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Phase transitions induced by concentration and thermodynamic magnetic fluctuations in chiral ferromagnets Fe$_{1-x}$Co$_x$Si

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ABSTRACT
Taking into account the results of LDA+U+SO-modeling of the electronic structure of Fe$_{1-x}$Co$_x$Si, temperature-prolonged magnetic phase transitions of the first order in strongly correlated alloys with a broken crystal structure of the B20 type are investigated. It is shown that such phase transitions are induced by concentration and thermodynamic fluctuations for compositions with 0.2 $<$ x $<$ 0.65 and are accompanied by a change in the sign of the mode-mode coupling parameter. In this case, an intermediate region appears between the long-range order phases and the paramagnetic phase, with the short-range spin order characterized by ferromagnetic and helicoidal spatial fluctuations. We have defined the intervals of external magnetic fields, at which skyrmion microstructures spatially limited by the crossover of helicoidal and ferromagnetic fluctuations appear in the considered region of the extended phase transition. The peculiarities of the temperature dependences of the magnetic susceptibility in an external magnetic field, characteristic of the appearance of skyrmions, are obtained.

I. INTRODUCTION

The crystal structure of helicoidal ferromagnets MnSi, Fe$_{1-x}$Co$_x$Si, Fe$_{1-x}$Mn$_y$Si, etc. belongs to the B20 structure type with the P2$_1$3 space group, in which there is no inversion symmetry.\textsuperscript{1} The latter removes prohibition of the existence of the antisymmetric relativistic Dzyaloshinskii–Moriya (DM) exchange, the occurrence of which is one of the reasons for magnetic chirality. In the region of magnetic phase transitions in these materials, the neutron diffraction experiment reveals an intermediate (between the helicoidal and paramagnetic phases) region of spin short-range order, in which fluctuations of the helix are observed.\textsuperscript{2} In this case, skyrmion microstructures appear in external magnetic fields, the nature of the formation of which remains unclear.

From the analysis of the Ginzburg–Landau functional it follows\textsuperscript{3} that the order of magnetic phase transitions observed in chiral ferromagnets is determined by the sign of the mode-mode coupling parameter. In particular, such a situation takes place in a helicoidal ferromagnet MnSi, where, using the Ginzburg–Landau functional optimized for spin fluctuations, it is shown that the magnetic phase transition is caused by a change in the sign of the mode-mode parameter due to a sharp suppression of zero-point spin fluctuations. In the ground state, on the contrary, there is a significant enhancement of zero-point spin fluctuations due to the peculiarity of the t-band associated with the location of the Fermi level in the region of the local minimum of DOS as calculated by LDA+U+SO simulation of the electronic structure of MnSi.

In the case of Fe$_{1-x}$Co$_x$Si, the chemical potential is in the t$_{2g}$-zone\textsuperscript{4} and zero-point fluctuations are noticeably weaker than in MnSi. However, in this group of compounds, significant concentration fluctuations of the magnetic moments of iron and cobalt occur, and for the region of compositions with 0.2 $<$ x $<$ 0.65, the chemical potential is near the local minimum of DOS.\textsuperscript{4}

In this regard, this work develops the concept of thermodynamic and concentration fluctuations in chiral ferromagnets. Taking into account the results of ab initio LDA+U+SO calculations of...
the DOS, phase transitions in ferromagnetic Fe₁₃Co₃Si with DM-interaction are investigated. On the basis of the obtained equations of magnetic state and expressions for irreducible spin correlators, we investigate ferromagnetic and helicoidal spatial fluctuations and spin microstructures that arise during a temperature-extended phase transition in Fe₁₃Co₃Si.

II. MODEL

We investigate the strongly correlated electronic system of Fe₁₃Co₃Si in the framework of the Hubbard Hamiltonian, extended by taking into account the difference in the intra-atomic Coulomb interactions at the sites occupied by Fe and Co atoms. Based on ab initio calculations of the electronic structure, the band motion of d-electrons will be considered in the LDA+U+SO-approximation. In addition, we include in the Hamiltonian the terms of the Zeeman splitting of electron energies by a uniform magnetic field \( \mathbf{h} = (0, 0, h_0, z) \) and the energy of the DM interaction, which, due to its relativistic smallness, will be considered in the mean field approximation:

\[
H = \mathbf{H}_0(x) + \delta H_{\text{int}} + \sum_{\mathbf{q}} \mathbf{h}_q^{(D)} \mathbf{S}_{\mathbf{q}}. \tag{1}
\]

where \( \mathbf{H}_0(x) = \sum_{\mathbf{k}, \mathbf{e}} \varepsilon_{\mathbf{k}}(x) \mathbf{n}_{\mathbf{k}}^e \mathbf{a}_{\mathbf{k}}^e \mathbf{a}_{\mathbf{k}}^e \) is the Hamiltonian of the band motion of strongly correlated d-electrons in the t₉-orbital state in the LDA+U+SO-approximation; \( \mathbf{h}_q^{(D)} = [\mathbf{M}_q \times \mathbf{d}_q] \) is the Dzyaloshinskii middle field, \( \mathbf{d}_q = id\mathbf{q} \).

\[
\delta H_{\text{int}} = x \Delta U \sum_{\mathbf{q}} \mathbf{n}_q \mathbf{Δ} \mathbf{n}_q + \sum_{\mathbf{q}} (U_{2z}(1 - \mathbf{p}_q) + U_{3z} \mathbf{p}_q) \times \left[ (\mathbf{S}_q)^2 - (\mathbf{n}_q)^2 / 4 \right]. \tag{2}
\]

Here \( \Delta U = U_{2z} - U_{3z}, 2n_0 = \sum_{\mathbf{q}} (n_q), x = N_0^{-1} \sum_{\mathbf{q}} p_q, N_0 \) is the number of lattice sites, \( \delta p_q = p_q - x, \delta H_{\text{int}} \) is the correction that includes electron density fluctuations due to interatomic correlations and differences in the Hubbard interaction parameters at sites occupied by cobalt or iron atoms.

The magnetization \( \langle \mathbf{M}_q \rangle = \langle \mathbf{M}^{(D)}_q \rangle = 2^{-1} (i\mathbf{M}_{qx} + j\mathbf{M}_{qy} + k\mathbf{M}_{qz}) \) magnetic susceptibility, and spin-spin Green’s function will be determined using the generating functional \( Z(x, \mathbf{h}_q') \):

\[
M_{qy} = -T \partial \ln Z(x, \mathbf{h}_q') / \partial h_{qz} \bigg|_{h_{qz} = -h_{qz}^{(D)}} \tag{3}
\]

\[
\xi_{q}^{(\tau)} = -T \partial \ln Z(x, \mathbf{h}_q') / \partial h_{qz} \bigg|_{h_{qz} = -h_{qz}^{(D)}} \tag{4}
\]

\[
\langle T_{\mathbf{q}} \mathbf{S}_q - (T_{\mathbf{q}} \mathbf{S}_q)^2 \rangle = T^2 \sum_{\mathbf{q}} \partial \ln Z(x, \mathbf{h}_q') / \partial h_{qz} \bigg|_{h_{qz} = -h_{qz}^{(D)}}. \tag{5}
\]

Here \( \mathbf{h}_q' \) is the generating field at the 4-vector \( q = (q, \omega_2n) \), which in all final expressions must be directed towards the uniform external field \( \mathbf{h} \) and the Dzyaloshinskii middle field \( \mathbf{h}_q^{(D)} \); \( \omega_2n \) is Matsubara’s Bose frequency;

\[
Z(x, \mathbf{h}_q') = \int_{0}^{\beta} (d\Omega) sT_{\tau} \times \exp \left[ -T^{-1} \left( H_0(x) + \sum_{\mathbf{q}} \Delta U \delta p_q \mathbf{n}_q^2 / 2 \right) - \int_{0}^{\beta} \sum_{\mathbf{q}} (U_{2z}(1 - \mathbf{p}_q) + U_{3z} \mathbf{p}_q) \right. \times \left[ (\mathbf{e}_q^s(\tau) \mathbf{S}_q(\tau))^2 - (\mathbf{n}_q(\tau))^2 / 2 \right] d\tau + \sum_{\mathbf{q}} \mathbf{h}_q' \mathbf{S}_{\mathbf{q}} \right] \]

is the generating functional, which coincides with the partition function for the generating fields \( \mathbf{h}_q' \) equal to zero with \( q = (0, q_0) \).

III. SADDLE POINT CONDITIONS FOR THE GENERATING FUNCTIONAL

To calculate the generating functional, one can use the previously described procedure for writing the partition function based on the Stratonovich–Hubbard transforms, which reduces the inclusion of Coulomb correlations to multidimensional integrals over the exchange (ξ) and charge (ρ) fields, fluctuating in space and time. Changing the integration variables: \( \xi_q \rightarrow (\xi_q - \mathbf{h}_q'/c) / \sqrt{2} \), we have

\[
Z(x, \mathbf{h}_q') = \int (d\xi_q)(d\mathbf{h}_q') \exp \left\{ -\sum_q [\xi_q - \mathbf{h}_q'/c]^2 / 2 \right\} \times Z(x, \xi, \mathbf{h}_q'), \tag{6}
\]

\[
\xi_{q}^{(\tau)} = c(\xi_{q}^{(\tau)} - (2U)^{-1} \Delta U \sum_{\mathbf{q}} \mathbf{p}_q \mathbf{n}_q) / \Delta U \mathbf{p}_q \mathbf{n}_q \tag{7}
\]

\[
c = (UT)^{1/2} \text{ uniform field in the } \mathbf{H}_{eff} \]
where $X_q = U(x_q^{(0)} - x_q^{(0)})$, $x_q^{(0)}$ is the Lindhard function at the 4-vector $q$, calculated in the LDA+U+SO-approximation.

Correction $X_q$ to the approximation of homogeneous local fields in (7) allows one to take into account the long-wavelength fluctuations arising during phase transitions and to consider long-periodic spin superstructures arising in Fe$_2$$_y$Co$_{1-x}$Si.

The final expression of the generating functional can be obtained after calculating the functional integrals (5) in the approximation of the saddle point method in variables: $\xi_q^{(v)} \equiv \Re \xi_q^{(v)}$, $\Im \xi_q^{(v)} = 0$), $\Re \xi_q^{(v)}$, and $\Im \xi_q^{(v)}$ with $q \neq 0$, $\xi_q^{(v)}$ with $q = (0, 0, n)$ at $\omega_n = 0$.

\[
\frac{\partial}{\partial \zeta} \ln \left( \int \frac{d^3q}{(2\pi)^3} e^{i\zeta \cdot q} \right) \frac{\partial}{\partial \Im \xi_q^{(v)}} = \frac{\partial}{\partial \zeta} \ln \left( \int \frac{d^3q}{(2\pi)^3} e^{i\zeta \cdot q} \right) \frac{\partial}{\partial \Re \xi_q^{(v)}} = 0
\]

An expression for the generating functional shows that there is a relation between the saddle values of the $\xi$-fields with irreducible spin correlators and the magnetizations:

\[
\xi_q^{(v)} = U^{-1}(2\gamma + 1), M_q^{(v)} = U^{-1}((\gamma - h_q)/\gamma).
\] (8)

Substituting (8) into the saddle point conditions and taking the requirement of a chaotic alloy ($\delta p_{\pi} \delta p_{\pi} = x(1-x)\delta_{\pi,\pi}$), from the saddle point conditions we obtain the magnetic state equations:

\[
M_q = \left[ D^{-1} + \kappa x(1-x)U^{-1} \Delta U / U \right]^{-1} X(q, 0) + \kappa (M_{q,0})^2 (1-\delta q, 0)
\]

Here $D$ is the exchange enhancement factor of the uniform magnetic susceptibility and $\kappa$ is the mode-mode coupling parameter (We refer the reader to Ref. 4 for the definition of many variables used in this manuscript). The chemical potential ($\mu$) is determined from the electroneutrality condition: $x = \sum_{a=1}^{Z} e^f(e, \mu) \delta_x + \delta_y + \delta_z = \mu_0(x, \mu + aU)$, where $\mu_0(x, \mu + aU)$ is the electronic density of states split by fluctuating exchange fields ($a = \pm 1$).

Even in the ground state concentration fluctuations of the amplitude of spin density are conserved: $\langle m_z^2 \rangle_x = x(1-x)U^{-1} \Delta U / M_q^2 + M_e^2$. In addition, according to the Lindhard model, with an increase in temperature, the amplitude of thermal spin fluctuations grows $m_z^2 / m_z^2 x = 4(3/4) C(T/U)^2 (D^{-1} + 2\kappa x M_q^2 + 2\kappa U^{-2} B_0^2)^{-1}$

\[
(D^{-1} + 2\kappa x M_q^2 + 2\kappa U^{-2} B_0^2 + A)^{-1}
\]

Here $B_0 = U M_q h_0 + h$ is the induction vector of a uniform magnetic effect of energy units, $C$ and $A$ are parameters of the Lindhard function,

\[
M_q = \left( 2\kappa x(1-x)U^{-1} \Delta U / U \right)^{1/2}
\]

\[
\times \left[ \left( D^{-1} + \kappa x(1-x)U^{-1} \Delta U / U \right)^{1/2} \right]^{-1/2}
\]

\[
\times \left[ \left( D^{-1} + \kappa x(1-x)U^{-1} \Delta U / U \right)^{1/2} \right]^{-1/2}
\]

\[
\times \left( D^{-1} + \kappa x(1-x)U^{-1} \Delta U / U \right)^{1/2} - \langle d(q, 0) \rangle / U
\]

\[
(10)
\]

IV. SOLUTIONS OF THE EQUATIONS OF MAGNETIC STATE WITH ALLOWANCE FOR SPATIAL FERROMAGNETIC AND HELICOIDAL FLUCTUATIONS

Analysis of Eq. (9) shows that for positive mode-mode coupling parameter ($\kappa>0$) and negative exchange enhancement factor ($D<0$ - ferromagnetism conditions), solutions of the magnetic state Eq. (9) correspond to a ferromagnetic helicoid, in which the sign of the Dzyaloshinskii constant is fixed:

\[
M_{q_0}^{(s)} = \pm M_{s}(q_0)/2, M_{q_0}^{(v)} = \pm i M_{s}(q_0)/2.
\]

According to (9), the change in the sign of the mode-mode coupling parameter changes the sign of the magnetic chirality.

Moreover, for $\kappa<0$ and $0>D^{-1} > -3d(q_0)/2$, we obtain solutions containing the Berry phase

\[
M_{q_0}^{(s)} = M_s \exp(\pm i\phi), M_{q_0}^{(v)} = \pm i M_s \exp(\pm i\phi)/2.
\]

In this case, by calculating the irreducible spin-spin correlator, one can see that in the region of ferromagnetic fluctuations the phase should be considered fixed. Outside this region, ferromagnetic and helicoidal spatial fluctuations ($M_s=0$) appear. Indeed, according to (3), the pair correlation function and the radius of spin ferromagnetic correlations are determined by the expressions:

\[
K^{(s)}(r) = \sum_q \xi_q^{(v)} \exp(iq r) = K_1(r) + K_2(r),
\]

\[
K_1(r) = (2k_0 / x \lambda) \exp(-r / \lambda),
\]

\[
K_2(r) = K_1(r) \left( |q_0| / \lambda \right) \sin(|q_0| r) - |q_0| / \lambda \right) \left( |q_0| / \lambda \right) \left( |q_0| / \lambda \right)
\]

where the correlation radius depends on $x$, temperature, and external field strength.

\[
R_C \equiv R_C(x, h, T) = k_0 \left( D^{-1} + 2\kappa M_s^2 + 2\kappa U^{-2} B_0^2 \right)^{-1/2}
\]

\[
(14)
\]

Expressions (13b) and (13c) describe ferromagnetic correlations ($K_1(r)$) and helical fluctuations ($K_2(r)$).

Under conditions when ferromagnetic correlations prevail, either spiral fluctuations appear, or for the values of an external uniform magnetic field determined by the inequality:

\[
h_0^{(s)} > d(q_0 |M_s| / (4|\kappa|))
\]

solutions of Eq. (9) with respect to inhomogeneous and uniform magnetizations correspond to skyrmion microstructures:

\[
M_{q_0}^{(s)} = M_s \cos(q_0 \gamma + \phi), M_{q_0}^{(v)} = \pm M_s \sin(q_0 \gamma + \phi).
\]

\[
M_{q_0}^{(v)} = \left( M_{q_0}^{(v)} / q_0 \right) \cos(q_0 \gamma + \phi) + \chi M_{q_0}^{(v)} / q_0
\]

\[
= \left( B_0^{(v)} / U \right)^2 - \left( (d(q_0 |M_s|) / (4U|\kappa|)) \right)^2.
\]

\[
(15a)
\]

\[
(15b)
\]
Here the wave vector $q'_{0}$ is fixed in modulus $|q'_{0}| = |q_{0}|$, and the value of the Berry phase differences ($\varphi$) is fixed in the space region limited by the correlation radius $R_{c}(x, h, T)$.

According to Eq. (9), prolongation of the first-order transition is possible. In this case, the local magnetization undergoes an abrupt decrease due to a change in the sign of $\kappa$ and the appearance of unstable ferromagnetism at the point $T_{C}$. This state of the magnetic subsystem disappears at the point of transition to the paramagnetic phase $T_{S}$. Moreover, it can be shown that

$$T_{S}^{2} = T_{C}^{2} + \left( \frac{U_{1}^{1/2} - U_{2}^{1/2}}{2U_{1}^{1/2}} \right)^{2} x (1 - x) d^2 / (UA).$$

(16)

An important factor in the change in the signs of $D$ and $\kappa$ can be concentration jumps in the amplitude of the local magnetization due to the change in the sign of the crystallographic chirality, which can lead to a local minimum of DOS near the Fermi level. Phase transitions of the first kind, arising due to the change in the sign of the mode-mode coupling parameter, are the cause of temperature jumps in the local magnetization.

V. h-T DIAGRAM OF MAGNETIC STATES IN THE MODEL OF THE Fe$_{1-x}$Co$_x$Si DOS

Let us use the densities of electronic states calculated earlier in the LDA+U+SO$^4$ method. In this case, the used structural data

FIG. 1. Temperature dependence of the magnetic susceptibility of the Fe$_{1-x}$Co$_x$Si alloy at different values of the external magnetic field: a) $x = 0.2$: 1- experimental data, 2-calculation in this work. Parameter $A = 1/12$; parameter $C = 1.3$; b) $x = 0.3$: 1- experimental data, 2-calculation in the present work. Parameter $A = 1/12$; parameter $C = 0.95$.

FIG. 2. Phase diagram of Fe$_{0.3}$Co$_{0.2}$Si and Fe$_{0.7}$Co$_{0.3}$Si alloys: 1- experimental data; 2-experimental data; 3-calculation in this work.

(17)

The values of the parameters of the Lindhard function, $A$ and $C$, included in the formulas for thermal fluctuations, can be determined by comparing the results of calculations of the DOS (particular positions of metal and silicon) for the studied alloys were borrowed from.

The values of the parameters of the Lindhard function, $A$ and $C$, included in the formulas for thermal fluctuations, can be determined by comparing the results of calculations of the
magnetic susceptibility

\[ \chi_0^{(xy)} = 2U^{-1} \times \left[ 2k(1 + x(1 - x)U^{-1}(U_{cb} - U_{ce}))M_0^{(y)} \right] \]

with experimental data\(^{1,12}\) (Fig. 1) at \( h = 0 \). The values of the DM parameters used in the calculations were borrowed from Ref. 6.

In the concentration regions 0.05 < \( x < 0.2 \) and 0.65 < \( x < 0.8 \), the helicoidal ferromagnetism transforms into a paramagnetic state through a second-order phase transition at \( T_C = T_S \). In addition, we find that for compositions 0.20 < \( x < 0.65 \) in the temperature range \( T_C < T < T_S \) at a nonzero value of the uniform external magnetic field \( (h^0(1+M_S)) > d\gamma_0M_S/(4|\kappa|) \) skyrmion “pockets” are formed on the calculated phase (\( h-T \))-diagrams. Examples of such phase diagrams are shown in Fig. 2.

A numerical analysis of the obtained expressions for irreducible spin correlators \(^{14}\) shows that skyrmion solutions appear in the region of ferromagnetic correlations and are suppressed as a result of the crossover of helicoidal and ferromagnetic fluctuations (see Fig. 3).

VI. CONCLUSION

In the present work, we have considered the main features of the concentration-temperature dependences of the magnetic properties of chiral ferromagnets Fe\(_{1-x}\)Co\(_x\)Si with the B20 crystal structure. The obtained temperature dependences of the magnetic susceptibility at various concentrations are in agreement with the experimental data in the region of the magnetic phase transition of the first and second order. It was found that in the external magnetic field a dip occurs in the temperature dependences of the magnetic susceptibility, and the equation of magnetic state has skyrmion solutions. The calculations describe the appearance of skyrmion phases in (\( h-T \))-diagrams and indicate that skyrmion states appear in the range from 0.2 to 0.65 of the concentration of cobalt monosilicide in Fe\(_{1-x}\)Co\(_x\)Si.

Analysis of the spin-spin correlator indicates the effect of suppression of skyrmions by spiral fluctuations outside the radius of ferromagnetic correlations (crossover of spatial ferromagnetic and helicoidal fluctuations). At transition to \( x = 0.65 \), where, according to Ref. 13, the DM interaction abruptly disappears, there is a simultaneous disappearance of skyrmions and spiral fluctuations, and the mode-mode coupling parameter becomes equal to zero. According to the expression for the pair spin-spin correlator, the ferromagnetic short-range order is preserved in this case. Understanding the reasons for the sharp zeroing of the DM interaction parameter requires microscopic calculations, which have not yet been possible.

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DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES