. 1 of [9].

The effective resolvent can be determined by the introduction of the following conditions:

$$G_{nn}(h) = \sum_{n=A, B} \sum_k P(k) \, G_{nn}^k C , \tag{12}$$

where $P(k)$ is the probability that a given cluster configuration is realized and depends upon the short-range order parameter of nearest-neighbour interaction as follows:

$$P(k) = \begin{cases} c[c + (1 - c) \alpha_1]^{n_A} [(1 - c)(1 - \alpha_1)]^{z_1 - n_A}; & \text{atom A is in the centre ,} \\ [(1 - c)(1 - c + c\alpha_1)]^{z_1 - n_A} [c(1 - \alpha_1)]^{n_A}; & \text{atom B is in the centre .} \end{cases} \tag{13}$$

C is the number of identical n_1-configurations, which is equal to

$$C = Z_1! \, [n_A!(Z_1 - n_A)!]^{-1} . \tag{14}$$

Equation (12) can be solved by iteration

$$h^{-1} = b^{-1} + \left[\sum_{n=A, B} \sum_k P(k) \, G_{nn}^k(b) \, C \right]^{-1} - G_{nn}^{-1}(b) , \tag{15}$$

where b is the value of h used in the calculations of the preceding step.

By means of the calculated effective resolvent h it is possible to determine the electron density of the alloy

$$\varrho(E) = -\frac{5}{\pi} \cdot \sum_{n=\text{A, B}} \gamma_n^{-2} \sum_k P(k) \, G_{nn}^k C \,. \tag{16}$$

In the first approximation of the effective resolvent the limit energy of the spectrum was calculated from the results obtained for virtual crystals. Next, h was calculated for all the energies for which the pertaining densities of states were not zero. For the determination of the configurational part of the energy $\varrho(E)$ was calculated as above

$$E_{\text{k}} = N \left\{ 2 \int\limits^{E_{\text{F}}} E \varrho(E) \, dE - U[cn_{\text{A}}^2 + (1 - c) \, n_{\text{B}}^2] + E_{\text{e}} \right\}, \tag{17}$$

where E_{F} is the Fermi energy of the metal determined by

$$2 \int\limits^{E_{\text{F}}} \varrho(E) \, dE = cn_{\text{A0}} + (1 - c) \, n_{\text{B}} \,, \tag{18}$$

N the number of atoms of the crystal, and E_{e} the configurational part of the electrostatic energy,

$$n_{\text{A}} = 2 \int\limits^{E_{\text{F}}} \varrho_{\text{A}}(E) \, dE \,, \qquad n_{\text{B}} = 2 \int\limits^{E_{\text{F}}} \varrho_{\text{B}}(E) \, dE \,, \tag{19}$$

and $\varrho_{\text{A}}(E)$ and $\varrho_{\text{B}}(E)$ are components of the density of states of the alloy

$$\left. \begin{aligned} \varrho_{\text{A}}(E) &= -\frac{5}{\pi} \operatorname{Im} [G_{nn}^{-1} + (z - E_{\text{A}}) \, \gamma_{\text{A}}^{-2} - h^{-1}]^{-1} \,, \\ \varrho_{\text{B}}(E) &= -\frac{5}{\pi} \operatorname{Im} [G_{nn}^{-1} + (z - E_{\text{B}}) \, \gamma_{\text{B}}^{-2} - h^{-1}]^{-1} \,. \end{aligned} \right\} \tag{20}$$

According to [7] the part of E_{e} in E_{k}, taking into consideration the nearest neighbours only, is

$$E_{\text{e}} = \frac{2}{\pi} \alpha_1 (1 - c) \, c (\Delta Z^*)^2 Z_1 \int q^2 \, \frac{\sin (qR)}{qR} \, e^{\frac{-q^2}{4\eta}} \, dq \,, \tag{21}$$

where

$$\Delta Z^* = Z_{\text{A}}^* - Z_{\text{B}}^*; \tag{22}$$

Z_{A} and Z_{B} are the effective valencies [8], R the radius of the first coordination sphere which can be defined by Vegard's rule, and η the Ewald parameter.

3. Discussion

Within the framework of the statistical theory of short-range order the calculated values of $\varrho(E)$ and E_{k} made the determination of α_1 possible by means of the equation

$$\alpha_1 = (1 - \alpha_1)^2 \, c(1 - c) \exp \left\{ -\frac{\partial E_{\text{k}}}{\partial \alpha_1} [N k_{\text{B}} T c (1 - c) \, z_1]^{-1} - 1 \right\}, \tag{23}$$

where k_{B} is the Boltzmann constant and T the temperature.

With the help of the pseudopotential approximation, originally developed for solid solutions, it is possible to calculate the type of atomic order and to determine the value of α_1 for a number of alloys. E_{k} is assumed to be a linear function of α_1 and the solution of (2) is traced back to finding the roots of an equation of second order. In the present paper E_{k} is not a linear function of α_1, thus the determination of α_1 from (2) requires a numerical method where it has to be added that $\partial E_{\text{k}}/\partial \alpha_1$ has a substantial influence on the convergence of iteration.

The numerical values obtained with the EVM BESM-6 computer are shown in Table 2 together with the values of α_1 obtained by the diffuse scattering method [1].

In the majority of the investigated systems, among which there are some short-range ordered alloys and plane-ordered ones, the signs of $\alpha_{1\,calc}$ and $\alpha_{1\,exp}$ agree, though the calculated absolute values of short-range order parameters are considerably higher than the experimentally obtained data.

Table 2

Comparison of the calculated and experimentally determined values of α_1

alloy	CuPt	CuPt	CuNi	NiPt	NiPt
concentration (at%)	29	50	50	11	31
$\alpha_{1\,calc}$	−0.18	−0.05	0.36	−0.12	−0.20
$\alpha_{1\,exp}$	−0.1	0.00	0.12	−0.13	−0.133
T (°C)	500	890	1021	1050	1050

This discrepancy is quite understandable: the first approximation used for the approximate calculation of α_1 is due to the rather coarse model, but at the same time it is characteristic that it was possible to calculate the appropriate signs of α_1 and to obtain a qualitatively correct relationship for the concentration dependence of short-range order. The results obtained for CuPt alloys are of theoretical importance. At relatively low Pt concentrations (up to 30 at% Pt) the alloy is ordered according to the type Cu_3Pt ($L1_2$), at equivalent (50–50 at%) concentration an order of the type CuPt ($L1_1$) develops. This transition distinguishes the alloy of equivalent composition from the other ordered alloys. Consequently, in the neighbourhood of Cu_3Pt the short-range order parameter has a high absolute value and is negative, and almost zero in the alloy of equivalent composition.

Thus, the α_1-values calculated in the present paper reflect the concentration changes, which means that our cluster model is in fairly good agreement with the experiments.

The essence of the model is, therefore, based on the assumption that the electron structure of the nearest-neighbour atoms in the alloy determines the fundamental properties of the density of states of a solid solution. It was taken into consideration that in the pseudopotential theory (which, when all is said and done, is a perturbation calculation of second order) the concentration dependence deviates only slightly from the parabolic rule. The results achieved in this work are based on the fact that it was tried to approach the realistic electron structure of the alloy.

At the same time, the $\varrho_0(E)$ used by us with a sharp maximum below the Fermi energy is a rather rough approximation of the density of states of transition metals having a face-centred cubic structure.

In the studies of α_1 of a wider range of alloys it seems therefore advisable to use an appropriate initial density of states from which a better agreement of the calculated and experimentally obtained data might be expected.

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