Magnetism and Local Distortions near Carbon Impurity in γ-Iron

D. W. Boukhvalov
Institute for Molecules and Materials, Radboud University Nijmegen, NL-6525 ED Nijmegen, the Netherlands
Institute of Metal Physics, Russian Academy of Sciences, Ural Division, Ekaterinburg 620041, Russia

Yu. N. Gornostyrev
Institute of Metal Physics, Russian Academy of Sciences, Ural Division, Ekaterinburg 620041, Russia
Institute of Quantum Materials Science, Ekaterinburg 620107, Russia

M. I. Katsnelson
Institute for Molecules and Materials, Radboud University Nijmegen, NL-6525 ED Nijmegen, the Netherlands

A. I. Lichtenstein
Institut für Theoretische Physik, Universität Hamburg, 20355 Hamburg, Germany
(Received 25 June 2007; published 13 December 2007)

Local perturbations of the crystal and magnetic structure of γ-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 ordering with substantial tetragonal distortions. Exchange integrals and solution enthalpy are calculated, the latter being in very good agreement with experimental data. The effect of the local distortions on the carbon-carbon interactions in γ-iron is discussed.

DOI: 10.1103/PhysRevLett.99.247205 PACS numbers: 75.20.En, 61.72.Ji, 71.20.Be, 75.30.Et

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

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

The most probable magnetic state of γ-iron is relevant for structural properties of its alloys. Its magnetic state is strongly frustrated, which leads to the existence of numerous complicated magnetic structures with very close energies [10–12]. The role of the lability of the magnetic structure and the frustrations has already been discussed in the context of the invar problem [4,5]. Here we present the results of *ab initio* calculations of the electronic structure, lattice, and magnetic properties of the carbon solid solution in γ-iron. It turns out that the carbon interstitial in the octahedron void results in an essential local magnetic polarization and strong lattice distortions, which should be taken into account, in particular, to obtain the correct value of the solution enthalpy.

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

$$H_{\text{eff}} = -\sum_{i,j} J_{i,j} \mathbf{S}_i \mathbf{S}_j$$

($\mathbf{S}_i$ 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'' [18]. We first optimized the structure and then used the implementation of the Green's function [19,20] into the linear muffin-tin orbitals (LMTO) method [21] to calculate the effective exchange parameters, which is not possible in the framework of SIESTA. Justification of this approach will be presented below, during the discussion of Table II.

To check the accuracy of our approach, we first studied structural relaxation effects in pure γ-Fe, which is known to result in tetragonal deformations of the initial fcc lattice [22,23]. The computational results presented in Table I demonstrate a reasonable agreement with the previous

TABLE I. Lattice parameters, magnetic moments, and energies of different magnetic configurations per atom for γ-Fe with atomic relaxation taken into account; the numbers in parentheses 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, μ_B	2.5	1.8	2.3
$E - E_{\mathrm{AFMD}}$, meV	33	45	0

calculations and with experimental data for the thin films of γ-Fe [22]. We have considered the following magnetic structures: ferromagnetic (FM), antiferromagnetic with the staggered magnetization in the $\langle 001 \rangle$ direction (AFM), and double antiferromagnetic (AFMD), or "$++--$" (see Fig. 1). The latter magnetic configuration is one of the most energetically favorable for γ-Fe [4,12].

Further, we have performed calculations for the $Fe_{32}C$ supercell with carbon in the octahedral void (Fig. 1). This concentration is close to the eutectic point (3.6 at. %) 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 II). Calculated exchange interactions for the first and second Fe–Fe bonds are shown in Fig. 2(a). These parameters agree well with previous calculations for fcc iron [5]. 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. 2(a) and $J_2 = 78$ K in Fig. 2(b)]. Interestingly, the relaxation makes the next-nearest-neighbor interactions even stronger than the nearest-neighbor ones [Fig. 2(c)]. 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.

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 the $Fe_{32}C$ unit cell; the numbers in parentheses are 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, μ_B NN	2.3 (2.1)	1.6 (1.8)	1.9 (1.9)
M, μ_B NNN	2.8 (2.7)	2.2 (2.4)	2.6 (2.5)
M, μ_B bulk	2.7 (2.5)	1.9 (2.2)	2.1 (2.3)
$E - E_{\mathrm{FM}}$, meV	0	47 (29)	16 (13)

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 [18] 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 states is in the limit of 25% (see Table II).

The mechanism of FM state stabilization by the carbon impurity can be understood by investigating Fe-C chemical bonding. We present the density of states (DOS) for Fe in a $Fe_{32}C$ supercell, together with the local DOS for carbon impurity, in Fig. 3. One can see that for a broad energy interval (± 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. 3(a)] than for both AFM ones [Figs. 3(b) and 3(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. 2(b)]. The effect of anisotropic structural

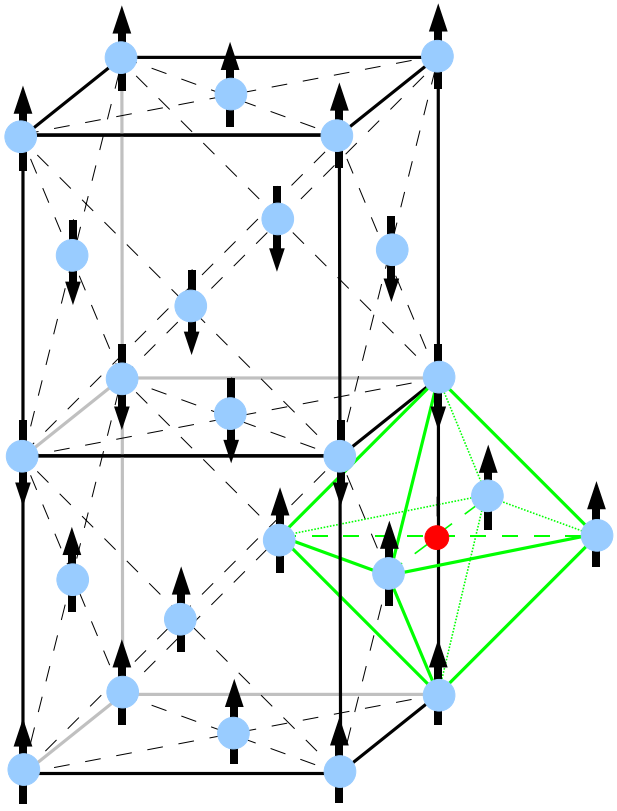

FIG. 1 (color online). Fragment of crystal and magnetic structure of γ-Fe for the AFMD magnetic ordering. Carbon interstitial impurity in octahedral position is shown by dark (red) circle.

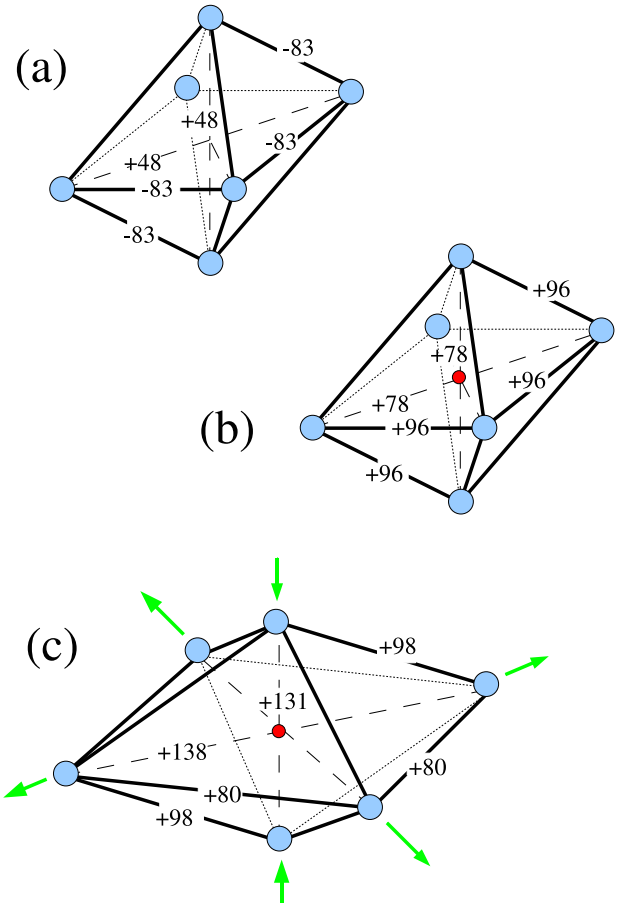

FIG. 2 (color online). Exchange parameters (in K) for different Fe-Fe pairs in original fcc lattice (a); in fcc lattice with carbon interstitial impurity without (b) and with (c) relaxation taken into account. Arrows indicate direction of atomic displacements during the relaxation.

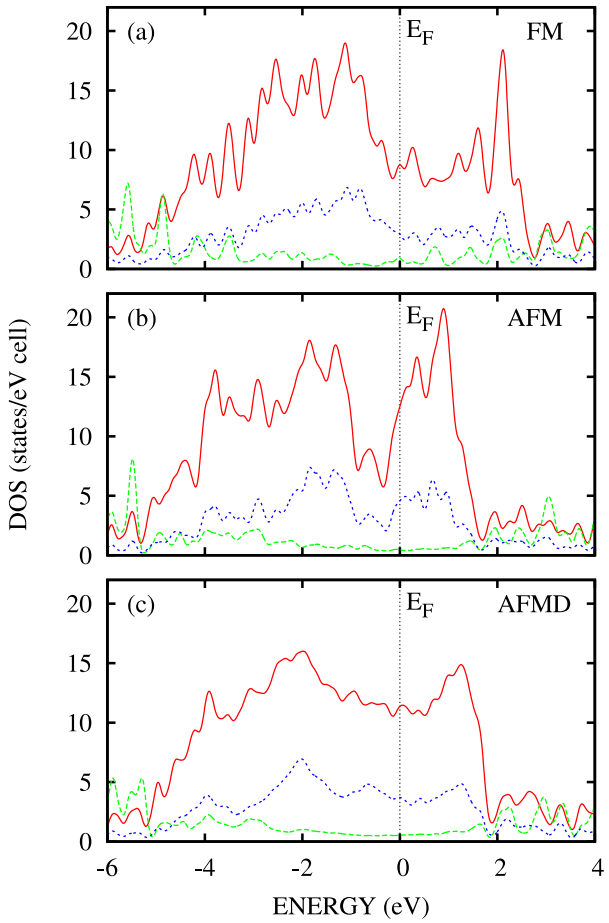

FIG. 3 (color online). Total DOS of iron atoms [solid (red) line], DOS of iron atoms from the first shell [dotted (blue) line], and for carbon atom [dashed (green) line] for relaxed $Fe_{32}C$ supercell with carbon in octahedral void for different magnetic configurations.

relaxation increases the formation of strong FM bonds [Fig. 2(c)] and reduces the total iron DOS at the Fermi level [Fig. 3(a)] in comparison with the original AFM states.

The solution enthalpy of carbon in γ-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 the experimental value is about 0.4 eV [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 [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 [25] give a value of order of 0.1 eV, which should be subtracted from our result.

We have also done calculations for the supercell $Fe_{108}C$ with the AFMD magnetic configuration. Starting from the 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 I). The corresponding values of local tetragonal distortions for the first shell near the carbon impurity is 3% and for the 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 the $Fe_{32}C$ supercell. The values of magnetic moments (in μ_B units) for the first three coordination spheres are 1.9, 2.5, and 2.6, respectively. Thus, local tetragonal distortion around a 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 [24]. Octahedral voids in the

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 the fcc host are much weaker since the voids are symmetric and the interstitial carbons are considered as purely dilatation centers [25]. We demonstrate that properly including the magnetic effects leads to the local tetragonal distortions around the 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 the 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 the understanding of structural distortions in the γ-iron alloy. Indeed, local magnetic configurations and, thus, local distortions can survive till relatively high temperatures. For the classical Heisenberg model on the 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 the order of 500 K (see Table II). Quantum effects for magnetic moments of the order of $2\mu_B$ increases this estimation by a factor of 2 [18,26], which allows one to assume that, at least, up to 10^3 K local magnetic correlations will survive. This temperature can be higher for a higher concentration of carbon. There is some direct experimental evidence that magnetic effects are important for the austenite-to-ferrite ($\alpha - \gamma$) 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 drastically changes carbon-carbon deformation interactions in the γ phase and, thus, should be relevant for the martensitic transformations in steel.

The work was supported by NWO (Project No. 047.016.005) and by FOM (Netherlands). D. W. B. acknowledges support from Funding by the Research Council of the President of the Russian Federation (Grant No. NSH-4640.2006.2). Y. N. G. acknowledges support by Russian Basic Research Foundation (Grant No. 06-02-16557).

[1] L. Kaufman, E. V. Clougherty, and R. J. Weiss, Acta Metall. **11**, 323 (1963).
[2] H. Hasegawa and D. G. Pettifor, Phys. Rev. Lett. **50**, 130 (1983).
[3] E. F. Wasserman, in *Ferromagnetic Materials*, edited by K. H. J. Buschow and E. P. Wolfarth (North-Holland, Amsterdam, 1990), Vol. 5, p. 237.
[4] M. van Schilfgaarde, I. A. Abrikosov, and B. Johansson, Nature (London) **400**, 46 (1999).
[5] A. V. Ruban *et al.*, Phys. Rev. B **71**, 054402 (2005).
[6] H. J. Goldschmidt, *Interstitial Alloys* (Plenum Press, New York, 1967).
[7] D. E. Jiang and E. A. Carter, Phys. Rev. B **67**, 214103 (2003).
[8] C. Domain, C. S. Becquart, and J. Foct, Phys. Rev. B **69**, 144112 (2004).
[9] J. A. Lobo and G. H. Geiger, Metall. Trans. A **7**, 1359 (1976).
[10] F. J. Pinski *et al.*, Phys. Rev. Lett. **56**, 2096 (1986).
[11] O. N. Mryasov *et al.*, J. Phys. Condens. Matter **3**, 7683 (1991).
[12] V. P. Antropov *et al.*, Phys. Rev. Lett. **75**, 729 (1995).
[13] E. Artacho *et al.*, SIESTA, Version 1.3, 2004.
[14] J. M. Soler *et al.*, J. Phys. Condens. Matter **14**, 2745 (2002).
[15] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[16] J. Izquierdo *et al.*, Phys. Rev. B **61**, 13639 (2000).
[17] A. V. Postnikov, P. Entel, and J. M. Soler, Eur. Phys. J. D **25**, 261 (2003).
[18] A. I. Liechtenstein, M. I. Katsnelson, and V. A. Gubanov, J. Phys. F **14**, L125 (1984); Solid State Commun. **54**, 327 (1985); A. I. Liechtenstein *et al.*, J. Magn. Magn. Mater. **67**, 65 (1987).
[19] O. Gunnarsson, O. Jepsen, and O. K. Andersen, Phys. Rev. B **27**, 7144 (1983).
[20] V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys. Condens. Matter **9**, 767 (1997).
[21] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975).
[22] P. M. Marcus, V. L. Moruzzi, and S. L. Qiu, Phys. Rev. B **60**, 369 (1999).
[23] M. Marsman and J. Hafner, Phys. Rev. B **66**, 224409 (2002).
[24] P. Haasen, *Physical Matallurgy* (Cambridge University Press, Cambridge, 1986).
[25] A. G. Khachaturyan, *Theory of Structural Transformation in Solids* (Wiley, New York, 1983).
[26] A. I. Lichtenstein, M. I. Katsnelson, and G. Kotliar, Phys. Rev. Lett. **87**, 067205 (2001).
[27] Y. Zhang *et al.*, J. Magn. Magn. Mater. **294**, 267 (2005).