First-Principles Study on Magnetism of ε-carbides

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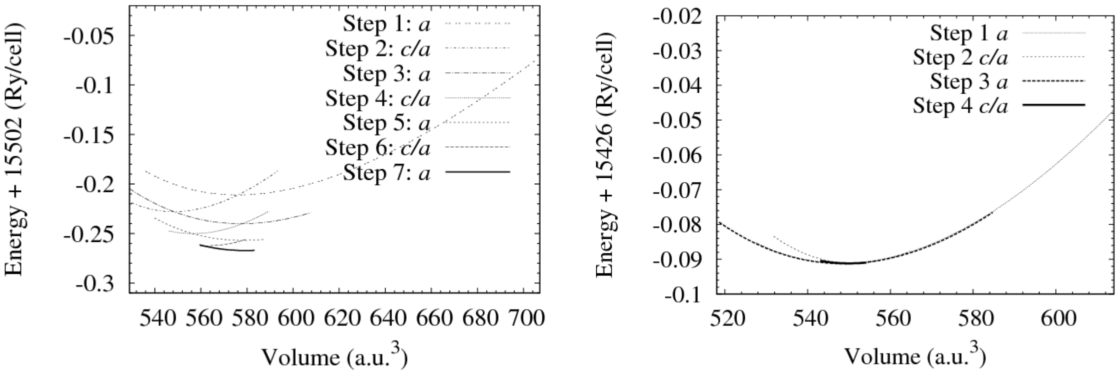
1. Introduction

During martensitic transformation, many forms of carbides can be found in a hardened structure consisting of tetragonal martensite and retained austenite, high-carbon steels. Those carbides are ε-carbide, θ-carbide (cementite), and x-carbide (Hägg carbide). Since the importance of quality of final products, it is necessary to understand their thermodynamics as well as magnetic properties. However, the controversial studies have been done on the structure of ε-carbide Fe_3C. The ε-carbide was proposed initially by Jack [1], based on the similarity of the X-ray diffraction patterns found in Fe_3N. The initially suggested crystal structure of ε-carbide was hexagonal close packed (hcp) structure with the lattice parameters, α=2.73 Å, c=4.33 Å, and c/α=1.58. However, Nagakura[2] studied the crystal structure by using the electron diffraction to reveal that the structure of ε-carbide should be in-plane doubled hcp structure with the lattice parameters, $\alpha=\sqrt{3}$ ah=4.767 Å and c=ch=4.354 Å. The possible Fe_2C stoichiometry was proposed by additional carbon occupation on the hexagonal lattice. The alternative study by Barton and Gale[3] claimed the structure ε-carbide being monoclinic, similar with the hcp structure, with the lattice paratmers, a=b=2.794 Å, c=4.360 Å, and $\gamma=120.92^o$ if one assume the formula Fe_2C. In 1983, Dirand and Afqir[4] confirmed by using a series of X-ray diffraction measurements on iron carbides, that the Nagakura's suggestion was correct: the space group of the ε-carbide structure is $P6_322$, which is the half group of $P6_3/mmc$, which is the hcp structure what previously considered structure.

On theoretical side, Faraoun *et al.*[5] studied the crystallin, electronic and magnetic structures of several carbides, but no calculation was done on ε-carbide. Very recently, Lv *et al.*[6] investigated the structural stability, electronic, and magnetic propertis of Fe_2C carbides by using a plane-wave-based-pseudo-potential method. However, the claims of Lv *et al.* are confusing on considering the crystal structure of ε-carbides: they claimed that they took the space group $P6_3/mmc$, with the half lattice parameter of a_h, which generates the unphysically small interatomic distances, *i.e.*, smaller than the atomic radius of iron atom. Unexpectedly, the calculated results by Lv *et al.* are in reasonable value ranges. Hence, it is required to reexamine the calculations in terms of a highly precise first-principles the all-electron total-energy full-potential linearized augmented plane-wave (FLAPW) method[7,8]. Here we tried to obtain the electronic structures and magnetism of the proposed hexagonal structure by Nagakura[3].

2. Computational Method

We adapt the crystal structure of ε-carbide being proposed by Nagakura[3] and confirmed later by Dirand and Afqir[4]. The Kohn-Sham equation[9] was solved self-consistently in terms of the FLAPW method as embodied in the QMD-FLAPW code within the generalized gradient approximation (GGA)[10] to the exchange-correlation potential. The LAPW basis set were expanded by plane wave cutoff of 22 Ry. Lattice harmonics with $l \leq 10$ were employed to expand the charge density, potential, and wave functions inside each muffin-tin (MT) sphere of radii of 2.15 a.u. for Fe atoms and 1.35 a.u. for C atoms. The core electrons are treated fully relativistically. The star-function cutoff of 260 Ry. was employed for depicting the charge density and potential in the interstitial region. Integrations inside the 3 dimensional (3D) Brillouin zone (BZ) were performed by improved tetrahedron method on a 13×13×13 mesh, which corresponds to 84 k-points inside the irreducible wedge of the 3D BZ. Self-consistency was assumed when the difference between input and output charge (spin) density was less than 1.0×10^{-5} electrons/a.u.3 Lattice constants were optimized and the internal atomic coordinates were relaxed by using the total-energy and the atomic formce minimization [11], which we assume the force zero when the atomic force is less than 2 mRy./a.u.



(a) (b)

Fig. 1. Multistep lattice constants optimization of (a) Fe_3C and (b) Fe_2C.

3. Results and Discussions

Fig. 1 shows the results of multistep lattice constants optimization of (a) Fe_3C and (b) Fe_2C. The optimized lattice constants of Fe_3C were calculated to be α=4.677 Å and c/α=1.080, while those of Fe_2C were evaluated to be α=4.691 Å and c/α=0.960, fatter and shorter hexagon than those of Fe_3C. These facts imply the possiblity that ε-carbides of non-integral stoichiometry will be stabilized not only by thermodynamic conditions, but also by mutual stress energy balance between the Fe_3C and Fe_2C phases. It is considered that the phase transition from the hexagonal ε-carbide to the orthorhombic η-carbide by the lattice mismatch between the Fe_3C and Fe_2C phases. The calculated local magnetic moment of the Fe atom in Fe_3C was 2.397 μB, while that in Fe_2C was 1.72 μB. The total magnetization of Fe_3C was calculated to be 1.68 T, while that of Fe_2C was calculated to be 1.32 T. The strong reduction of the local Fe magnetic moment and the corresponding reduction in the total magnetization of Fe_2C are thought to be originated by the strong Fe-C bonding, in the Fe_2C phase.

4. Conclusions

We reexamined the first-principles calculation of ε-carbide in both the Fe_3C and Fe_2C phases by using the all-electron total-energy FLAPW method based on the GGA. We found that the hexagonal crystal of Fe_2C is fatter and shorter than that of Fe_3C. Due to the stronger Fe-C bonding in Fe_2C than in Fe_3C, the local magnetic moment of Fe atom and the total magnetization of Fe_2C are reduced strongly.

5. References

[1] K. H. Jack, Acta Cryst. **3**, 392 (1950).

[2] S. Nagakura, J. Phys. Soc. Jpn. **14**, 186 (1959).

[3] G. H. Barton and B. Gale, Acta Cryst. **17**, 1460 (1964).

[4] M. Dirand and L. Afqir, Acta Metall. 31, 1089 (1983).

[5] H. I. Faraoun, Y. D. Zhang, C. Esling, and H. Aourag, J. Appl. Phys. **99**, 093508 (2006).

[6] Z. Q. Lv, S. H. Sun, P. Jiang, B. Z. Wang, and W. T. Fu, Comp. Mater. Sci. 42, 692 (2008).

[7] E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, Phys. Rev. B, **24**, 864, (1981), and references therein.

[8] M. Weinert, E. Wimmer, and A. J. Freeman, Phys. Rev. B, **26**, 4571, (1982).

[9] W. Kohn and L. J. Sham, Phys. Rev. **140**, A1133 (1965).

[10] J. P. Perdew, K. Burke, and M. Ernzernhof, Phys. Rev. Lett., **77**, 386 (1996); ibid. **78**, 1396(E), (1997).

[11] W. Mannstadt and A. J. Freeman, Phys. Rev. B **55**, 13298 (1997).