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How to Clarify the Relative Stability of Diamond and Graphite by Quantum Chemistry Calculations in Teaching

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Abstract: *In this article, the relative stability of graphite and diamond is calculated and compared by cp2k software. Quantum calculation proves that graphite is more stable than diamond, and the energy difference between them is about 612.449 kcal / mol if 192 carbon atoms are filled in one unit cell. All assignments are aimed at helping students gain practice with computational chemistry software while at the same time understanding the different stability between different crystal structures. Given the facts that CP2K is free, all calculations are simple, convenient and reliable, this work provides a solution to the similar problems encountered in Chemistry teaching, especially those about crystal structures.*

Keywords: *Relative Stability, Diamond, Graphite, CP2K*

1. Introduction

In the thermodynamics part of Inorganic Chemistry and Physical Chemistry, it is necessary to tell students about what is the most stable Elementary Substance of carbon. As we know, all textbooks or thermodynamic data sheets indicate that graphite is more stable than diamond [1]. However, this is not in line with the students' common understanding, because people usually think that diamond is very hard and graphite is very soft, so diamond should be more stable than graphite. How to explain this contradiction to the students?

In my teaching work, I found that this problem can be solved by Quantum Chemistry calculations, especially those calculations about crystal structures. In fact, CP2K is such good software. It is a quantum chemistry and solid-state physics software package that can perform atomistic simulations of solid state and crystal systems [2]. Based on the crystal structure of graphite and diamond, which has been clarified for a long time, it is convenient to calculate the energy of these two kinds of crystals. The smaller the energy, the more stable Elementary Substance is.

2. Computational steps and discussion

According to the Inorganic Crystal Structure Database (ICSD)[3], graphite and diamond can form at least four space group structures, i.e. Cmmm (No. 65 space group, graphite ICSD No. is 88812; Diamond ICSD No. is 88816), Cmma (No. 67 space group, graphite ICSD No. is 88811; diamond ICSD No. is 88815), R-3mR or R-3mH (both are No. 166 space group, graphite ICSD Nos. are 31829 and 53780; diamond ICSD Nos. are 44100, 66469 and 66470), P63/mmc (No. 194 space group, graphite ICSD Nos. are 52230, 53781 and 76767; diamond ICSD Nos. are 66465, 66467, 66468 and 88822). Our calculation results showed that no matter which crystal structure is selected, graphite is more stable than diamond in the same space group. So we choose the highest symmetric P63/mmc space group (belonging to the hexagonal crystal system) as our calculation crystal.

In order to facilitate the selection of multiple cells containing the same number of C atoms, we selected the crystal structures of ICSD No. 52230 and 66467 as the representative structures of graphite and diamond, respectively. Their crystal structure parameters are listed in Table 1.

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Table 1 Crystal structure parameters of selected graphite and diamond.

database_code_ICSD	52230(graphite)	66467(diamond)
a	2.460(2)	2.5221
b	2.46	2.5221
c	6.704(5)	12.3557
alpha	90.	90.
beta	90.	90.
gamma	120.	120.
volume	35.13	68.06
Z	4	12
space_group_name_H-M	'P 63/m m c'	'P 63/m m c'
Int_Tables_number	194	194

Theoretical method b97m RV (implemented by libxc Library) was selected and the basis set is 6-311G** [4-8]. All calculations were completed with CP2K 7.1 software package [2].

CP2K provides a general framework for different modeling methods such as DFT using the mixed Gaussian and plane waves approaches GPW and GAPW.

Because the crystal structure used in our calculation is the most stable one, there is no need to optimize the crystal structure again. Only the single point energies need to be calculated, so all calculations are easy to be completed. All calculations can be fulfilled even on personal computers.

The structures of two multiple cells are shown in fig. 1 and the results are listed in Table 2.

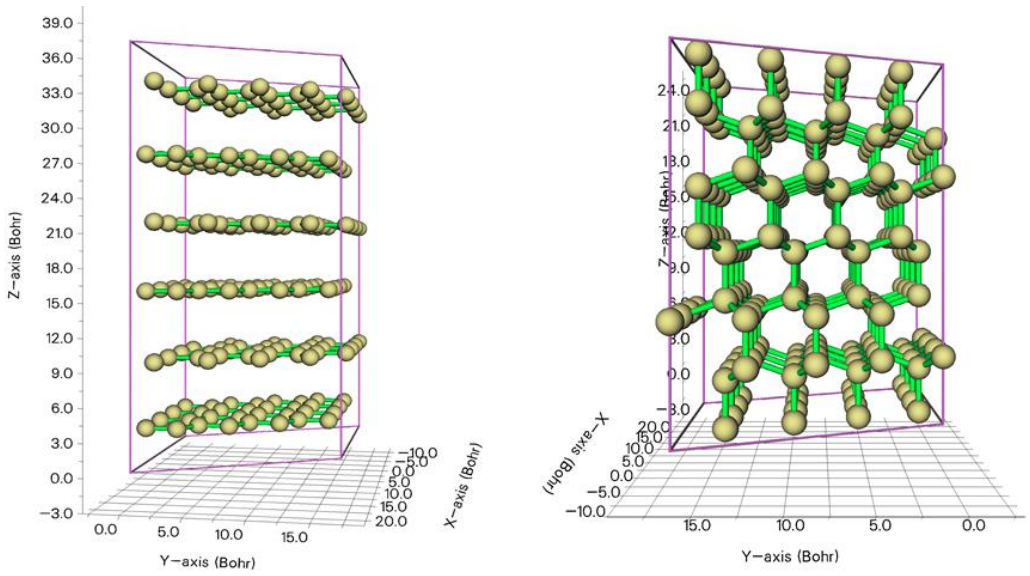

*Figure 1: Multiple cells structures of graphite (4*4*3, left) and diamond (4*4*1, right)*

Table 2: Comparison of calculation results between graphite and diamond.

database_code_ICSD	52230(graphite)	66467(diamond)
multiple cell	4*4*3	4*4*1
Atoms:	192	192
Shell sets	960	960
Shells:	1536	1536
Cartesian basis functions:	3648	3648
Number of electrons:	1152	1152
Number of occupied orbitals	576	576
Number of molecular orbital	576	576
Number of orbital functions	3456	3456
Total energy (a.u.)	-7323.522	-7322.546

It can be seen that the multiple cells of graphite and diamond all contain 192 atoms. The number of molecular orbitals is also the same, but the total energy is very different. Graphite is 0.976 a.u.

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(612.449 kcal / mol) more stable than diamond under the same crystal structure, which can explain the relative stability of graphite and diamond.

3. Conclusions

This article has described our calculation method and results about two typical crystal structures of graphite and diamond. As we know, CP2K software package is free, the crystal structure is easy to obtain, the calculation method is simple, and the conclusion is universal and reliable, which provides an idea for solving the same type of problems.

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