Effect of magnetic state on the $\gamma - \alpha$ transition in iron: First-principle calculations of the Bain transformation path

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Energetics of the fcc ($\gamma$) - bcc ($\alpha$) lattice transformation by the Bain tetragonal deformation is calculated for both magnetically ordered and paramagnetic (disordered local moment) states of iron. The first-principle computational results manifest a relevance of the magnetic order in a scenario of the $\gamma - \alpha$ transition and reveal a special role of the Curie temperature of $\alpha$-Fe, $T_C$, where a character of the transformation is changed. At a cooling down to the temperatures $T < T_C$ one can expect that the transformation is developed as a lattice instability whereas for $T > T_C$ it follows a standard mechanism of creation and growth of an embryo of the new phase. It explains a closeness of $T_C$ to the temperature of start of the martensitic transformation, $M_s$.

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Deeper understanding of mechanisms of polymorphous $\gamma - \alpha$ transformation in iron and its alloys is of fundamental importance for both metallurgical technologies and for a general theory of phase transitions in solids. Despite numerous investigations an issue of a mechanism of a new phase nucleation in the course of $\gamma - \alpha$ transformation remains open (see, e.g., discussion in Ref. [4]).

It is well known [1] that a character and rate of the transformation in iron and iron-based alloys is changed drastically below some temperature $M_s$, namely, at $T < M_s$ it occurs by a fast cooperative shear deformation of atoms (martensitic mechanism) whereas for higher temperatures (but lower than the temperature of phase equilibrium $T_{\gamma-\alpha}$) the transformation develop much slower and a formation and growth of grains of $\alpha$-phase is observed. In pure iron the temperature of start of the martensitic transformation $M_s \approx 1020 K$ [6,7] which is only 30 K lower than the Curie temperature of $\alpha$-Fe, $T_C$, in accordance with an old idea of Zener [8] suggesting that $M_s \approx T_C$. It is know also that in the system Fe-C a process of the $\gamma - \alpha$ transformation becomes much faster at a cooling down below $T_C$ [9]. It is commonly accepted now that magnetic degrees of freedom play a crucial role in the phase equilibrium in iron [10,11,12,13]. However, a mechanism of their effect on kinetics of the transformation remains unclear.

Several ways to transform the crystal lattice from fcc ($\gamma$) to bcc ($\alpha$) structures have been suggested, among them schemes of Bain [14] (a tetragonal deformation along the $<001>$ axis) and of Kurdumov-Zaks [1] (two shear deformations) are the best known. To determine the deformation path and estimate energy barriers calculations of total energy in a configurational space of lattice deformations are required. For the Kurdumov-Zaks path this is a rather cumbersome and computationally expensive problem. Therefore first-principle calculations of energetics of polymorphous transformation in iron were carried out, up to now, only for the Bain transformation path [12,13,16,17,18,19,20]. It turned out that energetics of the transformation is essentially dependent on magnetic structure of iron. In particular, ferromagnetic (FM) state of the fcc iron is unstable with respect to tetragonal deformation, with energy minima at $c/a$ ratio equal 1 (bcc) or $c/a \approx 1.5$ (fct structure) [12,15,16]. Antiferromagnetic (AFM) state of the fcc iron has lower energy than the FM one and show a monotonous increase of energy along $\gamma \rightarrow \alpha$ transformation path [12,16].

Since the magnetic ground state is different for $\alpha$- and $\gamma$-Fe, an investigation of energetics of the transformation path for a given colinear magnetic structure [12,15,16,17,18,19,20] is not enough to describe properly the $\alpha - \gamma$ transition. As was shown in Refs. [21,22,23] the true magnetic ground state of fcc Fe is rather complicated and, in general, noncollinear (depending on the lattice constant). Evolution of magnetic state of Fe along the Bain path was studied in Ref. [20] by the TB-LMTO method in atomic sphere approximation (ASA) [24].
was demonstrated that, for an essential part of the Bain path, noncollinear magnetic structures take place which are replaced by FM ordering for \( c/a \) smaller than some critical value.

The calculations \([13, 14, 15, 19]\) have been carried out for a fixed value of volume per atom or lattice constant \( a \) that corresponds to so-called epitaxial Bain path describing the transformation for iron films on a substrate. The latter leads to some restrictions on geometry of the transformation which takes place at low temperatures in magnetically ordered state. The results of Ref. \([20]\) allow us to predict a type of magnetic structures which can be realized in the epitaxial iron films. At the same time, the \( \gamma \rightarrow \alpha \) transformation in the bulk occurs at high temperatures when the magnetic state is disordered. To describe this situation, calculations for paramagnetic iron are required.

In this work we analyse in detail the Bain deformation path for both noncollinear and paramagnetic states using the methods of spin spirals (SS) and disordered local moments (DLM), respectively. As a result, we clarify the reasons for essential differences in mechanisms of the polymorphous transformation below and above the Curie temperature \( T_C \).

The calculations have been carried out using the VASP (Vienna Ab-initio Simulation Package) \([25, 26, 27]\) with first-principle pseudopotentials constructed by the projected augmented waves (PAW) \([28]\), and the generalized gradient approximation (GGA) for the density functional in a form \([29]\) with the parametrization \([30]\) (see also comments in Ref. \([31]\) concerning use of the GGA for noncollinear case). The PAW potential with energy mesh cutoff 530 eV, and uniform \( k \)-point 12\( \times \)12\( \times \)12 mesh in the Monkhorst-Park scheme \([32]\) were used.

To describe the noncollinear magnetic state the model of flat SS \([31]\) has been used with the magnetization rotation around wave vector of SS, \( \mathbf{q} \) which chosen along the axis of the Bain tetragonal deformation \( < \mathbf{001} > \). The values \( q = 0 \) and \( q = 0.5 \) (in units of \( 2\pi/c \)) correspond to the FM and AFM states, respectively. To calculate the energy of Fe with SS magnetic structure we employed the PAW formalism described in Ref. \([34]\) and implemented in the VASP code. We optimized the volume per atom for given values of \( q \) and tetragonal deformation.

Paramagnetic state of iron was modeled by the disordered local moment (DLM) method \([35]\). To this aim, we used 27-atom supercell (Fig. 1) with a given random distribution of magnetic moments (with zero total magnetic moment) which was kept fixed at the self-consistency process. The latter was provided by using constrained density functional approach \([36]\). As well as for the SS case we optimized the volume per atom for a given tetragonal deformation.

Computational results for SS are shown in Fig. 2. One can see that the minimum of the total energy is reached for bcc FM (curve 2) and fct AFM (curve 8), with a transition between these two states via noncollinear magnetic structure with the wave vectors \( q \approx 0.25 \) — 0.35. The energy difference between the FM and AFM states is small for \( 1.3 < c/a < 1.5 \) and increases, almost in order of magnitude, for \( c/a < 1.3 \). This agrees qualitatively with the previous results \([20]\) of the TB-LMTO-ASA calculations that the tetragonal deformation induces a magnetic transition.

Similar to Refs. \([20, 31, 33]\) we found that the energy minimum for the fcc Fe corresponds to \( q \approx 0.3 \) (curve 6 in Fig. 2). Optimization of the volume makes the \( q \)-dependence of the total energy rather flat, thus, the energy at \( q = 0.3 \) is only 6 meV/atom lower than for the AFM fcc state. The FM fcc structure (\( q = 0 \)) has the
energy in 54 meV/atom higher than for $q = 0.3$. It is characterized by much larger values of magnetic moment and volume per atom (11.86 Å$^3$ and 2.3 $\mu_B$ at $q = 0$ vs 10.74 Å$^3$ and 1.4 $\mu_B$ at $q = 0.3$). One can see in Fig. 2 that the FM state of fcc iron is unstable with respect to the tetragonal deformation; if one keeps the FM order the fcc iron will reconstruct spontaneously to bcc or fct phase, without essential changes of volume and magnetic moment per atom.

Fig. 3 presents the total energy along the Bain path for optimized (with a given $c/a$ ratio) SS magnetic structure, together with the results for the collinear (FM and AFM) case, for the paramagnetic case (DLM) and for partially disordered magnetic structure (DLM$_{0.5}$). The results for the FM and AFM magnetic structures are close to those obtained earlier by full-potential FLAPW method [13]. Taking into account noncollinear magnetic configurations allows us to describe a continuous transition between FM and AFM states and to estimate the energy barrier $E_b$ resulting from the Bain deformation. We have found $E_b \approx 20$ meV/atom for fcc-bcc and $E_b \approx 40$ meV/atom for fct-bcc transitions. The corresponding values found in Ref. [14] are 48 meV/atom and 63 meV/atom, respectively which is essentially larger than our data. The difference is mainly due to optimization of volume per atom used in our calculations (in Ref. [13] fixed values of the volume were used).

![FIG. 3: Variation of the total energy per atom along the Bain deformation path for different magnetic states. FM (empty triangles) and AFM (solid triangles) label collinear ferromagnetic and antiferromagnetic structures, SS (solid circles) - spin-spiral state, DLM (empty circles) - disordered local moments, DLM$_{0.5}$ (empty diamonds) - DLM state with the total magnetic moment equal to half of that for the FM state.]

Comparing Figs. 2 and 3 one can see that the barrier position corresponds to the value of tetragonal deformation where magnetic state switches from SS ($q \approx 0.3$) to FM ($q = 0$). Interestingly, the critical value of the Bain deformation found for the SS state turns out to be close to the crossing point of the corresponding curves for FM and AFM configurations.

For the paramagnetic (DLM) state the energy has a minimum corresponding to the fcc structure and is close to the energy of SS and AFM states for $1.3 < c/a < \sqrt{2}$ (Fig. 3). For $c/a < 1.3$ the energy grows monotonously with the $c/a$ decrease reaching the maximum for the bcc state ($c/a = 1$). This maximum is much higher than the energy for FM bcc and DLM fcc configurations (by 220 and 110 meV/atom, respectively). Thus, reconstruction of crystal lattice of Fe from fcc to bcc by the Bain deformation without change of magnetic configuration does not lead to any energy gain. To model the state of iron at finite temperatures below $T_C$ we have performed also calculations for the DLM state with total magnetization $M = 0.5M_{\text{max}}$ where $M_{\text{max}}$ is the magnetization in FM state for given $c/a$ ratio. The results are not essentially different from the paramagnetic case except for region close to bcc structure (compare the curves DLM and DLM$_{0.5}$ in Fig. 3). So, the energetics of the Bain transformation path changes drastically when the magnetic state becomes close to the ferromagnetic.

It is not surprising, of course, that the energy of bcc Fe is much higher in the DLM state than in ferromagnetic one, in light of a common opinion (originated from a seminal work by Zener [37]) that it is ferromagnetism that stabilizes $\alpha$-Fe. According to Ref. [38] a strong enough short-range magnetic order survives in iron above $T_C = 1043$ K which is probably essential to explain a stability of bcc phase in some temperature region above $T_C$ [13, 37]. To consider this problem quantitatively one has to be able to calculate phonon and magnetic contributions to entropy of different phases which is rather complicated. However, since $T_C$ is much higher than typical phonon energies the lattice vibration entropy in both phases are approximately constant in the temperature region under consideration and therefore the phonon contribution to the difference of free energies between $\alpha$- and $\gamma$-phases is a smooth function linearly dependent on the temperature. At the same time, magnetic contribution to the total energy is strongly dependent on the magnetic configuration and thus on the temperature, as follows from the presented results.

When cooling down iron in a temperature interval $T_C < T < T_{\gamma-\alpha}$, the bcc structure becomes preferable due to entropy contribution in free energy. Since the difference between free energies of the bcc and fcc phases is zero at $T_{\gamma-\alpha}$ and changes slowly with the temperature, the moving force of the phase transition is relatively weak. As a result, the $\gamma - \alpha$ transformation develops in this situation by the classical nucleation and growth mechanism.

When decreasing the temperature below $T_C$ the FM state of bcc Fe arises which has the energy much lower than that of paramagnetic fcc state (by 110 meV/atom).
At the same time, lattice reconstruction from paramagnetic fcc to FM bcc state requires to overcome a rather low barrier which height (≈ 20 meV/atom, or ≈ 250 K/atom) is small in comparison with the temperature $T \sim M_s$. Thus one can expect that cooling down to $T < T_C$ will initiate martensitic mechanism of $\gamma \rightarrow \alpha$ transformation, via a development of lattice instability [33]. This conclusion differs essentially from that of Ref. [12] where use the less accurate LMTO method with model Stoner parameters has resulted in three times larger barrier height than in our calculations.

Thus, $T_C$ of $\alpha$-Fe plays a role of a special point where kinetics of the transformation is changed, due to a crucial role of magnetic degrees of freedom in energetics of iron which is a main conclusion from our computational results.

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