Physics of the Solid State, 2023, Vol. 65, No. 5

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The influence of carbon atoms on the magnetic moment in the Fe—C system: calculation from the first principles

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Received March 13, 2023
Revised March 13, 2023
Accepted March 21, 2023

From the first principles, the influence of carbon content on the magnetic moment of theBCC- and BCC Fe-C systems was evaluated. The systems Fe-0.40C, Fe-0.79C and Fe-1.19C mass% with mass% were considered. It is shown that the tetragonality of the Fe—C system increases linearly with increasing carbon content and is in good agreement with experimental results. The average magnetic moment on Fe atoms also increases linearly with increasing carbon content. At the same time, the magnetic moment of Fe atoms located in the immediate vicinity of carbon atoms is less than in pure iron, and the atoms of the second coordination sphere, on the contrary, have more. It is shown that this is primarily due to the magneto-volume effect, whereas the effect of tetragonal distortion of the lattice is secondary.

Keywords: computer simulation, Fe—C, magnetic moment, tetragonality, magneto-volume effect.

DOI: 10.21883/PSS.2023.05.56039.33

1. Introduction

Carbon steels are important structural materials. Quenching of FCC phase of Fe—C containing up to 10 at.% of carbon is one of the methods of high strength property achievement in steels. In case of shock cooling, martensitic transformation occurs resulting in formation of a low tetragonal (BCT) structure which can be considered as a BCC iron lattice slightly extended along one axis [1]. Carbon forms a supersaturated solution which is, however, stable at room temperature for a long time. Tetragonality has a significant influence on strength and mechanical properties of steels. When carbon concentrations are higher than 10%, Fe3C release occurs. Thus, the BCC and BCT C solution existence region in iron permits a concentration up to 10 at.%.

Investigation of correlation between magnetic properties and tetragonality of Fe-C BCC alloys is of interest in terms od two aspects. First, determination of magnetic properties is one of the main methods allowing to determine $\gamma-\alpha$ transformation processes in steels. Second, available environmentally-friendly and cheap thin iron-carbon films are of great interest due to high strength and pronounced magnetic properties. At the same time, there is a lack of theoretical investigations of magnetic properties of such films [2,3].

It is well known [2,4] that addition of carbon increases magnetic moment of Fe, but the magnetic moment increase mechanism is not clearly understood at present time. In [5], an attempt was made to study this problem by ab initio computer-aided simulation methods using VASP software package. However, supercells containing one or two carbon impurity atoms were considered. A more detailed analysis of this problem with the increase in the number of carbon atoms in a supercell up to three and the use of more accurate full potential package WIEN-2k was carried out herein.

2. Calculation procedure

All calculations were performed by FP-LAPW full potential method taking into account the PBE-GGA generalized gradient approximation in WIEN-2k software package [6]. This is the most accurate method used within the density functional theory [7]. The study was carried out using the mainframe computers provided by the South Ural State University [8].

A BCC supercell containing 54 iron atoms with the following parameters was used as a model: $R_{\mathrm{mt}}K_{\max} = 6$ (10 for carbon-less systems), $R_{\mathrm{mt}}(\mathrm{Fe}) = 2.00$ a.u., $R_{\mathrm{mt}}(\mathrm{C}) = 1.20$ a.u., $E_{\mathrm{cut}} = -7$ Ry (340 eV). For reciprocal space integration and Brillouin zone electron density calculation, a Monkhorst-Pack scheme with $4 \times 4 \times 4$ k-point mesh was used. Accuracy of total energy of system, charge and interaction force between two atoms of max. 10^{-4} Ry, 10^{-3} e^- and 1 mRy/a.u. (0.025 eV/Å), respectively, was used as a convergence criterion in all cases. The listed simulation parameters ensured the system energy calculation accuracy of max. 0.01 eV.

3. Calculation results. Carbon influence on magnetic moment of iron atoms

Calculations of the total energy of BCC iron supercell containing one or two carbon atoms in insertion octapores

The number of s-, p- and d-electrons with various spin directions on pure iron atoms in Fe54C supercell and iron atoms adjacent to the carbon impurity in Fe54C cell where $N^{\uparrow(\downarrow)}$ is the number of electrons with different spin direction

Type	Fe54		Fe54C			
Atom	Random atom		Nearest neighbor		second-nearest-neighbor atom	
Spin	$N^{\uparrow}$	$N^{\downarrow}$	$N^{\uparrow}$	$N^{\downarrow}$	$N^{\uparrow}$	$N^{\downarrow}$
s	1.12	1.11	1.13	1.12	1.11	1.11
p	3.08	3.09	3.10	3.12	3.08	3.09
d	3.97	1.72	3.74	2.02	3.97	1.73
d-e_g	1.68	0.46	1.52	0.71	1.66	0.49
d-t_{2g}	2.29	1.24	2.22	1.31	2.31	1.24

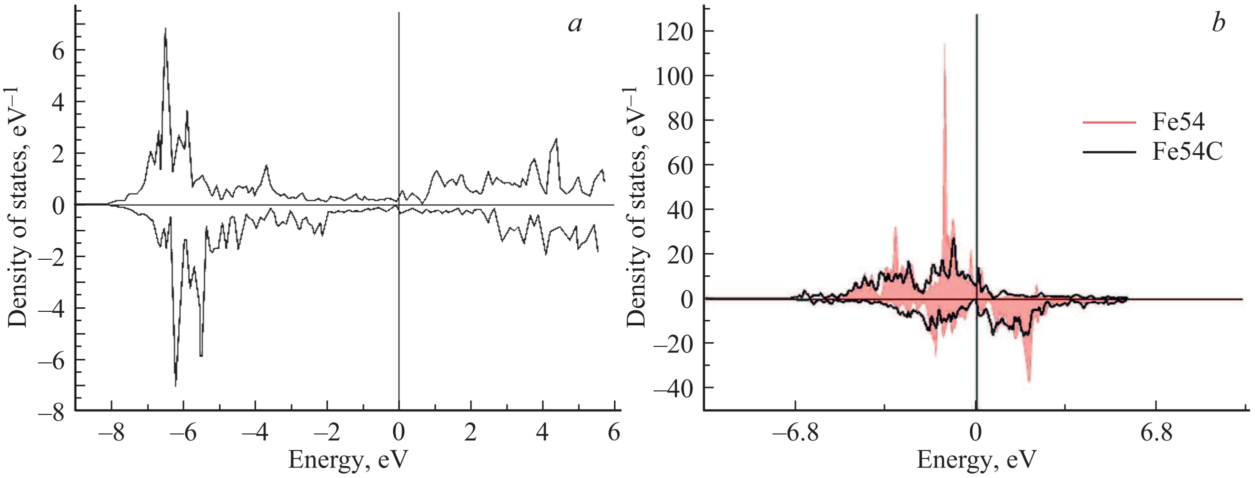

Figure 1. Local density: a — p-states of carbon impurity in Fe54C system; b- d-states on iron atoms in the first nearest neighbors of carbon in Fe54C system compared with local density for the same Fe in pure BCC.

were published earlier in[9]. The Table shows the analysis of variations of the number of s-, p- and d-electrons with different spin directions on the iron atoms adjacent to the carbon impurity (Fe54C supercell) compared with pure iron (Fe54 supercell).

According to the Table, the number of o s-, p-electrons on iron atoms varies negligibly with carbon dissolution; and the number of d-electrons with spin up in the second-nearest-neighbor atoms was unchanged and in the first-nearest-neighbor atoms significantly decreased, while the number of d-electrons with spin down n the second-nearest-neighbor atoms remained unchanged and in the first-nearest-neighbor atoms significantly increased Therefore, magnetic moment on the nearest neighbors of the interstitial carbon atom decreased significantly, and the presence of carbon has almost no influence on the second nearest neighbors.

Physical explanation of this phenomenon is simple and close to the mechanism offered in [10] for explanation of magnetic properties of non-transition impurities in transition metals. When mixing of p-orbitals of carbon atoms with d-orbitals of iron atoms, low-lying bonding state and higher by energy antibonding state are formed. In accordance with Pauli's principle, complete wave function of these states taking into account the spin shall be asymmetrical with respect to electron coordinate exchange. Since the bonding state coordinate function is symmetrical, then the spin function will be asymmetrical, i.e. electrons in this state shall have antiparallel spins.

Figure 1 shows the calculations of local electron state density on the carbon impurity atom and Fe atom in the first nearest neighbors for C atom in Fe54C supercell. As can be seen in Figure 1, a, mixing of p-orbitals of carbon primarily occurs with d-orbitals of spin up band, therefore p-electrons with spin up are involved in the bonding state. The coordinate wave function of the antibonding state is antisymmetric. Therefore, the spin wave function shall be symmetrical, i.e. electron spins involved in it are parallel. Therefore, primarily p-electrons with spin up will be primarily involved in this state which is shifter up by energy. Thus, the local electron density of p-electrons with spin down is shifted down and the density with spin up is lifted resulting in total increase in $N^{\downarrow}$ and decrease in $N^{\uparrow}$. Therefore, the moment of the carbon atom is opposite to the iron moment.

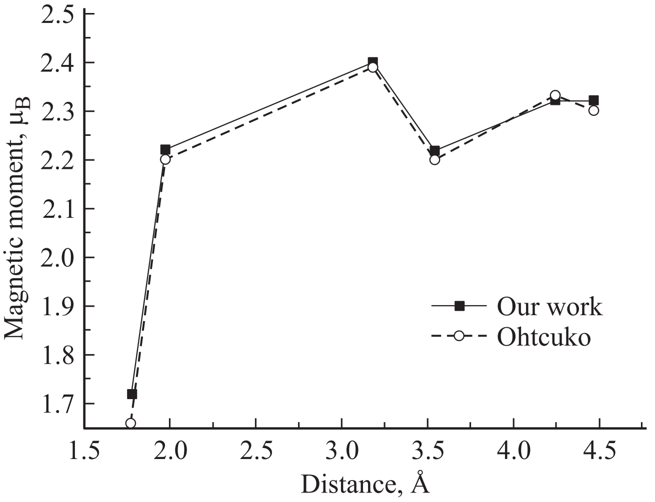

Figure 2. Dependence of magnetic moment on the iron atom on the distance to the carbon atom in tetragonal Fe54C supercell compared with Ohtsuka's study [4].

Increase in the number of $N^{\downarrow}$ on the impurity occurs primarily due to transition of d-electrons with spin up from iron atoms nearest to the impurity (Figure 1, b). This, in turn, causes electron deficiency , which violates the electroneutrality condition. The deficiency on the Fe atoms adjacent to the impurity is shielded by d-electrons with spin up. As a result, magnetic moment on the nearest iron atoms decreases, and this was found herein. This behavior results in occurrence of declining oscillation of the local magnetic moment that shields the electron gas impurity with distance from the carbon impurity, which was described by Friedel [11].

Figure 2 shows magnetic moments of Fe atoms depending on the distance to the carbon atom in Fe54C structure. The calculated magnetic moment of Fe atom in BCC-Fe54 is equal to $2.23\,\mu_{\mathrm{B}}$, which agrees well with the experimental data. The magnetic moment of the iron atom in the first nearest neighbors for the carbon atom is much lower than the magnetic moment of the pure iron atom (Fe54). With the increase in the distance between the carbon and iron atoms, the magnetic moment of the latter grows, and then varies near $2.3\,\mu$B.

As can be seen in Figure 2, declining magnetic moment oscillation on Fe atoms with distance from the carbon impurity is observed and agrees with the Friedel theory prediction [11] regarding the behavior of magnetic moment of the electron gas that shields the impurity.

Simulation of Fe54C2 and Fe54C3 supercells containing 2 and 3 interstitial carbon atoms in octapores gave various total energy levels of supercell and tetragonality depending on the configuration of octapores occupied by carbon atoms. If an atom occupies octapores of different types (e.g. x and y, or x, y, z, then tetragonality is low. If carbon atoms fill octapores of the same type, then tetragonality increases considerably and the total energy decreases according to the martensitic transformation theory developed by Khachaturyan [12]. This data was discussed in more detail earlier in [13]. The lowest energy was satisfied by configurations with the following tetragonality degrees $c\backslash a = 1.03$; 1.042 and 1.02 for 3, 2 and 1 carbon atoms, respectively.

Figure 3 shows the dependence of the calculated average magnetic moment of Fe atoms on carbon content and lattice cell volume, respectively.

According to 3, linear dependence of he average magnetic moment on carbon concentration is observed which is associated with magnetic volume effect and the presence of tetragonal lattice distortion. This conclusion is in line with [5] and empirical Schlosser equation and with Mitsuoka's experimental study [4]. However, the average magnetic moments of Fe found by us are a little lower than

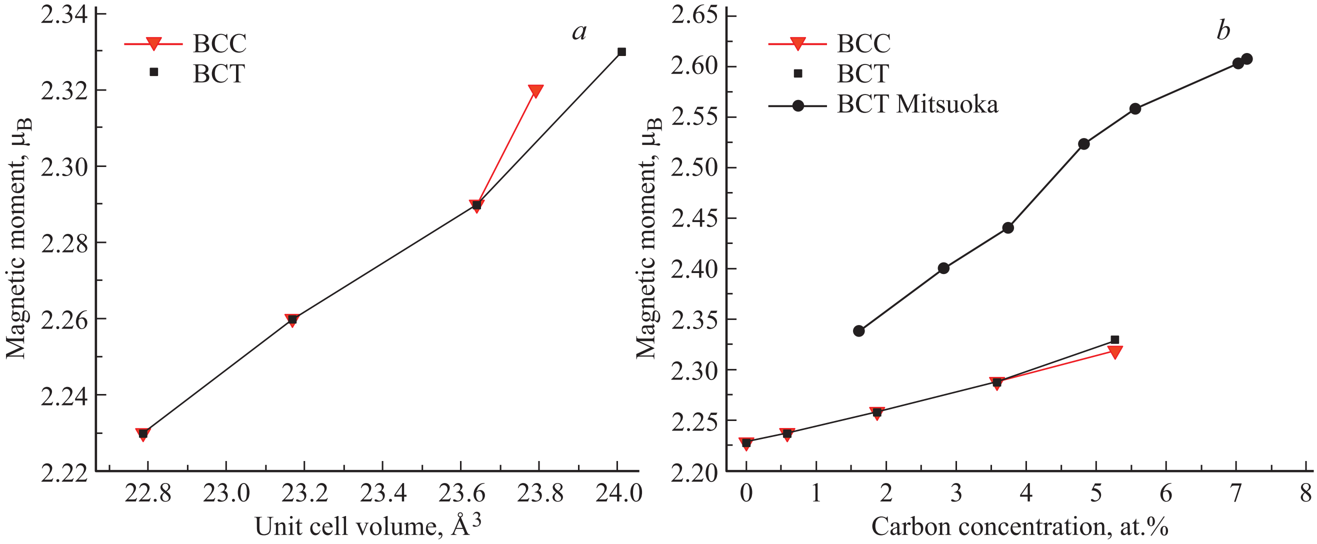

Figure 3. Dependence of the average magnetic moment in the iron atoms in BCC and BCT: a — on lattice cell volume, b — on carbon concentration.

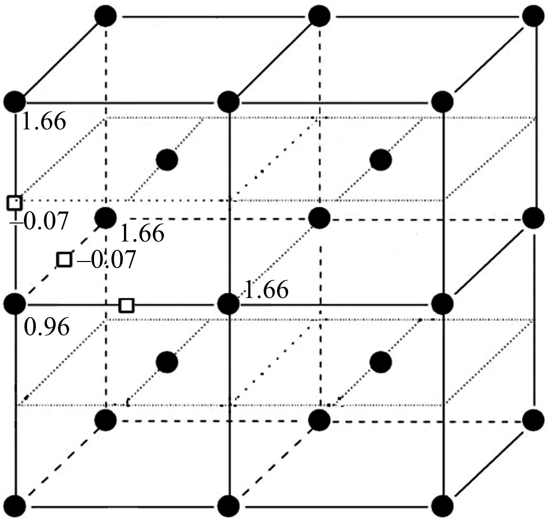

Figure 4. Magnetic moments on the atoms for Fe54C3 supercell: black circles – iron atoms, hollow squares — carbon atoms.

the experimental data [4]. This may be attributable to the fact that [4]used the assumption of zero magnetic moment on C atoms, while the obtained data indicates that negative magnetic moment $-0.09\,\mu_{\mathrm{B}}$ is present on the carbon atoms.

Figure 3, *b* also shows that the magnetic volume effect is most significant factor [14,15], while the tetragonality effect is low. This finding differs from the conclusion made in [5], where significant influence of the lattice tetragonality degree was pointed out. It should be also noted that as can be seen from the experimental data in [4], the average magnetic moment increase rate decreases considerably with further growth of carbon concentration.

It is known that iron carbides form hexagonal or orthorhombic structures during crystallization [16]. Therefore, there is no data on the behavior of magnetic moments of iron with higher carbon concentrations. However, there is a set of indirect data showing that, instead, the magnetic moment on iron atoms were decreasing at higher carbon concentrations. Thus, for example, in [3], where magnetic properties of amorphous $\mathrm{Fe}_x\mathrm{C}_{l-x}$ $(0.75 > x > 0.50)$ films were studied and it was shown that, starting from 30 at.%C, the average magnetic moment on iron atoms decreases monotonously and almost linearly with carbon content growth. This finding indirectly agrees with [17], where magnetic moments were measured in Fe4N with BCC structure which was equal to $2.14\,\mu_{\mathrm{B}}$, which is lower than that of pure iron. Nitrogen impurities act similarly to carbon impurities in many cases, therefore, this finding may indicate that the magnetic moment decreases for iron and carbon impurities with concentration about 25 at.%. Reduction of magnetic moments on the iron atoms at such concentrations is attributable to the growing number of iron atoms nearest to the carbon atoms whose magnetic moment, as shown in Figure 2, is decreasing from 2.23 to $1.72\,\mu_{\mathrm{B}}$. Moreover, for the iron atoms adjacent simultaneously to 2 or more carbon atoms, the magnetic moment may be lower, because the impurity influence mechanism described above causes a synergetic effect.

This may be illustrated by the calculated magnetic moments on the iron atoms for the Fe54C3 supercell configuration shown in Figure 4.

It can be seen that, for Fe atom which is the nearest neighbor of three carbon atoms simultaneously, the magnetic moment drops to a record-low value $0.96\,\mu_{\mathrm{B}}$. This effect explains the reduction of magnetic moments on the iron atoms id amorphous Fe-C alloys containing more than 30 at.%C which is observed experimentally.

4. Conclusions

The impact of various carbon impurity configurations on the magnetic properties of Fe-C systems was studied ab initio. The following results were obtained.

1. The average magnetic moment on Fe atoms grows linearly with an increase in carbon content up to 5 at.%C, which is in good agreement with the experimental and theoretical data [4,5].

2. It is shown that the magnetic moments of Fe atoms have low dependence on the lattice tetragonality, but a linear dependence of the magnetic moment on the equilibrium lattice cell volume at various carbon concentrations is observed. Therefore, it can be claimed that the magnetic effect is the cause of magnetic moment growth. This finding differs from the conclusion made in [5], where significant influence of the lattice tetragonality degree was pointed out.

3. The magnetic moment of Fe atoms being the nearest neighbors of a carbon atom is much lower than that of the pure iron and is about $1.72\,\mu_{\mathrm{B}}$. If Fe atom is adjacent simultaneously to two or more carbon atoms, then its magnetic moment is even lower down to $0.96\,\mu_{\mathrm{B}}$, this is attributed to the synergetic effect.

Funding

The study was supported financially by the Ministry of Science and Higher Education of the Russian Federation (governmental job-order on fundamental scientific research No. FENU-2023-0013 (2023013GZ)).

Conflict of interest

The authors declare that they have no conflict of interest.

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Translated by E.Ilyinskaya