Self-consistent mapping: Effect of local environment on formation of magnetic moment in $\alpha-\text{FeSi}_2$.

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The Hohenberg-Kohn theorem establishes a basis for mapping of the exact energy functional to a model one provided that their charge densities coincide. We suggest here to use a mapping in a similar spirit: the parameters of the formulated multiorbital model should be determined from the requirement that the self-consistent charge and spin densities found from the ab initio and model calculations have to be as close to each other as possible. The analysis of the model allows for detailed understanding of the role played by different parameters of the model in the physics of interest. After finding the areas of interest in the phase diagram of the model we return to the ab initio calculations and check if the effects discovered are confirmed or not. Because of the last controlling step we call this approach as hybrid self-consistent mapping approach (HSCMA). As an example of the approach we present the study of the effect of silicon atoms substitution by the iron atoms and vice versa on the magnetic properties in the iron silicide $\alpha-\text{FeSi}_2$. The DFT+GGA calculations are mapped to the model with intraatomic Coulomb and exchange interactions, hoppings to nearest and next nearest atoms and exchange of the delocalized electrons between iron atoms; the magnetic moments on atoms and charge densities of the material are found self-consistently within the Hartree-Fock approximation.

We find that while the stoichiometric $\alpha-\text{FeSi}_2$ is nonmagnetic, the substitutions generate different magnetic structures. For example, the substitution of three $Si$ atoms by the $Fe$ atoms results in the ferrimagnetic structure whereas the substitution of four $Si$ atoms by the $Fe$ atoms gives rise to either the nonmagnetic or the ferromagnetic state depending on the type of local environment of the substitutional $Fe$ atoms. Besides, contrary to the commonly accepted statement that the destruction of the magnetic moment is controlled only by the number of $Fe-Si$ nearest neighbors, we find that actually it is controlled by the $Fe-Fe$ next-nearest-neighbors hopping parameter. This finding led us to the counterintuitive conclusion: an increase of $Si$ concentration in $Fe_{1-x}Si_{2+x}$ ordered alloys may lead to a ferromagnetism. This conclusion is confirmed by the calculation within GGA-to-DFT approach.

I. INTRODUCTION

The method of mapping of first-principle density functional theory (DFT) calculations to the effective Heisenberg model for theoretical study of the magnetic properties of solids was developed in the series of works [1]. The role played by the electronic subsystem in this approach is reduced to formation of the lowest-order pairwise effective exchange interaction of classical spins. In order to have an opportunity to use the well-developed many-body perturbation theory and to obtain the physical picture of the formation of the magnetic and, especially, the non-magnetic properties of the matter by the electronic subsystem one either have to use Hedin’s GW approximation [2] or a detailed model which includes all atoms, their key orbitals and symmetry of the lattice in question, hopping parameters and Coulomb interactions. The GW approximation (even without the vertex corrections) is extremely time and computer-resources consuming. For this reason the route with more simple model Hamiltonians seems to be more efficient for highlighting the physics.

The construction of the hopping parameters for certain symmetries has been described by Slater and Koster [3].

Then, the phase diagram for the chosen model in the multidimensional space of these hopping parameters, Coulomb and exchange matrix elements can be constructed in a proper approximation. However, one point in this multi-parameter space corresponds to each real material, which can be described by such a model. A change of the external conditions for the material, like applying a pressure, temperature, or placing a film of the material on some substrate, will move this point from the initial position only slightly. Therefore, in order to be able to predict the behavior of real material, we have to know the material-in-question coordinates in the parameter space with good accuracy. Unfortunately, a unique receipt how to find the position of the material in the model parameter space does not exist. Here we suggest the following way to resolve this difficulty. Since the DFT-based calculations usually give a reasonably good description of metals and produce corresponding self-consistent spin- and charge densities, we can speculate in the DFT spirit: we use the requirement that the system with a model Hamiltonian has the spin- and charge densities as close as possible (ideally, the same) to the one obtained within the first-principle calculations for finding the parameters of the model. Then, having obtained some prediction within the model calculations we return to the first-principle ones in order to check the validity of the model prediction. This is an essence of the
suggested here hybrid self-consistent mapping approach (HSCMA). It may seem that such approach should work only within the validity domain of the chosen approximation for the DFT (in our case GGA-to-DFT). However, the largest contribution to the energy of the system and formation of the local charge density \( \rho_{DFT}(r) \) comes from the Hartree part of interaction, which is treated in DFT pretty well. That is why we want to start at least from the point in the model parameter space which provides \( \rho_{model}(r) \) close to \( \rho_{DFT}(r) \). Further the model with these parameters can be used for description of the phenomena beyond reach of DFT. Then the question arises why we want that the self-consistent model and DFT charge densities (magnetic moments) have to be close to each other? The matter is that we want to know the bare parameters of the model in order to be able to use the diagrammatic methods for dressing them and to avoid double counting. The most difficult question here is to find an approximation for the model calculation which would correspond to the one used in DFT. It clear, however, that the constraints in the accuracy of both methods allow to require a rough correspondence of charge densities. Indeed, on the one hand, in the DFT we use the exchange-correlation potential with restricted and, often, unknown validity domain (moreover, it is known that the calculations within the same approximation, but different packages, produce non-coinciding results). On the other hand, the model has to contain much smaller number of the interactions and hopping parameters (otherwise we will come to GW type of description at least). In spite of this uncertainty at the initial step this approach is attractive because it does not contain any fitting parameters, which should be taken from experiment. From this point of view it should be considered as first-principle approach. We have chosen to treat the model within the Hartree-Fock approximation.

The HSCMA is applied here for the analysis of the magnetic properties of \( \alpha - FeSi_2 \)-based ordered alloys.

The growth of Fe-silicides on silicon has been widely studied in recent years because, depending on their phase, crystal structure and composition, they can be semiconducting, metallic and/or ferromagnetic, and therefore offer a large variety of potential applications when integrated into silicon-based devices [4]-[6]. To this day, several Fe–silicide structures have been reported. At the Fe-rich side of the binary phase diagram, metallic as well as ferromagnetic \( Fe_5Si_3 \) and \( Fe_3Si \) (DO\(_3\) structure) [7,8] have already been established as key materials for spintronics [9,10]. The Si-rich side of the phase diagram contains several variants of a disilicide stoichiometric compound, such as the high-temperature tetragonal metallic \( \alpha - FeSi_2 \) phase [11], with applications as an electrode or an interconnect material [12,13], and the orthorhombic semiconducting \( \beta - FeSi_2 \) phase [14], which due to its direct band gap is an interesting candidate for thermoelectric, photovoltaic and optoelectronic devices [15]. While room-temperature stable \( \beta \)-phase is well-studied, tetragonal \( \alpha \)-phase do not attract great interest until recently. This is due to this phase is metastable and exist only at temperatures above 950°C [11]. However, the iron silicides, which do not exist in bulk, can be stabilized as films. In Refs. [12,16-19] a successful fabrication of thin films \( \alpha - FeSi_2 \) was reported. Also, while the magnetic order is not observed in bulk stoichiometric disilicide \( \alpha - FeSi_2 \), ferromagnetism was found [19] in the metastable phase \( \alpha - FeSi_2 \), which was stabilized in epitaxial-film grown on the silicon substrate. The authors of Refs. [13,20] reported that the magnetic moments on Fe atoms \( \mu = 1.8\mu_B \) [13] and \( \mu = 3.3\mu_B \) [20] in \( \alpha - FeSi_2 \) nanoslips and nano-stripes on Si (111) substrate arise. These experimental achievements have good perspective for the integration of the Fe\( Si \)-based magnetic devices into silicon technology, and, therefore, demands for the detailed understanding of the physics of the magnetic moment formation in these compounds.

Traditionally, the appearance of the magnetic structure in \( Fe-Si \) alloys is related to the increase of the concentration of Fe atoms. So, the unusual ferromagnetism in epitaxial-film form \( \alpha - FeSi_2 \) authors [19] explain by the appearance of substitutitional Fe atoms on Si sublattice. According to the \textit{ab initio} calculation in the framework of Coherent Potential Approximation (CPA) performed in [19] the ferromagnetism in thin films \( \alpha - FeSi_2 \) appears with the substitution of small percent of silicon atoms by the iron atoms. Particularly, when the concentration of substitution Fe atoms reaches 3.3%, these Fe atoms acquire magnetic moment \( \mu = 2.4\mu_B \). Similar explanation of anomalously high total magnetic moment was suggested also by the authors of Refs. [13,20]. The decrease of the magnetic moments of Fe atoms with the increase of the Si concentration was observed experimentally in the iron silicides \( Fe_xSi_{1+x} \) and discussed in the framework of the phenomenological local environment models [21]-[23]. It was noticed, that the changing of magnetic moment of Fe atom in iron silicides \( Fe_xSi_{1+x} \), rather depends on the number of Si atoms in the nearest local environment of iron and not on the concentration of Si atoms. In our work [24] the mechanism of magnetic moment formation in \( Fe_xSi \) is analysed in the framework of the multiorbital model, where it is shown that the neighboring Fe atoms along crystallographic axes as well as Si atoms in the first coordination sphere play the crucial role in the destruction of the Fe magnetic moments. Namely, the increase of the number of such Fe neighbors leads to the decrease of the Fe magnetic moment. Iron atoms in \( \alpha - FeSi_2 \) have only silicon atoms as the nearest neighbors and from the traditional point of view [21]-[25] it is naturally to assume that the absence of the magnetism in this silicide is caused by the nearest silicon environment. However, the specific feature of the \( \alpha - FeSi_2 \) structure is the presence of the alternating Fe and Si planes, which are perpendicular to the tetragonal axis of the cell (Fig.1). In such plane Fe atoms are surrounded only by Fe atoms arranged along the crystallographic axes. Our analysis [24] prompts that such mutual arrangement of Fe atoms should results in the...
magnetic moment destruction. The target of this work is to investigate the influence of local environment on the formation of the magnetic moments on iron atoms in the silicide $\alpha - \text{FeSi}_2$, its ordered $Fe - \text{rich}$ solid solutions with substitutional $Fe$ atoms $Fe_{1+x}\text{Si}_{2-x}$ and $Si - \text{rich}$ one with substitutional $Si$ atoms, $Fe_{1-x}\text{Si}_{2+x}$. Particularly, we will address the question about the role, played by second neighbors of $Fe$ ions in the physics of magnetic moment formation.

The paper is organized as follow. In Sec.II we provide the details of \textit{ab initio} and model calculations. The results of the \textit{ab initio} calculations of $\alpha - \text{FeSi}_2$ and its $Fe$-rich alloys are given in Sec. IIIA. The results of the model calculations of $\alpha - \text{FeSi}_2$ and its $Fe$-rich alloys and the dependence of magnetic moments on the hopping matrix elements are presented in Sec. IIIB. The results of the \textit{ab initio} investigation of $Si$-rich alloys of $\alpha - \text{FeSi}_2$ are described in Sec. IIIC. Sec.IV contains the summary of the obtained results and conclusions.

II. HSCMA: THE HYBRID \textit{AB INITIO} AND MODEL CALCULATION METHOD

In this work we combine the \textit{ab initio} calculations with the model one. We use the following scheme. First we perform the calculation of electronic and magnetic properties of the compound of interest within the framework of \textit{DFT-GGA} for different way of silicon atoms substitution by iron atoms taking into account the relaxation of atomic positions. Then we perform mapping the \textit{DFT-GGA} results to the multiorbital model, suggested in Ref.[23]. The guiding argument for the formulation of the model are: the model should 1) contain as little as possible parameters; 2) contain the specific information about the compound in question, \textit{i.e.}, contain proper number of orbitals and electrons, and to posses the symmetry of the corresponding crystal structure, and 3) contain main interactions, reflecting our understanding of the underlying physics. At last, we perform the mapping following the \textit{DFT} ideology: we find the parameters of the model from fitting the its self-consistent charge density to the one, obtained in the \textit{ab initio} calculations. The latter step distinguishes our approach from other ones [11][25][26]. Here we briefly outline the model Hamiltonian, the details of model calculation are described in [24]. We include into the Hamiltonian of our model set of interactions between the $d$-electrons of $Fe$ ($5d$-orbitals per spin) following Kanamori [27]. The structure contains neighboring $Fe$ ions, for this reason the interatomic direct $d$-$d$-exchange and $d$-$d$-hopping are included too. The $Si$ $p$-electrons ($3p$-orbitals per spin) are modeled by atomic levels and interatomic hoppings. Both subsystems are connected by $d - p$-hoppings. Thus, the Hamiltonian of the model is:

$$H = H^{Fe} + H_{J'}^{Fe-Fe} + H_0^{Si} + H_{hop},$$ (1)

where

$$H^{Fe} = H_0^{Fe} + H^{Fe}_{K},$$

$$H_0^{Fe} = \sum \varepsilon^{Fe}_n \hat{n}^{Fe}_n,$$

$$H_0^{Si} = \sum \varepsilon^{Si}_n \hat{n}^{Si}_n,$$

and the Kanamori’s part of the Hamiltonian

$$H_{hop} = \sum T_{n'n''}^{mm'} \hat{p}_{n'n''}^{\dagger} \hat{p}_{n'n''} + \sum t_{n'n''} \hat{d}_{n'n''}^{\dagger} \hat{d}_{n'n''} + \sum \left[ (t')_{n'n''} \hat{d}_{n'n''}^{\dagger} \hat{p}_{n'n''} + H.c. \right] + \hat{n}^{Fe}_n \hat{n}^{Si}_n \hat{n}^{Si}_n \hat{n}^{Fe}_n \equiv \sum \sigma_{\alpha\gamma} \hat{d}_{n'n''}^{\dagger} \hat{d}_{n'n''} \sigma_{\alpha\gamma} \hat{p}_{n'n''} \sigma_{\alpha\gamma} \hat{p}_{n'n''}.$$ (2)

Here $p_{n'n''}^{\dagger}$($p_{n'n''}$) and $d_{n'n''}^{\dagger}$($d_{n'n''}$) are the creation (annihilation) operators of $p$-electrons on $Si$- and $d$-electrons on $Fe$ -ions; $n$ is complex lattice index, (site, basis); $m$ labels the orbitals; $\sigma$ is spin projection index; $\sigma_{\alpha\gamma}$ are the Pauli matrices; $U, U' = U - 2J$ and $J$ are the intraatomic Kanamori parameters; $J'$ is the parameter of the intersite exchange between nearest $Fe$ atoms. At last, $T_{n'n''}^{mm'}$, $t_{n'n''}$, $(t')_{n'n''}$ are hopping integrals between $Si$-$Si$, $Fe$-$Fe$ and $Fe$-$Si$ atoms, correspondingly. The dependences of hopping integrals $T_{n'n''}^{mm'}$, $t_{n'n''}$, $(t')_{n'n''}$ of $k$ were obtained from the Slater and Koster atomic orbital scheme [2] in the two-center approximation using basic set consisting of five $3d$-orbitals per spin. In this two-centre approximation the hopping integrals depend on the distance $R = (lx + my + nz)$ between the two atoms, where $x, y, z$ are the unit vectors along cubic axis and $l, m, n$ are direction cosines. Then, within the two-center approximation, the hopping
integrals are expressed in terms of Slater – Koster parameters \( t_\sigma = (dd\sigma), t_\tau = (dd\pi) \) and \( t_\delta = (dd\delta) \) for Fe–Fe hopping, \( t_\Sigma = (pd\sigma), t_\Pi = (pd\pi) \) for Fe–Si and \( t_\Omega = (pp\pi), t_\Psi = (pp\sigma) \) for Si–Si hoppings \( \sigma, \pi, \delta \) specifies the components of the angular momentum relative to the direction \( \mathbf{R} \). Their k-dependence are given by the functions \( \gamma_\sigma(k), \gamma_\pi(k) \) and \( \gamma_\delta(k) \), where \( \gamma(k) = \sum_\mathbf{R} e^{i\mathbf{k}\mathbf{R}} \). The expressions for hopping integrals can be obtained in Table I from [3]. For example, \( t_{Fe–Fe}(k) = 2t_\pi [\cos(R_xk_x) + \cos(R_yk_y)] + 2t_\delta \cos(R_zk_z), \) etc. The number of points in the Brillouin zone was taken 1000. Monkhorst-Pack scheme [25] was used for generation of the k-mesh. The model is solved within the Hartree-Fock approximation (HFA). The band structure arises due to hopping parameters, which connect nearest neighbors (NN) and next NN (NNN) sites. The calculations were performed for three initial states: ferromagnetic (FM), antiferromagnetic (AFM) and paramagnetic (PM) states. After achieving self-consistency the state with minimal total energy was chosen. The last step was done with the help of the Galitsky-Migdal formula for total energy ((10) in [24]), which we adopted for our model.

All \textit{ab initio} calculations presented in this paper have been performed using the Vienna \textit{ab initio} simulation package (VASP) [29] with projector augmented wave (PAW) pseudopotentials [30]. The valence electron configurations \( 3d^64s^2 \) are taken for Fe atoms and \( 3s^23p^2 \) for Si atoms. The calculations is based on the density functional theory where the exchange-correlation functional is chosen within the Perdew-Burke-Ernzerhoff (PBE) parametrization [31] and the generalized gradient approximation (GGA) has been used. Throughout all calculations, the plane-wave cutoff energy is 500eV, and Gauss broadening with smearing 0.05eV is used. The Brillouin-zone integration is performed on the grid Monkhorst-Pack [28] special points \( 8 \times 8 \times 6 \). The optimized lattice parameters and atom’s coordinates were obtained by minimizing the full energy.

### III. RESULTS AND DISCUSSION

#### A. \textit{Ab initio} calculations

Stoichiometric compound \( \alpha – FeSi_2 \) has tetragonal space symmetry group \( P4/mmm \) with one formula unit per cell. The structure is shown in Fig. 1. The compound is nonmagnetic metal with lattice parameters from our \textit{ab initio} calculations \( a = 2.70 \text{Å}, c = 5.13 \text{Å} \) that are in a good agreement with experimental values [32]. The structure of \( \alpha – FeSi_2 \) consists of alternating planes of iron and silicon atoms \( Fe – Si – Si – Fe \), which are perpendicular to the tetragonal axis of the cell. Iron atoms are surrounded by 8 silicon atoms \( (R_{Fe–Si} = 2.36) \text{Å} \) located in the corners of slightly distorted in \([001] \) direction cube, the next nearest neighbors (NNN) of iron atoms are Fe atoms arranged along crystallographic axes \( x \) and \( y \), forming the iron plane \( (R_{Fe–Fe} = 2.70) \text{Å} \). The full density of states of \( \alpha – FeSi_2 \) was calculated in the works [33]-[35] and in our recent work [36], thus, in the present paper we give only partial spin-projected density (pDOS) of Fe d - electron states in Fig. 1. As seen, both \( t_{2g} \) and \( e_g \) electrons are delocalized in a wide energy range and a magnetism is absent.

However, as was mentioned in Introduction, several recent studies [13, 19, 20] discovered that a ferromagnetic state arises in the films of \( \alpha – FeSi_2 \). The explanation of the emergence of the magnetic structure, suggested in these works, is within the commonly accepted opinion, that the magnetism arises due to an increase of Fe concentration in the material. The used theoretical approaches, CPA in the Ref. [19] and phenomenological local environment models in Refs [13, 20], take into account, however, only a part of the local environment effects because full account of them is beyond the reach of the standard CPA methods by construction, whereas the local environment models [21, 22] take into account the nearest environment only. In Ref. [24] we found that the next nearest environment (NNN) plays a crucial role in the magnetic moment formation. This motivates us to include the NNN local environment effects into study of the magnetic properties of Fe - rich ordered alloys both in the framework of DFT calculations and subsequent analysis in the suggested multiorbital model too.

The different local environment of iron atoms was set by the different spatial arrangement and number of substitutional Fe atoms in the ordered alloys \( Fe_{1+x}Si_{2-x} \). In this part of paper we presented the results of our \textit{ab initio} calculations of some of ordered alloys \( Fe_{1+x}Si_{2-x} \). We used for the calculations the supercell \( 2a \times 2a \times c \), where \( a \) and \( c \) – the lattice parameters of stoichiometric \( \alpha – FeSi_2 \).

The ordered alloys considered in the present work are shown in Table I. Alloys A and B contain one and three substitutional Fe atoms at the Si sites in the Si planes, correspondingly. In the last three alloys C, D, E four Si atoms were replaced by Fe atoms in different ways: in the
plane perpendicular to \(c\) axis (C), in the plane parallel to \(c\) axis (D) or chess-mate replacement (E). The lattice parameters and calculated magnetic moments on the host iron atoms in \(Fe\) sublattice of \(\alpha - FeSi_2\) (\(Fe_0\)) and on the substitutional iron atoms (\(Fe_I\) and \(Fe_{II}\)) obtained after full optimization of geometry are given in Table I. The geometry optimization results in the elongation of all cells along \(c\) axis and to the compression in the \((ab)\) plane which are most pronounced for the C and E alloys.

| A | B | C | D | E |
|---|---|---|---|---|
| \(a=b=5.37\,\text{Å}\) | \(a=b=5.23\,\text{Å}\) | \(a=b=5.05\,\text{Å}\) | \(a=5.15\,\text{Å}\) | \(a=b=4.80\,\text{Å}\) |
| \(c=5.22\,\text{Å}\) | \(c=5.37\,\text{Å}\) | \(c=5.22\,\text{Å}\) | \(c=5.37\,\text{Å}\) | \(c=6.13\,\text{Å}\) |
| \(\mu(Fe_0)=0.2\,\mu_B\) | \(\mu(Fe_0)=0.5\,\mu_B\) | \(\mu(Fe_0)=0.0\,\mu_B\) | \(\mu(Fe_0)=1.5\,\mu_B\) | \(\mu(Fe_0)=2.0\,\mu_B\) |
| \(\mu(Fe_I)=2.7\,\mu_B\) | \(\mu(Fe_I)=2.6\,\mu_B\) | \(\mu(Fe_I)=2.1\,\mu_B\) | \(\mu(Fe_I)=2.5\,\mu_B\) | \(\mu(Fe_I)=1.3\,\mu_B\) |

The structures of some of ordered alloys, the optimized lattice parameters and the calculated magnetic moments; the colors encode: Si atoms by blue, host \(Fe_0\) atoms by grey, the substitutional \(Fe_I\) and \(Fe_{II}\) atoms by black and green, correspondingly.

Table I. (Color online) The structures of some of ordered alloys, the optimized lattice parameters and the calculated magnetic moments; the colors encode: Si atoms by blue, host \(Fe_0\) atoms by grey, the substitutional \(Fe_I\) and \(Fe_{II}\) atoms by black and green, correspondingly.

The substitution of one Si atom by iron (A) results in the appearance of the large magnetic moments \((\mu(Fe_I) = 2.7\,\mu_B)\) on the substitutional \(Fe_I\) atom. Although the alloy A is ordered the obtained result is coincides with the result obtained in CPA [19] for a random alloy. The value of the magnetic moment and pDOS on the substitutional \(Fe\) atom are in a good agreement with the ones from Ref. [19]. The general feature of both DOS is the sharp peak at the energy \(\sim -3\,\text{eV}\), which originates from the minority \(t_{2g}\) state of \(d\)-electrons (Fig. 2).

A further increase of substitutional Fe concentration leads to the non-trivial results that clearly illustrate the dependence of \(Fe\) magnetic moments on the local environment. As seen from the Table I the substitution of three Si atoms by Fe ones (alloy B) results in the appearance of the ferrimagnetic state: the substitutional \(Fe_I\) and \(Fe_{II}\) atoms become inequivalent: they acquire large magnetic moments, which are not equal to each other, and directed into opposite directions. The absolute values of magnetic moments are close to the ones in the alloy A. The alloy B presents only one of possible ways to order three substitutional Fe atoms in the supercell. Other nonequivalent ordering of the substitutional Fe atoms are shown in Table I. Our ab initio calculations show that the type of the magnetic structure, ferrimagnetic or ferromagnetic, is determined by the spatial arrangement of substitutional Fe atoms. Indeed, the first two alloys in Table I are ferrimagnetic, and the last three are ferromagnetic. The same dependence of the iron magnetic moments on the spatial arrangement (and hence on the the local environment) arises for the alloys with four substitutional Fe atoms on Si sites (C, D, E in Table I). The alloy C and \(\alpha - FeSi_2\) are non-magnetic, while the magnetic moments in the alloys D and E appear on the substitutional \(Fe_I\) and on the host \(Fe_0\) atoms. The pDOSs of substitutional \(Fe_I\) in alloys B, D, E are similar to ones in alloy A, pDOS of \(Fe_{II}\) in alloy B is mirror-symmetric to pDOS of \(Fe_I\). Notice that the \(t_{2g}\) states form peak in pDOS of substitutional \(Fe_I\) atom when the latter has magnetic moment while the pDOS of \(Fe_{II}\) \(d\)-electrons in the non-magnetic alloy C is similar to the one for the Fe atom in \(\alpha - FeSi_2\) (Fig. 1b): \(t_{2g}\) and \(e_g\) electron states are delocalized in the wide energy range.

Thus, our ab initio calculations confirm only part of the conclusions, derived from the local environment models [21][22]: the ferrimagnetism arises with an increase of the Fe concentration indeed, but the types of the magnetic structure of the ordered \(Fe_{1+x}Si_{2-x}\) alloys, which we obtain, are essentially different even at the same concentration of substitutional Fe atoms (Table I and Table II): the magnetic moments on Fe atoms are determined by the composition and the configuration of its local environment. These findings motivate us to investigate the role played by the different local environment on the magnetic moments formation in Fe–Si alloys more carefully.
Figure 2. (Color online) pDOS for host $F_{e_0}$ (left) and substitutional $F_{e_1}$ (right) in the alloy A. Black line shows $t_{2g}$ states, red line shows $e_g$ states. Zero on the energy axis is the Fermi energy.

Table II. (Color online) The ordered alloys with three substitutional Fe atom at the Si sites. Si atoms are shown by blue balls, host $F_{e_0}$ by grey, substitutional $F_{e_1}$ and $F_{e_2}$ atoms are shown by black and green balls, correspondingly.

| $\mu(Fe_0) = 0.2\mu_B$ | $\mu(Fe_1) = 2.7\mu_B$ |
|--------------------------|--------------------------|
| $\mu(Fe_0) = 2.6\mu_B$  | $\mu(Fe_1) = 0.3\mu_B$  |
| $\mu(Fe_0) = -2.4\mu_B$ | $\mu(Fe_1) = -2.0\mu_B$ |

Lattice parameter, Å  | 5.23 | 5.37 | 5.33 | 5.37 | 5.18 | 5.44

B. The model calculations

In this subsection we describe the results of model calculations for the stoichiometric $\alpha-FeSi_2$ and its ordered Fe-rich alloys $Fe_{1+x}Si_{2-x}$ (B, C and D in Table II). In all model calculations we have used the following parameters (see Sec.II): Hubbard $U = 1$, i.e. all other parameters are given in units of $U$; $J = 0.4$, $J' = 0.05$, $\varepsilon_{Si} = 6$, $\varepsilon_{Fe} = 0$. In the general case there are five hopping parameters: $t_1$ (Fe-Fe) and $t_2$ (Fe-Si) between the nearest neighbors (NN); $t_3$ (Fe-Fe), $t_4$ (Fe-Si) between next-nearest neighbors (NNN), and $t_5$ for Si-Si hoppings. The relation $t_\pi = \frac{1}{3}t_\sigma$ for NN and $t_\tau = \frac{1}{2}t_\sigma$ for NNN was kept in all model calculations; for this reason further everywhere we will use $t_\sigma \equiv t$. The values for these hopping parameters are found from the requirement that after achieving self-consistency in both the model and the ab initio calculations (GGA), the d-DOS and magnetic moments on Fe atoms have to be as close to each other as possible.

The best fit of the model magnetic moments and DOS to the ab initio ones can be achieved only when the hopping integrals are positive for the NN and negative for NNN. Along all model calculations we used equilibrium lattice parameter, obtained from the ab initio calculation (see Table I). We also take into account that the values of hopping integrals should correlate with the distance between neighbors in all ordered alloys and in $\alpha-FeSi_2$. The values of hopping parameters which provide the best fit are shown in the Table III.

1. $\alpha-FeSi_2$

We begin with the stoichiometric $\alpha-FeSi_2$ (Fig. Ia). It has the tetragonal lattice with the space group $P4/mmm$. Each of Fe atom in the $\alpha-FeSi_2$ has only Si atoms in the nearest local environment and only Fe atoms as the second neighbors, therefore, there are three hop-
The distances $d$ (Å) between nearest neighbors (NN) and next-nearest neighbors (NNN) and the values of hopping integrals $t$, which provide the best fit of the model charge densities to GGA-DFT ones.

|        | $\alpha$ − FeSi$_2$ | B | C | D |
|--------|----------------------|---|---|---|
| $d$    | $t$                  | $d$| $t$| $d$|
| Fe–Si (NN) | 2.36 | 1.0 | 2.38 | 0.95 | 2.37 | 1.0 | 2.39 | 0.95 |
| Fe–Fe (NN) | -   | -   | 2.40 | 0.9  | 2.44 | 0.85 | 2.43 | 0.85 |
| Fe–Si (NNN) | 2.70 | -0.65 | 2.60 | -0.70 | 2.58 | -0.75 | 2.56 | -0.72 |
| Si–Si (NN)  | 2.34 | 2.0  | 2.39 | 2.0  | 2.54 | 1.5  | 2.41 | 2.0  |
| Si–Si (NNN) | 2.80 | 1.0  | 2.61 | 1.5  | -    | -    | 2.78 | 1.0  |

|        | $\alpha$ − FeSi$_2$ | VASP | Model |
|--------|----------------------|-------|-------|
| $n_2^\uparrow$ | $n_2^\downarrow$ | $n_2^\uparrow$ | $n_2^\downarrow$ |
| $d_{xy}$     | 0.77 | 0.76 | $\mu = 0.1\mu_B$ | 0.69 | 0.66 | $\mu = 0.2\mu$ |
| $d_{xz}$     | 0.72 | 0.71 | $N_{el} = 6.6$ | 0.70 | 0.68 | $N_{el} = 6.6$ |
| $d_{yz}$     | 0.72 | 0.71 |               | 0.79 | 0.68 |               |
| $d_{xy} - y^2$ | 0.58 | 0.55 |               | 0.63 | 0.61 |               |
| $d_{z^2}$   | 0.67 | 0.63 |               | 0.70 | 0.60 |               |

Figure 3. (Color online) Top panel: Nearest and next-nearest neighbors of Fe$_{\alpha}$ with corresponding hopping integrals (Fe and Si atoms are shown by grey and blue balls correspondingly) and the $t_2$ − $t_3$-map of magnetic moments; the blue lines show the values of hopping integrals $t_2$ and $t_3$ from Table III. The map of the magnetic moment dependences on the hopping integrals $t_2$ and $t_3$ is shown in the top panel of Fig. 3. As seen the crucial role in the MM formation is played by hoppings between NNN Fe − Fe ($t_3$). Indeed, with $|t_3| > 0.6$ the experimentally existing nonmagnetic state is stable, a decrease of $|t_3|$ leads to the transition into ferromagnetic state. Furthermore, the boundaries between region with magnetic states and non magnetic ones are very sharp (Fig. 3 top panel): the MM decreases till zero very fast as a function of hopping $t_3$ between iron atoms. The hopping between NNN Fe − Si ($t_3$) has effect only on the magnitude of the MM in the ferromagnetic region. The mechanism of ferromagnetism destruction with hopping $t_3$ is clearly seen from the bottom panel of Fig. 3. Switching off the hopping between NNN Fe − Fe ($t_3 = 0$) makes the d-bands atom-like with the slight smearing. An increase of the $t_3$ hopping leads to a delocalization of these atom-like d-bands and destruction the magnetism. Hence, an increase of the distance between NNN (or, a decrease the hopping integral $t_3$) would results in the transition from nonmagnetic phase to magnetic one. This conclusion from the analysis of the model is confirmed by the ab initio calculation: the increase of the lattice parameters $a$ and $b$ of $\alpha$ − FeSi$_2$ (or the distance NNN Fe − Fe) by 7% ($a = b = 2.9\text{ Å}$, $c = 5.13\text{ Å}$) causes formation of MMs $\mu = 0.6\mu_B$ on the Fe atoms. Thus, it is rather the hopping integral between the NNN Fe − Fe atoms, not the NNN Fe − Si hopping, determines the existence of magnetic or nonmagnetic state in $\alpha$ − FeSi$_2$, because the NNN of Fe atom consist of Si atoms in the both cases.

In order to understand the effect of NN and NNN neighbors in the local environment on the magnetic moment (MM) formation we calculated the dependence of the MMs on the hopping integrals $t_2$ (NN Fe − Si) and $t_3$ (NNN Fe − Fe). The map of the magnetic moment dependences on the hopping integrals $t_2$ and $t_3$ is shown in the top panel of Fig. 3. As seen the crucial role in the MM formation is played by hoppings between NNN Fe − Fe ($t_3$). Indeed, with $|t_3| > 0.6$ the experimentally existing nonmagnetic state is stable, a decrease of $|t_3|$ leads to the transition into ferromagnetic state. Furthermore, the boundaries between region with magnetic states and non magnetic ones are very sharp (Fig. 3 top panel): the MM decreases till zero very fast as a function of hopping $t_3$ between iron atoms. The hopping between NNN Fe − Si ($t_3$) has effect only on the magnitude of the MM in the ferromagnetic region. The mechanism of ferromagnetism destruction with hopping $t_3$ is clearly seen from the bottom panel of Fig. 3. Switching off the hopping between NNN Fe − Fe ($t_3 = 0$) makes the d-bands atom-like with the slight smearing. An increase of the $t_3$ hopping leads to a delocalization of these atom-like d-bands and destruction the magnetism. Hence, an increase of the distance between NNN (or, a decrease the hopping integral $t_3$) would results in the transition from nonmagnetic phase to magnetic one. This conclusion from the analysis of the model is confirmed by the ab initio calculation: the increase of the lattice parameters $a$ and $b$ of $\alpha$ − FeSi$_2$ (or the distance NNN Fe − Fe) by 7% ($a = b = 2.9\text{ Å}$, $c = 5.13\text{ Å}$) causes formation of MMs $\mu = 0.6\mu_B$ on the Fe atoms. Thus, it is rather the hopping integral between the NNN Fe − Fe atoms, not the NNN Fe − Si hopping, determines the existence of magnetic or nonmagnetic state in $\alpha$ − FeSi$_2$, because the NNN of Fe atom consist of Si atoms in the both cases.
As it follows from *ab initio* calculation, the ordered alloy D reveals ferromagnetism, whereas the alloy C remains nonmagnetic (Table I). These ordered alloys have two nonequivalent Fe atoms: Fe0 is the host iron atom in the iron sublattice of α−FeSi2 and Fe1 is the substitutional Fe atoms in the Si sublattice. Different spatial arrangement of the substitutional Fe atoms results in the different environment of the host and substitutional Fe atoms in alloys D and C. These environments are shown in Fig. 4 (top panel). There is the important difference in the NNN environment of Fe0 and Fe1 in C and D alloys. In the C alloy both Fe0 and Fe1 atoms have four Fe atoms along crystallographic axes a and b as NNN at the same distances $R = 2.53\text{ Å}$ (Table III). The host Fe0 in the alloy D also has four NNN Fe atoms, but at different distances: two Fe neighbors along axis a with the distance $R = 2.56\text{ Å}$ and two ones along axis b with $R = 2.78\text{ Å}$. These inequal distances arise due to the different symmetry of crystal lattices: the C lattice is tetragonal with the space group $P4mm$, while the D one is orthorhombic with space group $Pmmn$. Thus, the distortions of the underlying tetragonal lattice of $\alpha−FeSi_2$...
arising in these alloys are different. Notice, that the distances between the NN Fe – Si and the NN Fe – Fe in both alloys are the same. Besides, the atom Fe1 has only two NNN Fe atoms at the distance R = 2.78Å in the alloy D. This distance is larger than the corresponding one in the alloy C. Therefore, we are forced to introduce in the alloy D two hopping integrals for the short $t_3^2$ and long $t_3^3$ distances between NNN Fe – Fe, while only one hopping integral $t_3$ is required for the description of the alloy C. The values of hopping integrals providing the best fitting to the ab initio calculation are given in Table III. The Hartree-Fock self-consistent MMs generated by the model at these values of hopping parameters are $\mu^{\text{mod}}(Fe_0) = \mu^{\text{mod}}(Fe_1) = 0$ in alloy C and $\mu^{\text{mod}}(Fe_0) = 1.4\mu_B$, $\mu^{\text{mod}}(Fe_1) = 2.5\mu_B$ in alloy D.

Let us compare the dependences of the Fe magnetic moments on the NN hopping integral $t_1$ and $t_2$ at fixed values of NNN hopping integral $t_3$ and $t_4$, shown at the middle panel of Fig.4. The range of the magnetic moments existence on both $Fe_0$ and $Fe_1$ atoms in the alloy D is restricted by the values of $|t_1| < 1$. The magnetic state with moments close to ab initio values ($\mu(Fe_0) = 1.5\mu_B$, $\mu(Fe_1) = 2.5\mu_B$) is on the narrow boundary between ferro- and paramagnetic phases. In the alloy C the nonmagnetic state is stable in all range of the hoppings between NN $t_1$ and $t_2$. Namely the circumstance that the magnetic moments are close to the instability line make them very sensitive to changes of the NNN hoppings. Indeed, which of solutions, magnetic or non-magnetic, will arise, is controlled by the value of hopping integral $t_3$: $t_3^2(Fe – Fe) = -0.75$ leads to formation of the paramagnetic state in the alloy C, whereas a decrease of $t_3$ in the alloy D, $t_3^D(Fe – Fe) = -0.60$ gives birth to a ferromagnetic state in the alloy D. The increase of $|t_3^2(Fe – Fe)|$ compared to $|t_3^D(Fe – Fe)|$ occurs due to shorter distance between Fe atoms in the NNN environment in alloy C (Table III). Moreover, a decrease of $|t_3|$ results in appearance of magnetic moments on both Fe atoms in the alloy C; at $t_3 = 0$ the map of magnetic moments in the alloy C becomes similar to one for the alloy D (Fig. 4 bottom panel). At first glance one could expect that the formation of the Fe-Si bond should destroy the moment on the Fe atom. However, the magnetic moments on Fe atoms happen to be much less sensitive to the hopping parameter $t_3$ between NN Fe and Si atoms. Indeed, all the $t_1 – t_2$-maps for Fe moments, calculated within this model, are elongated along the axis $t_2$.

The physics of the destruction of the magnetic moments on Fe atoms can be interpreted from the point of view of the d-band formation. The Fig. 5 illustrates this for the alloy C via the evolution of the $Fe_1$ d-electron pDOS and corresponding magnetic-moment maps with the increasing of only hopping integral $t_3$ at all other hopping integrals kept fixed. As seen, at first steps of increase of $t_3$ a gradual smearing of initially (at $t_3 = 0$) atom-like levels and a slight change of the map of magnetic moments occurs. Then, similar to the case of $Fe_1$ at $t_3 = 0$, the abrupt destruction of the magnetic moments arises and the difference between the minority and majority spin states in pDOS disappears.

Let us now discuss the origin of the unusual ferromagnetic state in the type of the alloy B (Table II), which contains three substitutional Fe atoms on the Si sites. The ordered alloy B has the tetragonal lattice with space group $P4mm$. There are three non-equivalent Fe atoms in the unit cell: $Fe_0$ is the host iron sublattice of $α – FeSi_2$, $Fe_2$ and $Fe_1$ are the non-equivalent substitutional Fe atoms in the Si sublattice. In accordance with ab initio calculations, the absolute values of magnetic moments on $Fe_2$ and $Fe_1$ atoms are close to each other, but have opposite directions: $\mu(Fe_2) = 2.3\mu_B$, $\mu(Fe_1) = -1.9\mu_B$. The model MMs obtained for the values of hopping integrals from Table II are $\mu^{\text{mod}}(Fe_2) = 2.8\mu_B$, $\mu^{\text{mod}}(Fe_1) = -2.1\mu_B$, and $\mu^{\text{mod}}(Fe_0) = 0.7\mu_B$. The specific feature of Fe-pDOS in the alloy B is that the $Fe_1$-pDOS is mirror-symmetric.
Thus, our analysis of the Hartree-Fock solutions of the multiorbital models of iron silicides and supporting them first-principle calculations allow to conclude that the decisive role in the destruction/formation of the iron magnetic moments is played by the NNN local environment or, more specifically, by the number of neighbors Fe–Fe and the by spacing between them. The results of our calculations show that the previous statement \[21-23\], that the destruction of magnetic moments in the iron silicides is caused by the increase of Si atoms in the NN environment is inaccurate. The obtained in our calculations strong influence of NNN Fe–Fe couples is caused by the peculiarity of the α–FeSi\(_2\) crystall structure, where the the iron atoms form planes. Since NNN Fe–Fe are arranged along crystallographic axes, the strong σ-bonds between Fe atoms are formed. So in the alloy C and α–FeSi\(_2\) which contains the iron (001) planes with the shorter distance between Fe–Fe than in the alloy D, these d-bonds result in the delocalization of the electrons and a decrease of the MMs up till their destruction (Fig. 5). At the same time in the alloys C and D Fe atoms have the same number of Si atoms in the NN environment and this does not prohibit them to have different MMs. It is very instructive to have a look from this point of view at the MM formation in the alloy A where the substitutional Fe atoms have maximal MMs compared to the ones in all other alloys considered here. The NNN environment of the substitutional Fe\(_{\alpha}\) atom in the alloy A (Table III first column) consists of only Si atoms; the hoppings between Fe–Fe which are responsible for the destruction of moment are absent. This facts lead to the formation of a large value of MM on this iron atom.

In order to demonstrate the decisive role of the d–d-hopping integral \(t_3\) between NNN Fe–Fe on the formation of the MM on Fe atoms we calculate the dependence of Fe MM on this hopping for \(\alpha–FeSi_2\) and the alloys C and B. This dependence is shown at Fig. 6. As seen, the increase of \(t_3\) in the alloy C and in \(\alpha–FeSi_2\) causes a destruction of the Fe MMs, whereas in the alloy B the abrupt flip of the Fe\(_{\alpha}\) moment magnetic is occurred with an increase \(t_3\). The model results are confirmed by the ab initio calculations. Obviously, the hopping integral \(t_3\) changes its value with an increase of the spacing between NNN Fe–Fe. Since the integral of the hopping matrix element contains an overlap of the wave functions, we assume that it depends on the distance \(R\) between the ions exponentially,

\[
t_3(R) = t_3^{\text{max}} \exp(\gamma \Delta R),
\]

where \(t_3^{\text{max}} = t_3(R_{\text{min}})\) and \(\Delta R = R - R_{\text{min}}(\text{Å})\). Taking the values \(t_3^{\text{max}} = -0.75\) and \(R_{\text{min}} = 2.53\) from Table III we have found the parameter \(\gamma = -0.8926(\text{Å}^{-1})\).
Using Eq. (3) we obtained the distances $R$ between NNN $Fe-Fe$ corresponding to the model parameters $t_3$. Then the values of the MM for the lattice parameters correspond to these distances have been calculated within GGA-to-DFT. These values are shown in Fig. 8 by dots. Remarkably, although the only $t_3$ hopping was changed with the distance $R$ in the model calculations (the values of the other hopping parameters were kept fixed according to Table III) we obtained the good agreement between the model and the ab initio magnetic moments. This again proves the significance of the NNN $Fe-Fe$ couplings for the MM formation.

C. Ab initio calculation of the Si-rich alloys.

Our model calculations lead to the conclusion that the $Fe$ local MM formation is controlled either by a decrease of the number of $Fe-Fe$ couples in $Fe$ layers or by an increase of the distance between $Fe$ atoms in pairs. Moreover, we can state that the increase of the cell’s magnetic moment with increase of $x$ in Fe-rich alloys $Fe_{1-x}Si_{2-x}$ is associated namely with the appearance of high-spin Fe species in the Si layers, which are surrounded mainly by the Si atoms. However, these conditions can be fulfilled also by an increase of the Si concentration. To make sure that this unexpected conclusion derived from the model is correct we carried out the ab initio GGA calculation of Fe magnetic moments for the Si-rich ordered alloys $Fe_{1-x}Si_{2+x}$. The alloy’s structures must satisfy the conditions listed above. By adding Si atoms into the iron planes we can decrease the number of the $Fe-Fe$ couples. Besides, the substitutional Si atoms increase the spacing between the Fe atoms.
Figure 8. (Color online) The dependence of MMs on the host Fe₀ and the substitutional Fe₁ and Fe₁₁ atoms on hopping \( t₃ \) in \( α-FeSi₂ \), the alloys C and B (from left to right). The solid lines are the dependences, obtained in model calculations, the dots show the MMs from \textit{ab initio} calculations at the distance \( R \) between NNN Fe-Fe, according to (3). The scale for the distances (in Å) is given on the tops of the figures.

Fig. 9 displays three different variants of substitution of Fe atoms in the Fe planes by the Si atoms. All calculations were carried out for the supercells \( 2a \times 2b \times 2c \) of \( α-FeSi₂ \), containing six iron atoms and two additional Si atoms. After full optimization of the supercells all considered alloys become magnetic, but the magnitude of the magnetic moment \( \mu \) per supercell depends on the particular arrangement of substitutional Si atoms: \( \mu = 3.2 \mu_B \) (Fig. 9a), \( \mu = 3.1 \mu_B \) (Fig. 9b), and \( \mu = 1.7 \mu_B \) (Fig. 9c). The emergence of local MM on different Fe atoms in the first two alloys (Fig. 9a, b) corresponds to the expectations, derived from the model. Indeed, since the number of iron NNN surrounded Fe₃ atom in the first alloy (Fig. 9a) is decreased by two, the local magnetic moment \( \mu(Fe₃) = 0.8 \mu_B \) on the Fe₃ atom arises. Similar local MM appears on the Fe₁ and the Fe₅ atoms in the second alloy (Fig. 9b) due to an increase of the distance between NNN Fe – Fe till \( ≃2.8 \text{Å} \). The third alloy (Fig. 9c), however, presents an example where, it seems, the model is oversimplified: the GGA calculation produces zero moment on the Fe₅ atom without Fe atoms in NNN surrounding, while according to our model the biggest local magnetic moment have to arise on the Fe₅ in this case. We assume that the term responsible for it and which is missed in our model is the crystal electric field (CEF), created by the Si surrounding. The Fe₅ in the third alloy (Fig. 9c) sits in the most symmetrical local surrounding \( P4/mmm \) by Si atoms, where the CEF splitting has to be stronger than in the first two cases (Fig. 9a, b).

The statement that the magnetic moments in Fe – Si alloys can arise due to an increase of the Si concentra-
tion allows us to suggest an alternative explanation of the ferromagnetism in the FeSi$_2$(111) film on Si(001) substrate, successfully stabilized by the authors of [19]. The authors of Ref. [19] explain the ferromagnetism of the α-FeSi$_2$ film by the small concentration (about 3%) of the additional substitutional Fe atoms. The calculation in [19] were performed in the framework of CPA, which is not able to take into account the local-environment effects. We assume that the observed moment arises not due to an increase of the Si concentration that arises due to a diffusion of the Si atoms from the Si substrate. For example, the lattice parameters in the considered here Si-rich alloys are such that the (111) elementary-cells sizes of the α-FeSi$_2$ are very close to the Si(001) − (3 × 2)(11.5 × 7.68Å): (11.83 × 7.89Å), (11.76 × 7.83Å), (11.67 × 7.93Å) for the first (Fig. 9a), second (Fig. 9b) and third (Fig. 9c) alloys, correspondingly. This corresponds to the mismatch about (−1.5%)−(−2.5%). Such a low mismatch presents an opportunity to stabilize the epitaxial films of the α-FeSi$_2$ structure with similar arrangements of Si atoms. The magnetic moment $\mu \approx 0.2$: $-0.4 \mu_B$/f.u., arises for all types of the substitutions shown in Fig. 9, which is consistent with the observed in Ref. [19] values.

IV. CONCLUSIONS

Today it is recognized, that the large, if not the decisive, role in the mechanism of the magnetic structure formation in different compounds is played by the local environment of the magnetic species. However, most of ab initio codes, based on DFT, are complicated and usually represents a “black box”, impedes the physical interpretation of the results. In particular, it is difficult to extract the contributions from different local environment of an atom. Effects of local environment are especially important in alloys, in which the slight difference in the local environment can result in significantly different magnetic structures. The substitutionally disordered systems such as metallic alloys play an increasingly important role in technological applications and, hence, a lot of efforts are invested into a theoretical understanding of their properties. Although CPA is nowadays the most successful ab initio theory for the calculations of disordered alloys, the standard formulation of it neglects the effects of NNN environment. Along with the development of the ab initio methods (as non local CPA[37]), the understanding of the certain property of the specific compound can be reached in the framework of the suitable models with the parameters obtained from the ab initio calculations for a given compound. Namely such combination of the ab initio calculations with the multiorbital model one for the iron silicides was used in our work. The feature which distinguish our model approach from other ones is that the parameters of the model are determined from the fitting its self-consistent charge density to the one, obtained by ab initio calculations. This allows to study the effects of NN and NNN local environment of the Fe atoms on the MM formation.

The presented study of the effect of silicon-atoms’ substitution by the iron atoms and vice versa on the magnetic properties in the iron silicide α-FeSi$_2$ within the suggested multiorbital model has shown that while the stoichiometric material α-FeSi$_2$ is nonmagnetic, the appearance of substitutional iron atoms in the α-FeSi$_2$ may result in different magnetic structures, either ferromagnetic or ferrimagnetic. Which particular structure emerges is determined by the number and the spatial arrangement of the substitutional iron atoms. The latter statement is strongly supported by the fact that different magnetic structures can appear at the same concentration of substitutional Fe atoms. Besides, as follows from the Hartree-Fock model calculations, the MMs formation is essentially determined not by the NN Si atoms but by the NNN environment, particularly, by the Fe atoms along the crystallographic axes: the MMs on iron atoms are very sensitive to the values of NNN Fe - Fe hopping parameters $t_3$. We demonstrated it by a comparison of the maps of moments dependence on the hopping parameters with and without taking into account NNN ones. It is important that the nonmagnetic states in the stoichiometric α-FeSi$_2$ arise at NNN $t_3 \neq 0$ only. The model with NN hoppings only, even if all NN to Fe atoms are Si atoms, does not have the solutions with zero moments on Fe. This allows to suggest that the magnetism in the nonmagnetic α-FeSi$_2$ can be induced by a negative pressure.

The various magnetic structures (ferro-, ferri- or non-magnetic) in Fe-rich alloys also controlled by the NNN Fe - Fe hopping parameters $t_3$. The different ways of Si atoms substitution by Fe atoms result in the diverse local distortions of the underlying lattice and, in turn, to quite different hopping parameters $t_3$ and magnetic properties. It is most clearly demonstrated by the magnetic behavior of several alloys with the same concentration of substitutional atoms, e.g., alloys C and D considered in this work (Sec.IIB). The comparison of the magnetic-moments maps reveals that different values of NNN Fe - Fe hopping parameters $t_3$ lead to the diverse magnetic behaviour: a nonmagnetic one in the alloy C and a ferromagnetic one in the alloy D. Notice, despite of the different lattice distortion, the spacing between NN (as well as number of NN Si atoms) is the same in the both cases, hence, the local environment models which do not take into account the NNN hoppings, cannot explain this distinction. Unlike the local environment models[21][22] we observe a weak dependence of the Fe magnetic moment on the hopping $t_2$ between NN Fe and Si atoms: all the $t_1 - t_2$-maps for Fe moments, calculated within this model, are elongated along the axis $t_2$. One more characteristic feature of these maps is the presence of sharp boundaries between magnetic states region and nonmagnetic one as a function of NN Fe – Fe hopping integral $t_1$. In general, our conclusion about the decisive
role of NNN local environment in the magnetic moment formation contradicts to the conclusions of earlier (much less detailed) models of local environment, where a decrease of the moment on Fe atoms was ascribed to the increase of number of Si in NN sphere. According to our calculations the main role in formation of local magnetic moment is played by decreasing of the number of Fe−Fe pairs along the crystallographic axes and/or increasing of the distance between them. This conclusion is especially interesting since most of models do not take the NNN hoppings into account.

The unexpected and somewhat counter-intuitive conclusion, produced by the model calculations, is that not only an increase of the Fe concentration can lead to the emergence of local magnetic moment on Fe atoms, but also of the metalloid concentration. Indeed, the number of the Fe−Fe pairs can be reduced by replacing of the Fe atoms in iron planes by Si atoms. Moreover the distances between Fe atoms in these planes are increased due to the distortion of the underlying lattice. So, the conditions leading to the emergence of magnetism are met. The ab initio calculation of the ordered Si-rich alloys confirms this conclusion. Hence we can explain the ferromagnetism in the α − FeSi2(111) film, obtained by the authors of Ref.[19], in a more realistic way. In our opinion, the observed in Ref.[19] moment results from the increase of Si concentration due to a diffusion of the Si atoms from the Si substrate, but not due to an increase of the Fe concentration.

Based on the presented analysis, we can formulate the conditions promoting the appearance of a magnetism in the iron silicides. The key parameters responsible for the magnetism are the hoppings between Fe atoms t4 and t3, which are the most sensitive parameters to different types of pressure. The latter can be done by either byfitting the lattice parameter of the substrate for α − FeSi2 film (chemical pressure), or by a substitution of Fe or Si atoms. As was pointed out in Ref.[20], the best orientation relationships, that stabilize the epitaxial α − FeSi2 are α − FeSi2(201)||Si(110), α − FeSi2(110)||Si(111) or α − FeSi2(111)||Si(001). Such planes contain additional Si atoms in Si-rich alloys from Fig. and the sizes of corresponding unit cells are very close to the Si-substrate one. Small mismatch has place for the all mutual orientations of film and substrate and presents an opportunity to stabilize the epitaxial films of the α − FeSi2 structure. Moreover the possibility of tuning the hopping parameter t3 in iron silicides has the large technological interest, because it gives an opportunity to control the appearance of different magnetic configurations in the cause of fabrication of new alloys or nanostructures with the prospective magnetic properties. At last, the existence of the region with sharp transition from ferro- to paramagnetic or from ferro- to ferrimagnetic state strongly improves the perspectives of the practical applications of iron silicide films and, hopefully, will stimulate technologists to find a way to make the films near the instability line with desirable characteristics.

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