

10

Dr. András SZÁSZ

phys. stat. sol. (b) 100, 479 (1980)

Subject classification: 13; 13.2; 21

M. V. Lomonosov State University, Moscow (a)
and Institute for Solid State Physics, Eötvös Loránd University, Budapest¹⁾ (b)

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

By

I. G. BATIREV (a), A. A. KATSNELSON (a),
L. KERTÉSZ (b), and A. SZÁSZ (b)

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 band 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.

Die Dichte der Elektronenzustände binärer Übergangsmetallegierungen mit Nahordnung wird mittels der Näherung des kohärenten Potentials gefunden. Auf der Grundlage dieser berechneten Werte wird der Beitrag der Bandstrukturenergie zum Konfigurationsanteil der Gesamtenergie bestimmt und der Gleichgewichtswert des Nahordnungsparameters von der ersten Koordinations-sphäre berechnet. Die erhaltenen Ordnungsparameter befinden sich für die meisten betrachteten Systeme im Vorzeichen in Übereinstimmung mit den experimentellen Werten.

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⁾ Muzeum 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_cB_{1-c} (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_k , of the solid solution is determined on this presumption

$$E_k = 2N \int_0^{E_F} E g(E) dE - U(cn_A^2 + (1-c)n_B^2) + E_c, \quad (1)$$

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,

$$n_A = 2 \int_0^{E_F} g_A(E) dE, \quad n_B = 2 \int_0^{E_F} g_B(E) dE,$$

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

$$g(E) = cg_A(E) + (1-c)g_B(E),$$

and E_c is the configurational part of the electrostatic energy. The Fermi level of the alloy is determined from the condition

$$2 \int_0^{E_F} g(E) dE = cn_A^0 + (1-c)n_B^0, \quad (2)$$

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_k 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

$$E_c = \frac{2}{\pi} C_1 (\Delta Z^*)^2 \alpha_1 c(1-c) \int \frac{\sin(qR)}{qR} \exp\left(\frac{-q^2}{4\eta}\right) dq, \quad (3)$$

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 η the Ewald parameter.

If E_k is known, the main task of this paper can be solved, namely the equilibrium value of α_1 can be determined for various systems of the transition elements from the equation

$$\alpha_1 = (1 - \alpha_1)^2 c(1-c) \left[\exp\left(-\frac{1}{N} \frac{\partial E_k}{\partial \alpha_1} / C_1 k_B T c(1-c)\right) - 1 \right], \quad (4)$$

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

$$H = \sum_n |n\rangle \varepsilon_n \langle n| + \sum_n \sum_{m \neq n} |n\rangle h_{nm} \langle m|, \quad (5)$$

where ε_n is the atomic d-level in the pure component. ε_n can have one of two possible values, ε_A or ε_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 neighbours. The values of these off-diagonal elements are h_{AA} , h_{AB} , and h_{BB} transition integrals when the neighbouring 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 ($w_A = C_1 h_{AA}$ and $w_B = C_1 h_{BB}$) 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, $h_{AB} = \frac{1}{2}(h_{AA} + h_{BB})$, with the help of which the Hamiltonian can be written as follows:

$$H = H^B + \sum_n |n\rangle \delta_n \langle n| + \sum_n \sum_{m \neq n} h_n(|n\rangle \langle m| + |m\rangle \langle n|),$$

where H^B is the Hamiltonian of the crystal of type B, $\delta_n = \varepsilon_n - \varepsilon_B$, h_n 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 $h_B = 0$. The effective average is characterized by the following Hamiltonian:

$$\bar{H} = \sum_n |n\rangle \Sigma \langle n| + \sum_n \sum_{m \neq n} |n\rangle h_{nm} \langle m| + \sum_n \sum_{m \neq n} h_{nm} \Sigma_2(|n\rangle \langle m| + |m\rangle \langle n|),$$

where Σ and Σ_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

$$\rho_B^0(E) = \sum_{i=1,2,3} 2w_B^{-2} M_i^{-1} \sqrt{w_B^2 - \frac{(E - E_i)^2}{N_i}}, \quad (6)$$

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 $\rho_B^0(E)$ 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

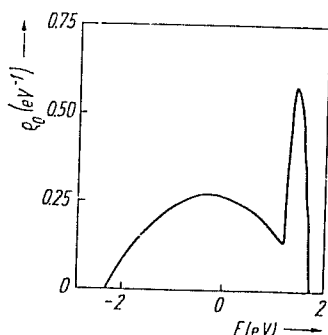


Fig. 1. The model density of states of a f.c.c. metal

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 $\varrho_n^0(E)$.

With respect to the two neighbouring atoms on sites n and m in the effective average, for this pair correlation cluster the operator of scattering $t_{nm}^{(2)}$ can be written as the sum of the two terms, $t_n^{(2)}(m) + t_m^{(2)}(n)$, where $t_n^{(2)}(m)$ and $t_m^{(2)}(n)$ 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, $t_n^{(2)}(m)$, is related to the one-site scattering operators t_n and t_m as follows:

$$t_n^{(2)}(m) = t_n + t_n \bar{G} (1 - t_m \bar{G} t_n \bar{G})^{-1} t_m (1 + \bar{G} t_n), \quad (7)$$

where

$$\langle n | t_n | n \rangle = (\epsilon_n - \Sigma) [1 - (\epsilon_n - \Sigma) \bar{G}_{nm} - 2(h_n - h_{BB} \Sigma_2) \bar{G}_{nm}]^{-1},$$

$$\langle n | t_n | m \rangle = 2(h_n - h_{BB} \Sigma_2) [1 - (\epsilon_n - \Sigma) \bar{G}_{nm} - 2(h_n - h_{BB} \Sigma_2) \bar{G}_{nm}].$$

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

$$\bar{G}_{nm} = [(z - \Sigma) \bar{G}_{nn} - 1] [(1 + 2\Sigma_2) h_{BB} C_1]^{-1}.$$

The coherent potentials Σ and Σ_2 are determined from the following system of equations:

$$\langle\langle n | t_{nm}^{(2)} | n \rangle\rangle = 0, \quad \langle\langle n | t_{nm}^{(2)} | m \rangle\rangle = 0, \quad (8)$$

where $t_{nm}^{(2)}$ is the configurational average

$$\langle t_{nm}^{(2)} \rangle = P_{AA} t_{AA}^{(2)} + P_{AB} (t_{AB}^{(2)} + t_{BA}^{(2)}) + P_{BB} t_{BB}^{(2)},$$

where $P_{AA} = c[c + (1 - c)\alpha_1]$, $P_{AB} = (1 - c)c(1 - \alpha_1)$, $P_{BB} = (1 - c)(1 - c + c\alpha_1)$ 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 α_1 . The system of (8) was solved by means of the Newton-Rawson iteration method. In addition to the obtained values of Σ and Σ_2 the total density $\varrho(E)$ and the components of the density $\varrho_n(E)$ for $n = A$ and B were also calculated

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

$$\varrho_n(E) = -\frac{5}{\pi} \text{Im} \{ \bar{G}_{nn} [1 - (\epsilon_n - \Sigma) \bar{G}_{nn} - 2(h_n - h_{BB} \Sigma_2) \bar{G}_{nm}]^{-1} -$$

$$- (\bar{G}_{nm})^2 \langle\langle n | t_n | n \rangle\rangle - \bar{G}_{nn} \bar{G}_{nm} \langle\langle n | t_n | m \rangle\rangle \},$$

where

$$\bar{G}_{nn} = (1 + 2\Sigma_2)^{-1} \int \frac{\dot{\varrho}_B(E') dE'}{(z - \Sigma)(1 + 2\Sigma_2)^{-1} - E'}; \quad z = E + i0.$$

3. Discussion

The numerical calculation of the system of equations for α_1 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

Relationsh

f.c.c. latt
needed fo
character
band str
and $2w_B$
and the c
each com

Table
of (6), t
of state
mental
[6]. A c
parameter
taken p
causes
and Cu
and ca
noted t

compo

α_1 exp.
 α_1 calc.
 α_1 calc.
 $T(^{\circ}\text{C})$

32 ph

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 bandwidths $2w_A$ and $2w_B$, the number of electrons on the atoms, n_A^0 and n_B^0 (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

i	$\epsilon_i - \epsilon_{Ni}$ (eV)	$2w_i$ (eV)	n_i^0 (electrons/atom)
Fe	1.6	4.0	7.4
Co	0.8	4.0	8.4
Ni	0	4.0	9.45

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

i	$\epsilon_i - \epsilon_{Pt}$ (eV)	$2w_i$ (eV)	n_i^0 (electrons/atom)
Co	3	4.0	8.3
Ni	2	4.0	9.45
Cu	1	3.5	9.95
Pt	0	7.0	9.55

Table 3 gives the results of calculations of α_1 calc calculated from $g_B(E)$ with the help of (6), the short-range order parameters α_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 α_1 calc with α_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 α_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 α_1 in comparison with the theoretical results

compound	NiCo	FeNi	CuNi	NiPt (21 at% Pt)	CoPt (20 at% Co)	CuPt (29 at% Pt)
α_1 exp	0	-0.103	0.12	-0.092	-0.09	-0.1
α_1 calc	-0.2	-0.21	0.43	-0.16	-0.16	-0.19
α_1' calc	-0.2	-0.21	0.4	-0.15	-0.16	-0.22
$T(^{\circ}C)$	930	100	1021	1050	1000	500

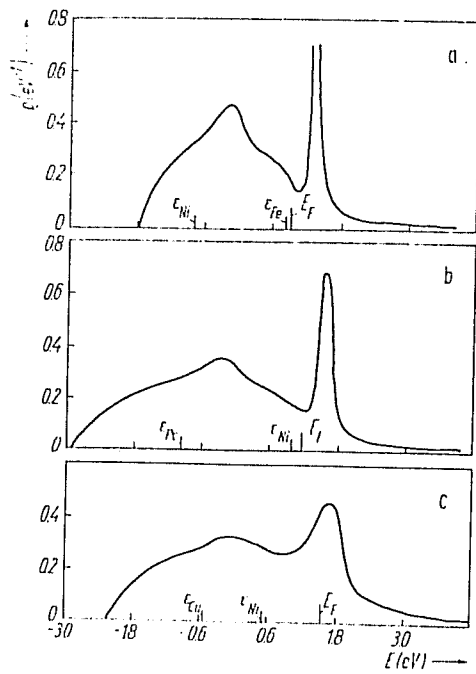


Fig. 2. Calculated density of states of alloys for obtained equilibrium values of short-range order parameters. a) FeNi: $c = 0.5$, $\alpha_1^{\text{calc}} = -0.21$; b) NiPt: $c = 0.21$, $\alpha_1^{\text{calc}} = -0.16$; c) CuNi: $c = 0.5$, $\alpha_1^{\text{calc}} = 0.43$

NiCo alloys, but the existence of a long-range order at temperatures below the Curie point, T_C , indicates the negative sign of α_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 $\alpha_1^{\text{calc}} = 0.23$, while $\alpha_1^{\text{exp}} = 0.00$. 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. 2c). 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 α_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 α_1 , results agreeing with the experimentally obtained ones have been achieved and it has been shown

Relationsh

that in so
tically t
esting fac
a greater

- [1] J. VAN
- [2] J. VAN
- [3] J. VAN
- [4] A. A.
- [5] A. O.
- [6] V. I. I
Nauka
- [7] L. SCH
- [8] V. SUR
- [9] F. HER
London
- [10] FARID
11 (197
- [11] B. VEL
- [12] M. YAS
- [13] P. C. C

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

- [1] J. VAN DER REST and F. GAUTIER, *J. Phys.* F 5, 2883 (1975).
- [2] J. VAN DER REST, F. GAUTIER, and F. BROUERS, *J. Phys.* F 5, 995 (1975).
- [3] J. VAN DER REST, *J. Phys.* F 7, 1051 (1977).
- [4] A. A. KATSNELSON, V. M. SILONOV, and FARID A. KHWAJA, *phys. stat. sol. (b)* 91, 11 (1979).
- [5] A. O. E. ANIMALU, *Phys. Rev. B* 8, 3542 (1973).
- [6] V. I. IVERONOVA and A. A. KATSNELSON, *Blizhnii porjadok v tverdkh rast vo rakh*, Izd. Nauka, Moskva 1977.
- [7] L. SCHWARTZ and H. EHRENREICH, *Phys. Rev. B* 6, 2923 (1972).
- [8] V. SRIVASTAVA, D. KUMAR, and S. K. JOSHI, *Solid State Commun.* 21, 25 (1976).
- [9] F. HERMAN and S. SKILMAN, *Atomic Structure Calculations*, Englewood Cliffs Prentice Hall, London 1963.
- [10] FARID A. KHAVADZHA, V. M. SILONOV, and A. A. KATSNELSON, *Izv. vuzov, Ser. fiz.* No. 1, 11 (1977).
- [11] B. VELICKY, S. KIRKPATRICK, and H. EHRENREICH, *Phys. Rev.* 175, 747 (1968).
- [12] M. YASUKI, E. HAYASHI, and M. SHIMIZU, *J. Phys. Soc. Japan* 29, 1446 (1970).
- [13] P. C. CLAPP, *Acta metall.* 22, 563 (1974).

(Received December 13, 1979)