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Determination of Crystal Lattice Structure and Cohesive Energy of 3d Transition Metal Carbides by First-Principles Calculation

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Abstract We obtained the optimal atomic coordinates using the experimental lattice constants (a=0.452 6nm, b=0.508 9nm, c=0.674 3nm) of cementite Fe_3C. We calculated and analyzed the electron density distribution to make analysis about the nature of chemical bonds in the cementite structure. After determination of lattice constant parameters, we obtained the cohesive energy by subtracting the total energy of the crystal from the summation of total energies of atoms composing the crystal and dividing it by the number of atoms. Next, we inserted metal atoms into graphite structure, calculated the total energy and estimated the subtraction between the total energies of isolated metal atom and graphite crystal.

Key words diamond, M_3C, cohesive energy

Introduction

The great leader Comrade **Kim Il Sung** said as follows.

"We should further strengthen scientific research and rapidly develop science and technology so that any scientific and technical problems in economic construction can be solved as soon as they arise and thus successfully make the national economy scientific and fully ensure that it becomes Juche-orientated and modern."("**KIM IL SUNG** WORKS" Vol. 35 P. 312)

Now the catalytic transition metal elements Fe, Ni, Co, Mn and Cr are used in diamond synthesis most widely. Catalysis metal element Fe, Ni, Co, Mn form metastable carbides with a structure similar to that of Fe_3C where each carbon is surrounded by six iron atoms in the process of diamond synthesis[2].

In the paper[4, 5] it proposed a combinative mechanism of HP-HT catalytic synthesis of diamond based on X-ray data obtained from synchrotron radiation and other experimental results. In this mechanism, they suggested that metal atoms of the `catalyst-solvent` diffuse between the graphite layers to form weakly bonded graphite intercalation compounds(GICs).

We considered the typical transition metal carbides of cementite structure (M_3C: M for metal, space group of Pnma) to investigate the interaction characteristics between transition metal elements and carbon atom. Based on the pseudopotential plane wave (PP-PW) method and the projector augmented wave (PAW) method within density functional theory (DFT), we have performed the first-principles simulations for determining the optimal crystal lattice constants of carbides containing the transition metal elements, Mn, Fe, Co and Ni, and first-row element C, compared with experimental ones, and calculated the binding energy (or cohesive energy)[1, 3].

1. Simulation of Crystal Lattice Structure

First of all, we obtained the optimal atomic coordinates using the experimental lattice constants (a=0.452 6nm, b=0.508 9nm, c=0.674 3nm) of cementite Fe_3C. The atomic coordinates in cementite structure are shown in Table 1.

Table 1. The atomic coordinates in cementite structure.

Crystallographic coordinates			Atom
x_1	1/4	z_1	
$-x_1$	3/4	$-z_1$	4c
$1/2-x_1$	3/4	$1/2+z_1$	C
$1/2+x_1$	1/4	$1/2-z_1$	
x_2	1/4	z_2	
$-x_2$	3/4	$-z_2$	4c
$1/2-x_2$	3/4	$1/2+z_2$	Fe
$1/2+x_2$	1/4	$1/2-z_2$	
x_3	y_3	z_3	
$-x_3$	$-y_3$	$-z_3$	
$1/2+x_3$	$1/2-y_3$	$1/2-z_3$	
$1/2-x_3$	$1/2+y_3$	$1/2+z_3$	8d
$-x_3$	$1/2+y_3$	$-z_3$	Fe
x_3	$1/2-y_3$	z_3	
$1/2-x_3$	$-y_3$	$1/2+z_3$	
$1/2+x_3$	y_3	$1/2-z_3$	

Fig. 1 shows the atomic structure of cementite structure. The atomic position parameters to be determined are 7 (x_1, z_1, x_2, z_2, x_3, y_3, z_3).

Fe atoms make the high dense packed structure and carbon atoms are inserted among them, forming the inserting phase.

The atomic coordinate parameters obtained in the simulations are (0.877, 0.440, 0.038, 0.837, 0.176, 0.068 and 0.332) in Fe_3C, which are well agreed with the experimental ones (0.890, 0.450, 0.036, 0.850, 0.186, 0.063 and 0.328). These values in other carbides Mn_3C, Co_3C, Ni_3C are also well agreed with the experimental ones within the negligible error of 10^{-2} magnitude. Next we performed the crystal lattice optimization. The obtained lattice constants are a=0.451 6nm, b=0.506 3nm, c=0.674 1nm in Fe_3C, which are very close to the experimental ones. The situations are similar in other carbides.

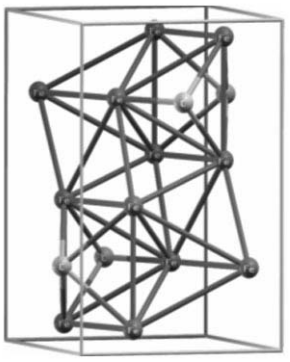
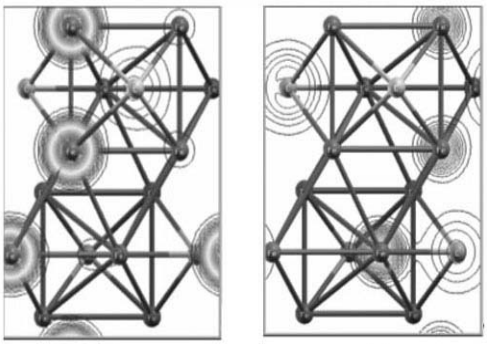


Fig. 1. Unit cell of cementite structure

We calculated and analyzed the electron density distribution to make analysis about the nature of chemical bonds in the cementite structure (Fig. 2).



a) b)

Fig. 2. Contour plot of electron density in cementite Fe$_3$C

As shown in the Fig. 2, the electron density is distributed intensively with almost spherical symmetric shape around Fe atom, while small amount of electron density is visible around C atom.

Such thing tells us that the electrons transferred from C to Fe atom, Fe atoms are bonded with strong metallic bond and weak ionic bonding between Fe and C atoms exists. The carbon atoms, therefore, can be taken out of crystal.

2. Determination of Binding Energies of Crystals

After determination of lattice constant parameters, we obtained the cohesive energy by subtracting the total energy of the crystal from the summation of total energies of atoms composing the crystal and dividing it by the number of atoms. Since the structure factor is 4 in the cementite structure, the cohesive energy is as follows.

$$E_{\mathrm{coh}} = [(12E_{\mathrm{M}} + 4E_{\mathrm{C}}) - E_{\mathrm{M_3C}}]/16$$

where E_{M} and E_{C} are the total energies of isolated metal atom and carbon atom respectively and $E_{\mathrm{M_3C}}$ is one of the crystal composed of 4 M_3C units, that is, unit cells containing 16 atoms.

The obtained cohesive energies are shown at table 2.

The bond length between carbon and metal atoms in considered M_3C-type carbides are 0.204 and 0.206nm.

Next, we inserted metal atoms into graphite (Fig. 3), calculated the total energy and estimated the subtraction between the total energies of isolated metal atom and graphite crystal. In table 3 the total energies and the subtractions are shown. The total energy of the pure graphite crystal is 22.794 31Ha.

Table 2. Cohesive energies of carbides

Carbides	Cohesive energy/(eV · atom^{-1})	
	Calc.	Exp.
Mn_3C	6.87	—
Fe_3C	6.53	5.05
Co_3C	6.28	—
Ni_3C	5.75	—

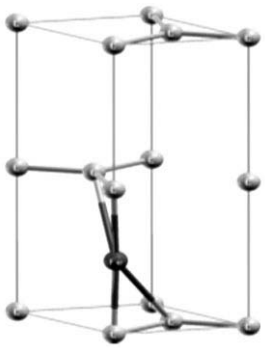


Fig. 3. The crystal structure of graphite inserted metal atoms

From the table 3, we can see that the insertion of Mn makes the structure more stable, while other metals make the structure more unstable increasing the atomic number. The atomic radii of Fe, Co and Ni are similar (0.126, 0.125, 0.124nm).

Table 3. Total energies and the subtraction

Element	Isolated Atom/Ha	graphite+metal/Ha	Subtraction/eV
Mn	−13.672 50	−36.514 519	1.30
Fe	−19.375 46	−42.089 635	−2.18
Co	−26.222 52	−48.721 306	−8.04
Ni	−34.590 56	−56.499 039	−24.10

1Ha =27.211 383 4eV= 4.359 742 5·10^{-18}J

Conclusion

When considering the variation characteristics in the cementite structure of Mn, Fe, Co, and Ni compared with the experimental ones, it is shown that their catalytic behaviors are different as the catalysis for synthesizing diamond. We can fabricate better diamond if the catalysis for synthesizing diamond could be developed considering such behaviors.

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