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# Bulk and surface magnetic properties of dilute FeCr alloys

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## Abstract

The electronic and magnetic structures of dilute FeCr alloys have been investigated in the framework of the periodic Anderson model. The theory involves only a few phenomenological parameters, which can be determined via magnetic properties of pure Fe and Cr samples. Some examples are considered: the perturbation of magnetic moments of Fe atoms due to Cr impurities both in the bulk and near the surface; the electronic structure of the Cr protective monolayer covering the Fe surface; and the properties of Fe/Cr superlattices.

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## 1. Introduction

Investigations of transition metal dilute alloys are significant from the applications viewpoint (because they allow the creation of new materials with exotic properties), as well as from fundamental one (since they provide unique information about the nature of d-metal magnetism). The magnetic properties of surfaces, superlattices and other low-dimensional systems are of special interest. Their magnetic and electronic structures differ from those of the bulk, and this leads to a number of new physical phenomena, which have been recently discovered.

As an example of such a new class of phenomena we note the oscillating dependence on the thickness of the non-magnetic spacer of the exchange magnetic coupling between magnetic slabs in metallic superlattices [1,2]. In these superlattices, giant magnetore-

sistance has been detected which was caused by a change in the magnetic structure when an external magnetic field is switched on [3]. The interfaces in the superlattices are not perfectly smooth and during superlattice production the replacement of different atoms and changing of the properties of interface take place. Note that namely these atoms determine the interface roughness and the conductivity of the sample [4].

Among a number of experimental methods [5], one of the most promising for investigations of magnetic structure is the method based on Mössbauer spectroscopy. This is connected with the local character of the information that can be obtained from the Mössbauer spectra (MS). If, for example, one of the atomic layers in the superlattice, where Fe is used as the magnetic material, is made of <sup>57</sup>Fe, whereas the other iron layers contain <sup>56</sup>Fe, then the spectra obtained give information about the hyperfine fields (hff) of the <sup>57</sup>Fe atomic layer [6].

On the other hand, it is possible to investigate the

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surface when the total external reflection of Mössbauer radiation takes place and the role of subsurface layers increases significantly [7].

It should be noted that for MS interpretation it is necessary to develop a model that relates the shape of the spectra to the magnetic properties. It is usually assumed that hff on the nuclei emerge due to the polarization of inner s-shells by the localized magnetic moment on a given atom as well as the direct contact interaction of the s-conductivity band [8]. The first contribution is proportional to the localized magnetic moment; the second is determined by the polarization of the s-conductivity band. Hence, for a theoretical description of the spectra obtained, it is necessary to calculate both the localized magnetic d-moments and the polarization of itinerant s-electrons.

One of the most advanced methods for describing the electron structure is *ab initio* calculations based on the density functional formalism [9–12]. These calculations predict a considerable increase in magnetic moments on the surface of Fe, Co and Cr. Calculations of the electron structure of metallic magnetic superlattices have been performed in the framework of this method [13–15]. These computations are rather elaborate and time consuming but it is not yet possible to consider non-homogeneous in-plane states and the effects of adsorbed atoms on the magnetic properties of non-perfect surfaces [16].

On the other hand, some results of the calculation in the density functional approach were found to disagree with experiment. For example, the energy of magnetic coupling in the superlattices turns out to be an order of magnitude greater than the experimental value [13,17]. Moreover these calculations do not allow to get a simple intuitive picture of the phenomena and to discern which interactions from a number of those taken into account are responsible for the properties under consideration. Note that recent calculations [14,15] give values of coupling energies that are in more reasonable agreement with the experimental data. At the same time there are studies where the *ab initio* method was exploited for the selection of the simple mechanism of coupling phenomena [18].

Another approach to the description of magneto-ordering in quasi-two-dimensional systems is connected with the application of model Hamiltonians,

such as the Hubbard Hamiltonian. This leads to equations for Green functions which are usually solved in the nearest-neighbour approximation.

In spite of the fact that the calculations in this case are not so complex, they are laborious as well and this approach is limited to describe non-homogeneous complex systems. Furthermore, the results of the calculations are sometimes in contradiction with the data of more precise experiments. For instance, the period of the magnetic coupling calculated for a Fe/Cr/Fe sandwich system in the approximation of a perfectly smooth interface [19] does not agree with experimental data obtained for wedge-like samples [20]. Note that in recent studies in the frame of the Hubbard Hamiltonian some surface and interface structures with broken two-dimensional periodicity have been successfully described [21,22]. In particular, in Ref. [22] the experimental results [20] were interpreted using the calculations of magnetic properties for high-Miller-index surfaces. Such systems have not been described by any of the *ab initio* methods.

These circumstances make it important to develop a simple theory with a minimum number of phenomenological parameters which will allow a description of magnetically ordered non-homogeneous systems. A version of such a theory based on the periodic Anderson model was developed for description of surfaces and stratified magneto-ordered systems [23]. In this approach, the conclusion about an enhancement of magnetic properties on the surface was confirmed. The dependence of the surface magnetic moment on the surface orientation was demonstrated [24]. In Ref. [25] a new method of mass-operator calculation was developed which allows to take into account d–d interactions inside an arbitrary number of coordinate spheres; the correlation between the band and cluster approach was also discussed.

In the present paper the problem of describing the magnetic structure of dilute alloy FeCr near the surface or interface is studied. We consider the perturbation of the host magnetic moments by impurity atoms in dependence on their mutual positions. Then we calculate the magnetic and electronic structure of the Fe surface covered by a protective Cr monolayer. After that we apply the theory developed to describe the properties of the dilute alloy near the

surface. The possibility of using the data obtained for interpretation of the Mössbauer spectra is considered.

## 2. The model

We consider d-metals in the framework of Anderson's periodic model and assume that the electron spectrum is described by a two-band approach, which corresponds to s and d subsystems. For the localized d-electrons we use the Wannier, and for the itinerant s-electrons the Bloch function representation.

Let us write the equations for the Green function matrix elements in the form:

$$\sum_j [\omega \delta_{i,j} - E_{i,j}] G_{j,i'} - \sum_k V_{i,k} G_{k,i'} = \delta_{i,i'}, \quad (1)$$

$$[\omega - E_k] G_{k,i} - \sum_j V_{k,j} G_{j,i} = 0, \quad (2)$$

$$[\omega - E_i] G_{i,k} - \sum_{k'} V_{i,k'} G_{k',k} = 0, \quad (3)$$

$$[\omega - E_k] G_{k,k'} - \sum_j V_{k,j} G_{j,k'} = \delta_{k,k'}. \quad (4)$$

where  $E_{i,i}$  and  $E_k$  are the energies of a d-electron localized on site  $i$  and an itinerant s(p) electron with quasi-momentum  $k$ ,  $V_{i,k}$  and  $V_{k,i}$  describe inter-band hybridization,  $E_{i,j}$  are direct transitions from site  $i$  to  $j$ . If the direct transitions are omitted, then the system (1)–(4) is reduced to Anderson equations for a single impurity [26]. Our approach implies that the s–d interaction on the site is large enough compared to s–d interactions on different sites. In this case we construct a resonant d-state, which has a definite width, as in Ref. [26], and after that the interaction between different atoms is taken into account.

Extracting the functions  $G_{k,i}$  from (2), the set of equations for  $G_{i,i'}$  is obtained:

$$[\omega - E_i] G_{i,i'} - \sum_j V_{i,j} G_{j,i'} = \delta_{i,i'}, \quad (5)$$

where the d-electron energy

$$E_i = E_{i,i} + \sum_k \frac{V_{i,k} V_{k,i}}{\omega - E_k},$$

and the ‘hopping’ integral between the localized sites

$$V_{i,i'} = E_{i,i'} + \sum_k \frac{V_{i,k} V_{k,i'}}{\omega - E_k},$$

are renormalized by the s–d interaction.

Note that  $E_i$  includes an imaginary part, which is determined by the s–d interaction:

$$\Gamma_i = \text{Im} \sum_k \frac{V_{i,k} V_{k,i}}{\omega - E_k}.$$

In the following we take the parameters  $V$  and  $\Gamma$  to be independent of site coordinate  $i$ .

Iteration of Eq. (5) leads to the following expression for the d-electron Green function:

$$G_{i,i'} = \frac{1}{\omega - E_i} \left[ \delta_{i,i'} + \frac{V_{i,i'}}{\omega - E_i} + \sum_{j,l} \frac{V_{i,j} V_{j,l} V_{l,i'}}{(\omega - E_j)(\omega - E_l)} + \dots \right]. \quad (6)$$

For the diagonal matrix element we obtain

$$G_{i,i} = (\omega - E_i - \sigma_i)^{-1} \quad (7)$$

where the mass operator  $\sigma_i$  is defined as follows:

$$\sigma_i = \sum_j \frac{V_{i,j} V_{j,i}}{\omega - E_j} + \sum_{j,l} \frac{V_{i,j} V_{j,l} V_{l,i}}{(\omega - E_j)(\omega - E_l)} + \dots \quad (8)$$

The summation in (8) is carried out over all transition paths which start and finish at the  $i$ -site and, moreover, do not pass through it.

To make the system (6)–(8) definite we use the simplest self-consistent condition, which is analogous to the Hartree–Fock approach:

$$E_i^\alpha = E_{0i} + U_i n_i^{-\alpha}, \quad (9)$$

where  $n_i^{-\alpha}$  is the number of d-electrons with spin  $-\alpha$  on the  $i$ -site. The initial energy  $E_{0i}$  and the Coulomb integral  $U_i$  depend on the sort of atoms on the  $i$ -site. We consider these parameters as phenomenological ones in the spirit of the Fermi liquid theory.

Note that an analogous model was exploited to describe the magnetic properties of metals with a half-filled d-band and thin films of these metals [27,28]. The approach used there corresponds to the inclusion in the first order of perturbation theory of electron transitions between neighbouring sites. As an initial approach the density of states for a single impurity was used. Such a theory does not allow us to consider a complex, non-homogeneous state, such as clusters of different chemical atoms near the

sample surface. That is why we use another method, which makes it possible to calculate the mass operator taking into account d–d transitions inside a given number of coordinate spheres [25].

To calculate the mass operator  $\sigma$ , let us take a certain set of atoms  $\mathfrak{S}$  and consider only the transitions through atoms of this set. Then

$$\sigma_i = \sum_{j \in \mathfrak{S}} V_{i,j} S_{j,i}, \quad (10)$$

where  $S_{i,j}$  is the contribution from all paths beginning on the  $i$ -site and finishing on the  $j$ -site. For  $S_{i,i}$  it is possible to write the following set of equations:

$$(\omega - E_j) S_{j,i} = V_{j,i} + \sum_{l \in \mathfrak{S}} V_{j,l} S_{l,i}. \quad (11)$$

If the set  $\mathfrak{S}$  is the first coordinate sphere of atoms under consideration, for  $\sigma$  in the case of the bcc lattice one obtains:

$$\sigma_i = \frac{8V^2}{\omega - E}, \quad (12)$$

and for the fcc lattice it is:

$$\sigma_i = \frac{12V^2}{\omega - E - 8V}. \quad (13)$$

In (12) and (13) it is assumed that energies  $E_i^\alpha = E^\alpha$  for all  $i$ , as it is for ferro- and paramagnetic order in a homogeneous sample.

Analogous, but more cumbersome formula, can be derived for space non-homogeneous systems. The appearance of the ‘hopping’ parameter  $V$  in the denominator (13) is connected with the fact that for an fcc lattice in the first coordinate sphere of the atom under consideration there are as long paths as possible which give a contribution to  $S_{j,i}$ , whereas for a bcc lattice only a direct transition is available, which corresponds to the first term on the right-hand side of (11).

Now the d-electron state occupation numbers are given by the expression

$$n_i^\alpha = -\frac{1}{\pi} \int d\omega f(\omega) \operatorname{Im} G_i^\alpha(\omega - i0),$$

where  $f(\omega)$  is the Fermi–Dirac function. Now we have a full set of equations for self-consistent determination of  $n_i$ ,  $E_i$ .

The phenomenological parameters of the model

are the energy  $E$ , the Coulomb integral  $U$ , the ‘hopping’ integral  $V$  (which we assume to be non-zero only for nearest neighbours) and the level width  $\Gamma$ . Note that in most cases it is more convenient to use dimensionless variables:

$$x_i = \frac{(E_{0i} - \epsilon_F)}{\Gamma}, \quad y_i = \frac{U_i}{\Gamma}, \quad \frac{V}{\Gamma}.$$

In this case all the energies are expressed in  $\Gamma$ -units. We assume that the parameters  $x_i$ ,  $y_i$  and  $V/\Gamma$  have been determined from calculations of the properties of a homogeneous sample, and  $V/\Gamma$  is taken to be the same for different materials.

To calculate the s-band polarization we use Eqs. (3) and (4). Making an iterated expansion, one finds

$$G_{k,k'}^{(s),\alpha} = \frac{\delta_{k,k'}}{\omega - E_k} + \frac{1}{(\omega - E_k)(\omega - E_{k'})} \sum_{j,j'} V_{k,j} V_{j',k'} G_{j,j'}^\alpha. \quad (14)$$

The first term on the right-hand side is spin-independent, corresponding to a free s-electron contribution, and the second term takes into account the polarization of the s-band caused by the d-subsystem. The matrix elements  $V_{k,j}$  are assumed to be the same as in the space homogeneous case:

$$V_{k,j} = V_k \exp(i\mathbf{k}\mathbf{R}_j).$$

Turning to the Wannier representation for s-electrons and neglecting the dependence of  $V_k$  on  $k$ , for the Green function  $G_{j,j}^{(s),\alpha}$  we obtain:

$$G_{j,j}^{(s),\alpha} \equiv \frac{1}{N} \sum_{k,k'} \exp[i(\mathbf{k} - \mathbf{k}')\mathbf{R}_j] G_{k,k'}^{(s),\alpha} = G_{j,j}^{(s)(0)} + \sum_{l,m} G_{j,l}^{(s),\alpha(0)} G_{l,m}^\alpha G_{m,j}^{(s),\alpha(0)}, \quad (15)$$

where  $G_{j,j}^{(s),\alpha(0)}$  is the Green function for the free s-electrons. For calculation of the d-subsystem Green functions  $G_{m,n}^\alpha$  in (15) one can use the technique described above.

If one assumes the perturbation caused by an impurity to be local, i.e. only the terms in (15) contain  $G_{j,j}^\alpha$  (where  $j$  is an impurity site) are changed, then the results of RKKY theory may be reproduced from (15). Namely, the electron density oscillates

with the amplitude, which decreases as  $R^{-3}$ , while the distance  $R$  increases. Such an approach is often used for the interpretation of Mössbauer spectra.

It should be noted that in the framework of the theory developed it is possible to consider the perturbation of the localized magnetic moments near the impurity atom and its influence on the conductivity band polarization in a general form, in the cases when the RKKY approach appears insufficient. It is important for a description of materials close to the ferromagnetic state (such as Pd) where the magnetic moment of the impurity induces a strong polarization of the host atoms in a few coordinate spheres. It may be necessary to go beyond the framework RKKY theory when the effective attraction between the impurities occurs and the structure of the clusters formed substantially determines the polarization of the conductivity band.

### 3. Electronic and magnetic structures of dilute FeCr alloys

We now exploit the theory developed to describe the electronic and magnetic structures of Cr impurity atoms in an Fe matrix. If the Cr concentration is low enough, we can take into account clusters that contain no more than two Cr atoms. We consider transitions in the first coordinate sphere of the atom in question and assume that the impurity atoms which are farther than the second coordinate sphere do not change the magnetic moments of Fe atoms. This implies that the Fe atoms whose electron structure is perturbed by the impurity are able to change only the magnetic structure of their neighbours. Our calculations reveal that the perturbation of magnetic moments in the second sphere of the impurity is much less than in the first one.

Note that for a space homogeneous metal with bcc lattice mass operator and Green functions of d-electrons were worked out for the cases when the d–d interaction was taken into account in the 1, 2, 3 and 7 coordinate spheres of the atom under consideration [25]. It was shown that the main features of the magnetic behaviour can be reproduced in the simplest model of nearest neighbours but with the corresponding value of the effective hopping parameter. This is also likely to be true in dilute bcc alloys.

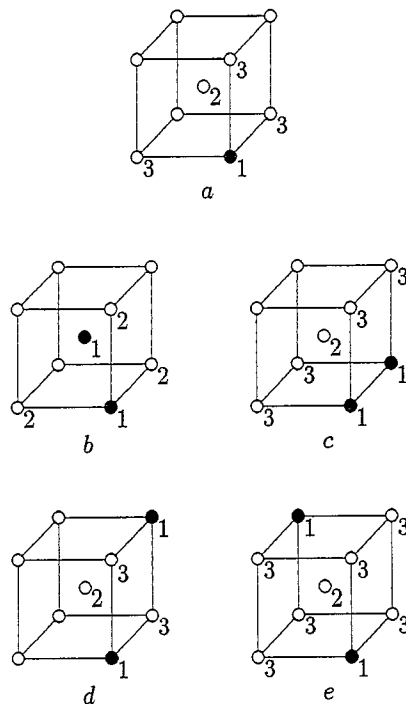


Fig. 1. Impurity Cr atoms (full) in the Fe matrix (empty).

All the possible configurations of 1 and 2 impurity atoms in the first coordinate sphere of the Fe atom are shown in Fig. 1 (a–e). These are:

(a) A single Cr atom (1) in the Fe lattice and Fe atoms in the first (2) and second (3) coordinate spheres of the impurity (Fig. 1a).

(b) Two neighbouring impurity Cr atoms (1) in the Fe lattice and Fe atoms which contain one Cr atom in the first and second coordinate spheres (Fig. 1b).

(c) Two Cr atoms – second neighbours (1) in the Fe lattice, and Fe atoms which contain two Cr atoms among the nearest neighbours (2) and second neighbours (3) (Fig. 1c).

(d) Cr atoms at a distance of  $a\sqrt{2}$  (where  $a$  is the lattice constant) (1), and Fe atoms which contain two impurity atoms in the first (2) and second (3) coordinate spheres (Fig. 1d).

(e) Two Cr atoms which are along the diagonal of the cube (1), Fe atoms which contain these Cr impurities among nearest neighbours (2), and Fe atoms which contain impurities in the second and third coordinate spheres (Fig. 1e).

The model parameters for Fe and Cr atoms were chosen so that the properties of the corresponding spatially homogeneous materials (the number of d-electrons per atom  $N_{\text{Fe}} = 7.0$ ,  $N_{\text{Cr}} = 5.0$ , and the magnetic moments  $M_{\text{Fe}} = 2.2 \mu_{\text{B}}$  for ferromagnetic ordering,  $M_{\text{Cr}} = 0.6 \mu_{\text{B}}$  for antiferromagnetic ordering) were reproduced. Note that in the Cr samples the state of spin density wave with an amplitude of about  $0.6 \mu_{\text{B}}$  is realized. This state is close to the unstable one and leads to some difficulties in calculations of Cr-containing systems [19].

As an initial approximation for the self-consistent calculation we use the populations of the electron states which correspond to the pure ferromagnetic Fe and antiferromagnetic Cr. At an initial stage, it was possible to choose the magnetic moment of Cr impurity atoms to be both ferro- and antiferro-ordered with respect to the moment of Fe. The mass operator in our approach is determined by the atoms in the first coordinate sphere of the atom under consideration. For example, for the configuration shown in Fig. 1(c), every Cr atom (1) is surrounded by four Fe atoms of kind (2) and four Fe atoms of kind (1) from Fig. 1(a); every Fe atom of kind (2) is enclosed by two Cr atoms (1), four Fe atoms of kind (3) and, in our approach, two Fe atoms, like atoms in pure ferromagnetic Fe. Finally, the Fe atom of kind (3) has, among its nearest neighbours, two atoms Fe (2), two atoms Fe (3) from Fig. 1(a), and four atoms of 'pure' Fe.

The self-consistent calculation of the occupation numbers for the localized d-state being fulfilled, one can find the magnetic moment and the number of d-electrons per atom. Although our system includes both localized d and itinerant s(p) subsystems, one should demand that the electroneutrality condition for the clusters which consist of impurity atoms and Fe atoms with perturbed state under the action of the impurity, is governed only by d-electrons. This condition can be changed if the equations for both subsystems are solved and the Fermi level has to be shifted for all electrons. The electroneutrality condition for Fig. 1(c) configuration reads:

$$2n(\text{Cr}_{c(1)}) + 4n(\text{Fe}_{c(2)}) + 8n(\text{Fe}_{c(3)}) + 8n(\text{Fe}_{a(2)}) + 2n(\text{Fe}_{a(3)}) = 2n(\text{Cr}) + 22n(\text{Fe}).$$

Here the literal indices and the numbers refer to the

Table 1

Magnetic moments and number of d-electrons on Fe atom near the impurities. Letter in the first column corresponds to Fig. a–c, cipher – number of atoms on this figure

	Magnetic moment ( $\mu_{\text{B}}$ )	Number of d-electrons
a(2)	2.06	7.04
a(3)	2.22	7.03
b(2)	2.07	7.04
c(2)	1.93	7.05
c(3)	2.19	7.07
d(2)	1.95	7.03
d(3)	2.23	7.05
e(2)	1.99	7.00
e(3)	2.23	7.04

configurations in accordance with Fig. 1, and the kind of the atom within it, respectively. The right-hand side contains the corresponding values for pure metal.

We now turn our attention to the results of numerical calculations.

(1) The magnetic moments of Cr impurity atoms for the self-consistent solution turn out to be ordered antiferromagnetically relative to the magnetic moments of Fe. This result does not depend on the initial magnetic ordering (i.e. on the magnetic ordering which was assumed at the very first step of the calculations). Note that the same behaviour was obtained in the ab initio calculation and in the experimental data [9].

(2) The magnetic moment of Cr impurity atoms exceeds considerably the magnetic moment in the pure antiferromagnetic Cr. The interaction between Cr atoms leads to a reduction of the moments, and the closer the Cr are, the greater is this reduction (Table 1).

Table 2

Localized magnetic moment on Cr impurity atoms as a function of the distance between impurity atoms

Distance between impurities (in lattice constant)	Magnetic moment ( $\mu_{\text{B}}$ )
$\frac{1}{2}\sqrt{3}$	1.79
1	2.13
$\sqrt{2}$	2.16
$\sqrt{3}$	2.18
$\infty$	2.19

(3) The calculations demonstrate that Fe atoms reveal a small decrease in the magnetic moments under the action of Cr impurities (Table 2). However, this is not additive with respect to the number of impurity atoms but depends on their mutual positions. In particular, the decrease in magnetic moments for the Cr atom (2) in Fig. 1(b) is less than that for atom (2) in Fig. 1(a), although atom  $\text{Fe}_{b(2)}$  has one impurity atom in the first and one in the second coordinate sphere, whereas atom  $\text{Fe}_{a(2)}$  has only one atom in the first sphere. This could be explained by the strong mutual influence of neighbouring Cr atoms.

(4) The increase in the localized magnetic moments is accompanied by a decrease in the number of d-electrons on the same atom. In our approach, this leads to the lowering of the Fermi level relative to the bottom of the band and to the redistribution of electrons between atoms of a cluster.

#### 4. Stratified systems: surface and superlattices Fe/Cr

The main factor that influences the magnetic properties of surface atoms is connected with the variation of the number of nearest neighbours and with the subsequent effective shrinking of the d-band. For both Fe and Cr this leads to a considerable enhancement of the surface magnetic properties. These results were obtained for surfaces and thin films in the framework of the density functional formalism [10–12], as well as in the tight-binding approximation [28]. With our model, it is easy to explain the dependence of the magnetic structure on the orientation of the surface with respect to the crystal axes.

For example, in a bcc lattice the surface atoms have six nearest neighbours for (110) surface orientation and only four such atoms for (100) orientation. It seems reasonable that narrowing of the d-band and deviation of magnetic moments from the bulk values would be less in the last case. Namely, this behaviour, which completely corresponds with the results obtained in the framework of density functional calculations [10], has been found in our theory.

In the numerical calculation of the magnetic moment distribution the following procedure is used.

The values of the occupation numbers of d-electrons are determined successfully, starting with the surface layer. For an initial approximation we take the bulk values of the occupation numbers. To find the mass operator for an  $i$ -layer we need to specify energies in layers  $i - 1$  and  $i + 1$ . For  $E_{i-1}$  we use the value found immediately before this at the same iteration, whereas for  $E_{i+1}$  we use the value of the previous iteration. This procedure is repeated until the magnetic moments and the numbers of d-electrons in each layer remain unchanged.

If a layer containing nonequivalent atoms (such as for the calculation of the FM/AFM interface, where AF ordering of magnetic moments occurs in the superficial layer), it is necessary to perform self-consistent calculations for every nonequivalent atom. Here we suggest, as in the case of a dilute alloy problem, that the total number of d-electrons in the sample is preserved. This condition significantly affects the results of calculations for thin films and superlattices with a short period, because it leads to a redistribution of electrons between layers. For a semi-infinite metal the shift of the Fermi level and the electron redistribution appear to be weak, since the electron structure changes only in a few subsurface layers.

For the pure  $\alpha$ -Fe surface (100) it was found that the magnetic moment of the surface layer increases to  $2.54\mu_B$  from the value  $2.23\mu_B$  in the bulk. The number of d-electrons per atom decreases from 7.0 in the bulk to 6.86. The enhancement of magnetic properties near the surface turns out to be less than predicted with the density functional formalism. However, the results obtained are closer if the d-magnetic moment and the number of d-electrons are taken to be  $2.3\mu_B$  and 7.0, respectively [23].

The changing of the d-electron number in the subsurface layers leads due to the local electroneutrality condition, to the s(p) band polarization. Ab initio calculations also predict that the s(p) band polarization is antiferromagnetic relative to the localized magnetic moment [10]. This makes it difficult to observe an increase in the magnetic properties in the MS experimental studies.

In the second layer from the surface the magnetic moment is moderately less than in the bulk. Then it approaches the bulk value.

In experimental studies of the Fe superlattice it is

important to bear in mind the influence of adsorbed atoms on the magnetic properties. Such atoms often suppress the surface magnetism [6]. That is why investigations of electronic and magnetic structure of surface covered by protective monolayers (an example is Cr on Fe surface) are of special interest.

As discussed above, the impurity atoms decrease the moments of the surrounding Fe atoms. It seems to be natural that the increase in the magnetic moments of atoms at the Fe surface is less in the case when the surface is covered by a Cr monolayer. Actually, as our calculations have demonstrated, the moment of the interface Fe layer is less than in the bulk:  $2.07\mu_B$ . A fair increase in the moment (up to  $2.32\mu_B$ ) due to surface effects is exhibited only in the next Fe layer.

Note that, as distinct from the magnetic moment, the number of d-electrons per atom in the interface Fe layer is found to be almost the same as without the Cr layer. This results in a redistribution of the s(p)-electrons near the interface.

Magnetic ordering in the protective Cr layers is ferromagnetic and magnetic moments are ordered antiparallel relative to the Fe moments. The value of the magnetic moments for Cr atoms is  $2.75\mu_B$ , which is much greater than both in the bulk and in the FeCr alloy. The reason for such a considerable increase in magnetic properties lies in the fact that the protective layer is the surface one and has fewer nearest neighbours than the inner layers. In addition, for the surface (100) all the Cr adjacent atoms are Fe atoms, and there is no direct interaction between Cr atoms. This leads to an increase in the magnetic moment. The results of recent experimental studies of Cr layers on Fe surfaces [29,30] are in good agreement with our data. Note that calculations of the properties of the free Cr surface give a giant enhancement of magnetic moments up to  $3.63\mu_B$  [31]. Experiments demonstrate the magnetic phase transition occurs at a temperature 2.5 times larger than that of the bulk [32].

In the Fe/Cr superlattice (the classic system with antiferromagnetic coupling and giant magnetoresistance) the same peculiarities are exhibited in electronic and magnetic structures as for the Cr monolayer on the Fe surface. If the superlattice is considered where the Fe film consists of three layers, our calculations show that the interface layer has a lower

magnetic moment ( $2.0\mu_B$ ), whereas the moment of the central layer is greater than that of the bulk ( $2.5\mu_B$ ) in accordance with the results of other calculations [19,33]. When the thickness of the Fe film increases the same structure can be observed as for two independent Fe surfaces covered by Cr.

As for magnetic ordering in the Cr mediator, we found that the magnetic moment for the (100) interface is always ordered antiferromagnetically to Fe. That is why for ferromagnetic ordering of Fe slabs in the superlattice and for an even number of layers in the Cr mediator (for antiferromagnetic ordering of Fe slabs in the superlattice and an odd number of layers in the Cr mediator) in the Cr slabs the magnetic state with a fold superposed on antiferromagnetic order is observed. In the centre of the Cr slab the magnetic moment vanishes. The possibility of such states in the frame of the Anderson periodic model was discussed in Ref. [23]. The state with the fold has a higher energy. Therefore, for superlattices with perfectly smooth interfaces one can expect short-range oscillations of the magnetic coupling with a period of two lattice constants.

## 5. Cr impurities near the Fe surface

To conclude this study, we consider the problem of describing the perturbation of the electronic and magnetic structures caused by impurity atoms near the sample surface. On the one hand, the presence of the surface leads to an increase in the magnetic moments. However, the influence of Cr impurities results in a decrease of these values. What happens if both factors are taken into account? Let us consider the two configurations in Fig. 2.

In Fig. 2(a) the Cr impurity atom (full) is on the surface, and in Fig. 2(b) it is on the next layer. As an

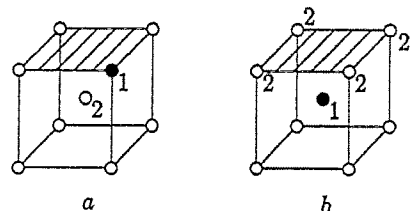


Fig. 2. Impurity Cr atom (full) on the Fe surface (a) and in the second after surface layer (b).



initial approximation for the occupation numbers in our calculations we use the values that correspond to the homogeneous antiferromagnetic Cr for Cr atoms and a semi-infinite Fe sample for Fe atoms.

In all cases, the self-consistent solution reveals antiparallel ordering of neighbouring Fe and Cr magnetic moments. The value of Cr moments on the surface ( $2.8\mu_B$ ) appears to be close to that of Cr in the Cr monolayer on the Fe surface. In the layer next to the surface, the Cr atoms have a magnetic moment of  $2.27\mu_B$ , which is larger than that for an impurity Cr atom in the bulk.

For Fe atoms surrounding the impurity, it is possible to keep track of the influence of both the impurity and the surface. If an impurity atom is on the surface, nearest-neighbour Fe atoms from the second layer have a magnetic moment of  $2.5\mu_B$ . The impurity atom in the first coordinate sphere causes a decrease in the surface magnetic moment of Fe to  $2.44\mu_B$ . The perturbation of the magnetic moments by the Cr impurity is substantial only in the first coordinate sphere.

Note that when Cr atoms pass through the Fe surface they reduce the magnetic moments of their neighbours and could give rise to the giant decrease in the sample magnetic moment in the magnetometer experiments [16].

## 6. Conclusions

We have presented the theory that allows us to calculate the d-electron occupation numbers for a specially non-homogeneous system. As an example of such a system, dilute FeCr alloys were considered, as well as the surfaces of the pure metal, (Fe) covered by the protective (Cr) layer, FeCr alloy near the surface of the sample. Now we summarize the results of our calculations.

(1) In all cases the Cr impurity atom has a magnetic moment unparallel to the Fe moment of the matrix.

(2) The interaction between Cr atoms leads to a decrease in the magnetic moment. The replacement of Cr by Fe atoms in the system of interacting Cr atoms results in an increase in Cr magnetic moments.

(3) The increase in the magnetic moment per atom is followed by a decrease in the number of

d-electrons on the same site. The electroneutrality condition leads to a redistribution of itinerant electrons and their polarization.

(4) The Cr impurity atoms cause a decrease in the magnetic moments of the surrounding Fe atoms. However, this decrease is not additive with respect to the number of impurities, but depends on their mutual positions. This is a result of the interaction of the impurities and the subsequent decrease in their magnetic moments.

(5) The surface changes the magnetic properties of atoms through the reduction in the number of nearest neighbours. This results in a considerable increase in magnetic moments near the surface of pure metals (both Fe and Cr).

(6) The protective Cr layer on the Fe surface depresses the interface Fe magnetic moment down to a value that is less than that in bulk Fe. However, in the next (after the interface) layer the magnetic moment appears to be larger than that in the bulk. Similarly, for Fe/Cr superlattices the interface Fe atoms have a moment that is less than that in the bulk; but the central layer has a higher magnetic moment.

(7) Calculations of the electronic and magnetic structures of Fe/Cr superlattices show that self-consistent solutions exist for both ferro and antiferromagnetically ordered Fe slabs in the superlattice. One of this solutions always has a fold, where the magnetic moment falls to zero. This solution has a higher energy and hence is unstable.

(8) The Cr impurities near the Fe surface induce a reduction in the magnetic moments of surrounding atoms. It is significant in the first coordinate sphere and much less in the second. It is possible to follow the influence of both impurities and the surface on the distribution of magnetic moments. The perturbation of magnetic moments determines the hyperfine fields on Fe nuclei and can be used for the interpretation of Mössbauer experiments. However, for this purpose it is urgent to calculate more precisely the s(p) band polarization. Such calculations are now in progress.

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