Magnetoelastic coupling in $\gamma$-iron

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Exchange interactions in $\alpha$- and $\gamma$-Fe are investigated within an ab-initio spin spiral approach. We have performed total energy calculations for different magnetic structures as a function of lattice distortions, related with various cell volumes and the Bain tetragonal deformations. The effective exchange parameters in $\gamma$-Fe are very sensitive to the lattice distortions, leading to the ferromagnetic ground state for the tetragonal deformation or increase of the volume cell. At the same time, the magnetic-structure-independent part of the total energy changes very slowly with the tetragonal deformations. The computational results demonstrate a strong mutual dependence of crystal and magnetic structures in Fe and explain the observable “anti-Invar” behavior of thermal expansion coefficient in $\gamma$-Fe.

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I. INTRODUCTION

Iron-based alloys are still among the most important industrial materials. The thermodynamic properties and mechanism of phase transformations in these materials have been discussed intensively last years. Nevertheless, the fundamental properties of iron have not been completely understood up to now. Main difficulties are related with a non-trivial combination of the itinerant and localized behavior and correlation effects of 3$d$-electrons determining electronic, magnetic and structural properties of iron. It is commonly accepted now that magnetic degrees of freedom play a crucial role in the stability of different iron phases which makes the situation even more complicated. Interplay between magnetic and lattice degrees of freedom in different crystallographic phases of iron remains still unresolved problem.

One of the most complicated example related $\gamma$-phase of iron with highly frustrated magnetic structure. There are many magnetic configurations of $\gamma$-Fe with almost the same total energies and the ground state is crucially depends on the value of lattice parameter. The sensitivity to dilatation has been studied in detail by many groups in the context of a so called moment-volume instability. At the same time, the energy dependence on the tetragonal deformation which is closely related with the Bain deformation path of $\alpha \rightarrow \gamma$ phase transformation also deserves a serious attention. We discussed this issue in our previous work and found that the transition of $\gamma$-Fe to the ferromagnetic state can trigger the martensitic transformation without noticeable energy barriers. In more detail, the effect of tetragonal deformations on magnetism and vice versa was discussed in relation with the Invar behavior observed in Fe–Ni alloys. A magnetoelastic spin-lattice coupling plays also an important role in structural phase transitions in $\gamma$-Mn and Cr-based alloys, as well as in the magnetic shape-memory alloy Ni$_2$MnGa. A soft-mode phonon behavior, as a precursor of the $\gamma \rightarrow \alpha$ transformation, was recently observed in Fe–Ni alloys.

In contrast with Fe–Ni alloys, the equilibrium $\gamma$-phase in pure Fe exists only at high temperatures $T > 1200$ K where thermal fluctuations are very strong and magnetic moments are disordered. Observation of the so-called “anti-Invar” behavior of $\gamma$-Fe can be related with the fact that the spin–lattice coupling is strong enough to affects the thermodynamic properties up to very high temperatures.

In this paper we investigate quantitatively a variation of the exchange parameters in $\alpha$- and $\gamma$-Fe as functions of tetragonal Bain-deformations and dilatation. Whereas the sensitivity of the exchange parameters to the dilatation has been studied previously, an information about the tetragonal deformations have been missing until now. Based on the calculated magnetic exchange data we discuss the origin of the anti-Invar behavior of $\gamma$-Fe.

II. COMPUTATIONAL APPROACH

The standard approach to study magnetic properties of itinerant-electron transition-metal systems related with
the mapping of density functional total energies on the
effective classical Heisenberg model:
\[ H_{ex} = - \sum_{i<j} J_{i,j} \mathbf{e}_i \mathbf{e}_j \]  
\[ (1) \]

were \( \mathbf{e}_i \) is the unit vector in direction of the magnetic
moment at site \( i \). In this notation the value of on-site atomic magnetic moments \( M_i \) is included into the
exchange parameters \( J_{i,j} \). Therefore the total energy of
the system is a sum of a magnetic-structure independent
contribution \( E_0 \) and the “Heisenberg-exchange” part:
\[ E = E_0 + H_{ex}, \]
where \( E_0 \) is a function of deformations and the magnitude of local moments: \( E_0(\Omega, c/a, M) \). A
similar decomposition was used earlier in Ref. \[ 27 \]. One
should stress that \( E_0 \) is dependent on the values of mag-
netic moments \( M_i \) and is therefore essentially different
from the energy of a non-spin-polarized state, which attri-
bute is zero all magnetic moments: \( M_i = 0 \).

There are two main approaches to the mapping onto
magnetic Hamiltonian. An analytical scheme is based on
the use of so-called “magnetic force theorem” \[ 25,26 \], when
the exchange interactions are obtained from variations
of the total energy with respect to infinitesimal devia-
tions of the magnetic moments from a collinear state. In
this paper we use more accurate numerical method based
on the density functional calculations of the spin spiral
magnetic structures, where the neighboring magnetic mo-
mments are rotated relative to each other by a finite angle
(for review, see Ref. \[ 23 \]). This scheme includes a spin-
and charge-density relaxation for large moment fluctua-
tions. The energy per atom of the spin spiral with the
wave vector \( \mathbf{Q} \) can be presented as:
\[ E(\mathbf{Q}) = E_0 - \frac{1}{N} \sum_{i<j} J_{i,j} \exp(i \mathbf{Q} \cdot \mathbf{R}_{i,j}) \]
\[ = E_0 - \sum_n Z_n J_n \exp(i \mathbf{Q} \cdot \mathbf{R}_n), \]
\[ (2) \]

where \( N \) is the number of magnetic atoms, \( Z_n \) is the num-
ber of the \( n \)-th nearest neighbor atoms, \( E_0 \) is a magnetic-
structure-independent contribution to the total energy of
the system, \( \mathbf{R}_{i,j} \) is the vector connecting sites \( i \) and \( j \),
\( n \) labels the coordination shell. The exchange param-
ters \( J_n \) can be found from Eq. \[ 2 \] by using the discrete
Fourier transformation:
\[ J_n = -\frac{1}{K} \sum_k E(\mathbf{Q}_k) \exp(i \mathbf{Q}_k \cdot \mathbf{R}_n), \]
\[ (3) \]

where the summation runs over a regular \( \mathbf{Q} \)-vector mesh
in Brillouin zone with the total number of points \( K \). As
follows from Eq. \[ 3 \] the value \( E_0 \) is the average value of spin
spiral energies over all \( \mathbf{Q}_k \),
\[ E_0 = \frac{1}{K} \sum_k E(\mathbf{Q}_k). \]
\[ (4) \]

In principle, one can find the dependence of total energy
on magnitude of \( M \) within a constrained moment spin-
spiral calculations, but this lay beyond a scope of present
paper. A parameter of total exchange energy
\[ J_0 = \sum_n Z_n J_n \]
\[ (5) \]
characterizes a ferromagnetic contribution to the total energy. Note that the decomposition of the total energy
used in Ref. \[ 27 \] differs from that used in this work by a
shift by \( J_0 \).

In general, the exchange parameters found from the
planar spin spiral calculations and from the magnetic force
theorem are different and only the value of a spin
stiffness constant should be the same\[ 25,26 \]. Note that
parameters obtained by the use of infinitesimal spin
deviations\[ 25,26 \] give a correct description of a magnon
spectra, while parameters found from a direct calculation
of the spin spiral total energies are supposed to be
more accurate for descriptions of thermodynamic
properties\[ 29 \]. The difference of \( J_n \) obtained within these
two approaches characterizes a non-Heisenberg charac-
ter of magnetic interactions which is expected for itin-
erant magnets such as iron\[ 40 \]. Another manifestation
of the non-Heisenberg behavior related with the fact that
the magnitude of the magnetic moments dependent on
the spin spiral wave vector \( \mathbf{Q} \). Therefore, the values \( J_n \)
obtained in the framework of spin spiral approach are
considered as effective exchange parameters.

The total energy calculations of Fe with spin spirals
magnetic structure is performed using VASP (Vienna Ab-
initio Simulation Package)\[ 24,25 \] with first-principle pseu-
dopotentials constructed by the projected augmented
wave method (PAW)\[ 25 \]. Following an experience on non-
collinear magnetic investigation\[ 23 \] we employed the gen-
eralized gradient approximation (GGA) for the density
functional in a form by Perdew and Wang (1991)\[ 32 \]
with the spin-interpolation\[ 26 \]. The PAW potential without
core states and with energy mesh cutoff 530 eV, and the
uniform \( k \)-point \( 12 \times 12 \times 12 \) mesh in the Monkhorst-Park
scheme\[ 27 \] with 1728 \( k \)-points are used. The calculations
are done for a single-atom unit cell subjected by two
types homogeneous deformations, namely, dilatation (a
change of the volume for a fixed \( c/a \) ratio) and tetragonal
ones (a change of \( c/a \) ratio at a fixed volume). For given
lattice parameters, the energy set \( E(\mathbf{Q}_k) \) is calculated on
a uniform \( 16 \times 16 \times 16 \) mesh and the Fourier transforma-
tion (Eq. \[ 3 \]) is used to determine the exchange parameters
\( J_n \).

\[ \text{III. COMPUTATIONAL RESULTS} \]

The local magnetic moments \( M(\mathbf{Q}) \) and total ener-
gies for the spin spiral states \( E(\mathbf{Q}) \), calculated for dif-
ferent values of volume and tetragonal deformations are
presented in Figs. \[ 1 \] and \[ 2 \] respectively. We show the
results only for the symmetric directions of the wave vec-
tor \( \Gamma - Z - W(\mathbf{U}) \) in Brillouin zone parallel to \( \langle 001 \rangle \) and
\( \langle 012 \rangle \) in lattice with cubic (tetragonal) symmetry\[ 23 \].
The magnetic moments depend strongly on the spin spiral wave vector \( Q \), as one can see from Fig. 1. This fact confirms the non-Heisenberg character of magnetic interactions in iron. The magnitude of magnetic moments gradually decrease by about 30% along \( \Gamma - Z \) direction for all considered structures except for fcc iron at small volume \( \Omega = 11.0 \, \text{Å}^3 \). Large difference of magnetic moments for fcc Fe at \( Q \)-point at a small volume \( \Omega = 11.0 \, \text{Å}^3 \) and bigger ones (\( \Omega \geq 11.44 \, \text{Å}^3 \)) results from a well known magnetovolume instability which was discussed in the context of the Invar problem\(^ {17} \).

According to our results (Fig. 2) the ground state of fcc iron is spin spiral with \( Q \) varying nearby \( 0.5 \langle 001 \rangle \) (in \( 2\pi/c \) units) with volume and \( c/a \) ratio for a broad interval \( 10.5 < \Omega < 12.0 \, \text{Å}^3 \). The magnetic ground state of fcc iron is a controversial issue up to now. The antiferromagnetic double layer structure (AFMD), equivalent the spin spiral with \( 0.5 \langle 001 \rangle \) has been discussed in a series of papers\(^ {11,48,49} \). The later publications\(^ {13,14,51} \) show, rather incommensurate ground states with \( Q \)-vector depending on lattice parameters. Our result are in agreement with the recent calculations\(^ {13,14,38,39,47,51} \).

An increase of iron volume further \( \Omega > 12.0 \, \text{Å}^3 \) results in the transition from spin spiral to ferromagnetic (FM) structure (Fig. 2). The energy difference \( \Delta E_M \) between FM and antiferromagnetic (AFM) states (or spin spiral structure with \( Q = \langle 001 \rangle \)) gives a scale of the exchange interaction energy which decreases monotonously with increasing of the volume and finally changes the sign near \( \Omega_{\text{exp}} = 11.44 \, \text{Å}^3 \). This volume corresponds to an experimental value for precipitates of \( \gamma \)-Fe in Cu at low temperatures\(^ {50} \).

Our results demonstrate that the magnetic structure of fcc iron is strongly dependent on the lattice deformations (Fig. 2). This conclusion agrees well with the previous investigations of iron\(^ {13,18,51} \). In particular, the spin spiral ground state is changed to the ferromagnetic one within the tetragonal deformation region along the Bain path from the fcc \( (c/a = 1) \) to bcc iron \( (c/a = 1/\sqrt{2}) \). A magnetic transition to the FM state and its role in the martensitic transformation have been discussed earlier in
In the opposite case, when $c/a > 1$, the tetragonal deformation leads to a weaker dependence of $E(Q)$. The spin spiral structure represents a ground state at $c/a \approx 1.1$ and a transition to the ferromagnetic ground state appeared at $c/a \geq 1.2$. This magnetic transformations are in agreement with a previously obtained phase diagram.\(^\text{31}\)

The results for exchange parameters $J_n(c/a, \Omega)$ as function of lattice distortions are presented in Fig. 3. Positive values indicate that the ferromagnetic type of ordering is preferable. The dependence $E(Q)$ determined by Eq. 2 with obtained exchange parameters $J_n$ give a perfect interpolation to the calculated spin spiral energies (lines and symbols in Fig. 2). A striking feature of this curves is that the total exchange energy $J_0$ behaves similar to $Z_1J_1$ ($Z_i$ corresponds to number of $i$-th neighbors ) for all deformations considered. This means that the contributions of longer-range exchange interactions ($n > 1$) are canceled out. Similar results have been obtained by analytical calculations of exchange parameters\(^\text{16}\) for the volume variation of fcc iron.

Effects of volume variation on the exchange parameters in fcc structure is very noticeable and $J_1$ demonstrates a non-monotonous behavior (Fig. 3b). At low volumes ($\Omega < \Omega_{\text{exp}}$) total exchange parameter $J_0$ becomes negative showing the tendency to antiferromagnetic–type coupling. For atomic volumes near $\Omega_{\text{exp}}$ the parameter $J_1$ is close to zero and the exchange energy $J_0$ is small and negative. In this case the value $J_0$ is determined by all exchange parameters $J_n$ with $n > 1$. Therefore, computational results for $\Omega \approx \Omega_{\text{exp}}$ appear to be quite sensitive to the details of the approximation used\(^\text{12}\) (e.g. the exchange-correlation functional, energy cut-off, number of k-points, etc.). Such behavior of exchange parameters can likely be related to a complex magnetic structure discussed in the experimental work by Tsumoda and co-workers\(^\text{26}\).

Parameter $J_0$ changes the sign at a volume which is close to zero and the exchange energy $\gamma$ behaves similar to $Z_1J_1$ ($Z_i$ corresponds to number of $i$-th neighbors ) for all deformations considered. The dependence of the total exchange energy $J_0$ on both types of deformations is shown in Fig. 4 as a contour plot $J_0(\Omega, c/a)$. One can see that the total exchange energy together with the increase in volume enhance significantly the exchange interaction energy in $\gamma$-Fe. The value $J_0 \approx 70$ meV is reached for the experimental volume of $\gamma$-Fe $\Omega \approx 12 \AA^3$ and $(c/a - 1) \approx 5\%$.

Calculated exchange parameters $J_n$ are presented in the Fig. 5 as functions of interatomic distances. The exchange interactions in fcc iron have a very long-ranged behavior at the volumes $\Omega \approx \Omega_{\text{exp}}$. Such a strong Friedel oscillations was already found in Ref. 16. This is a reason of magnetic frustrations and existence of numerous complex magnetic structures with low energies in the fcc Fe\(^\text{12,16,38,50}\). A tetragonal deformation of the fcc structure changes dramatically the behavior of $J_n$ due to a sharp increase of $J_1$ contribution which becomes a dominant one. The increase of volume acts in a similar way. One can see from Fig. 5 that the exchange interactions depend not only on interatomic distance $R_n$ but also very sensitive to particular values of $c/a$. Therefore, correct lattice deformations should be necessarily taken into account explicitly for a correct description of magnetic structures in Fe.

**IV. DISCUSSION AND CONCLUSIONS**

We can determine the magnetic-structure independent contribution $E_0$ by subtracting the Heisenberg-like contribution with calculated exchange parameters from the total energy. In order to do this one can use the energy of ferromagnetic state in the spin-spiral framework $Q = 0$ from the Eq. 2 and the following expression: $E_0 = E_{\text{FM}} - J_0$. As was mentioned earlier, $E_0$ essentially differs from a total energy obtained in the non-spin-polarized calculations because of implicit dependence of $E_0$ on the magnetic moment $M$. They are equal only for the systems with zero magnetic moments of all atoms.

The results for $E_0$ are shown in Fig. 6 together with the total energies of FM ferrite and AFM ferrite states obtained by the reconstruction from $E_0$ and $J_n$. For comparison, the total energies of $E_{\text{NM}}$ obtained from calculations by VASP are also shown. These results agree very well with the previous ab-initio calculations\(^\text{49}\) and demonstrate the dramatic difference between $E_0$ (see
**FIG. 3:** (Color online) Exchange parameters $J_n$ for $n = 1, 2, 3, 4, 5$ for different lattice parameters: dependence $J_n$ on a volume of fcc (a) and bcc (b) Fe; dependence $J_n$ on $(c/a)$ at fixed volumes $\Omega = 11.44 \, \text{Å}^3$ (c) and $\Omega = 12.0 \, \text{Å}^3$ (d), respectively.

**FIG. 4:** (Color online) Dependence of the total exchange parameter $J_0$ on volume $\Omega$ and $c/a$ ratio as a contour plot $J_0(\Omega, c/a)$.

**FIG. 5:** (Color online) The exchange parameter as a function of interatomic distance to the $n$-th neighbour $J_n(R_n)$ for different $c/a$ ratios.

For fcc iron the magnetic-structure independent contribution $E_0$ is rather close to the energy of AFM and AFMD states. For bcc iron the difference between $E_0$ and ground-state energy $E_{FM}$ is larger but rather weakly volume dependent compare to fcc states. At the same time, the energy of FM fcc state shows two minima at low and high volumes. This behavior of fcc total energy drastically differs from the $E_0$ curve. The difference is larger for higher volumes and has entirely magnetic origin due to increase of the exchange parameters with $\Omega$ (Fig. 3). Quantitatively, the values of bulk modulus for fcc iron obtained from the Birch-Murnaghan equation of state Eq. (4) and $E_{NM}$.

The situation with tetragonal deformations is quite unusual. One can see in Fig. 5 that $E_0$ depends on $c/a$ very weakly. This means that the Heisenberg-like contribution is dominant in the shear modulus $C''$, as well as in the whole energy curve along the Bain path. This is main origin of anomalously strong coupling between the magnetic and lattice degrees of freedom in iron, where the tetragonal deformation plays a special role. The curve $E_0(c/a)$ has a minimum at $c/a = 1$ (fcc structure) whereas both $E_{FM}$ and $E_{AFM}$ have no minima at this point which means instability of fcc phase in both magnetic structures. The minima correspond to bcc (FM) and fct (AFM, AFMD) states with $c/a > 1$. 

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Our calculations reveal another unusual feature of the magnetic interactions in fcc iron related with a growth of the exchange parameter $J_1$ and, as a consequence, $J_0$ with the volume increase at $\Omega > \Omega_{\text{exp}}$ (see Fig. 3). This behavior corresponds to the rising branch of the Bethe-Slater curve $J(\Omega)$ which have been used for a semi-quantitative interpretation of the Invar anomaly. This region of volumes corresponds to observed high-temperature phase of $\gamma$-Fe; for further increase of interatomic distances the overlap of $d$-orbitals becomes weaker and the exchange interactions $J_n$ decreases.

Here we show that the calculated dependence of $J_n(\Omega)$ can explain the anti-Invar phenomenon in $\gamma$-Fe. If a magnetic subsystem is well described by the Heisenberg-like model (1) its contribution to pressure according to the Hellman-Feynman theorem is

$$ P_m = -\frac{1}{N} \left\langle \frac{\partial H_{\text{ex}}}{\partial \Omega} \right\rangle = \frac{1}{N} \sum_{i<j} \frac{\partial J_{i,j}}{\partial \Omega} \langle e_i e_j \rangle $$

$$ \approx Z_1 \frac{\partial J_1}{\partial \Omega} \langle e_0 e_1 \rangle $$

(6)

where $Z_1$ is the number of nearest neighbors. We assume that the nearest-neighbor interaction is the strongest one which is supported by our first-principle calculations. For a purpose of qualitative discussions, we will treat exchange interactions perturbatively assuming $Z_1 J_1 \ll T$ ($T$ is the temperature and $k_B = 1$). Then one has $\langle e_0 e_1 \rangle \approx J_1/3T$ and therefore

$$ P_m = Z_1 \frac{\partial J_1^2}{6T} \frac{\partial^2}{\partial \Omega} $$

(7)

This means that the pressure induced by magnetic exchange interactions is positive and decreases with the temperature increase.

The thermal expansion coefficient

$$ \alpha = \frac{1}{\Omega} \left( \frac{\partial \Omega}{\partial T} \right)_P = \left( \frac{1}{B} \right)_T \left( \frac{\partial P}{\partial T} \right)_\Omega $$

(8)

can be divided into magnetic-structure independent part ($\alpha_0$) and one related with magnetic exchange interactions ($\alpha_m$): $\alpha = \alpha_0 + \alpha_m$. The magnetic exchange part is equal to

$$ \alpha_m = \frac{1}{B} \left( \frac{\partial P_m}{\partial T} - B_m \alpha_0 \right) $$

(9)

Here $B$ is isothermal bulk modulus $B = B_0 + B_m$, $B_0$ is the magnetic-structure independent part of $B$, and $B_m = -\partial(P_m/\partial T)$. Usually, the second term in Eq. (9) is neglected. Since $\partial P_m/\partial T < 0$ one can assume that the expression (7) should lead to the Invar behavior, and hence to the negative contribution to the thermal expansion coefficient. A strong volume dependence of the
exchange parameter $J_1$ can lead to the opposite conclusion. Substitutes Eq. (7) into Eq. (9) one finds

$$\alpha_m = -\frac{1}{B_0} \frac{Z_1 \partial J_1^2}{6 \lambda T} \left[ 1 - \alpha_0 T \left( \frac{\partial \ln (\partial J_1^2 / \partial \Omega)}{\partial \ln \Omega} \right) \right]$$

(10)

Using calculated volume dependence $J_1(\Omega)$ (Fig. 4) and values $\alpha_0$, $\Omega$ obtained from the experiment, one can find that the second term in square brackets in the right-hand side of Eq. (10) is approximately 1.1 at the temperature of 1200 K. Therefore, a total magnetic exchange contribution to the thermal expansion coefficient (10) has positive sign. This corresponds to the anti-Invar behavior, in a qualitative agreement with the experimental data.22

The negative magnetic exchange contribution to the thermal expansion coefficient $\alpha_m$ in the Invar materials usually is associated with a thermal dependence of the spontaneous magnetostriction, while the positive contribution (anti-Invar behavior) is often considered to be related to thermal volume changes due to magnetic fluctuations.24,25 The present investigation allows us to explain the anti-Invar effect of high-temperature $\gamma$ phase of iron within a simple Heisenberg-like model in terms of magnetic softening of the bulk modulus, without any assumptions about two magnetic states of iron atoms with high and low volume.17

Due to the thermal expansion effective exchange parameters increases with the temperature increase,

$$J_0^f = J_0 + \lambda T,$$

(11)

with a positive constant $\lambda > 0$. If we substitute this formula into the mean-field expression for the magnetic susceptibility

$$\chi = \frac{m^2}{3(T - 2J_0^f/3)}$$

(12)

one can see that corresponding temperature dependence leads to an increase of the effective magnetic moment, $m^2 \rightarrow m^2/(1 - 2\lambda/3)$ and the Curie temperature, $T_C \rightarrow T_C/(1 - 2\lambda/3)$.

To conclude, we have carried out a systematic study of exchange parameters in $\alpha$- and $\gamma$-Fe as functions of the volume and tetragonal deformation. The computational results demonstrate a strong coupling between lattice and magnetic degrees of freedom which should be taken into account in thermodynamic properties of Fe, especially its thermal expansion. Accurate analysis of the magnetic-structure independent contribution $E_0$ allows us to conclude that a response of fcc and bcc Fe to deformations is mainly controlled by the magnetic exchange.

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