Magnetism and local distortions near carbon impurity in $\gamma$-iron

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Local perturbations of crystal and magnetic structure of $\gamma$-iron near carbon interstitial impurity is investigated by ab initio electronic structure calculations. It is shown that the carbon impurity creates locally a region of ferromagnetic (FM) ordering with substantial tetragonal distortions. Exchange integrals and solution enthalpy are calculated, the latter being in a very good agreement with experimental data. Effect of the local distortions on the carbon-carbon interactions in $\gamma$-iron is discussed.

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Steel is a material playing unique role in our civilization. Its main chemical composition is very simple, this is just iron and carbon. Nevertheless, surprisingly, basic microscopic physics determining phase and structural states of the steel is rather poorly understood yet. In particular, mechanisms of development of lattice instability and martensitic transformation at cooling down of $\gamma$-Fe are still unknown. It is commonly accepted now that magnetism is of crucial importance for the phase stability of iron and its alloys \cite{1,2}, however, more or less detailed theoretical studies have been carried out only for a particular case of Invar Fe-Ni alloys \cite{3,4,5}.

Commonly used steel is based on the low-temperature ($\alpha$) bcc phase of iron. However, morphology of its microstructure which is decisive for all practical applications is formed during the quenching process from high-temperature fcc ($\gamma$) phase. Kinetics of the $\gamma$ – $\alpha$ transition is very sensitive to carbon concentration. The state of carbon in $\alpha$-iron was a subject of numerous investigations \cite{6,7,8}. The state of carbon in $\gamma$-iron is much less understood, and even its solution enthalpy calculated by state-of-art ab initio approach strongly disagrees with the experimental data \cite{9} which is quite unusual.

The most probably, magnetic state of $\gamma$-iron is relevant for structural properties of its alloys. Its magnetic state is strongly frustrated which leads to existence of numerous complicated magnetic structures with very close energies \cite{10,11,12}. Role of the lability of magnetic structure and the frustrations is discussed already in the context of Invar problem \cite{4,5}. Here we present the results of ab initio calculations of the electronic structure, lattice and magnetic properties of carbon solid solution in $\gamma$-iron. It turns out that the carbon interstitial in octahedron void results in an essential local magnetic polarization and strong lattice distortions which should be taken into account, in particular, to obtain correct value of the solution enthalpy.

We used the SIESTA package of first-principles electronic structure calculations \cite{13,14} with the generalized gradient approximation for the density functional \cite{15}. Earlier the same approach has been successfully used to calculate various properties of bulk and surface iron \cite{16} as well as Fe clusters \cite{17}. To calculate exchange interactions of the effective Heisenberg model

$$H_{\text{eff}} = - \sum_{i,j} J_{i,j} S_i S_j$$

($S_i$ are the classical spins defined by the direction and magnitude of obtained magnetic moments) a standard density functional approach has been used based on the “magnetic force theorem” \cite{18}. We optimized first the structure and then use the implementation of the Green’s function \cite{19,20} into the LMTO method \cite{21} to calculate the effective exchange parameters which is not possible in the framework of SIESTA. Justification of this approach will be presented below, at the discussion of the Table \cite{11}

To check accuracy of our approach we first studied structural relaxation effects in pure $\gamma$-Fe which is known to result in tetragonal deformations of initial fcc lattice \cite{22,23}. The computational results presented in the Table \cite{11} demonstrate a reasonable agreement with the previous calculations and with experimental data for thin films of $\gamma$-Fe \cite{22}. We have considered the following
TABLE I:
Lattice parameters, magnetic moments, and energies of different magnetic configurations per atom for γ-Fe with atomic relaxation taken into account; numbers in parenthesis are taken from Ref.[22].

|        | FM  | AFM | AFMD |
|--------|-----|-----|------|
| a Å    | 3.58 (3.45) | 3.44 (3.45) | 3.57 (3.49) |
| c/a    | 1.08 (1.18) | 1.09 (1.09) | 1.05 (1.09) |
| $M_{B}$, $\mu_B$ | 2.5 | 1.8 | 2.3 |
| $E - E_{AFMD}$, meV | 33 | 45 | 0 |

magnetic structures: ferromagnetic (FM), antiferromagnetic with the staggered magnetization in $<001>$ direction (AFM), and double antiferromagnetic (AFMD), or “++−−” (see Fig. 1). The latter magnetic configuration is one of most energetically favorable for γ-Fe \[4,12\].

FIG. 1: (color online) Fragment of crystal and magnetic structure of γ-Fe for the AFMD magnetic ordering. Carbon interstitial impurity in octahedral position is shown by red (dark) circle.

Further, we have performed calculations for Fe$_{32}$C supercell with carbon in the octahedral void (Fig. 1). This concentration is close to the eutectic point (3.6 at.% at 1180 K) at the phase diagram Fe-C \[24\] which is the most interesting from the point of view of metallurgy. Calculations of the total energy and magnetic moments, as well as optimization of positions of all atoms in the supercell have been carried out for FM, AFM, and AFMD structures (see Table 1). Calculated exchange interactions for the first and second Fe–Fe bonds have shown in Fig. 2a. These parameters agree well with previous calculations for fcc iron \[25\]. Carbon in the octahedral void, even without relaxation, changes the sign of nearest-neighbor exchange parameters from AFM ($J_1$=-83 K) to FM ($J_1$=+96 K).

Another effect is an essential increase of the next-nearest-neighbor exchange parameter ($J_2=48$ K in Fig. 2a and $J_2=78$ K in Fig. 2b). Interestingly, the relaxation makes the next-nearest-neighbor interactions even stronger than the nearest-neighbor ones (Fig. 2c). Probably, the gain of magnetic energy related to this effect is one of the driving mechanisms of the local tetragonal distortion. The main magnetic characteristics calculated in the SIESTA and in the LMTO are similar which confirms that our exchange parameters are reliable enough, at least, for qualitative discussions.

It turned out that, in contrast with the case of pure γ-iron, the FM ordering has the lowest energy in the presence of carbon. The exchange parameters \[15\] calculated for the FM configuration presented in Fig. 2 also confirm that this magnetic configuration is stable. The accuracy of the Heisenberg model estimated from the difference of exchange parameters and values of magnetic moments in the FM and AFMD state is in the limit of 25% (see Table II).

TABLE II:
Lattice parameters, tetragonal deformations, magnetic moments for nearest neighbors (nn) and next nearest neighbors (nnn), and total energy differences per iron atom for Fe$_{32}$C unit cell; numbers in parenthesis calculated within LMTO values

|        | FM  | AFM | AFMD |
|--------|-----|-----|------|
| a Å    | 3.73 | 3.56 | 3.61 |
| c/a, nn | 0.94 | 0.98 | 0.93 |
| c/a, nnn | 0.99 | 1.04 | 1.00 |
| c/a, bulk | 0.97 | 1.04 | 1.00 |
| $M_{B}$, $\mu_B$ nn | 2.3 (2.1) | 1.6 (1.8) | 1.9 (1.9) |
| $M_{B}$, $\mu_B$ nnn | 2.8 (2.7) | 2.2 (2.4) | 2.6 (2.5) |
| $M_{B}$, $\mu_B$ bulk | 2.7 (2.5) | 1.9 (2.2) | 2.1 (2.3) |
| $E - E_{FM}$, meV | 0 | 47 (29) | 16 (13) |

The mechanism of FM state stabilization by the carbon impurity can be understood by investigation of Fe-C chemical bonding. We present the density of states (DOS) for Fe in Fe$_{32}$C supercell, together with the local DOS for carbon impurity, in Fig. 3. One can see that for a broad energy interval ($\pm 2$eV) near the Fermi level the hybridization of the sp-states of carbon with the d-states of iron is much more pronounced for the FM state (Fig. 3a) than for both AFM ones (Fig. 3b,c). This can lead to the energy stabilization of FM states in fcc Fe-C alloys, which results in positive exchange interactions even without structure relaxation (Fig. 2b). The effect of anisotropic structural relaxation increases formation of strong FM bonds (Fig. 2c) and reduce the total iron DOS at the Fermi level (Fig. 3c) in comparison with the original AFM states.
The solution enthalpy of carbon in $\gamma$-iron has been calculated from the total energies of FM Fe$_{32}$C and of AFMD fcc Fe (which have the lowest energies among trial magnetic configurations), together with the ground state energy of graphite. The result is 0.55 eV whereas experimental value is about 0.4 eV \cite{9}. Keeping in mind that ab initio calculations without taking into account local distortions and correct magnetic ground state give just a wrong sign for this quantity \cite{7} one can say that the agreement is rather good. Actually, this is even better since our calculations have been done for high enough carbon concentration and thus a fictitious carbon-carbon interaction presents. Estimations of this effect according to the standard elasticity theory \cite{25} gives a value of order of 0.1 eV which should be subtracted from our result.

We have done also calculations for the supercell Fe$_{108}$C with the AFMD magnetic configuration. Starting from third coordination sphere of the carbon atom the tetragonal deformation $c/a - 1$ is approximately 7% which is close to the value for pure iron (see Table \ref{table1}). The corresponding values of local tetragonal distortions for the first shell near the carbon impurity is 3% and for second shell is already 6%. This means that respective to the tetragonal deformation of the host carbon produces local distortion of its nearest surrounding at approximately 4% which is a bit smaller than for Fe$_{32}$C supercell. The values of magnetic moments (in $\mu_B$ units) for the first three coordination spheres are 1.9, 2.5, and 2.6, respectively. Thus, local tetragonal distortion around carbon atom can be considered, indeed, as an effect of single impurity.

Interactions between carbon atoms via lattice distortions (deformation interactions) determine decomposition and carbon ordering processes in steel which are important for microstructure formation \cite{24}. Octahedral voids in bcc lattice are asymmetric themselves which results in local tetragonal distortions around carbon interstitial impurity and rather strong deformation interactions. It is commonly accepted that the deformation
interactions in fcc host are much weaker since the voids are symmetric and the interstitial carbons are considered as purely dilatations centers [25]. We demonstrate that proper including the magnetic effects leads to the local tetragonal distortions around carbon in γ-Fe of the same order of magnitude as in α-Fe and, thus, traditional views on the importance of the deformation interactions in different phases should be reconsidered.

These local deformations are intimately connected with the effect of carbon on local magnetic configurations of iron. It turns out that carbon changes signs of some exchange integrals from AFM to FM. Similar effects of strong distortion dependence of exchange interactions has been discussed earlier for fcc Fe-Ni alloys [5]. We show here that in addition to above mentioned distance dependence of effective exchange interaction the effect of Fe-C chemical bonding is also important.

It should be noted, that our calculations are done for the ground-state case whereas an interesting temperature interval for Fe-C steels is above 10^3 K. Nevertheless, the investigated magnetic effects can be very important for understanding of structural distortions in γ-iron alloy. Indeed, local magnetic configurations and thus local distortions can survive till relatively high temperatures. For the classical Heisenberg model on fcc lattice, the mean-field estimation for the Curie temperature is equal to the energy difference between FM and AFM configurations which gives a value of order of 500 K (see Table 11). Quantum effects for magnetic moments of order of 2 μ_B increases this estimation by a factor of 2 [18, 26] which allows to assume that, at least, up to 10^5 K local magnetic correlations will survive. This temperature can be higher for higher concentration of carbon. There are some direct experimental evidences that magnetic effects are important for the austenite-to-ferrite (α − γ) transformation in steel [27].

In conclusion, the complex magnetic state with strong tetragonal distortions is predicted for γ-iron near carbon impurities. The calculated exchange interactions show the strong tendency to formation of local FM clusters. This effect changes drastically carbon-carbon deformation interactions in γ-phase and thus should be relevant for the martensitic transformations in steel.

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