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LOCAL SPIN DENSITY FUNCTIONAL APPROACH TO THE THEORY OF EXCHANGE INTERACTIONS IN FERROMAGNETIC METALS AND ALLOYS

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Rigorous expressions for the exchange parameters of classical Heisenberg model applied to crystals are obtained using a local spin density functional (LSDF) approach and KKR-Green functions formalism. The spin wave stiffness constant and Curie temperature (T_c) of ferromagnetic metals are obtained without any model assumptions as to the character of exchange interactions. The concentration dependence of T_c for binary ferromagnetic alloys is investigated in the framework of the single-site CPA-theory. The corresponding calculations are carried out for simple metals Fe, Ni and disordered Ni–Pd alloys.

1. Introduction

Recently significant progress has been achieved in the understanding of the magnetic nature of transition metals in the scope of spin-fluctuation theories [1-5]. It has been shown that the main contributions to thermodynamic properties of the itinerant-electron magnets originate from collective spin excitations which may be connected with the local magnetic moment rotations. However, the calculations of these excitations are based, up to now, on some model assumptions (single-band Hubbard Hamiltonian, "static approximation" etc.), which do not allow consideration of these approaches as the basis for quantitative magnetic theory. Oguchi et al. [6], Gyorffy et al. [7] and Oswald et al. [8] have attempted to calculate the exchange interactions and the thermodynamic properties of crystals based on the real electronic structure.

Unfortunately, the basic assumptions used were that the exchange interactions in metals could be described by the usual quantum Heisenberg Hamiltonian [6]. Also, the exchange parameters J_{ij}, calculated in these works are only the sums of one-electron energies, and should be considered as being only approximate for the total energy differences in the framework of the local spin density functional [9,10]. Therefore, the KKR-Green function calculations of indirect spin interactions between two magnetic impurity atoms in Cu and Ag matrices [8] show strong dependence of exchange parameter on magnetic configurations. Thus, the estimation of these quantities in terms of the total energy differences between ferro- and antiferromagnetic configurations [11] give only some averaged values. Note also, that only paramagnetic states of metals were considered [6,7], and generalization of these treatments to the ferromagnetic ground states is not a straightforward one.

In the present paper we discuss the meaning of the exchange parameter J_{ij} usually introduced for magnetic metals and their alloys, obtain the rigorous expressions for J_{ij} in LSDF approach and propose the methods for calculation of spin wave stiffness constants and Curie temperatures. The expressions for J_{ij} are applicable for any crystal ground state magnetic configurations.

Applicability of the approach developed is illustrated taking the results of real space Green function calculations for Fe, Ni metals and disordered Ni–Pd alloys.

2. Exchange parameters and spin-wave stiffness

It is common practice to consider magnetic properties of metals and alloys with the local magnetic moments in the framework of quantum Heisenberg model. However, in this way, one faces a number of difficulties such as the non-integral values of the magnetic moments M (in terms of the Bohr magneton), the strong dependence of M on the local environment, and the type of magnetic ordering in the crystal [12,13]. These effects are mainly connected with the essentially itinerant character of d-electrons even in the metals where magnetic moments may be considered to be localized [14]. Spin fluctuation theories [3,15] show that only an effective classical Heisenberg Hamiltonian can be introduced for metals:

$$H_{\mathrm{ex}} = -\sum_{ij}{}' J_{ij} \boldsymbol{e}_i \cdot \boldsymbol{e}_j \tag{1}$$

($\boldsymbol{e}_i$ is the unit vector in the direction of the ith site magnetization, J_{ij} are the exchange parameters), and Hamiltonian (1) is applicable only for small spin deviations from the ground state. The expression (1) can be considered as the phenomenological exchange energy of weakly inhomogeneous spin density distributions [16,17], when the inhomogeneous character of the spin density is not small, the dependence of J_{ij} on the magnetic configuration is not negligible. Therefore, the definition of J_{ij} through the difference of the energies of pair atoms in ferro- and antiferromagnetic configurations, as it was ordinary proposed [6,8], does not seem correct anymore. This limitation is not very severe for the magnetic insulator, where J_{ij} appears to be almost constant for any magnetic configurations [6].

Our purpose is to find a way for first-principle calculations of J_{ij} basing on LSDF approach. The most suitable version of the band theory in order to obtain the exchange energy (1) is the multiple scattering technique with the MT-form of potential (the KKR-Green function method). The spin-dependent electron density $\rho_\sigma(\boldsymbol{r})$, ($\sigma = \uparrow, \downarrow$) is written then as the sum over non-overlapped WS-cells Ω_i

$$\rho_\sigma(\boldsymbol{r}) = \sum_i \rho_{i\sigma}(\boldsymbol{r} - \boldsymbol{R}_i). \tag{2}$$

Then the magnetic moment for the ith "site" in the ferromagnetic state is defined by the relation

$$M_i = \int_{\Omega_i} \mathrm{d}\boldsymbol{r} \left[\rho_{i\uparrow}(\boldsymbol{r}) - \rho_{i\downarrow}(\boldsymbol{r})\right]. \tag{3}$$

In order to determine the exchange parameters J_{ij} one must calculate the total energy variation δE for small deviations of some magnetic moments from the ground-state magnetic configuration. For example, considering the local magnetic excitation connected with the rotation of one spin moment at site 0 on the angle θ from the ferromagnetic state one can determine the effective exchange parameter J_0 for the interactions of atom under consideration with the whole crystal. The Eq. (1) in this case results in the expression:

$$\begin{aligned} \delta E_0 &= 2\sum_j J_{0j}(1-\cos\theta) \approx J_0\theta^2, \\ J_0 &= \sum_j J_{0j}. \end{aligned} \tag{4}$$

The pair interaction parameters J_{ij} may be determined from the rotation energy of two spin moments at sites i and j on opposite angles $\pm\theta/2$. It is also necessary to subtract interaction energies of the ions i and j with the environment:

$$\begin{aligned} \delta E'_{ij} &= \delta E_{ij} - \delta E_i - \delta E_j \\ &= J_{ij}(1-\cos\theta) \approx \tfrac{1}{2} J_{ij}\theta^2. \end{aligned} \tag{5}$$

Thus, the first principle determination of exchange parameters is reduced to the calculations of total energy variations for the whole crystal corresponding to small spin density perturbations. The total energy calculation in the LSDF approach is rather complicated [13]. Fortunately, we are only interested in small perturbations from the ground state and therefore Andersen's "local force theorem" [18–20] may be successfully used (its extension for the spin-polarised case is given in appendix A). According to this theorem the total energy variation δE coincides with the sum of one-particle energy changes for the occupied states at the fixed ground state potential. In the first order on the perturbations of the charge and spin densities one can find the following relation:

$$\delta E = \int^{\epsilon_F} \mathrm{d}\epsilon\, \epsilon\, \delta n(\epsilon) = \epsilon_F\, \delta z - \int^{\epsilon_F} \mathrm{d}\epsilon\, \delta N(\epsilon)$$
$$= -\int^{\epsilon_F} \mathrm{d}\epsilon\, \delta N(\epsilon). \qquad (6)$$

here $n(\epsilon) = \mathrm{d}N/\mathrm{d}\epsilon$ is the density of electron state, ϵ_F is the Fermi energy. In the case of magnetic excitation the change of total number of electrons δz equals zero.

The rotation of ith site magnetization can be found through the change of the one-particle density matrix [6,7,21]

$$\hat\rho_i = \tfrac{1}{2}(\rho_{i\uparrow} + \rho_{i\downarrow}) \times \hat 1 + \tfrac{1}{2}(\rho_{i\uparrow} - \rho_{i\downarrow}) \times (\boldsymbol{e}_i \cdot \boldsymbol{\sigma}), \qquad (7)$$

where $\hat 1$ is the unit 2×2 matrix, $\boldsymbol{\sigma}$ are Pauli matrices.

At the perturbation corresponding to the rotation of the site 0 magnetic moment on a small angle θ from ferromagnetic configuration the charge density $n(\boldsymbol{r})$ is not changed, whereas the variation of the spin density $m(\boldsymbol{r})$ is of the order of θ^2:

$$\delta m(\boldsymbol{r}) = \delta\, \mathrm{Tr}\,|\hat{\boldsymbol{\sigma}}\hat{\boldsymbol{\rho}}(\boldsymbol{r})| \approx \delta\rho_{\uparrow\uparrow}(\boldsymbol{r}) - \delta\rho_{\downarrow\downarrow}(\boldsymbol{r}) + \frac{2\,\delta\rho_{\uparrow\downarrow}(\boldsymbol{r})\,\delta\rho_{\downarrow\uparrow}(\boldsymbol{r})}{|\rho_{\uparrow\uparrow}(\boldsymbol{r}) - \rho_{\downarrow\downarrow}(\boldsymbol{r})|}. \qquad (8)$$

In order to find $\delta N(\epsilon)$ in eq. (6) corresponding to spin moment rotations on site $i = 1, 2, \ldots, n$, we use the multiple scattering approach [22,23].

According to Lloyd's formula [22]

$$N(\epsilon) = N_0(\epsilon) + \frac{1}{\pi}\,\mathrm{Im\,Tr\,ln}\,\hat T(\epsilon). \qquad (9)$$

The scattering path operator $\hat T$ is formally expressed in the usual way [23]:

$$(\hat T^{-1})^{ij}_{L\sigma,L'\sigma'} = t^{-1}_{iL\sigma\sigma'}\delta_{ij}\delta_{LL'} - G^{ij}_{LL'}\delta_{\sigma\sigma'}, \qquad (10)$$

here t is the single site scattering matrix [22].

Let us define the scattering path operator corresponding to the perturbed state ($\hat T'$) in the following form [24]:

$$\hat T' = \hat T(1 + \delta\hat t^{-1} \cdot \hat T)^{-1}, \qquad (11)$$

where

$$\delta\hat t^{-1} = \begin{cases} \hat t_i'^{-1} - \hat t_i^{-1}, & i = 1, 2, \ldots, n, \\ 0, & \text{otherwise.} \end{cases}$$

Here $\hat t$ and $\hat T$ are evaluted for the ground state. Substitution of eqs. (9) and (11) in (6) results in the following expression:

$$\delta E = \frac{1}{\pi}\int^{\epsilon_F} \mathrm{d}\epsilon\; \mathrm{Im\,Tr\,ln}(1 + \delta\hat t^{-1} \cdot \hat T). \qquad (12)$$

In order to find $\delta\hat t^{-1}$-matrix one uses the spinor structure of the scattering t-matrix [6,7], which is similar to eq. (7):

$$\hat t_i = \tfrac{1}{2}(\hat t_{i\uparrow} + \hat t_{i\downarrow}) \times \hat 1 + \tfrac{1}{2}(\hat t_{i\uparrow} - \hat t_{i\downarrow}) \times (\boldsymbol{e}_i \cdot \hat{\boldsymbol{\sigma}}). \qquad (13)$$

Hence

$$\delta\hat t_i^{-1} = \tfrac{1}{2}\left(\hat t_{i\uparrow}^{-1} - \hat t_{i\downarrow}^{-1}\right) \times (\delta\boldsymbol{e}_i \cdot \hat{\boldsymbol{\sigma}}). \qquad (14)$$

Let us consider the rotation of one spin moment at the site 0:

$$\delta\boldsymbol{e}_0 = (\sin\theta,\ 0,\ \cos\theta - 1),$$

then

$$\delta\hat t^{-1} = \tfrac{1}{2}\delta_{i0}\left(\hat t_{i\uparrow}^{-1} - \hat t_{i\downarrow}^{-1}\right) \times \begin{pmatrix} \cos\theta - 1 & \sin\theta \\ \sin\theta & 1 - \cos\theta \end{pmatrix}. \qquad (15)$$

Using the condition $\mathrm{Tr\,ln}\,\hat T = \mathrm{ln\,det}\,\hat T$, and the fact that

$$\det{}_{iL\sigma}(1 + \delta\hat t^{-1} \cdot \hat T) = \det{}_{L\sigma}(1 + \delta\hat t_0^{-1} \cdot \hat T^{00})$$

one may calculate the determinant in eq. (12) in the spin space. Taking into account that in the ground ferromagnetic state

$$\hat T^{00} = \begin{pmatrix} \hat T^{00}_{\uparrow} & 0 \\ 0 & \hat T^{00}_{\downarrow} \end{pmatrix} \qquad (16)$$

we obtain:

$$\delta E_0(\theta) = \frac{1}{2\pi}\int^{\epsilon_F} \mathrm{d}\epsilon\; \mathrm{Im\,Tr}_L\,\mathrm{ln} \times \left\{1 - \tfrac{1}{2}\left[\Delta_0\left(\hat T^{00}_{\uparrow} - \hat T^{00}_{\downarrow}\right) + \Delta_0\hat T^{00}_{\uparrow}\Delta_0\hat T^{00}_{\downarrow}\right](1 - \cos\theta)\right\}, \qquad (17)$$

where $\Delta_i = (\hat{t}_{i\uparrow}^{-1} - \hat{t}_{i\downarrow}^{-1})$, Tr_L is the trace over the orbital variables of scattering matrices. It is worthwhile to note that eq. (17) is valid only in the first order of magnitude in $\delta m \sim \theta^2$. Therefore, the expanding of eq. (17) in the series up to θ^2 and comparison the result with the eq. (4) lead to the relation:

$$J_0 = -\frac{1}{4\pi}\int^{\epsilon_F} \mathrm{d}\epsilon \ \mathrm{Im}\ \mathrm{Tr}_L\left\{\Delta_0\left(\hat{T}_\uparrow^{00} - \hat{T}_\downarrow^{00}\right) + \Delta_0\hat{T}_\uparrow^{00}\Delta_0\hat{T}_\downarrow^{00}\right\}. \tag{18}$$

Note that eq. (18) gives the expression for the effective exchange interaction parameter of the spin moment at site 0 with the whole magnetic crystal. In the one-site limit ($T^{00} = t_0$, $G^{ij} = 0$) one has $J_0 = 0$. Therefore J_0 is determined by the interatomic interactions. It should be noted that the exchange parameter J_0 is not simply proportional to the spin splitting of the energy bands, which is mainly connected with the intra-atomic exchange interaction [25].

Considering in the same way the rotation of two magnetic moments on the sites i and j on the opposite angles $\pm\theta/2$ (see appendix B) and compare the result with the eq. (5) we get:

$$J_{ij} = \frac{1}{4\pi}\int^{\epsilon_F} \mathrm{d}\epsilon \ \mathrm{Im}\ \mathrm{Tr}_L\left\{\Delta_i\hat{T}_\uparrow^{ij}\Delta_j\hat{T}_\downarrow^{ji}\right\}. \tag{19}$$

This formula gives the expression for the pair exchange interaction parameter in the classical Heisenberg model (1). It is interesting to trace the connection between J_0 and J_{ij}. Using the relation:

$$\left(\hat{T}_\uparrow^{-1} - \hat{T}_\downarrow^{-1}\right)_{ij} = \Delta_i\delta_{ij} \tag{20}$$

which follows from eq. (10), one may obtain:

$$\hat{T}_\uparrow^{00} - \hat{T}_\downarrow^{00} = -\sum_j \hat{T}_\uparrow^{0j}\Delta_j\hat{T}_\downarrow^{j0}. \tag{21}$$

Substitution of eq. (21) into eq. (18) and taking into account eq. (19) results in:

$$J_0 = \sum_{j\neq 0} J_{0j} \tag{22}$$

which is in agreement with eq. (4) and confirms sufficient correctness of the classical Heisenberg model (1) for small spin deviations. The physical meaning of the parameter will be disscussed in section 3.

The real elementary excitations connected with spin rotations are spin waves. In order to calculate the energy of a classical spin spiral $E(\boldsymbol{q})$ we choose θ_i in the form $\theta_i = \boldsymbol{q}\cdot\boldsymbol{R}_i$, $\boldsymbol{q}$ being the wave vector. For $\boldsymbol{q} \to 0$ the corresponding spin density perturbation is small: $\delta m \sim \boldsymbol{q}^2$ therefore one may use the local force theorem to calculate the spin wave stiffness tensor, which is determined in the phenomenological theory [16,17] by the following expression:

$$D_{\alpha\beta} = \frac{2}{M}\frac{\partial^2 E}{\partial q_\alpha \partial q_\beta}, \tag{23}$$

The corresponding calculations results in the formula [26]:

$$D_{\alpha\beta} = \frac{1}{2\pi M}\int^{\epsilon_F} \mathrm{d}\epsilon \ \mathrm{Im}\ \mathrm{Tr}_L \sum_{\boldsymbol{k}} \Delta\frac{\partial\hat{T}_\uparrow^{\boldsymbol{k}}}{\partial k_\alpha}\Delta\frac{\partial\hat{T}_\downarrow^{\boldsymbol{k}}}{\partial k_\beta} = \frac{2}{M}\sum_j J_{0j}R_{j\alpha}R_{j\beta}, \tag{24}$$

where $\boldsymbol{R}_j$ is the lattice vector, $\hat{T}_\sigma^{\boldsymbol{k}}$ is the scattering path operator for the crystal in the $\boldsymbol{k}$-representation, the summation over $\boldsymbol{k}$ is carried out over the Brillouin zone. Eq. (24) is consistent with the Heisenberg model (1) which gives the following result:

$$E(\boldsymbol{q}) = \sum_j J_{0j}\left\{1 - \exp\left(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_j\right)\right\}, \tag{25}$$

where J_{0j} is determined by eq. (19).

It should be noted that in order to find any other contributions to the spin-wave spectrum (of the order of $\boldsymbol{q}^4$, $\boldsymbol{q}^6$, ..., etc.) it is necessary to make the self-consistent total-energy calculation for the spin spiral [20], and eq. (25), generally speaking, is not correct any longer.

3. The Curie temperature

As is shown in section 2 it is not quite difficult to calculate the characteristics of magnetic excitations in framework of LSDF approach for the temperature $T=0$. However, the consideration of the finite temperature case meets serious difficulties [7]. A correct expression for the temperature dependence of the exchange-correlation functional (which seems to be determined by complicate processes of spin fluctuation interactions [4] rather than Fermi distribution functions) is not known yet. Therefore, the theory of itinerant electron magnetism at finite temperature cannot be formulated so far with the same accuracy as that for $T=0$. Here we present the approximate method of calculation of the Curie temperature T_c, which is some development of Slater's magnetic transition state approach [25], generalized earlier by us for the case of metals [27].

We start with the generalized mean field scheme and write the energy E of magnetic moment M at the given site in the following form:

$$E = -\boldsymbol{h}\cdot\boldsymbol{M}, \tag{26}$$

where $\boldsymbol{h}=\lambda\langle\boldsymbol{M}\rangle$ and λ is the mean field parameter. The critical temperature T_c is determined by the condition of the appearance of nontrivial solutions of self-consistent equations:

$$\langle\boldsymbol{M}\rangle = \frac{\operatorname{Tr}\boldsymbol{M}\exp\{(1/T)(\boldsymbol{h}\cdot\boldsymbol{M})\}}{\operatorname{Tr}\exp\{(1/T)(\boldsymbol{h}\cdot\boldsymbol{M})\}}. \tag{27}$$

It results in the relation:

$$T_c = \lambda\langle\boldsymbol{M}^2\rangle/3, \tag{28}$$

where λ, $\langle\boldsymbol{M}^2\rangle$ is calculated at $T=T_c$. The parameter λ is connected with the energy of local spin excitations considered in section 2:

$$E(\theta) = -\lambda M_0^2\cos\theta, \tag{29}$$

here M_0 is the site 0 moment value at $T=0$. If we consider ferromagnetic crystal with well-defined local magnetic moments, λ, $\langle\boldsymbol{M}^2\rangle$ and M show to be weakly temperature dependent (according to Pindor et al. [21] this is a good approximation for iron but rather a bad one for nickel), thus, assuming that $\lambda(T=T_c)\approx\lambda(T=0)$ and comparing eq. (29) with eq. (5) one obtains:

$$\lambda = 2J_0/M_0^2, \tag{30}$$

J_0 is determined by eq. (18). Substituting eq. (30) for eq. (28) results in

$$T_c = \tfrac{2}{3}J_0\eta. \tag{31}$$

The factor $\eta=\langle\boldsymbol{M}^2\rangle/M_0^2$ (which equals $(S+1)/S$ in the Heisenberg model) takes into account the quantum nature of spin moment. This quantum factor cannot be calculated exactly in one-electron LSDF approach, because $\langle\boldsymbol{M}^2\rangle$ is expressed in terms of four-fermion averages on the site [28]. It should be noted that the change $\eta\to 1$ in expression (31) (corresponds to classical spin statistics) improves the agreement between the theory and experiment significantly [7,28]. Probably it is just the result of mutual cancellation of various effects (such as temperature dependence of J_0, M, errors in expressions for η and for T_c in the mean-field approximation). Therefore we use $\eta=1$ in this paper (as Gyorffy et al. [7], in contrast with our previous work [28].

Let us compare the approach proposed with the magnetic transition state method by Slater [25] (note that Hubbard [3] used similar scheme in his calculation of T_c in the functional integral method). According to this model, in order to calculate T_c it is necessary to find the energy of spin flip on a given site. This energy reduces to the difference of the sums of one-electron energies in the magnetic transition state only approximately [25]. The approach proposed here is based on the calculation of the energy variation at small spin deviations, so one may use the rigorous LSDF-scheme local force theorem. Besides that, it is possible to take into account also the case when the value of exchange interactions themselves depends on the spin configuration. For magnetics with rather badly defined local magnetic moments it is more accurate to calculate values involving, in eq. (31), for the paramagnetic phase by means of the KKR-CPA method for a random spin configuration [6,7,21]. Then one should substitute the single-site CPA-expressions for the off-diagonal T-matrix [29]:

$$\begin{aligned}\hat{T}^{ij} = {} & \left[1+\hat{T}_c^{00}\left(\hat{t}_i^{-1}-\hat{t}_c^{-1}\right)\right]^{-1}\\ & \times T_c^{ij}\left[1+\left(\hat{t}_j^{-1}-\hat{t}_c^{-1}\right)\hat{T}_c^{00}\right]^{-1}\end{aligned} \tag{32}$$

in eq. (19) in order to find J_{ij} and then J_0 through eq. (22). Here $\hat{t}_c$ and $\hat{T}_c$ are the effective scattering matrices for the paramagnetic state. It is interesting to note, that the expression for J_{ij} obtained in this approximation (eqs. (19) and (32)) coincides (after some manipulations) with the J_{ij} defined by eq. (6) in the paper by Oguchi et al. [7]. Furthermore the formulae for J_{ij} obtained by Gyorffy et al. [7] for the paramagnetic state reduce to the same expressions, provided that only single-site terms in derivatives of t_c are used.

4. Ferromagnetic alloys

The approach developed here may be generalized for the case of binary ferromagnetic alloys. We suppose that the electronic Green functions for the disordered system A_cB_{1-c} (c – concentration) is calculated making use of the single-site KKR-CPA scheme [23,29]. In order to estimate the temperature of the magnetic phase transition one may use the mean-field approximation for classical spin statistics (section 3):

$$T_{\text{Curie}}(c) = \tfrac{2}{3} J_0(c), \quad J_0(c) = \left.\frac{\mathrm{d}^2 E(c)}{\mathrm{d}\theta^2}\right|_{\theta=0}, \tag{33}$$

here $E(c)$ is the total LSDF-energy of ferromagnetic alloy, θ is an angle of magnetization rotation on the given site. It has been shown in section 2 that spin-density variation from ferromagnetic state is of the order of θ^2 in this case. Therefore local force theorem (eq. (6)) may be used in calculations of $J_0(c)$. For this purpose we wrote the well-known formula for alloy's integrated density of states by Gyorffy and Stocks [23] in the following "matrix" form:

$$N_c(\epsilon) = cN_A(\epsilon) + (1-c)N_B(\epsilon), \tag{34}$$

where

$$N_i(\epsilon) = N_0(\epsilon) + \frac{1}{\pi} \operatorname{Im} \operatorname{Tr} \ln \hat{T}_i(\epsilon),$$

$$\hat{T}_i(\epsilon) = \hat{T}_c\left\{1 + \left(\hat{t}_i^{-1} - \hat{t}_c^{-1}\right)\hat{T}_c\right\}.$$

here $i = (A, B)$, $\hat{t}_c$ and $\hat{T}_c$ are the effective single-site t-matrix and scattering path operator for binary alloy [23], $\hat{t}_A$ and $\hat{t}_B$ are single-site t-matrices of atom A and B in system A_cB_{1-c}.

The rotation of magnetization at the site 0 results in the change of $\hat{t}_A$ and $\hat{t}_B$ matrices only. From eq. (16) one finds

$$\left.\frac{\partial \hat{t}_i^{-1}}{\partial \theta}\right|_0 = -\tfrac{1}{2}\delta_{i0}\left(\hat{t}_{i\uparrow}^{-1} - \hat{t}_{i\downarrow}^{-1}\right) \cdot \hat{\sigma}_x,$$
$$\left.\frac{\partial^2 \hat{t}_i^{-1}}{\partial \theta^2}\right|_0 = \tfrac{1}{2}\delta_{i0}\left(\hat{t}_{i\uparrow}^{-1} - \hat{t}_{i\downarrow}^{-1}\right) \cdot \hat{\sigma}_z. \tag{35}$$

Calculating the $J_0(c)$ by means of eqs. (33)–(35) leads to:

$$J_0(c) = cJ_A(c) + (1-c)J_B(c), \tag{36}$$

where

$$J_i(c) = -\frac{1}{4\pi}\int^{\epsilon_F} \mathrm{d}\epsilon \operatorname{Im} \operatorname{Tr}_L\left\{\Delta_i\left(\hat{T}_{i\uparrow}^{00} - \hat{T}_{i\downarrow}^{00}\right) + \Delta_i \hat{T}_{i\uparrow}^{00} \Delta_i \hat{T}_{i\downarrow}^{00}\right\}, \quad (i = A, B).$$

The main advantage of eq. (36) is that effective exchange interactions in alloys are expressed through the same scattering matrices as in ordinary single-site CPA-theory. Therefore it is not difficult to estimate the concentration dependence of Curie temperature for binary alloys in the framework of spin-polarized KKR-CPA calculations.

5. Results and discussion

In order to find the exchange interaction parameters for magnetic metals one should carry out the self-consistent band structure calculation of the scattering path operator [6]:

$$T_{LL'}^{ij}(\epsilon) = \sum_{k}\left[t^{-1}(\epsilon) - G(\boldsymbol{k}, \epsilon)\right]_{LL'}^{-1} \times \exp\left\{\mathrm{i}\boldsymbol{k} \cdot \left(\boldsymbol{R}_i - \boldsymbol{R}_j\right)\right\}. \tag{37}$$

An easier way is to calculate $\hat{T}$ in the real space taking into account the finite number of scattering in the free electron gas [30]. Then the scattering path operator is obtained by direct inversion of eq. (10) for finite clusters of atoms. We have used this technique and calculate the exchange interactions in Fe and Ni metals.

The real-space Green function method [30] has been applied to the three-shell clusters in bcc Fe

($FeFe_8Fe_6$) and fcc Ni ($NiNi_{12}Ni_6$). The exchange-correlation functional by Gunnarsson and Lundqvist [10] was used. The crystal potential was constructed by superposition of charge densities for renormalized atoms. The self-consistency for the ground state was achieved according to the s–d configurations of renormalized atoms [31]. It is worth noting that the octahedral point symmetry of the clusters under consideration allows the calculation of J_{ij} from eq. (19) with the symmetrized $\hat{T}$-matrix and to introduce the exchange interaction parameters of the central atom with the first ($z_1 J_1$) and second ($z_2 J_2$) coordination spheres (z_i is the number of atoms in the ith shell). The calculation results for J_1 and J_2 are presented in the table 1 as well as the spin wave stiffness constant D calculated from eq. (24) and Curie temperature T_c. Rather good agreement of calculated values of D with the experimental ones shows that the contribution from the exchange interactions from the larger distances becomes negligible due to their oscillating RKKY-characters [6,32]. In order to study the applicability of the theory presented in the case of disordered alloys we considered the ferromagnetic system Ni_cPd_{1-c} in the whole range of concentrations. The self-consistent spin-polarizaed electronic structure of Ni–Pd alloys was calculated for the three-shell clusters in the framework of KKR-CPA scheme [33]. The total density of states for the Ni-Pd alloy shown in fig. 1 for $c = 0.1$, are compared with the results of band KKR-CPA calculation [34]. The Curie temperature of Ni–Pd alloys was estimated through the expressions (33), (36). The concentration dependence of T_c was shown in fig. 2. The agreement with experimental curve [35] appears to be rather good.

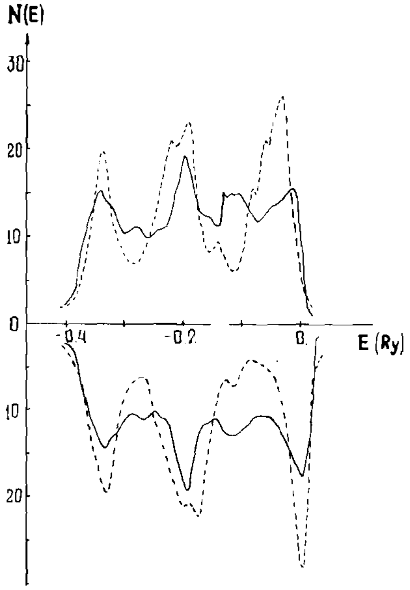

Fig. 1. Total density of states for disordered alloy $Ni_{0.1}Pd_{0.9}$ as calculated by three-shell cluster CPA scheme (dashed line) and KKR-CPA method [34] (full line).

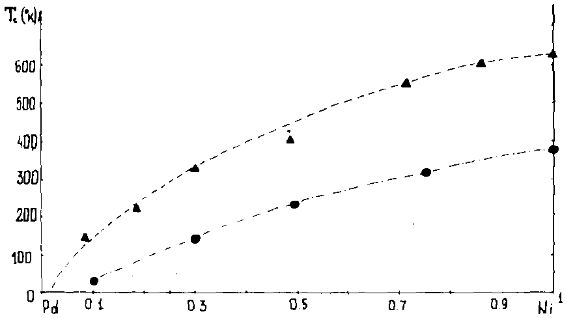

Fig. 2. Concentration dependence of Curie temperature for Ni–Pd alloys as calculated by cluster KKR-CPA method (dots) in comparison with the experimental curve [35] (triangles).

Table 1

Values of exchange interaction parameters calculated by the cluster Green's function method

Metal	J_0 (meV)	T_c (K)	T_c^{expt} (K)	J_1 (meV)	J_2 (meV)	D (meV Å^2)	D^{expt} (meV Å^2)
Fe	155.7	1200	1040 [a]	20.5	−3.4	294	314 [b]
Ni	49.1	380	630 [a]	1.9	0.23	386	395 [c]

[a] J. Crangle and G.M. Goodman, Proc. Roy. Soc. A321 (1971) 477.

[b] M.W. Stringfellow, J. Phys. C1 (1968) 950.

[c] P. Mitchell and D. McK Paul, Phys. Rev. B23 (1985) 3272.

onclusions

The main result of the present paper is the construction of the method for rigorous determination of exchange parameters within the LSDF approach (within the MT-potential model) through the properties of the ground state.

The essential feature of the method developed is the use of the "local force theorem" which allows, in the one-hand, to justify the expressions obtained and, on the other hand, to simplify the calculational procedure. The results of the Green function calculations carried out demonstrate rather good accuracy of the present scheme. Possible future developments may include the use of more accurate methods of band calculations for the scattering path operator [36]. In the calculations of the Curie temperature we have not used any model assumptions about the nature of exchange interactions except for the mean-field approximation in general form. As is obvious, T_c cannot be calculated with the same accuracy as the characteristics of magnetic excitation at $T = 0$, e.g. the spin-wave stiffness constant.

Appendix A. Local force theorem in LSDF method

The proof of the local force theorem presented below includes the case of spin perturbations, contrary to previous considerations [18–20].

We proceed with the one-electron LSDF equation [10] (in atomic units):

$$\sum_{\beta}\left\{\left(-\tfrac{1}{2}\Delta + V_0 - \int\frac{n(\boldsymbol{r}')\,d\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}\right)\delta_{\alpha\beta} + V^{\mathrm{xc}}_{\alpha\beta}\right\}\psi_{i\beta}(\boldsymbol{r}) = \epsilon_i\psi_{i\alpha}(\boldsymbol{r}), \tag{A.1}$$

where V_0 is the external potential (e.g. that due to nuclei),

$$V^{\mathrm{xc}}_{\alpha\beta} = \partial\left[nE^{\mathrm{xc}}(n,\, m)\right]/\partial\rho_{\beta\alpha} \tag{A.2}$$

is the exchange-correlation potential, α, β are spin variables, $\rho_{\alpha\beta}(\boldsymbol{r}) = \langle\psi^{\dagger}_{\alpha}(\boldsymbol{r})\psi_{\beta}(\boldsymbol{r})\rangle$ is the one-particle density matrix, $n = \mathrm{Tr}\,\hat{\rho}$, and $m = |\mathrm{Tr}\,\hat{\sigma}\hat{\rho}|$ are the charge and spin density, respectively, E^{xc} is the exchange-correlation energy density [10] which is locally dependent on $\hat{\rho}$ through n and m. Then any small perturbation is determined by the variation of the independent variable $\delta n(\boldsymbol{r})$, $\delta m(\boldsymbol{r})$ and one obtains:

$$\begin{aligned} V^{\mathrm{xc}}_{\alpha\beta} &= \frac{\partial\left[nE^{\mathrm{xc}}(n,\, m)\right]}{\partial n}\frac{\partial n}{\partial\rho_{\beta\alpha}} + \frac{\partial\left[nE^{\mathrm{xc}}(n,\, m)\right]}{\partial m}\frac{\partial m}{\partial\rho_{\beta\alpha}} \\ &= \frac{\partial(nE^{\mathrm{xc}})}{\partial n}\delta_{\alpha\beta} + \frac{1}{m}\frac{\partial(nE^{\mathrm{xc}})}{\partial m}\sigma_{\alpha\beta}\,\mathrm{Tr}(\hat{\sigma}\hat{\rho}). \end{aligned} \tag{A.3}$$

Then the expression for the total energy in LSDF approach has the usual form [18–20]:

$$E = E_{\mathrm{sp}} + E_{\mathrm{dc}},\quad E_{\mathrm{sp}} = \sum_{i}^{\mathrm{occ}}\epsilon_i \tag{A.4}$$

$$\begin{aligned} E_{\mathrm{dc}} &= \tfrac{1}{2}\int\!\!\int\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}' + \int\mathrm{d}\boldsymbol{r}\left[\mathrm{Tr}(\hat{\rho}\hat{V}^{\mathrm{xc}}) - nE^{\mathrm{xc}}\right] \\ &= \tfrac{1}{2}\int\!\!\int\frac{n(\boldsymbol{r})n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}' + \int\mathrm{d}\boldsymbol{r}\left[n\frac{\partial(nE^{\mathrm{xc}})}{\partial n} + m\frac{\partial(nE^{\mathrm{xc}})}{\partial m} - nE^{\mathrm{xc}}\right], \end{aligned}$$

where E_{sp} and E_{dc} are the sum of single-particle energies over the occupied states, and the "double counted" terms, respectively. The variation of E_{sp} at small perturbations in system under consideration consists from the variation $\delta^{*}E_{\mathrm{sp}}$ at the fixed $n(\boldsymbol{r})$ and $m(\boldsymbol{r})$ and the sum of the variations of the single particle energies resulting from the relaxation of the potential $\delta_1 E_{\mathrm{sp}}$ [19]. In the first order of the perturbation theory one finds:

$$\begin{aligned} \delta_1 E_{\mathrm{sp}} &= \sum_{i}\sum_{\alpha\beta}\int\mathrm{d}\boldsymbol{r}\,\psi_{i\alpha}\left\{\int\frac{\delta n(\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}'}{|\boldsymbol{r}-\boldsymbol{r}'|}\delta_{\alpha\beta} + \delta V^{\mathrm{xc}}_{\alpha\beta}(\boldsymbol{r})\right\}\psi_{i\beta} \\ &= \int\!\!\int\frac{n(\boldsymbol{r})\delta n(\boldsymbol{r}')}{|\boldsymbol{r}-\boldsymbol{r}'|}\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}' + \mathrm{Tr}(\hat{\rho}\delta\hat{V}^{\mathrm{xc}}). \end{aligned} \tag{A.5}$$

The last term in eq. (A.5) may be rewritten in the form:

$$\mathrm{Tr}\left(\hat{\rho}\delta\hat{V}^{\mathrm{xc}}\right)=\frac{\partial^2(nE^{\mathrm{xc}})}{\partial n^2}n\delta n+\frac{\partial^2(nE^{\mathrm{xc}})}{\partial m^2}m\delta m+\frac{\partial^2(nE^{\mathrm{xc}})}{\partial n\,\partial m}(n\delta m+m\delta n)+\frac{\partial(nE^{\mathrm{xc}})}{\partial m}\rho_{\beta\alpha}\delta\left[\frac{1}{m}\sigma_{\alpha\beta}\,\mathrm{Tr}(\hat{\sigma}\hat{\rho})\right] \tag{A 6}$$

taking into account eq. (A.3). It is easy to show by direct calculations that the latter term in the right side of eq. (A.6) equal to zero. Then we find, similarly to the usual proof of local force theorem for non-magnetic case [18–20], that (A.5) cancels exactly with the first variation of E_{dc} and hence:

$$\delta E=\delta^{*}E_{\mathrm{sp}} \tag{A 7}$$

in the first order in $\delta n(\boldsymbol{r})$ and $\delta m(\boldsymbol{r})$.

Appendix B. The energy of pair exchange interactions

Let us consider the variation of the total energy of the crystal at the rotations of pairs of spin moments on sites i and j on the opposite angles $\pm\theta/2$. Note that one must exclude the interaction energy of the moments i and j with the crystal environment [6]. According to eq. (12), we get:

$$\delta E'_{ij}=\frac{1}{\pi}\int^{\epsilon_{\mathrm{F}}}\mathrm{d}\epsilon\,\mathrm{Im}\,\mathrm{Tr}\,\ln\Big\{1-\left(1+\delta t_i^{-1}T^{ii}\right)^{-1}\times\delta t_i^{-1}T^{ij}\times\left(1+\delta t_j^{-1}T^{jj}\right)^{-1}\delta t_j^{-1}T^{ji}\Big\}. \tag{B.1}$$

Taking into account that

$$\delta\hat{t}_i^{-1}=\tfrac{1}{2}\Delta_i(\delta\boldsymbol{e}_i\cdot\hat{\boldsymbol{\sigma}}),$$
$$\hat{T}^{ij}=\tfrac{1}{2}\left(\hat{T}^{ij}_{\uparrow}+\hat{T}^{ij}_{\downarrow}\right)\times\hat{1}+\tfrac{1}{2}\left(\hat{T}^{ij}_{\uparrow}-\hat{T}^{ij}_{\downarrow}\right)\times(\boldsymbol{e}_0\cdot\hat{\boldsymbol{\sigma}}), \tag{B.2}$$

where

$\delta\boldsymbol{e}_{i(j)}=(\pm\sin\theta/2,\,0,\,\cos\theta/2-1)$, $\boldsymbol{e}_0=(0,\,0,\,1)$,

we find in the second order in θ;

$$\begin{aligned}\delta E'_{ij}&\simeq-\frac{1}{\pi}\int^{\epsilon_{\mathrm{F}}}\mathrm{d}\epsilon\,\mathrm{Im}\,\mathrm{Tr}\left\{\delta\hat{t}_i^{-1}\hat{T}^{ij}\delta\hat{t}_j^{-1}\hat{T}^{ji}\right\}\\&=-\frac{1}{16\pi}\int^{\epsilon_{\mathrm{F}}}\mathrm{d}\epsilon\,\mathrm{Im}\,\mathrm{Tr}_L\Big\{\Delta_i\left(\hat{T}^{ij}_{\uparrow}+\hat{T}^{ij}_{\downarrow}\right)\Delta_j\\&\quad\times\left(\hat{T}^{ji}_{\uparrow}+\hat{T}^{ji}\right)(\delta\boldsymbol{e}_i\cdot\delta\boldsymbol{e}_j)+\Delta_i\left(T^{ij}_{\uparrow}-T^{ij}_{\downarrow}\right)\Delta_j\\&\quad\times\left(T^{ji}_{\uparrow}-T^{ji}_{\downarrow}\right)\big[(\delta\boldsymbol{e}_i\cdot\boldsymbol{e}_0)(\delta\boldsymbol{e}_j\cdot\boldsymbol{e}_0)\\&\quad-(\delta\boldsymbol{e}_i\times\boldsymbol{e}_0)(\delta\boldsymbol{e}_j\times\boldsymbol{e}_0)\big]\Big\}\\&\approx\frac{1}{4\pi}\int^{\epsilon_{\mathrm{F}}}\mathrm{d}\epsilon\,\mathrm{Im}\,\mathrm{Tr}_L\left\{\Delta_i\hat{T}^{ij}_{\uparrow}\Delta_j\hat{T}^{ji}_{\downarrow}\right\}\theta^2/2\end{aligned} \tag{B.3}$$

Since $(\delta\boldsymbol{e}_i\cdot\delta\boldsymbol{e}_j)\sim\theta^2$, $(\delta\boldsymbol{e}_i\times\boldsymbol{e}_0)\cdot(\delta\boldsymbol{e}_j\times\boldsymbol{e}_0)\sim\theta^2$, $(\delta\boldsymbol{e}_i\cdot\boldsymbol{e}_0)(\delta\boldsymbol{e}_j\cdot\boldsymbol{e}_0)\sim\theta^4$ and $(\delta\boldsymbol{e}_i\times\delta\boldsymbol{e}_j)\cdot\boldsymbol{e}_0=0$ Comparising the result obtained in eq. (B.3) with eq. (5) we get the final expression (19) for the exchange parameters J_{ij}.

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