Coherent Potential Approximation
of the Relationship between Short-Range Order and the
Position of the Fermi Level on the State Density Curves

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The density of electron states of binary alloys of transitional elements with short-range order is found using the coherent potential approximation. On the base of these calculated values the contribution of the bond structure energy to the configurational part of the total energy is determined and the equilibrium value of the short-range order parameter on the first coordination sphere is evaluated. The order parameters obtained for most the considered systems agree in sign with the experimental data.


1. Introduction

Application of the coherent potential approximation to the cluster model of binary alloys of transition metals made it possible to calculate the magnetic susceptibility of alloys and the energy of formation of non-ordered solid solutions. In this case a certain agreement was found between the calculated and experimental results [1 to 3].

It has, however, been proved by numerous measurements that, as a rule, a non-chaotic distribution of the mixtures of the various types of atoms exists in the state of equilibrium. The short-range order model of alloys seems to be more realistic; this model involves the calculation of the energy parameters of alloys by means of the quantum theory of solids.

Of the quantum theoretical methods that of pseudopotentials proved to be the most useful one which enabled the prediction of the sign of the short-range order parameters for a relatively wide range of alloys.

Nevertheless, so far no definite rule was found with the help of which it would be possible to predict the cases when the experimental results will agree with the calculated ones. Further theories will be used therefore to promote the study of the effects of short-range order.

The aim of the present work is the calculation of the short-range order parameters in alloys of transition metals by means of the method of coherent potential approximation and the comparison of the calculated results with the available experimental data.

1) Muszum krt. 6-8, Budapest VIII, Hungary.
2. Calculations

The density of the d-electron states, \( g(E) \), with short-range order will be calculated for the binary alloy \( A_xB_{1-x} \) (where \( c \) is the concentration of the component A), with the help of parameters characteristic of pure metals [1, 3]. The correlation between the atoms is taken into consideration only up to the nearest neighbours, the configurational part of the total energy, \( E_v \), of the solid solution is determined on this presumption

\[
E_v = 2N \int E g(E) dE - U(\eta n_A^x + (1 - c) n_B^x) + E_F,
\]

where \( N \) is the number of atoms in the lattice, \( E_F \) the Fermi level of the alloy, \( U \) the effective integral of the electron-electron interaction within the atom (which is considered twice in the first term [2]); \( n_A \) and \( n_B \) are the numbers of electrons of the components A and B, respectively,

\[
n_A = 2 \int g_A(E) dE, \quad n_B = 2 \int g_B(E) dE,
\]

where \( g_A(E) \) and \( g_B(E) \) are the components of the density of state of the alloy and are related to the total density

\[
g(E) = c g_A(E) + (1 - c) g_B(E),
\]

and \( E_F \) is the configurational part of the electrostatic energy. The Fermi level of the alloy is determined from the condition

\[
2 \int g(E) dE = c n_A^0 + (1 - c) n_B^0,
\]

where \( n_A^0 \) and \( n_B^0 \) are the numbers of electrons of atoms in the pure metals A and B, respectively. The increment of the electrostatic term in \( E_v \) has been analysed fairly thoroughly [4], thus in the present work the expression given in [4] for \( E \) will be used, as limited to the first coordination sphere

\[
E_v = \frac{n}{\pi} C_1(\Delta Z^*)^2 \alpha_1 m(1 - c) \int \frac{\sin(qR)}{qR} \exp \left( \frac{-q^2}{4\eta} \right) dq,
\]

where \( q \) is the wave vector; \( R \) the radius of the first coordination sphere, \( \Delta Z^* = Z_A^* - Z_B^* \) where \( Z_A^* \) and \( Z_B^* \) are the effective valencies of the pure metals [5], \( C_1 \) is the first coordination number (the number of nearest-neighbour atoms), and \( \eta \) the Ewald parameter.

If \( E_v \) is known, the main task of this paper can be solved, namely the equilibrium value of \( \alpha_1 \) can be determined for various systems of the transition elements from the equation

\[
\alpha_1 = (1 - \alpha_1^2) \eta m(1 - c) \left[ \exp \left( -\frac{1}{N} \frac{\partial E_v}{\partial \alpha_1} \right) C_1k_B Tc(1 - c) - 1 \right],
\]

where \( k_B \) is the Boltzmann constant and \( T \) the temperature. To have a closed system of (1) to (4) the density of electron states of the alloy has to be calculated.

There are a number of generalizations of the coherent potential approximation [11] which take into account all possible repeated scatterings starting from the pair of atoms [7, 8]. The methods evolved in these works can be utilized in the study of alloys with short-range order, taking into account the correlations between the pairs of atoms in the nearest neighbourhood.

Considering the Hamiltonian of a binary alloy in the Wannier representation, let us suppose that the alloy is concentrated and therefore the degeneration of the d-states
can be neglected, so

\[ H = \sum_n |n⟩⟨n| + \sum_{n,m=A,B} h_{nm} |n⟩⟨m|, \]

where \( \epsilon_n \) is the atomic d-level in the pure component. \( \epsilon_n \) can have one of two possible values, \( \epsilon_A \) or \( \epsilon_B \) depending upon the occupation of the site \( n \) by an atom of type A or B.

The off-diagonal elements of the Hamiltonian will differ from zero only for the nearest neighbors. The values of these off-diagonal elements are \( h_{AA}, h_{AB}, \) and \( h_{BB} \) transition integrals when the neighboring sites \( n \) and \( m \) are occupied by atom pairs of the type A and A, A and B, and B and B. A structure dependence of the transition integrals has to be supposed, as the half-widths of the bands of the pure components \( (\omega_A = C_1 h_{AA} \) and \( \omega_B = C_2 h_{BB} \) have substantially different values for some of the elements under investigation, as can be seen in Table 2.

It has been shown [1] that in the calculation of the energy of formation by means of the geometric mean approximation when \( h_{AB} = (h_{AA} \cdot h_{BB})^{1/2} \) the off-diagonal error is significant. We have used in our model the arithmetic mean approximation, \( h_{AB} = (h_{AA} + h_{BB})/2 \), with the help of which the Hamiltonian can be written as follows:

\[ H = H^0 + \sum_n |n⟩⟨n| \delta_n \epsilon_n + \sum_{n,m=A,B} h_{nm} |n⟩⟨m| + |m⟩⟨n|, \]

where \( H^0 \) is the Hamiltonian of the crystal of type B, \( \delta_n = \epsilon_n - \epsilon_B \); \( h_{nm} \) depends only upon the type of atom occupying site \( n \) and can have one of the two following values \( h_A = h_{AB} + h_{BB} \) and \( h_A = 0 \). The effective average is characterized by the following equation:

\[ \bar{H} = \sum_n |n⟩⟨n| + \sum_{n,m=A,B} |n⟩h_{nm} |m⟩ + \sum_{n,m,A,B} h_{mn} \Sigma_2 |n⟩⟨m| + |m⟩⟨n|, \]

where \( \Sigma \) and \( \Sigma_2 \) are the coherent potentials to be determined.

For the modelling of the density of states of the "pure" metal B a simple analytical model was chosen which, as a result of earlier calculations [12], approaches the form

\[ g_B^0(E) = \sum_{i=1,2,3} 2\omega_n^2 M_i^{-1} \sqrt{\frac{\omega_n - (E_i - E)^2}{N_i}}, \]

where \( M_i, N_i, \) and \( E_i \) are parameters by means of which we gain again the shape of the density of states of the f.c.c. structure as shown in Fig. 1.

The "tail" of \( g_B^0(E) \) at the top of the band is related to the distortion of the density of d-states due to s-d hybridization. However, this phenomenon which in the approximation used by us was only partly considered, has no great importance in the
calculation of the short-range order parameters as will be shown later in the discussion of the results.

Let us next suppose that the five d-orbits of the transition element B are independent of one another, and that the corresponding densities of states are identical and equal to \( \bar{\varrho}_B(E) \).

With respect to the two neighboring atoms on sites \( n \) and \( m \) in the effective average, for this pair correlation cluster the operator of scattering \( \bar{\varrho}_{nm}(z) \) can be written as the sum of the two terms, \( \bar{\varrho}_{nm}(z) = \bar{\varrho}_{nm}(\omega) + \bar{\varrho}_{nm}(\omega') \), where \( \bar{\varrho}_{nm}(\omega) \) and \( \bar{\varrho}_{nm}(\omega') \) describe the primary scattering on sites \( n \) and \( m \), respectively, as well as all the possible multiple scatterings on the \( n \)-\( m \) pair of atoms. The first term, \( \bar{\varrho}_{nm}(\omega) \), is related to the one-site scattering operators \( t_n \) and \( t_m \) as follows:

\[
\bar{\varrho}_{nm}(\omega) = t_n + t_n \bar{G}(1 - t_m \bar{G}(\omega))^{-1} t_m (1 + \bar{G}(\omega)),
\]

where

\[
\langle n | t_n | m \rangle = \frac{\langle n - \Sigma \rangle}{2} (\bar{G}_{nn} - 2(\omega - h_{nm} \Sigma_2) \bar{G}_{nm})^{-1},
\]

\[
\langle m | t_m | m \rangle = \frac{\langle m - \Sigma \rangle}{2} (\bar{G}_{mm} - 2(\omega - h_{nm} \Sigma_2) \bar{G}_{nm})^{-1}.
\]

In (7) the indices of the nearest neighbors are \( n \) and \( m \), \( \bar{G}_{nm} \) and \( \bar{G}_{mn} \) are the off-diagonal and diagonal matrix elements of the Green function of the medium, \( \bar{G}_{nm} = (z - \omega)^{-1} \), given in site representation. The correlation between \( \bar{G}_{nm} \) and \( \bar{G}_{mn} \) is

\[
\bar{G}_{nm} = \frac{(z - \omega)^{-1} ((1 + 2 \Sigma_2) h_{nm} G_{nm})^{-1}.}
\]

The coherent potentials \( \Sigma \) and \( \Sigma_2 \) are determined from the following system of equations:

\[
\langle n | \bar{\varrho}_{nm}^{(n)} | m \rangle = 0, \quad \langle m | \bar{\varrho}_{nm}^{(m)} | m \rangle = 0,
\]

where \( \bar{\varrho}_{nm}^{(n)} \) is the configurational average

\[
\langle \bar{\varrho}_{nm}^{(n)} \rangle = P_{AA} \bar{\varrho}_{AA}^{(n)} + P_{AB} \bar{\varrho}_{AB}^{(n)} + P_{BB} \bar{\varrho}_{BB}^{(n)}.
\]

where \( P_{AA} = c(1 - c) \bar{\varrho}_A \), \( P_{AB} = (1 - c) (1 - c) \bar{\varrho}_A \), \( P_{BB} = (1 - c) (1 - c) \bar{\varrho}_B \) are the probabilities of the realization of the configurations A-A, A-B, and B-B up to the short-range order characterized by the parameter \( \alpha \). The system of (8) was solved by means of the Newton-Rawson iteration method. In addition to the obtained values of \( \Sigma \) and \( \Sigma_2 \) the total density \( \varrho(E) \) and the components of the density \( \varrho_n(E) \) for \( n = A \) and \( B \) were also calculated

\[
\varrho(E) = -\frac{5}{2\pi} \text{Im} \bar{G}_{nn}(z),
\]

\[
\varrho_n(E) = -\frac{5}{2\pi} \text{Im} \{ \bar{G}_{nn} - (\omega - \Sigma) \bar{G}_{nn} - 2(\omega - h_{nm} \Sigma_2) \bar{G}_{nn} \}^{-1} - \langle \bar{G}_{nn} \rangle \langle n | t_n | m \rangle - \bar{G}_{nn} \langle n | t_n | m \rangle,
\]

where

\[
\bar{G}_{nn} = (1 + 2 \Sigma_2)^{-1} \int \frac{\bar{\varrho}_B(E') \varrho E'}{(z - \Sigma) (1 + 2 \Sigma_2)^{-1} - E'} ; \quad z = E + i\theta.
\]

3. Discussion

The numerical calculation of the system of equations for \( \alpha \) was performed on the computer BESM-6. The parameters of the short-range order in the first coordination sphere were calculated for a series of solid solutions of the transition elements 3d and 5d. The systems under investigation, as well as their pure components, form

| Table of (8), the values of state parameters for each component | | | | |
|---|---|---|---|
| A | B | C | D |
| \( \alpha_A \) | \( \alpha_B \) | \( \alpha_C \) | \( \alpha_D \) |
| T(°C) | \( \Sigma \) | \( \Sigma_2 \) | \( \varrho_0 \) |
| \( \varrho_0 \) | \( \varrho_0 \) | \( \varrho_0 \) | \( \varrho_0 \) |
| \( \varrho_0 \) | \( \varrho_0 \) | \( \varrho_0 \) | \( \varrho_0 \) |
| \( \varrho_0 \) | \( \varrho_0 \) | \( \varrho_0 \) | \( \varrho_0 \) |

Note: \( \varrho_0 \) denotes the density at zero temperature.
f.c.c. lattices at the temperatures used for the calculations. The lattice parameters needed for the calculation of $E_k$ were obtained by Vegard's method. The parameters characterizing the pure elements and used in the calculation of the energy $E_k$ of the band structure are the relative position of the energy levels, the bandwidth $2\sigma_A$ and $2\sigma_B$, the number of electrons on the atoms, $n_A^*$ and $n_B^*$ (given in Tables 1 and 2), and the effective integral $U$ of the electron-electron interaction which is 3.2 eV for each component (see [1, 3, 9]).

### Table 1
Characteristic parameters for pure elements of the first transition d-series

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\varepsilon_i - \varepsilon_{Ni}$ (eV)</th>
<th>$2\sigma_i$ (eV)</th>
<th>$n_i^*$ (electrons/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>1.6</td>
<td>4.0</td>
<td>7.4</td>
</tr>
<tr>
<td>Co</td>
<td>0.8</td>
<td>4.0</td>
<td>8.4</td>
</tr>
<tr>
<td>Ni</td>
<td>0</td>
<td>4.0</td>
<td>9.45</td>
</tr>
</tbody>
</table>

### Table 2
The values of the parameters for pure elements belonging to different transition groups

<table>
<thead>
<tr>
<th>$i$</th>
<th>$\varepsilon_i - \varepsilon_{Pt}$ (eV)</th>
<th>$2\sigma_i$ (eV)</th>
<th>$n_i^*$ (electrons/atom)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>3</td>
<td>4.0</td>
<td>8.3</td>
</tr>
<tr>
<td>Ni</td>
<td>2</td>
<td>4.0</td>
<td>9.45</td>
</tr>
<tr>
<td>Cu</td>
<td>1</td>
<td>3.5</td>
<td>9.55</td>
</tr>
<tr>
<td>Pt</td>
<td>0</td>
<td>7.0</td>
<td>9.55</td>
</tr>
</tbody>
</table>

Table 3 gives the results of calculations of $\alpha_{1,calc}$ calculated from $\varphi(B)$ with the help of (6), the short-range order parameters $\alpha_{1,calc}$ were obtained from the initial density of states with the horizontal "plateau" on the top of the band, as well as the experimental results obtained by means of the method of diffuse short-range order scattering [6]. A comparison of $\alpha_{1,calc}$ with $\alpha_{1,calc}$ leads to the conclusion that the sign of the parameter of short-range order is not influenced by the fact that s-d hybridization was taken partly into consideration within the framework of our approximation. This causes an only negligible change in the value of this parameter in the CuNi, NiPt, and CuPt alloys. Table 3 shows the agreement between the experimentally determined and calculated signs of $\alpha_1$ in the alloys under investigation. It should, however, be noted (Table 3) that no measurements with diffuse scattering were carried out with

### Table 3
Theoretical evaluation of the $\alpha_1$ in comparison with the theoretical results

<table>
<thead>
<tr>
<th>compound</th>
<th>NiCo</th>
<th>FeNi</th>
<th>CuNi</th>
<th>NiPt (21 a1% Pt)</th>
<th>CoPt (20 a1% Co)</th>
<th>CuPt (20 a1% Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_{1,exp}$</td>
<td>0</td>
<td>-0.103</td>
<td>0.12</td>
<td>-0.092</td>
<td>-0.09</td>
<td>-0.1</td>
</tr>
<tr>
<td>$\alpha_{1,calc}$</td>
<td>-0.2</td>
<td>-0.21</td>
<td>0.43</td>
<td>-0.16</td>
<td>-0.16</td>
<td>-0.19</td>
</tr>
<tr>
<td>$\alpha_{1,calc}$</td>
<td>-0.2</td>
<td>-0.21</td>
<td>0.4</td>
<td>-0.15</td>
<td>-0.16</td>
<td>-0.22</td>
</tr>
<tr>
<td>$T$(°C)</td>
<td>930</td>
<td>100</td>
<td>1021</td>
<td>950</td>
<td>1000</td>
<td>500</td>
</tr>
</tbody>
</table>

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NiCo alloys, but the existence of a long-range order at temperatures below the Curie point, $T_C$, indicates the negative sign of $\alpha_1$. It should be stressed that the signs of the parameters of short-range order were correctly calculated for all alloys under investigation.

As has already been shown, the order of $50\%$ Cu-$50\%$ Pt alloys cannot be described correctly at least to the second coordination sphere without taking into account the formation and ordering energies of the clusters. It is, therefore, not surprising that the calculated short-range order parameter in this solid solution is $\alpha_{calc} = 0.23$, while $\alpha_{exp} = 0.00$. This discrepancy points to the unsatisfactory nature of our two-site approximation.

If the filling of the d-bands of the other alloys is analysed, an interesting correlation appears between the relative position of $E_F$ to the curve of density of states and the sign of the short-range order parameter. Thus, in the CuNi system ($\alpha_1 > 0$) the Fermi level is in the vicinity of the maximum density of states characteristic of the structure (Fig. 2e). At the same time, the $E_F$ of all alloys with negative short-range order parameters (e.g. FeNi, NiPt, see Fig. 2a, b) are outside of this maximum, in a domain where $\rho(E)$ is more smooth. This property is most likely not general, but at the current level of development of the theory of short-range order of the electron structure of alloys it appears to be possible. The results obtained in this way can be brought into agreement with the qualitative assessment of the effect of the density of electron states on the short-range order pattern [10]. When in this paper the sign of $\alpha_1$ is analysed on the basis of the rigid-band model, it has been assumed that the small density of states at $E_F$ which indicates an unsatisfactory screening of the core ion by valence electrons, leads to an increase of the repulsion between ions of identical type (AA or BB). Hence, atoms of the same type will repel one another and a short-range ordering with $\alpha_1 < 0$ will appear. Increase of the density of states at the Fermi level causes an intense screening of the ions and can lead to a reduction of the repulsion between atoms of identical type (AA or BB), and this will result in a short-range order parameter $\alpha_1 < 0$. It can be seen from Fig. 2a, b, and c and Table 3 that the results of calculations performed by means of the method suggested by us do not contradict the above statement.

Thus, by means of the method suggested by us for the calculation of $\alpha_1$, results agreeing with the experimentally obtained ones have been achieved and it has been shown...
that in solid solutions the sign of the short-range order parameter can influence noticeably the position of $E_F$ in relation to the curve of state density. This is a very interesting fact, but before it can be considered a rule more research has to be done on a greater number of alloys and using more realistic state densities.

References


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