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Effect of magnetic state on the γ-α transition in iron: First-principles calculations of the Bain transformation path

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Energetics of the fcc (γ)-bcc (α) lattice transformation by the Bain tetragonal deformation is calculated for both magnetically ordered and paramagnetic (disordered local moment) states of iron. The first-principles computational results manifest a relevance of the magnetic order in a scenario of the γ-α transition and reveal a special role of the Curie temperature of α-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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I. INTRODUCTION

Deeper understanding of mechanisms of polymorphous γ-α transformation in iron and its alloys is of fundamental importance for both metallurgical technologies[1,2] and for a general theory of phase transitions in solids.[3–5] Despite numerous investigations an issue of a mechanism of a new phase nucleation in the course of γ-α 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 $T_{\gamma\text{-}\alpha}$) the transformation develops much slower and a formation and growth of grains of α-phase is observed. In pure iron the temperature of start of the martensitic transformation $M_s \approx 1020$ K (Refs. 6 and 7) which is only 30 K lower than the Curie temperature of α-Fe, T_C, in accordance with an old idea of Zener[8] suggesting that $M_s \approx T_C$. It is known also that in the system Fe-C a process of the γ-α 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.[10–13] However, a mechanism of their effect on kinetics of the transformation remains unclear.

Several ways to transform the crystal lattice from fcc (γ) to bcc (α) structures have been suggested, among them schemes of Bain[14] (a tetragonal deformation along the $\langle 001 \rangle$ 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-principles calculations of energetics of polymorphous transformation in iron were carried out, up to now, only for the Bain transformation path.[12,15–20] 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 in energy along $\gamma \rightarrow \alpha$ transformation path.[15,16]

Since the magnetic ground state is different for α- and γ-Fe, an investigation of energetics of the transformation path for a given collinear magnetic structure[12,15–19] is not enough to describe properly the α-γ transition. As was shown in Refs. 21–23 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 tight-binding linear muffin-tin orbital (TB-LMTO) method in atomic sphere approximation (ASA).[24] It 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[15–17,19] 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

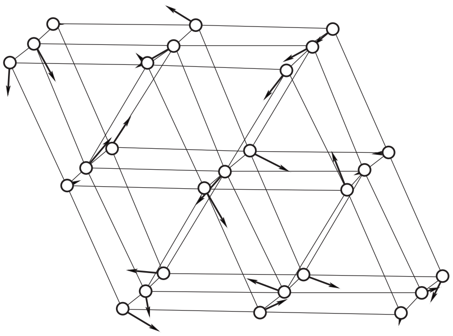

FIG. 1. Supercell used in the DLM calculation. Arrows show the magnetic moments.

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 γ-α 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 analyze 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.

II. METHOD OF CALCULATIONS AND RESULTS

The calculations have been carried out using the VASP (Vienna *Ab initio* Simulation Package)[25–27] with first-principles pseudopotentials constructed by the projected augmented waves (PAW),[28] and the generalized gradient approximation (GGA) for the density functional in a form[29] based on interpolation scheme[30] (see also comments in Ref. 31 concerning use of the GGA for the noncollinear case). The PAW potential with energy mesh cutoff 530 eV, and uniform k-point $12\times12\times12$ mesh in the Monkhorst-Park scheme[32] were used.

To describe the noncollinear magnetic state the model of flat SS (Ref. 31) has been used with the magnetization rotation around the wave vector of SS, $\mathbf{q}$ chosen along the axis of the Bain tetragonal deformation $\langle 001\rangle$. 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 into 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 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.

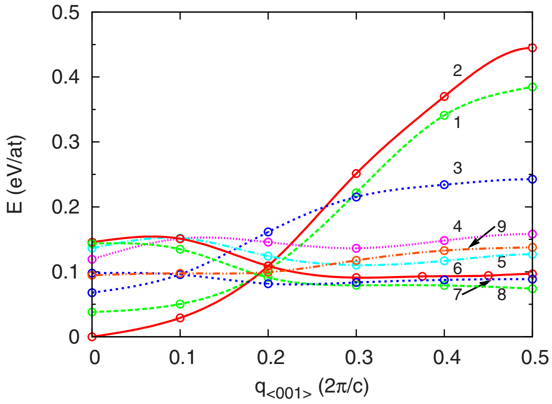

FIG. 2. (Color online) Dependence of the total energy per atom for SS on the wave vector $\mathbf{q}\parallel\langle 001\rangle$ for different values of tetragonal deformation. Curves 1 to 9 correspond to $c/a=0.9;1.0;1.2;1.3;1.35;\sqrt{2};1.5;1.6;1.7$, respectively; $c/a=1$ for bcc and $c/a=\sqrt{2}$ for fcc structures.

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 $q\simeq0.25-0.35$. 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, 33, and 31 we found that the energy minimum for the fcc Fe corresponds to $q\simeq0.3$ (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 in volume and magnetic moment per atom.

Figure 3 presents the total energy along the Bain path for optimized 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 ($\mathrm{DLM}_{0.5}$) with the total magnetization $M=0.5M_{\max}$ where $M_{\max}$ is the magnetization in FM state for a given c/a ratio. We choose as an optimal SS magnetic structure the structure with the wave vector $\mathbf{q}$ providing minimum of the energy $E(\mathbf{q})$ for a given c/a ratio (see Fig. 2).

The results for the FM and AFM magnetic structures are close to those obtained earlier by full-potential linearized augmented plane-wave method.[15] 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 homogeneous Bain deformation. We have found E_b

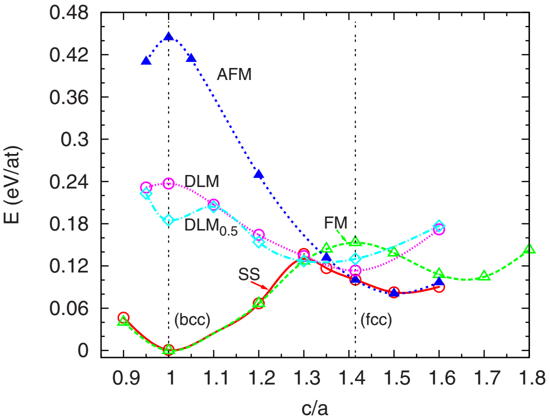

FIG. 3. (Color online) Variation in the total energy per atom along the Bain deformation path for different magnetic states. FM (empty triangles) and AFM (solid triangles) label collinear ferromagnetic and antiferromagnetic structures, SS (empty circles)—spin-spiral state, DLM (crosses)—disordered local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

$\simeq 20$ meV/atom for fcc-bcc and $E_b \simeq 40$ meV/atom for fct-bcc transitions. The corresponding values found in Ref. 15 are 48 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. 15 fixed values of the volume were used).

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 in Fig. 3.

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 240 and 120 meV/atom, respectively). For fcc structure the energy of DLM configuration is lower (by 40 meV/atom) in comparison with FM state. Note that the obtained energy differences between DLM and FM states for bcc and fcc iron are in good agreement with results of previous coherent potential approximation–disordered local moment calculations.[37,38]

Thus, reconstruction of crystal lattice of Fe from fcc to bcc by the Bain deformation without change in magnetic configuration does not lead to any energy gain. To model the state of iron at finite temperatures slightly below T_C we have performed also calculations for the partially disordered $\mathrm{DLM}_{0.5}$ state. The results are not essentially different from the paramagnetic case except for the region close to bcc structure (compare the curves DLM and $\mathrm{DLM}_{0.5}$ in Fig. 3) where partial magnetization leads to the local energy minimum. So, the energetics of the Bain transformation path changes drastically when the magnetic state becomes close to the ferromagnetic.

III. DISCUSSION AND CONCLUSIONS

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[39]) that it is ferromagnetism that stabilizes α-Fe. According to Ref. 40 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.[11,39] 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. Anharmonic effects in the phonon subsystem are, in general, important for lattice properties of metals at high temperatures, as was demonstrated recently for bcc phases of Y, Sc, Ti, Zr, Hf (Refs. 41 and 42) and Mo.[43] It is natural to expect, in particular, that they stabilize high-temperature δ phase of iron above $T_{\gamma\text{-}\delta} = 1700$ K. However, phonon contributions to thermodynamic properties of α and γ phases cannot be strongly temperature dependent in the relatively narrow temperature interval $T_C < T < T_{\gamma\text{-}\delta}$ where paramagnetic bcc iron exists. At the same time, as follows from the presented computational results, the magnetic contribution to the free energy difference ΔF_{mag}, is strongly dependent on the magnetic configuration and thus on the temperature. As result, it is the magnetic free energy that plays a decisive role among all factors determining the relative stability of the two phases.

When cooling down iron in a temperature interval $T_C < T < T_{\gamma\text{-}\alpha}$, the bcc structure becomes preferable due to entropy contribution in free energy. Since the difference between free energies of the bcc and fcc phases ΔF_{tot} is zero at $T = T_{\gamma\text{-}\alpha}$ and changes slowly with the temperature for $T_C < T < T_{\gamma\text{-}\alpha}$ (see Ref. 44), the moving force of the phase transition is relatively weak. In addition, as follows from Fig. 3, there is no lattice instability of γ iron in paramagnetic state. As a result, the γ-α 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 or 1300 K/atom) and $\gamma \rightarrow \alpha$ transformation occurs under a large driving force. 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 M_s. Thus one can expect that cooling down to $T < T_C$ will initiate martensitic mechanism of γ-α transformation, via a development of lattice instability.[45] 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.

It is worthwhile to note that the calculated energy barrier E_b for the Bain path due to homogeneous deformation gives only an estimation from below for the enthalpy of α-phase nucleation; the latter includes also and interface energy and energy of elastic strain. However, it probably does not effect on the main conclusion about a dramatic change in the transformation kinetic when iron is cooling down below T_C. The results shown in Fig. 3 clearly point out that $\alpha \rightarrow \gamma$ transformation upon heating is related with the lattice instability (see DLM curve), in contrast with $\gamma \rightarrow \alpha$ transformation depending on the overcooling temperature.

Thus, the Curie temperature T_C of α-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.

An essential reconstruction of the potential relief for the Bain transformation path clarifies a microscopical origin of the experimentally observed proximity of the start martensitic transformation temperature M_s and T_C specifying the suggestion[8,44] which was based on purely thermodynamic analysis.

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