APPENDIX A.

Following [12] we give here the block-scheme and brief description of the code, developed by us for the analysis of the model. The eigenvalues of model Hamiltonian (1) are found in the Hartree-Fock approximation by Green function method (HFA). After standard HFA decoupling and Fourier transformation we obtain the matrix equation for the Green's functions $G^{\sigma}_{i_1 m_1, i'm'}$ for each spin for spin-homogeneous states:

$$\left(E\delta_{ii_1}\delta_{mm_1} - \Omega^{\sigma}_{im,i_1 m_1}(k) \right) G^{\sigma}_{i_1 m_1, i'm'}(k,E) = \delta_{ii'}\delta_{mm'},$$

(A1)

where m stands for orbital and i labels atom in the basis. Particularly, for the α-$FeSi_2$ the matrix Ω has size 11×11 for each spin. The matrix $\Omega^{\sigma}_{im,i_1 m_1}$ consist of the blocks,

$$\Omega(k) = \begin{pmatrix} \Omega_{FeFe}(k) & \Omega_{FeSi}(k) \\ \Omega^{\dagger}_{FeSi}(k) & \Omega_{SiSi}(k) \end{pmatrix},$$

(A2)

which have the form

$$[\Omega_{FeFe}(k)]^{\sigma}_{\lambda i,\mu j} = \delta_{\lambda\mu}\delta_{ij}\varepsilon^{Fe}_{i\sigma} - t^{\lambda\mu}_{ij}(k), \quad [\Omega_{FeSi}(k)]^{\sigma}_{\lambda i,\mu j} = [t'(k)]^{\lambda\mu}_{ij},$$

(A3)

$$[\Omega_{SiSi}]^{\sigma}_{\lambda i,\mu j}(k) = \delta_{\lambda\mu}\delta_{ij}\varepsilon^{Si}_{i\sigma} - T^{\lambda\mu}_{ij}(k)$$

(A4)

with

$$\varepsilon^{Fe}_{i\sigma} = \varepsilon^{Fe}_0 + Un^{d,\bar\sigma}_{i\lambda} + U'\sum_{m\neq\lambda} n^d_{im} - 2J\eta(\sigma)\sum_m \sigma^{d,z}_{im} - 2J'\eta(\sigma)\sum_{l,m}\sigma^{d,z}_{lm}$$

(A5)

$$n^{d,\bar\sigma}_{i\lambda} = \sum_k \langle d^{\dagger}_{k,i\lambda\bar\sigma} d_{k,i\lambda\bar\sigma}\rangle, \quad n^{d,\sigma}_{i\lambda} = \sum_k \langle d^{\dagger}_{k,i\lambda\sigma} d_{k,i\lambda\sigma}\rangle, \quad \sigma^{d,z}_{im} = \frac{1}{2}\sum_{\sigma}\sigma n^{d,\sigma}_{im}.$$

(A6)

And $\sigma = \uparrow,\downarrow; \eta(\uparrow) = 1, \eta(\downarrow) = -1$. Then the self-consistent equations for population numbers are expressed in terms of eigenvalues $\varepsilon^{\sigma}_{\nu}(k)$ and eigenvectors $u^{\nu\sigma}_{im}(k)$ of matrix $\Omega^{\sigma}_{im,i_1 m_1}(k)$:

$$n^{d,\sigma}_{im}(k) = \langle d^{\dagger}_{k,im\sigma} d_{k,im\sigma}\rangle = \sum_{\nu} [u^{\nu\sigma}_{im}(k)]^* f\left(\varepsilon^{\sigma}_{\nu}(k) - \mu\right) u^{\nu\sigma}_{im}(k).$$
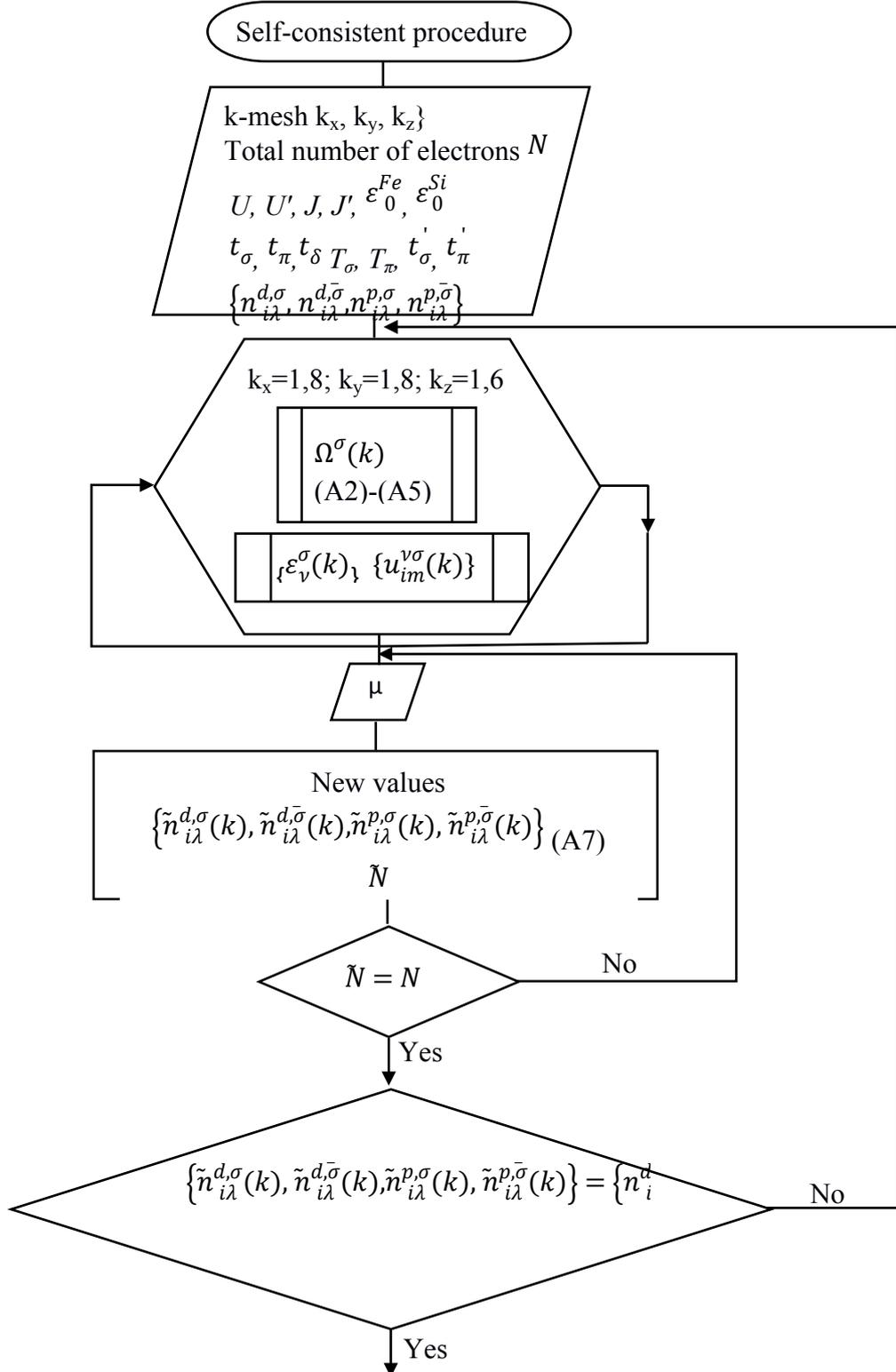
(A7)

The function $f(x) = [1 + exp(x/T)]^{-1}$ is Fermi function, chemical potential μ is found, as usual, from the full number of electrons per the cell.

The dependences of hopping integrals $t^{mm'}_{nn'}$, $(t')^{mm'}_{nn'}$, $T^{mm'}_{nn'}$ on k were obtained from the Slater and Koster atomic orbital scheme [18] in the two-center approximation using basic set consisting of five $3d$ orbitals for each spin on each Fe and three $3p$ orbital for each spin on each Si. In *two-centre approximation* the hopping integrals depend on the displacement $R=(l\mathbf{x}+m\mathbf{y}+n\mathbf{z})$ between the two atoms, where $\mathbf{x, y, z}$ 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 $t_\sigma \equiv (dd\sigma)$, $t_\pi \equiv (dd\pi)$ and $t_\delta \equiv (dd\delta)$ for $Fe - Fe$ hopping and $t_\sigma \equiv (pd\sigma)$, $t_\pi \equiv (pd\pi)$ for Fe- Si and $Si - Si$ hoppings (σ, π, δ specifies the component of the angular momentum relative to the direction $\boldsymbol{R}$). Their $\boldsymbol{k}$-dependence are given by the functions $\gamma_\sigma(\boldsymbol{k})$, $\gamma_\pi(\boldsymbol{k})$ and $\gamma_\delta(\boldsymbol{k})$, where $\gamma(k) = \sum_R e^{ikR}$. The expressions for hopping integrals can be obtained with Table I from [31]. For example, $t_{Fe-Fe}^{xy,xy}(k) = 2t_\pi(cos(R_x k_x) + cos(R_y k_y)) + 2t_\delta cos(R_z k_z)$, etc.

Self-consistent procedure

k-mesh k_x, k_y, k_z}
Total number of electrons N
U, U', J, J', ε_0^{Fe}, ε_0^{Si}
t_σ, t_π, t_δ T_σ, T_π, t_σ', t_π'
$\{n_{i\lambda}^{d,\sigma}, n_{i\lambda}^{d,\bar{\sigma}}, n_{i\lambda}^{p,\sigma}, n_{i\lambda}^{p,\bar{\sigma}}\}$

$k_x = 1,8$; $k_y = 1,8$; $k_z = 1,6$

$\Omega^\sigma(k)$
(A2)-(A5)

$\{\varepsilon_\nu^\sigma(k)\}$ $\{u_{im}^{\nu\sigma}(k)\}$

μ

New values
$\{\tilde{n}_{i\lambda}^{d,\sigma}(k), \tilde{n}_{i\lambda}^{d,\bar{\sigma}}(k), \tilde{n}_{i\lambda}^{p,\sigma}(k), \tilde{n}_{i\lambda}^{p,\bar{\sigma}}(k)\}$ (A7)
$\tilde{N}$

$\tilde{N} = N$ — No

Yes

$\{\tilde{n}_{i\lambda}^{d,\sigma}(k), \tilde{n}_{i\lambda}^{d,\bar{\sigma}}(k), \tilde{n}_{i\lambda}^{p,\sigma}(k), \tilde{n}_{i\lambda}^{p,\bar{\sigma}}(k)\} = \{n_i^d$ — No
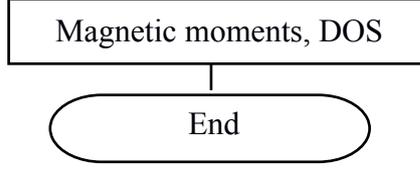
Yes

Figure A1. The block diagram of self-consistent procedure

The population numbers $n_{im}^{d,\sigma}(k),\ n_{im}^{p,\sigma}(k)$ have been found self-consistently with the accuracy $o(10^{-3})$. The number of point in the Brillouin zone was taken 864 (8×8×6) for the *simple tetragonal* lattice. The Monkhorst-Pack scheme [16] was used for generating of the k-mesh. The block-diagram of the self-consistent procedure for the population numbers is presented in Fig. A1. Both types of initial states, the magnetic and the paramagnetic ones, have been tested in the calculations. 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, which we adopted for our model. Within HFA it acquires the form:

$$E_{tot} = \frac{1}{2}\sum_{ij\lambda\mu}\sum_{vk}[u_{im}^{v\sigma}(k)]^*\left(\tau_{ij}^{\lambda\mu}(k) + \varepsilon_v^\sigma(k)\right)f\left(\varepsilon_v^\sigma(k) - \mu\right)u_{im}^{v\sigma}(k),$$

(A8)

with

$$\tau_{ij}^{\lambda\mu}(k) = \delta_{ij}\delta_{\lambda\mu}\varepsilon_i^0 + t_{ij}^{\lambda\mu} + (t')_{ij}^{\lambda\mu} + T_{ij}^{\lambda\mu}$$

(A9)

(*i,j* label the sorts of atoms).

The model charge densities, obtained self-consistently, have to be as close as possible to the GGA ones, i.e. the model parameters can be found from minimization of the difference between the *ab initio* electron density $\rho_{GGA}(k,\sigma)$ and the model one $\rho_{model}\left(k,\sigma;U,U',J,J',\{t,T,t'\}\right)$

$$Y = [\rho_{GGA}(k,\sigma) - \rho_{model}\left(k,\sigma;U,U',J,J',\{t,T,t'\}\right)]^2$$

with respect to interaction parameters *[10,12]*. Since the Hartree-Fock equations have to be solved self-consistently for each set of the model parameters, we simplified the problem further and instead of minimization of function Y (*i.e.*, the differences of the model and VASP electron spin densities in each point of space) we've chosen to fit the occupation numbers of d-electrons ($n_{i\lambda}^{d,\sigma}$), the magnetic moments of Fe atoms (m_{Fe}) and partial d-densities of states (g_{Fe}) for Fe atoms

$$Y = (n_{i\lambda}^{d,\sigma}[GGA] - n_{i\lambda}^{d,\sigma}[model])^2 + (m_{Fe}[GGA] - m_{Fe}[model])^2 +$$

$$+ (g_{Fe}[GGA] - g_{Fe}[model])^2$$

(A10)

A self-consistent procedure is performed for several sets of parameters ($U,\ U',\ J,\ J',\ \varepsilon_0^{Fe},\ \varepsilon_0^{Si},\ t_\sigma,$ $t_\pi, t_\delta\ T_\sigma,\ T_\pi,\ t_\sigma',\ t_\pi'$). Then we choose the set of parameters, providing the best fit to ab initio calculations, i.e. min *Y*.