

THE THERMODYNAMIC POTENTIAL FOR ELECTRONS AND PHONONS IN A DISORDERED CRYSTAL

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We obtain a cluster expression for the two-time retarded Green's functions and the thermodynamic potential of a disordered crystal taking the electron-phonon and electron-electron interactions into account. The electron states of the system are described in the framework of a multiband tight-binding model. The calculations are based on the diagram techniques for temperature Green's functions. The coherent potential approximation is chosen as a zero-order one-site approximation in this cluster expansion method. We show that the contributions from the processes of scattering of elementary excitations by clusters decrease as the number of sites in the cluster increases in accordance with certain small parameters. Analytic estimates of the influence of the electron-phonon interaction on the energy spectrum of electrons of an ordered alloy are obtained in a one-band model. The applicability of these results to describing the influence of strong electron correlations on the electron structure and properties of alloys of transition metals with narrow energy bands is illustrated with the example of a Fe-Co alloy. Our results suggest possible ways to generalize the one-band Hubbard model, well-known in the theory of magnetism, to describe the influence of strong electron correlations on the electron structure and properties of disordered alloys of transition metals with narrow energy bands.

Introduction

Success in the investigation of the properties of disordered systems (alloys, disordered semiconductors, amorphous materials) is connected with the progress of the electronic theory. The alloys are the most investigated systems among them.

The traditional notions about properties of alloys are based on the Born approximation and not applicable in case of the alloys of transition metals with the large impurity potential of scattering. The essential successes in the description of such systems are stipulated by using the method of multiple scattering and especially the coherent potential approximation [1]. The coherent potential approximation (CPA) is the best single-site approximation for studying the properties of alloys [1]. However, for research of the alloys properties essentially in dependence on the interatomic correlations, it is necessary to go beyond the scope of the single-site approximation, i.e. to account the scattering by clusters. The set of works is devoted to this problem. The cluster generalizations of CPA, based on a single cluster in an effective medium, do not provide the analyticity and translation

invariance of configuration-averaged Green's function [1]. Among the cluster generalizations of CPA, it is necessary to note the method of 'augmented space' [2 - 4] and the approximation of 'travelling cluster' [5]. These approaches solve the problem of construction of a self-consistent approximation by taking into account the scattering by clusters and saving the analyticity and translation invariance of the configuration-averaged Green's function of a system. The equivalence of the approximation of 'travelling cluster' [5] to the method of 'augmented space' [2 - 4] is proved in [6]. The generalization of the method of 'augmented space' to the case of alloys with a short-range order is developed in [7 - 10]. However, in the mentioned approaches it is difficult to estimate the accuracy of offered approximations, because no small parameter has used.

In [11 - 16], the method for calculation of a configuration-averaged Green's function and the free energy of electrons of an alloy is based on the T -matrix expansion in one-center scattering operators. The average of the one-center operators product is decomposed into a product of averaged pair operators. CPA is chosen as the zero approximation. The small parameter of expansion is introduced in [17]. However, the problem of accuracy of these approximations remains unsolved. The applications of this method to the calculation of the density of electronic states and ordering energy of partially ordered alloys [11 - 12], parameters of a short-range order and effective interatomic interactions [14 - 15], and the definition of stability of ordered structures [16] were developed as well.

In [18, 19], a method is advanced for accounting the statistical correlations on the base of a cluster expansion for one- and two-particle Green's functions, which define, correspondingly, the energy spectrum of electrons and electrical conductivity of alloys. CPA is chosen as the zero approximation in this method. Corrections to CPA are found by summing up the contributions from the processes of scattering by clusters of two, three, etc. atoms. It is shown that the contributions of the corresponding processes of scattering decrease with increasing the number of particles in the cluster on a small parameter, which is similar to one introduced earlier in [17]. The study

of this parameter [12, 18 - 20] shows that it can be small in a wide range of the alloy characteristics (including the component concentrations), excepting a narrow energy interval at the band edge.

The specified approach is used in [18, 19] for the investigation of the influence of interatomic correlations (short-range and long-range ordering) upon the energy spectrum of electrons (density of states) and the electrical conductivity of alloys. It is shown that the density of electronic states under the short-range ordering in an alloy exhibits a characteristic dip which transforms into a quasigap under the long-range ordering. It is established that the behaviour of electrical conductivity under the atomic ordering and the character of ordering essentially depend on a position of the Fermi level in relation to the mentioned quasigap.

However, in the works mentioned above, the descriptions of electronic states did not take into account the oscillations of a crystal lattice and the electron-phonon interaction, which can give the significant contributions into the ordering energy and interatomic correlations parameters and essentially affect the alloy properties. It is necessary to note that, in [21, 22], the attempt of accounting the contribution of the electron-phonon interaction to the thermodynamic potential and electronic heat capacity of an alloy is made. In [23, 24], the influence of the electron-phonon interaction on the electrical conductivity of disordered alloys is investigated. However, in [21 - 24], the interatomic correlations were not taken into account, and the electron-phonon interaction was considered as weak. Moreover, expressions obtained in [24] are true only at high temperatures, when the thermal displacements of atoms can be described by the semiclassical limit.

In the present work, the cluster expansion for Green's functions and the thermodynamic potential of a system of electrons and phonons in a disordered alloy is obtained. The electronic states of the system are described in a many-band tight-binding model. In the present expansion, CPA is chosen as the zero single-site approximation. It is shown that the contributions of the scattering processes by clusters decrease with increasing the number of atoms in the cluster on some small parameter. The equation for the parameters of interatomic correlations (short-range and long-range orders) is obtained. The possibility of application of the obtained results to the investigation of the influence of strong electronic correlations on the electronic structure and properties of alloys of transition metals with narrow energy bands is shown.

1. Hamiltonian of the System

The Hamiltonian of the system of electrons and phonons in a disordered crystal (metal alloy,

disordered semiconductor) in the Wannier representation takes the form

$$H = H_0 + H_{\text{int}}. \tag{1}$$

The Hamiltonian in the zero approximation in (1),

$$H_0 = \Phi_0 + H_{f0} + H_{e0}, \tag{2}$$

consists of the Hamiltonian of the subsystem of noninteracting electrons

$$H_{e0} = \sum_{\substack{n_1 i_1 \gamma_1 \\ n_2 i_2 \gamma_2}} h_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{(0)} a_{n_1 i_1 \gamma_1}^+ a_{n_2 i_2 \gamma_2}, \tag{3}$$

the Hamiltonian of the subsystem of noninteracting phonons

$$H_{f0} = \sum_{n i \alpha} \frac{P_\alpha^2 \binom{n}{i}}{2M_A} + \frac{1}{2} \sum_{\substack{n_1 i_1 \alpha_1 \\ n_2 i_2 \alpha_2}} \Phi_{\alpha_1 \alpha_2}^{(0)} \binom{n_1}{i_1} \binom{n_2}{i_2} u_{\alpha_1} \binom{n_1}{i_1} u_{\alpha_2} \binom{n_2}{i_2}, \tag{4}$$

and the energy of the electrostatic interaction of ions Φ_0 .

The Hamiltonian of the perturbation in (1),

$$H_{\text{int}} = H_{ei} + H_{ef} + H_{ee} + H_{fi} + H_{ff}, \tag{5}$$

consists of the Hamiltonian of electron-ion (electron-impurity) interaction

$$H_{ei} = \sum_{\substack{n_1 i_1 \gamma_1 \\ n_2 i_2 \gamma_2}} w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} a_{n_1 i_1 \gamma_1}^+ a_{n_2 i_2 \gamma_2}, \tag{6}$$

the Hamiltonian of electron-phonon interaction

$$H_{ef} = \sum_{\substack{n_1 i_1 \gamma_1 \\ n_2 i_2 \gamma_2}} v_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} a_{n_1 i_1 \gamma_1}^+ a_{n_2 i_2 \gamma_2}, \tag{7}$$

the Hamiltonian of pair electron-electron interaction

$$H_{ee} = \frac{1}{2} \sum_{\substack{n_1 i_1 \gamma_1 \\ n_2 i_2 \gamma_2 \\ n_3 i_3 \gamma_3 \\ n_4 i_4 \gamma_4}} v_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2, n_3 i_3 \gamma_3, n_4 i_4 \gamma_4}^{(2)} a_{n_1 i_1 \gamma_1}^+ a_{n_2 i_2 \gamma_2}^+ a_{n_3 i_3 \gamma_3} a_{n_4 i_4 \gamma_4}, \tag{8}$$

the Hamiltonian of phonon-ion (phonon-impurity) interaction

$$H_{fi} = \frac{1}{2} \sum_{\substack{n_1 i_1 \alpha_1 \\ n_2 i_2 \alpha_2}} \Delta M_{\alpha_1 \alpha_2}^{-1} \begin{pmatrix} n_1 & n_2 \\ i_1 & i_2 \end{pmatrix} P_{\alpha_1} \begin{pmatrix} n_1 \\ i_1 \end{pmatrix} P_{\alpha_2} \begin{pmatrix} n_2 \\ i_2 \end{pmatrix} + \frac{1}{2} \sum_{\substack{n_1 i_1 \alpha_1 \\ n_2 i_2 \alpha_2}} \Delta \Phi_{\alpha_1 \alpha_2} \begin{pmatrix} n_1 & n_2 \\ i_1 & i_2 \end{pmatrix} u_{\alpha_1} \begin{pmatrix} n_1 \\ i_1 \end{pmatrix} u_{\alpha_2} \begin{pmatrix} n_2 \\ i_2 \end{pmatrix}, \quad (9)$$

$$\Delta M_{\alpha_1 \alpha_2}^{-1} \begin{pmatrix} n_1 & n_2 \\ i_1 & i_2 \end{pmatrix} = \left(\frac{1}{M_{n_1 i_1}} - \frac{1}{M_A} \right) \delta_{n_1 n_2} \delta_{i_1 i_2} \delta_{\lambda_1 \lambda_2},$$

$$\Delta \Phi_{\alpha_1 \alpha_2} \begin{pmatrix} n_1 & n_2 \\ i_1 & i_2 \end{pmatrix} = \Phi_{\alpha_1 \alpha_2} \begin{pmatrix} n_1 & n_2 \\ i_1 & i_2 \end{pmatrix} - \Phi_{\alpha_1 \alpha_2}^{(0)} \begin{pmatrix} n_1 & n_2 \\ i_1 & i_2 \end{pmatrix},$$

and the Hamiltonian of phonon-phonon interaction

$$H_{ff} = \frac{1}{3!} \sum_{\substack{n_1 i_1 \alpha_1 \\ n_2 i_2 \alpha_2 \\ n_3 i_3 \alpha_3}} \Phi_{\alpha_1 \alpha_2 \alpha_3} \begin{pmatrix} n_1 & n_2 & n_3 \\ i_1 & i_2 & i_3 \end{pmatrix} \times u_{\alpha_1} \begin{pmatrix} n_1 \\ i_1 \end{pmatrix} u_{\alpha_2} \begin{pmatrix} n_2 \\ i_2 \end{pmatrix} u_{\alpha_3} \begin{pmatrix} n_3 \\ i_3 \end{pmatrix}. \quad (10)$$

Here, $a_{ni\gamma}^+$, $a_{ni\gamma}$ are the creation and destruction operators for electrons in the states that described by Wannier functions $\varphi_{ni\gamma}(\xi) = \langle \xi | n i \gamma \rangle$; $\xi = (\vec{r}, \sigma)$; index γ includes both the number of an energy band and the projection of a spin σ on the axis Z , n is the number of an elementary cell of the crystal, i is the number of a site sublattice in the elementary cell; $h_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{(0)}$ are the matrix elements of the one-electron Hamiltonian for a pure crystal, $\vec{u} \begin{pmatrix} n \\ i \end{pmatrix}$ is the operator of atom displacement at the site (ni) ; $P_{\alpha} \begin{pmatrix} n \\ i \end{pmatrix}$ is the operator of the α -projection of the atom momentum; $\Phi_{\alpha_1 \alpha_2} \begin{pmatrix} n_1 & n_2 \\ i_1 & i_2 \end{pmatrix}$, $\Phi_{\alpha_1 \alpha_2 \alpha_3} \begin{pmatrix} n_1 & n_2 & n_3 \\ i_1 & i_2 & i_3 \end{pmatrix}$ are the force constants.

The operator of the potential energy of an electron in the field of ionic skeletons of the crystal, $V(\vec{r})$, is presented as

$$V(\vec{r}) = \sum_{ni} v^{ni}(\vec{r} \rhd \vec{r}_{ni}^{\rhd}), \quad \vec{r}_{ni}^{\rhd} = \vec{r}_{ni} + \vec{u} \begin{pmatrix} n \\ i \end{pmatrix},$$

where \vec{r} is the radius-vector of the electron, $\vec{r}_{ni}^{\rhd} = \vec{r}_n + \vec{\rho}_i^{\rhd}$ is the radius-vector of the equilibrium position of the atom at the site (ni) of the crystal lattice. The random contributions to the matrix element of the one-electron Hamiltonian for a pure crystal which are connected with an impurity read

$$w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} = \sum_{ni} w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{ni},$$

$$w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{ni} = \sum_{\lambda} c_{ni}^{\lambda} w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{\lambda ni},$$

$$w_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{\lambda ni} = v_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{\lambda ni} - v_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{Ani},$$

where

$$v_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}^{\lambda ni} = \int \varphi_{n_1 i_1 \gamma_1}^*(\xi) v^{\lambda}(\vec{r} \rhd \vec{r}_{ni}^{\rhd}) \varphi_{n_2 i_2 \gamma_2}(\xi) d\xi. \quad (11)$$

Here, c_{ni}^{λ} are the random filling numbers which adopt the values 1 or 0 in dependence on the presence or absence of the atom of the λ sort at the site (ni) .

In (7), the values $v'_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}$ are expressed through the operators of coordinates $u_{\alpha} \begin{pmatrix} n \\ i \end{pmatrix}$ of the crystal lattice:

$$v'_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} = \sum_{ni\alpha} v'^{ni\alpha}_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} u_{\alpha} \begin{pmatrix} n \\ i \end{pmatrix},$$

$$v'^{ni\alpha}_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2} = \sum_{\lambda} c_{ni}^{\lambda} v'^{\lambda ni\alpha}_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}$$

where $v'^{\lambda ni\alpha}_{n_1 i_1 \gamma_1, n_2 i_2 \gamma_2}$ are determined by (11), in which it is necessary instead of $v^{\lambda}(\vec{r} \rhd \vec{r}_{ni}^{\rhd})$ to substitute

$$- e_{ni\alpha} \frac{d}{d|\vec{r} \rhd \vec{r}_{ni}^{\rhd}|} v^{\lambda}(|\vec{r} \rhd \vec{r}_{ni}^{\rhd}|), \quad \vec{e}_{ni} = \frac{\vec{r} \rhd \vec{r}_{ni}^{\rhd}}{|\vec{r} \rhd \vec{r}_{ni}^{\rhd}|}.$$

2. Free Energy and Parameters of Interatomic Correlations

The thermodynamic potential of the system is determined by the expression

$$\Omega = - \Theta \ln \text{Sp} (e^{-H/\Theta}), \quad \text{where } H = H - \mu_e N_e. \quad (12)$$

From (12), we get

$$\Omega = \Omega_0 + \Omega', \quad \Omega' = - \Theta \ln \langle \sigma(1/\Theta) \rangle_0, \quad (13)$$

where $\sigma(\tau) = T_\tau \exp \left[- \int_0^\tau H_{\text{int}}(\tau') d\tau' \right]$,

$$H_{\text{int}}(\tau) = e^{H_0\tau} H_{\text{int}} e^{-H_0\tau},$$

$$H_0 = H_0 - \mu_e N_e, \langle A \rangle_0 = \text{Sp}(\rho_0 A), \rho_0 = e^{(\Omega_0 - H_0)/\Theta}.$$

Let's redefine the interaction Hamiltonian H_{int} (5) by multiplying it by some parameter λ and putting $H_{\text{int}}(\lambda) = \lambda H_{\text{int}}$.

Differentiating (13) with respect to the parameter λ , we get the equation

$$\frac{\partial \Omega'(\lambda)}{\partial \lambda} = \frac{\Theta}{\lambda} \int_0^{1/\Theta} d\tau \langle T_\tau H_{\text{int}}(\tau, \lambda) \sigma(1/\Theta, \lambda) \rangle_0 / \langle \sigma(1/\Theta, \lambda) \rangle_0. \tag{14}$$

Integrating (14) under the condition $\Omega'(0) = 0$, $\Omega'(1) = \Omega'$, we obtain

$$\Omega' = \Theta \int_0^1 \frac{d\lambda}{\lambda} \int_0^{1/\Theta} d\tau \langle T_\tau H_{\text{int}}(\tau, \lambda) \sigma(1/\Theta, \lambda) \rangle_0 / \langle \sigma(1/\Theta, \lambda) \rangle_0. \tag{15}$$

For calculations of the thermodynamic potential Ω' (15), it is possible to advance a diagram technique similar to the diagram technique for temperature Green functions [25]. Fulfilling the Fourier transformation of the integrand, we obtain

$$\begin{aligned} \Omega' = & - \frac{1}{\pi} \text{Im} \int_0^1 \frac{d\lambda}{\lambda} \int_{-\infty}^{\infty} d\varepsilon [f(\varepsilon) \langle \text{Sp}(w(\lambda) + \Sigma_{ef}(\varepsilon, \lambda) + \\ & + \Sigma_{ee}(\varepsilon, \lambda)) G^{aa^+}(\varepsilon, \lambda) \rangle + \\ & + \frac{1}{2} \text{cth} \left(\frac{\varepsilon}{2\Theta} \right) \langle \text{Sp}(\Delta M^{-1}(\lambda) G^{PP}(\varepsilon, \lambda) + \\ & + (\Delta \Phi(\lambda) + \Sigma_{ff}(\varepsilon, \lambda) G^{uu}(\varepsilon, \lambda)) \rangle], \end{aligned} \tag{16}$$

where $f(\varepsilon)$ is the Fermi function.

The density of electron states per atom is

$$g_e(\varepsilon) = - \frac{1}{\pi v N} \text{Im Sp} \langle G^{aa^+}(\varepsilon) \rangle, \tag{17}$$

and the density of phonon states is

$$g_f(\varepsilon) = - \frac{1}{\pi v N} 2 \frac{\varepsilon}{\hbar^2} M_A \text{Im Sp} \langle G^{uu}(\varepsilon) \rangle. \tag{18}$$

In (17), (18), brackets $\langle \rangle$ designate the average over various dispositions of atoms (configuration average).

We execute the cluster expansion for the Green functions $G^{aa^+}(\varepsilon)$, $G^{uu}(\varepsilon)$ by presenting mass operators as sums of single-site operators and choosing the single-site approximation of a Green function for the effective medium as the zero approximation. The specified expansion is a generalization of the cluster expansion for the Green function $G^{aa^+}(\varepsilon)$ in a neglect of the multiparticle interaction [18, 19]. The Green function of the effective medium for the subsystem of electrons is determined by the expression

$$\begin{aligned} \tilde{G}^{aa^+}(\varepsilon) = & [[G_0^{aa^+}(\varepsilon)]^{-1} - (\Sigma_{ef}^A(\varepsilon) + \\ & + \Sigma_{ee}(\varepsilon) + \sigma_e(\varepsilon))]^{-1}, \end{aligned} \tag{19}$$

where the mass operator of electron-phonon interaction for the pure crystal equals

$$\Sigma_{ef}^A(\varepsilon) = \sum_{\substack{n_1 i_1 \\ n_2 i_2}} \Sigma_{ef}^{A n_1 i_1, A n_2 i_2}(\varepsilon).$$

The Green function of the effective medium for the subsystem of phonons is determined by the expression

$$\tilde{G}^{uu}(\varepsilon) = [[G_0^{uu}(\varepsilon)]^{-1} - (\Sigma_{fe}^A(\varepsilon) + \Sigma_{ff}(\varepsilon) + \sigma_f(\varepsilon))]^{-1}, \tag{20}$$

where

$$\Sigma_{fe}^A(\varepsilon) = \Sigma_{fe}^{AA}(\varepsilon).$$

In (19), (20), $\sigma_e(\varepsilon)$, $\sigma_f(\varepsilon)$ are the potentials of the effective medium (coherent potentials), whose values will be defined below.

Fulfilling the transformations [18, 19] of the functions $G^{aa^+}(\varepsilon)$, $G^{uu}(\varepsilon)$, we get

$$G(\varepsilon) = \tilde{G}(\varepsilon) + \tilde{G}(\varepsilon) T(\varepsilon) \tilde{G}(\varepsilon), \tag{21}$$

where the T -matrix of scattering is represented as a series, whose terms describe the scattering by clusters with various numbers of centers:

$$T = \sum_{(n_1 i_1)} t^{n_1 i_1} + \sum_{(n_1 i_1) \neq (n_2 i_2)} T^{(2) n_1 i_1, n_2 i_2} + \dots \tag{22}$$

Here,

$$T^{(2)n_1i_1, n_2i_2} = [I - t^{n_1i_1} \tilde{G} t^{n_2i_2} \tilde{G}]^{-1} \times \\ \times t^{n_1i_1} \tilde{G} t^{n_2i_2} [I + \tilde{G} t^{n_1i_1}].$$

In (22), $t^{n_1i_1}$ is the operator of scattering by a single site

$$t^{n_1i_1} = [I - \tilde{\Sigma}^{n_1i_1} \tilde{G}]^{-1} \tilde{\Sigma}^{n_1i_1}, \quad (23)$$

where, for the subsystem of electrons,

$$\tilde{\Sigma}^{n_1i_1}(\epsilon) = \Sigma_e^{n_1i_1}(\epsilon) - \sigma_e^{n_1i_1}(\epsilon),$$

$$w + \Sigma_{ef}(\epsilon) - \Sigma_{ef}^A(\epsilon) = \sum_{(n_1i_1)} \Sigma_e^{n_1i_1}(\epsilon),$$

$$\sigma_e(\epsilon) = \sum_{(n_1i_1)} \sigma_e^{n_1i_1}(\epsilon),$$

and, for the subsystem of phonons,

$$\tilde{\Sigma}^{n_1i_1}(\epsilon) = \Sigma_f^{n_1i_1}(\epsilon) - \sigma_f^{n_1i_1}(\epsilon),$$

$$\frac{\epsilon^2}{\hbar^2} \Delta M + \Delta \Phi + \Sigma_{fe}(\epsilon) - \Sigma_{fe}^A(\epsilon) = \sum_{(n_1i_1)} \Sigma_f^{n_1i_1}(\epsilon),$$

$$\sigma_f(\epsilon) = \sum_{(n_1i_1)} \sigma_f^{n_1i_1}(\epsilon).$$

As shown in [18, 19], the contributions of the processes of scattering by clusters to the configuration-averaged Green function decrease with increasing the number of centers in a cluster on some small parameter. Fulfilling the configuration averaging in (22) and passing to the k -representation, in a neglect of processes of scattering by clusters of the three and more centers, we have the averaged T -matrix of scattering for the subsystem of electrons

$$\langle T_{i\gamma, i'\gamma'}(\vec{k}, \epsilon) \rangle = \sum_{i_1} \sum_{\substack{\lambda_1, \lambda_2 \\ (n_2i_2 \neq (0i_1)) \\ n, n'}} \langle c_{0i_1}^{\lambda_1} c_{n_2i_2}^{\lambda_2} \rangle \times \\ \times T_{ni\gamma, n'i'\gamma'}^{(2)\lambda_1 0i_1, \lambda_2 n_2i_2} e^{ik(\vec{r}_n + \vec{p}_i - \vec{r}_n - \vec{p}_i)}. \quad (24)$$

The expression for the T -matrix of scattering for the subsystem of phonons follows from (24) by replacing the energy band index γ by the projection α of a vector in the Cartesian coordinate system.

In (24), $\langle c_{n_1i_1}^{\lambda_1} c_{n_2i_2}^{\lambda_2} \rangle = c_{i_1}^{\lambda_1} c_{i_2}^{\lambda_2} + \epsilon_{n_1i_1, n_2i_2}^{\lambda_1 \lambda_2}$ are the probabilities of the substitution for sites (n_1i_1) and (n_2i_2) by atoms of the λ_1 and λ_2 sorts; $\langle c_{ni}^\lambda \rangle = c_i^\lambda$ is the probability of the substitution for a site of the i -th sublattice by an atom of the λ sort. In the case of crystals of the cubic symmetry for a binary alloy, we have $c_i^A = x_i = c^A - \frac{v_2}{v} \eta$, $c_i^B = y_i = 1 - x_i$ for the

v_1 sublattice of the first type and $x_i = c^A + \frac{v_1}{v} \eta$ for the v_2 sublattice of the second type; $v = v_1 + v_2$; η is the long-range parameter; $c^A, c^B = 1 - c^A$ are the concentrations of A - and B -components in the crystal; $\epsilon_{n_1i_1, n_2i_2}^{AA} = \epsilon_{n_1i_1, n_2i_2}^{AA} = \langle (c_{n_1i_1}^A - c_{i_1}^A)(c_{n_2i_2}^A - c_{i_2}^A) \rangle$ are the parameters of pair interatomic correlations.

The thermodynamic potential Ω_0 in (13) in the absence of interaction equals

$$\Omega_0 = \Omega_c + \Omega_{0e} + \Omega_{0f} \quad (25)$$

The thermodynamic potential for the electronic subsystem is

$$\Omega_{0e} = -vN\Theta \int_{-\infty}^{\infty} \ln \left(1 + e^{\frac{\mu_e - \epsilon}{\Theta}} \right) g_{0e}(\epsilon) d\epsilon. \quad (26)$$

The thermodynamic potential for the subsystem of phonons is

$$\Omega_{0f} = vN\Theta \int_{-\infty}^{\infty} \ln \left(1 - e^{\frac{-\epsilon}{\Theta}} \right) g_{0f}(\epsilon) d\epsilon. \quad (27)$$

In (26), (27), $g_{0e}(\epsilon), g_{0f}(\epsilon)$ are given by (17), (18), in which $G^{aa^+}(\epsilon), G^{uu}(\epsilon)$ are replaced by the Green functions in the zero approximation, $G_0^{aa^+}(\epsilon), G_0^{uu}(\epsilon)$.

The configuration component of the thermodynamic potential Ω_c in (25), depending on the atom distribution over sites of the crystal lattice, equals

$$\Omega_c = \langle \Phi_c \rangle - \Theta S_c,$$

where $S_c = -\langle \ln P_c \rangle$ is the configuration entropy, $P_c(\{c_{ni}^\lambda\})$ is the distribution function of atoms over sites of the lattice.

In neglecting the electron-phonon, electron-electron, and phonon-phonon interactions, expression (13) for the thermodynamic potential becomes essentially simpler. Supposing in (16) $\Sigma_{ef}(\epsilon) = \Sigma_{ee}(\epsilon) =$

$= \Sigma_{ff}(\epsilon) = 0$ and decomposing the Green functions $G^{aa^+}(\epsilon)$, $G^{uu}(\epsilon)$ in ascending power series, we obtain

$$\Omega = \Omega_c + \Omega_e + \Omega_f, \tag{28}$$

where Ω_e, Ω_f are given by (26), (27), in which $g_{0e}(\epsilon), g_{0f}(\epsilon)$ are displaced by $g_e(\epsilon), g_f(\epsilon)$ (see (17), (18)).

The expression for Ω_e in (28), obtained in the specified particular case, corresponds to that in [11–14].

Taking into account only the electron-electron interaction in Hamiltonian (5) and neglecting terms small as $O(\lambda^2)$ in integral (16), we come to an approximate expression for the thermodynamic potential of the electronic subsystem Ω_e , obtained in [26] (see also [21, 22]). The free energy F as a function of the system volume V , temperature T , number of electrons N_e , and parameters of interatomic correlations $(\epsilon_{n_1 i_1, n_2 i_2}, \eta)$ is connected with the thermodynamic potential Ω by the relation $F = \Omega + \mu_e \langle N_e \rangle$ and equals

$$F = \langle \Phi_0 \rangle - \Theta S_c + \Omega_{0e} + \Omega_{0f} + \Omega' + \mu_e \langle N_e \rangle. \tag{29}$$

The configuration part of the entropy of an alloy S_c in (29) is connected with the probabilities of the atom distribution over the lattice sites $P_{n_1 i_1}^{\lambda_1}, P_{n_2 i_2}^{\lambda_2}$ by the relation [27, 28]

$$S_c = - \left[\sum_{(n_1 i_1) \lambda_1} P_{n_1 i_1}^{\lambda_1} \ln P_{n_1 i_1}^{\lambda_1} + \frac{1}{2} \sum_{\substack{(n_1 i_1) \neq (n_2 i_2) \\ \lambda_1, \lambda_2}} P_{n_1 i_1, n_2 i_2}^{\lambda_1 \lambda_2} \ln \frac{P_{n_1 i_1, n_2 i_2}^{\lambda_1 \lambda_2}}{P_{n_1 i_1}^{\lambda_1} P_{n_2 i_2}^{\lambda_2}} + \dots \right], \tag{30}$$

where

$$P_{ni}^{\lambda} = \langle c_{ni}^{\lambda} \rangle, \quad P_{n_1 i_1, n_2 i_2}^{\lambda_1 \lambda_2} = \langle c_{n_1 i_1}^{\lambda_1} c_{n_2 i_2}^{\lambda_2} \rangle.$$

Equilibrium values of the parameters of interatomic correlations $(\epsilon_{0i_1, n_2 i_2}, \eta)$ are determined from the condition of minimum for the energy of an alloy:

$$\frac{\partial F}{\partial \epsilon_{0i_1, n_2 i_2}} = 0, \quad \frac{\partial F}{\partial \eta} = 0.$$

In neglecting the contributions of the processes of scattering by clusters of three and more atoms, we

get the equation connecting the parameters $\epsilon_{0i_1, n_2 i_2}$ and η

$$\ln \left\{ 1 + \frac{\epsilon_{0i_1, n_2 i_2}}{[x_{i_1} y_{i_2} - \epsilon_{0i_1, n_2 i_2}][y_{i_1} x_{i_2} - \epsilon_{0i_1, n_2 i_2}]} \right\} = \frac{2}{\pi \Theta} \text{Im} \int_0^{\infty} \frac{d\lambda}{\lambda} \left[\int_{-\infty}^{+\infty} d\epsilon f(\epsilon) Sp Y_{0i_1, n_2 i_2}^e(\epsilon, \lambda) + \int_{-\infty}^{+\infty} d\epsilon \frac{1}{2} \text{cth} \left(\frac{\epsilon}{2\Theta} \right) Sp Y_{0i_1, n_2 i_2}^f(\epsilon, \lambda) \right] - w_{0i_1, n_2 i_2}^2 / \Theta, \tag{32}$$

where

$$\begin{aligned} Y_{0i_1, n_2 i_2}(\epsilon, \lambda) &= X_{0i_1, n_2 i_2}^{(2)AA}(\epsilon, \lambda) - X_{0i_1, n_2 i_2}^{(2)AB}(\epsilon, \lambda) - \\ &- X_{0i_1, n_2 i_2}^{(2)BA}(\epsilon, \lambda) + X_{0i_1, n_2 i_2}^{(2)BB}(\epsilon, \lambda), \\ X_{0i_1, n_2 i_2}^{e(2)\lambda_1 \lambda_2}(\epsilon, \lambda) &= (w \lambda_1^{0i_1}(\lambda) + h_{ef}^{\lambda_1 0i_1}(\epsilon, \lambda)) \times \\ &\times \tilde{G}^{aa^+}(\epsilon, \lambda) (t^{e\lambda_2 n_2 i_2}(\epsilon, \lambda) + T^{e(2)\lambda_1 \lambda_2}(\epsilon, \lambda) \tilde{G}^{aa^+}(\epsilon, \lambda) + \\ &+ \left(w \lambda_2^{n_2 i_2}(\lambda) + h_{ef}^{\lambda_2 n_2 i_2}(\epsilon, \lambda) + \frac{1}{N} \Sigma_{ee}^A(\epsilon, \lambda) + \right. \\ &+ \left. \frac{1}{N} \Sigma_{ee}(\epsilon, \lambda) \right) \tilde{G}^{aa^+}(\epsilon, \lambda) T_{0i_1, n_2 i_2}^{e(2)\lambda_1 \lambda_2}(\epsilon, \lambda) \tilde{G}^{aa^+}(\epsilon, \lambda), \\ X_{0i_1, n_2 i_2}^{f(2)\lambda_1 \lambda_2}(\epsilon, \lambda) &= \left(\frac{\epsilon^2}{\hbar^2} \Delta M \lambda_1^{0i_1}(\lambda) + h_{\Delta\Phi}^{\lambda_1 0i_1}(\lambda) \right) \times \\ &\times \tilde{G}^{uu}(\epsilon, \lambda) (t^{f\lambda_2 n_2 i_2}(\epsilon, \lambda) + T_{0i_1, n_2 i_2}^{f(2)\lambda_1 \lambda_2}(\epsilon, \lambda)) \times \\ &\times \tilde{G}^{uu}(\epsilon, \lambda) + \left(\frac{\epsilon^2}{\hbar^2} \Delta M \lambda_2^{n_2 i_2}(\lambda) + h_{\Delta\Phi}^{\lambda_2 n_2 i_2}(\epsilon, \lambda) + \right. \\ &+ \left. \frac{1}{N} \Sigma_{ff}(\epsilon, \lambda) \right) \tilde{G}^{uu}(\epsilon, \lambda) T_{0i_1, n_2 i_2}^{f(2)\lambda_1 \lambda_2}(\epsilon, \lambda) \tilde{G}^{uu}(\epsilon, \lambda), \end{aligned}$$

$$w_{0i_1, n_2 i_2}^{(2)} = w_{0i_1, n_2 i_2}^{AA} - w_{0i_1, n_2 i_2}^{AB} - w_{0i_1, n_2 i_2}^{BA} + w_{0i_1, n_2 i_2}^{BB},$$

$w_{0i_1, n_2 i_2}^{\lambda_1 \lambda_2} = \frac{Z_{\lambda_1} Z_{\lambda_2} e^2}{4 \pi \epsilon_0 |\vec{r}_{0i_1} - \vec{r}_{n_2 i_2}|}$ is the interaction energy of two ions with the valencies $Z_{\lambda_1}, Z_{\lambda_2}$, which equal the numbers of electrons in the considered energy bands of the components λ_1, λ_2 of the alloy.

The Fermi level μ_e is determined from the equation

$$\langle Z \rangle = \int_{-\infty}^{\infty} f(\epsilon, \mu_e) g_e(\epsilon) d\epsilon, \quad (33)$$

where $g_e(\epsilon)$ is given by (17). $\langle Z \rangle = \langle N_e \rangle / vN$ is the average number of electrons per atom, $\langle Z \rangle = c^A Z_A + c^B Z_B$; Z_A, Z_B are the numbers of electrons per atom in the considered energy bands of components A, B of the alloy.

The equilibrium values of the interatomic correlation parameters can be applied to the calculation and analysis of the X-ray diffraction scattering. The diffraction scattering intensity for disordered solutions in neglecting the distortions and oscillations of the crystal lattice is

$$I(\mathbf{q}) = N(f_A - f_B)^2 \left[xy + \sum_{m \neq 0} \epsilon_{0m} \cos(\mathbf{q}\mathbf{r}_m) \right], \quad (34)$$

where f_A, f_B are the atomic scattering factors of atoms A and B , respectively; \mathbf{r}_m is the radius-vector of the crystal lattice site; \mathbf{q} is the scattering vector.

Conclusions

The obtained results allow one to take into account the influence of strong electronic correlations on the electronic structure and properties of transition metals' alloys with narrow energy bands.

For this purpose, we account the inhomogeneous distribution of the electronic density by assuming that in the free energy of a system F (29), the number of electrons $Z_{ni\gamma\sigma}^{m_{\lambda i}}$ in a state $(ni\gamma\sigma)$, i.e. the number of electrons per atom at the site (ni) for the energy band γ and the spin projection σ , depends on the sort of an atom (λ) and the local magnetic moment $m_{\lambda i}$ at the given site (ni) . The value $Z_{ni\gamma\sigma}^{m_{\lambda i}}$ is determined by (33), in which the density of electronic states $g_e(\epsilon)$ is replaced by the conditional partial density of states $g_{ni\gamma\sigma}^{m_{\lambda i}}(\epsilon)$ for the energy band γ and the spin projection σ . The density of states

$$g_{ni\gamma\sigma}^{m_{\lambda i}}(\epsilon) = -\frac{1}{\pi} \text{Im} \langle G_{ni\gamma\sigma, ni\gamma\sigma}^{aa+}(\epsilon) \rangle \Big|_{(ni) \in m_{\lambda i}},$$

in which the average will be carried out under the condition that, at a site (ni) , the sort of an atom is λ and the projection of the localized magnetic moment of electrons is $m_{\lambda i}$. If we denote the probability of a

specified event through $P_{ni}^{m_{\lambda i}}$, it is possible to write $\sum_{\lambda, m_{\lambda i}} P_{ni}^{m_{\lambda i}} = 1$.

It is possible also to write the equations

$$Z_{\lambda i \gamma} = Z_{ni\gamma\sigma}^{m_{\lambda i}} + Z_{ni\gamma-\sigma}^{m_{\lambda i}}, \quad m_{\lambda i \gamma} = Z_{ni\gamma\sigma}^{m_{\lambda i}} - Z_{ni\gamma-\sigma}^{m_{\lambda i}}, \quad (35)$$

where $Z_{\lambda i} = \sum_{\gamma} Z_{\lambda i \gamma}$, $m_{\lambda i} = \sum_{\gamma} m_{\lambda i \gamma}$ are, accordingly, the number of electrons and the value of the α -projection of the magnetic moment of an atom of the sort λ at the site (ni) .

It follows from (35) that, together with fluctuations of the localized magnetic moment $m_{\lambda i}$, there can be fluctuations of the charge density $Z = \frac{1}{v} \sum_{\lambda, i} c_i^{\lambda} Z_{\lambda i}$ in the system relatively to the averaged value $\langle Z \rangle$ (33).

From (35), we have

$$Z_{ni\gamma\sigma}^{m_{\lambda i}} = \frac{Z_{\lambda i \gamma} + m_{\lambda i \gamma}}{2}, \quad Z_{ni\gamma-\sigma}^{m_{\lambda i}} = \frac{Z_{\lambda i \gamma} - m_{\lambda i \gamma}}{2}.$$

The fluctuations of the localized magnetic moment $m_{\lambda i}$ arise at rather large values of the potential of Coulomb repulsion of electrons with opposite spins at one site $\tilde{v}_{ni\gamma\sigma, ni\gamma-\sigma}^{(2)ni\gamma\sigma, ni\gamma-\sigma}$ in the mass operator of the electron-electron interaction $\Sigma_{ee}(\epsilon)$, which occurs in the case of transition metals with narrow energy bands.

In the one-band approximation, these effects are described by the Hubbard model well known in the theory of magnetism, which takes into account the Coulomb repulsion of electrons with opposite spins at one site and the interaction of electrons at the nearest sites. The configuration entropy of an alloy S_c in (29) is determined by the probabilities of the distribution of atoms and localized magnetic moments over lattice sites (ni) in the correspondence with (30), where it is necessary to make the replacement $\lambda \rightarrow m_{\lambda i}$, $\sum_{\lambda} (...) \rightarrow \sum_{\lambda, m_{\lambda i}} (...)$.

The projections of the localized magnetic moments $m_{\lambda i}$ and the parameters of correlations in a disposition of atoms and the orientation of magnetic moments at lattice sites are determined from the condition of minimum of the free energy F (29).

As an example, we calculated the free energy F given by Eq. (29), localized magnetic moments, and correlation parameters for the atom arrangement and the orientation of magnetic moments at sites of the bcc lattice for the equiatomic alloy Fe-Co. Fig. 1 shows the density of electron states $g_e(\epsilon)$ given by Eq. (17) for the Fe-Co alloy at temperatures $T = 0$ K and

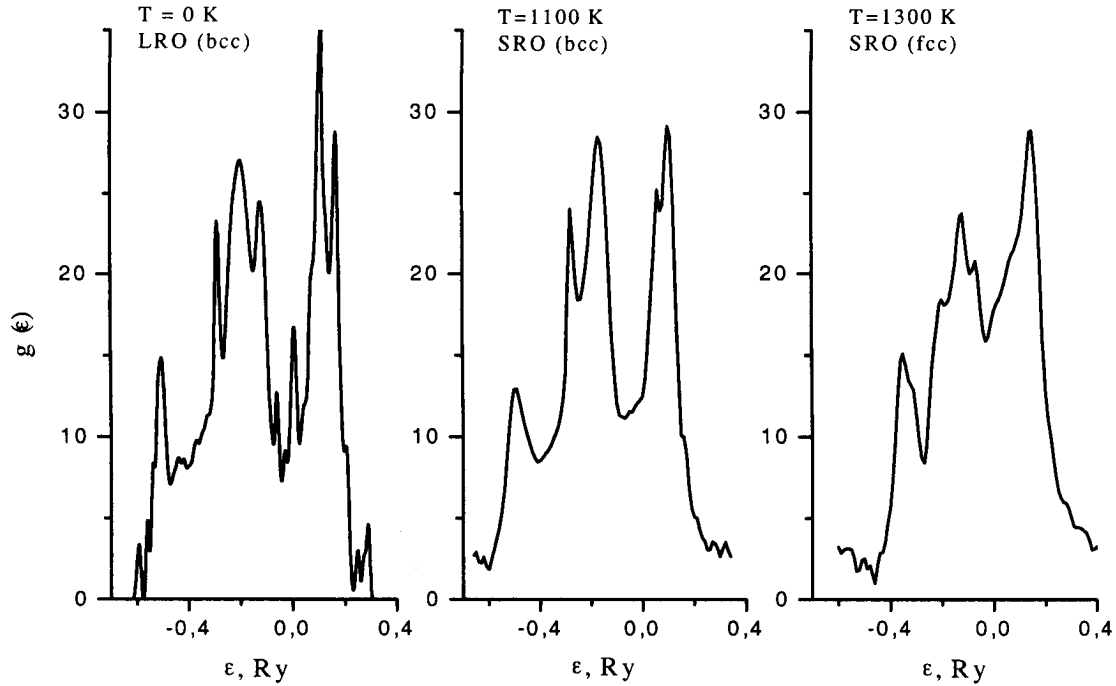


Fig. 1. Density of electron states for a Fe⁻Co alloy

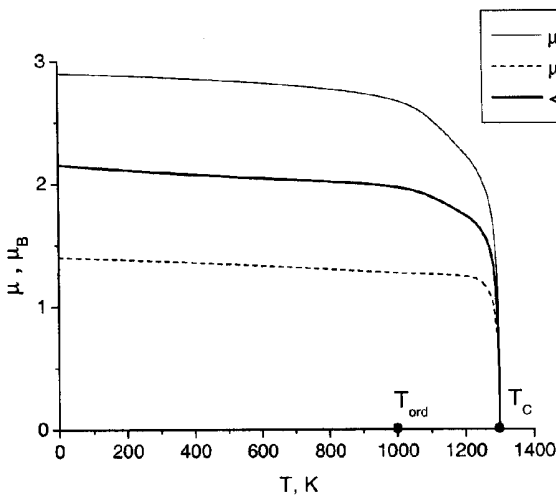


Fig. 2. Temperature dependence of localized magnetic moments

$T = 1100$ K and for a paramagnetic Fe⁻Co alloy with the fcc lattice at $T = 1300$ K.

The matrix elements of Hamiltonian (1) in the multiband s - p - d tight-binding model were calculated using the wave functions and the potentials of isolated atoms through the Slater - Coster method [29], [30]. The basis was orthogonalized using the Löwdin method [31]. For simplicity, we carried out the calculations without taking the lattice vibrations into account. Only

the terms corresponding to the Coulomb repulsion of electrons in the d state with opposite spins at the same site, i.e., the terms in $\Sigma_{e n i d \sigma, n i d \sigma}^{(1)}(\epsilon)$ that depend on the number of the same site ($n i$), were taken into account in the electron-electron interaction mass operator $\Sigma_{e e}(\epsilon)$. This means that the statistical fluctuations of the charge density and the spin density in the one-site approximation described above were taken into account, while the dynamic fluctuations, in particular, the waves of the charge density and the spin density described by the nondiagonal (with respect to the site number ($n i$)) matrix elements of $\Sigma_{e e}(\epsilon)$ were neglected. We also assumed that the projection of the magnetic moment of an atom of the sort λ takes two values $m_{\lambda} = \pm \mu_{\lambda}$.

As was noted, the equilibrium values of localized magnetic moments, parameters of interatomic correlations ($\epsilon_{0 i_1, n_2 i_2}^a, \eta^a$), and correlations in the orientation of magnetic moments ($\epsilon_{0 i_1, n_2 i_2}^m, \eta^m$) are determined from the minimum condition of the free energy F . The correlation parameters of nearest neighbors were accounted for two coordination spheres and denoted as $\epsilon_1 = \epsilon_{01,02}$ and $\epsilon_2 = \epsilon_{01,11}$.

The temperature dependence of the localized magnetic moments and correlation parameters is presented in Figs. 2 and 3, that are connected with changes in the electron energy spectrum during the ordering and changes in the filling of electron states.

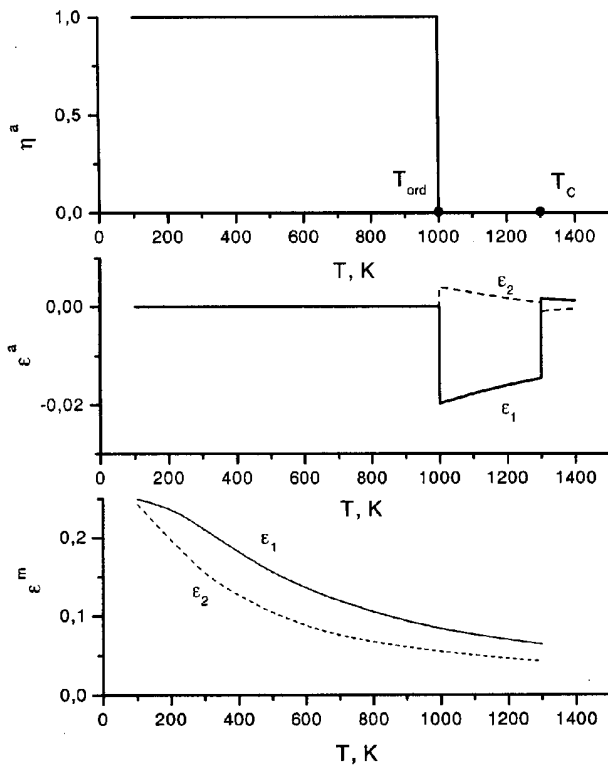


Fig. 3. Temperature dependence of correlation parameters

The well-known Heisenberg model does not take these effects into account.

The positive sign of the parameters of correlations in the orientations of magnetic moments at $T = 0$ K and $T = 1100$ K (see Fig. 3), according to their definition, corresponds to the ferromagnetic phase. The values of the localized magnetic moments and the parameters of correlations decrease with increase of temperature up to the Curie temperature T_C . The calculated temperature for the phase order-disorder transition $T_{ord} = 1000$ K and the Curie temperature $T_C = 1300$ K are in good agreement with experimental data.

Our results suggest possible ways to generalize the one-band Hubbard model well known in the theory of magnetism to describe the influence of strong electron correlations on the electron structure and properties of disordered alloys of transition metals with narrow energy bands.

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