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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

**THEORETICAL STUDY OF THE STRUCTURAL
STABILITY OF BINARY SEMICONDUCTOR ALLOYS
AND CAGE-LIKE ALLOY CLUSTERS**

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NANYANG TECHNOLOGICAL UNIVERSITY**

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of Binary Semiconductor Alloys and Cage-like Alloy Clusters

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Summary

With the statistical method and first principle calculations, the properties of alloy materials can be addressed properly. In this work, we develop two new theories to deal with the semiconductor alloy systems and cage-like cluster alloy systems, by combined with first principle methods. Based on the consideration of the thermodynamics of the growth process of semiconductor alloy, quasi-ordered structure (QOS) method is built by using the concept of factor group in group theory. Based on the consideration of the effect of the local environments of the chemical bonds, color bond graph (CBG) theory is made in order to search the stable configurations in the huge configuration space of cage-like alloys.

With QOS model, the structural and electronic properties of the ZnO-based semiconductor alloys, including $\text{Be}_x\text{Zn}_{1-x}\text{O}$, $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, and $\text{ZnO}_{1-x}\text{S}_x$, are systematically studied by the first principle methods. For isostructural phase alloys $\text{Be}_x\text{Zn}_{1-x}\text{O}$, we find some alloy configurations with the same concentration can have very different band-gaps and predict the ordered metastable states is possible to be obtained in experiment. For nonisostructural phase alloys $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, we suggest the concept about mixing regions of phases can be used for theoretical analysis. We also have drawn the mixing regions of phases for the three alloys. For $\text{ZnO}_{1-x}\text{S}_x$, we predict the bowing coefficient for wurtzite structure is very different from that for zincblende structure.

With CBG theory and bond-counting rule, we systematically investigate the structural stability of superhard alloy BC_2N and search the low-energy configurations of cage-like alloys $(\text{BN})_6\text{C}_{12}$ and $\text{Si}_n\text{C}_{60-n}$. For superhard BC_2N alloy, it is found the hardness of configuration is correlated with the stability and there are many high-density alloy configurations with low energies in configuration space. It is predicted that a mixture of high-density alloy configurations is likely to occur in the experimental samples. For cluster $(\text{BN})_6\text{C}_{12}$, the substitutions of BN units in the cage are found to follow a rule of “continuity” pattern. We also predict that these alloy phases can be synthesized under the high temperature and nonequilibrium experimental conditions. With the study on the low-energy configurations of alloy cage $\text{Si}_n\text{C}_{60-n}$, we find that silicon atoms have the tendency of aggregation on the fullerene ball. Due to the low formation energy of these configurations, it is predicted that the alloy phase in carbon-rich region is possible to synthesize in experiment.

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Publications during my Ph. D. study at NTU

Journal publications related to the thesis

1. **X.F. Fan**, H.Y. Wu, Z.X. Shen and Jer-Lai Kuo, “*A First Principles Study on High-density Pseudo-cubic BC_2N* ”, *Diamond and Related Materials* **18**, 278 (2009)
2. **X.F. Fan**, Z.X. Shen, Y.M. Lu and Jer-Lai Kuo, “*A Theoretical Study of Thermal Stability and Electronic Properties of Wurtzite and Zincblende ZnO_xS_{1-x}* ”, *New Journal of Physics* **11**, 093008 (2009)
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Chapter 1

Introduction

1.1 First principle calculation for material modeling

In order to design a material for a special purpose, the traditional approach is to pick the best candidate from a set of existing materials and then tune its properties by controlling various processing steps. Experimental trial-and-error approach is blindfold and expensive, therefore theoretical calculations have received increasing attention to assist in narrowing down the number of the possibilities and providing further guidance for material design¹. In the last four decades, a powerful theoretical tool, computer simulations at the atomic level based on first principle theory (atomistic simulation), is developed to understand the microscopic processes of material growth and search effectively for new materials^{2,3}.

Atomistic simulation has several advantages that drive the rapid development of the methodologies. Firstly, it offers an unprecedented level of control over experimental conditions. For example, it can offer a 100% purity material, which is impossible in practical experiments and some extreme conditions such as high vacuum levels, high pressure, low temperature, and high temperature which exceed the limit to conditions attainable in the laboratory. Secondly, it can offer unlimited characterization capabilities. Any candidate material can be tested for desirable properties before attempting to synthesize them. Thirdly, the cost for performing a computer simulation has been dramatically reduced due to the increasing of raw computational power and development of theoretical algorithms.

With the development of various density functional methods and simulation techniques, the accuracy of atomistic simulation has been improved dramatically in the last two decades⁴. Nowadays, properties of the bulk materials, such as elastic, mechanical, electronic, optical, ferroelectric, and ferromagnetic properties can be predicted with sufficient accuracy. Other important questions of materials, such as point defects, interface states, chemical catalysis, and surface adsorption can also be

examined by simulations. Furthermore, first principle methods have also been applied to deal with the physical systems of low dimensionality, such as quasi-2D interface, surface with restricted surface size, quasi-1D nano-wire with restricted radius and medium-sized quasi-0D cluster.

Although first principle methods are highly successful, their applications to alloys are still hindered by an astronomical number of possible alloy structures. In order to circumvent the alloy problems, one strategy is to treat an alloy as a substitutionally disordered system. Along this line, there are two major approaches: special quasi-random structure (SQS) method^{5,6} and coherent potential approximation (CPA) method^{7,8}. Based on such methods, first principle results can be integrated with statistical mechanics to yield the thermo-dynamical properties. However, for some metal and semiconductor alloy systems, one important task is to search the most stable ordered structures or intermediate-phase structures. Therefore, one has to tackle the fundamental difficulty in the alloy system that is to search over millions of structures (the 2^N question in binary alloys). To treat this with first-principles accuracy, one can ‘coarse-grain’ the many-body Hamiltonian into a ‘model Hamiltonian’^{9,10}, such as Connolly-Williams approach^{11,12}. Whatever, there is not a universal method for all alloy systems with the first-principle accuracy. For different alloy system, we may need a special method to deal with.

Alloys, suitable solid mixtures of some mother materials, have long been used to optimize the key material parameters such as the hardness, lattice constants and fundamental band gap. For the development of material science, it is highly desirable to have the ability of accurate theoretical analysis of the alloy problems. In this thesis, we present our theoretical studies on the optoelectronic ZnO-based semiconductor alloys and super-hard BCN alloy. Development of nano-technologies has told us that change of the size can result in the dramatic change of the physical and chemical properties of materials. We also look into the possibility of composition controlling and size effects, which may induce the new properties of traditional IV-IV and III-V elements.

1.2 Semiconductor alloy system and alloy cluster system

1.2.1 Wide band gap ZnO-based semiconductor alloy

Semiconductor alloys provide a natural means of tuning the magnitude of the band gap and other material parameters so as to optimize the performance and widen the application of semiconductor devices¹³. For example, quasi-binary (ternary) alloys of III-V semiconductor family can tune the band gaps to span the range from 0.18 eV to 2.4 eV. In order to develop the optoelectronic applications (such as full-color displays, full-color indicators and light sources for lamps), wide band gap semiconductors attract much attention in recent twenty years¹⁴. Intensive research has been carried out on green-, blue- and ultraviolet- light-emitting diodes (LEDs) and laser diodes (LDs). II-VI materials such as ZnSe-based material¹⁵, III-V nitride such as GaN^{16,17} and IV-IV materials such as SiC¹⁸⁻²⁰ have been investigated intensively for a long time.

Recently, ZnO has been recognized as the next generation UV light emitting material due to its wide band gap (3.37 eV at RT) and large exciton binding energy (60 meV)²¹⁻²⁴. For the development of ZnO-based optoelectronic devices^{25,26}, ZnO-based alloys can offer a flexible band gap modulation in the range of short wavelength that allows the construction of quantum-well and super-lattice based on ZnO material. To explore suitable materials, we engaged a systematic theoretical study of structural stability and electronic properties of a few novel ZnO-based alloys.

1.2.2 Superhard materials-BCN alloy system

Ultra-hard materials are used in many applications, including abrasives, cutting and polishing tools, wear-resistant coatings, and high-pressure devices. From the macroscopic view, a material can be considered to be hard if it can resist plastic deformation. Plastic deformation usually involves irreversible motion of the atoms that will induce the movement and/or creation of dislocations. This mechanical property is difficult to be estimated accurately. However, two microscopic parameters, bulk modulus and shear modulus, are typically used as indication for pre-screening super-hard materials²⁷.

Based on the above idea, superhard materials can be divided into two main categories. Firstly, light elements including beryllium, boron, carbon, nitrogen, oxygen, and so on, are combined to form the compounds with short covalent bonds. Secondly, light elements are combined with the heavy elements that have high densities of valence electrons. Here, we are interested in the first category of superhard materials (to combine some light elements with proper crystal structure). Diamond is the hardest material with near 100GPa²⁸, cubic boron nitride with a hardness of 50 GPa comes closest to matching the diamond²⁹. With the combination of these two excellent materials, cubic BC_xN (*c*-BC_xN) is an ideal candidate for super-hard materials^{30,31}. Recent debates on the hardness of *c*-BC₂N have inspired us to carry out a thorough examination of its mechanical and thermal-dynamical properties.

1.2.3 Nano-electronic materials: cage-like alloy clusters (BCN, SiC alloy cage)

Following Moore's law, the miniaturization of the Si microelectronic devices requires the understanding of nano-sized materials. In the size of nanometer (clusters with about 2 to 1000 atoms), the quantum size effects become important and the structural, physical and chemical properties of clusters can be very different from their bulk counterparts. These make the study of the structures and properties of nano-clusters very popular in past twenty years.

Small covalently bonded semiconductor clusters are worth studying in order to understand the microscopic reaction mechanism³². For example, silicon clusters have been studied extensively due to both the intrinsic interest to chemical structure and bonding (chemical reactivity of silicon clusters) and the potential technological applications for cluster-assembled materials. Since the discovery of fullerene C₆₀, carbon clusters have rapidly become an active area of research due to the potential technological importance in electrochemistry^{33,34}, ferromagnetism and superconductivity³⁵. Furthermore, stable cage-like carbon clusters can be considered as a potential building block for cluster-assembled micro-electric devices.

The research field of the alloy clusters is relatively new and still in its infancy

compared with the study of the elemental clusters. This may be due to the additional complexity of the alloy clusters (such as substitution pattern). In order to overcome the combinatorial complexity of the alloy clusters, we build up a method named color bond graph (CBG) theory. Based on this new method, we can efficiently simulate ternary alloy cluster BCN and binary cluster SiC to study the structural stability and other properties.

1.3 Major contribution of the thesis

1.3.1 Quasi-ordered alloy structures and ZnO-based semiconductor alloy systems

For semiconductor alloys, size mismatch between the atomistic constituents usually leads to the disordered alloy system with positive mixing enthalpy. Special quasi-random structure (SQS) method is usually used to study the properties of the semiconductor alloys. Today, the optoelectronic materials are usually grown in form of thin films under low temperature by advanced epitaxial growth techniques (P-MBE, LMBE, and RP-MOCVD). These epitaxial growth techniques typically operate at a nonequilibrium thermodynamics environment for material growth. At this low-temperature nonequilibrium condition, the phase separation is kinetically limited and local stable alloy clusters with lower formation enthalpy will be formed. Therefore, it is considered that the alloy films can be synthesized with local quasi-ordered structure for large range of the alloy concentration region. Based on the above consideration, we make a new method named as quasi-ordered structure (QOS) method. In this method, all the quasi-ordered structures in a supercell can be constructed by the application of space group of the parent materials. Then the results from the first principle are combined with statistical mechanics to study the properties of the alloy film.

The QOS method has been applied to the ZnO-based alloy systems for the analysis of electronic properties and structural stability. For isostructural phase alloys $\text{Be}_x\text{Zn}_{1-x}\text{O}$, we found the structures that have the same periods along the [0001] direction as the parents are relatively more stable. By constructing a $2 \times 2 \times 2$ supercell with 16 cations, three metastable-ordered states with Be concentrations of 25%, 50%

and 75% were found. For the electronic properties, it was found that the band gap was sensitive to the configurations and some alloy configurations with the same concentration can have band gaps differed by ~ 1.5 eV. For the nonisostructural phase alloys $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, we identified the structural metastable regions with $0.25 < x < 0.375$, $0.75 < x < 0.875$ and $0.375 < x < 0.5$, by considering the relative stability of $B1$ and $B4$ phases. This means the alloys $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ with stable wurtzite structure can be fabricated with the ranges of $0 < x < 0.25$, $0 < x < 0.75$ and $0 < x < 0.375$. The Γ -point band gaps were calculated and the bowing parameters were found to be 1.03 and 0.87 eV for alloys $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ by alloy statistical average. For the nonisostructural phase alloys $\text{ZnS}_x\text{O}_{1-x}$, the local stable single-phase $\text{ZnO}_{1-x}\text{S}_x$ alloy with zincblende structure can be obtained at the range of concentration $0 \leq x \leq 0.5$, under the nonequilibrium thermodynamics condition. The bowing coefficient for wurtzite structure is very different from that for zincblende structure in alloy $\text{ZnO}_{1-x}\text{S}_x$.

1.3.2 Color bond graph (CBG) theory and application in cage alloy system

To treat the combinatorial complexity of cage-like alloy clusters with first-principles accuracy, a model Hamiltonian with proper parameters is needed. From the view of chemical bonds, it is normally anticipated that the stability of the chemical bonds is directly linked to the stability of the molecule structure. The stability of the alloy configurations may be studied by counting the number of different bonds. However, the bond counting rules (BCR) is so simple that it should don't evaluate quantitatively the stability of an alloy structure. It is well known that the same chemical bonds will have different strength intensity and bond length in the different chemical environments. Based on the consideration of the effect of local environments of the chemical bonds, we make a method named color bond graph (CBG) theory in which the energy of the alloy configurations can be recast in a general form

$$E(\sigma) = E_0 + \sum_i \alpha_1^i C_1^i(\sigma) + \sum_{i,k} \alpha_{2,k}^i B_{2,k}^i(\sigma) + \sum_{i,k} \alpha_{3,k}^i A_{3,k}^i(\sigma) + \sum_{i,k} \alpha_{4,k}^i F_{4,k}^i(\sigma) + \cdots \quad (1.1)$$

where the parameters α 's represent the interaction energies, C_i 's are the energy of vertex i ($i=1$ to N), B_2 's, A_3 's and F_4 's are the generalized correlation functions for different types of "bonds" to include contributions from two-vertex (the B_2 's), three-vertex (the A_3 's) terms and four-vertex (the F_4 's).

The BCR rule has been proven to be as a effective guide for searching the low-energy stable structures in cage-like cluster $(\text{BN})_6\text{C}_{12}$. Then BCR rule was applied the bulk alloy system BC_2N for choosing stable/metastable ground states. The CBG theory has been tested in alloy cage-like cluster $(\text{BN})_6\text{C}_{12}$ to predict the ground states. Then CBG model was applied the alloy system about heterofullerenes $\text{Si}_n\text{C}_{60-n}$ ($0 \leq n \leq 30$).

1.4 Organization of the Thesis

This thesis is organized as follows. In chapter 2, we summarize first principle quantum calculation for material simulations. In chapter 3, we give a brief introduction on the general alloy theory. In chapter 4, we present the application of space group theory to gain quasi-ordered structures in the first half and a new method, color bond graph theory, for the alloy questions in cage-like clusters is presented in the second half. In chapter 5, 6 and 7, we present our study on wide band gap ZnO-based semiconductor alloys, including alloys BeZnO , CaZnO , MgZnO , CdZnO and ZnSO . For each alloy system, we systematically study the structural stability and the electronic properties. In chapter 8, we systematically analyze the super-hard alloy material, high-density pseudo-cubic BC_2N alloy. In chapter 9, by color bond graph theory, we try to predict the stability of $\text{C}_{12}\text{B}_6\text{N}_6$ fullerene. In chapter 10, by combining the color bond graph theory and genetic algorithms method, the structural stability of heterofullerenes $\text{Si}_n\text{C}_{60-n}$ ($0 \leq n \leq 30$) are studied systematically. In chapter 11, the works are concluded with indications on future work.

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Chapter 2

First Principle Quantum Calculation

In this chapter, we introduce first principle quantum calculation for material simulations. With Born-Oppenheimer approximation and Bloch's theorem, the density functional theory (DFT) has become a footstone for theoretical study of solid-state materials. With Kohn-Sham equations, DFT is turned into a practical tool for calculating the properties of real materials under local density approximation (LDA).

2.1 Quantum mechanics of materials

In 1926, Schrödinger gave the quantum explanation of the time evolution of a physical process by wave mechanism. Then quantum theory of atoms and molecules was quickly established. For any solid system, it is easy to write down a Hamiltonian representing the kinetic energy of the electrons and nuclei and all the Coulomb interactions between the particles like

$$H = \sum_i \frac{P_i^2}{2m} + \sum_n \frac{P_n^2}{2M} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i,j;i \neq j} \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_n \sum_i \frac{Z_n e^2}{|r_i - R_n|} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{n,l;n \neq l} \frac{Z_n Z_l e^2}{|R_n - R_l|}, \quad (2.1)$$

where Ze and M are the charge and mass of the nucleus, R_n is the location of the n -th nucleus, e and m are the charge and mass of the electrons, and r_j is the location of the j -th electron. However, as Dirac pointed out in 1929, the difficulty is that the exact application of quantum theory leads to equations much too complicated to be solved. In the actual application, some approximations with the light of physics insight must be constructed¹.

In the past 80 years, there have been important advances in solids due to the great simplification of Hamiltonian². In the solid, there are large numbers of atoms that interact strongly with each other. The interaction results in the broadening of electronic spectra and various collective effects³. Together with the development of

modern computers, these advances of solid state theory have enabled us to understand the properties of real materials now⁴. For example, by *ab initio* calculations, the electronic properties of materials can be obtained and the problem such as the electronic origin of the optical properties of semiconductors and the mechanism of antiferromagnetism and ferromagnetism can be solved⁵. By the first principle structural optimization, the questions such as the stability of the structure and the structural phase transition can be solved.

However, first principle methods have their shortage. Firstly, a lot of approximations result some important low energy phenomena can't be described in detail with physics insight just by *ab initio* calculation⁶. In order to describe the low energy phenomena such as plasmons, magnons, excitons, polarons, Cooper pairs and the fractionally charged excitations, some physics models are needed. Secondly, the large and complex system cannot be solved due to the need of very large computer resources. In order to solve the complex questions, such as the alloy systems, we need combine the first principle calculation with statistic mechanism. Whatever, now we have learned to harvest from combination between *ab initio* calculation for electronic and structural properties and some physics models in understanding some physics phenomena.

2.2 First-principle calculation of solid

Solving an interacting many-body system ($\sim 10^{23}$) with the form of quantum mechanics certainly is a formidable task. Some important approximation and theory are developed in order to simplify the interaction system.

The first basic approximation is the adiabatic approximation of Born and Oppenheimer which allows one to decouple the nucleus movement from the electronic movement in a solid, considering the very large difference between nuclear and electronic mass^{7,8}. Under this approximation, the Hamiltonian of the electron can be written as

$$H_{BO} = \sum_i \frac{P_i^2}{2m} + \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{i,j;i \neq j} \frac{e^2}{|r_i - r_j|} - \frac{1}{4\pi\epsilon_0} \sum_n \sum_i \frac{Z_n e^2}{|r_i - R_n|} + E_N(R)$$

$$E_N(R) = \frac{1}{4\pi\epsilon_0} \frac{1}{2} \sum_{n,l;n \neq l} \frac{Z_n Z_l e^2}{|R_n - R_l|} \quad (2.2)$$

Obviously, In the Hamiltonian of the electron, the motion of the nuclei is neglected. Then the task will be to find the minimum of the electron Hamiltonian by changing the positions of the nuclei (note that within Born and Oppenheimer approximation, the nuclei are treated on a classical footing since their ground state is determined as the minimum of their potential energy, neglecting quantum fluctuations)⁹.

Based on the periodic crystal structure of solid, Bloch proves the famous Bloch theorem, which brings the concept of electronic energy band structure in solid. This theorem states that with a periodic potential in solid, the eigenstates of the electron Hamiltonian can be written in the form of a plane waves times a periodic function like $\Phi_K(r) = e^{iK \cdot r} u_K(r)$ and $u_K(r) = u_K(r + R)$. (2.3)

Based on the above approximation and theorem, different formalisms of theory are developed such as Hartree-Fock orbital theory, density functional theory (DFT) and GW approximation based on many-body perturbation theory. Now, most electronic structure calculation for solids still is based on DFT. Here a general introduction of DFT will be given in the following sections.

2.3 The density function theory with local density approximation

The kernel of DFT is that the ground state total energy of a many electron system can be expressed as a functional solely on the electron density. Working with the density as a fundamental variable will result in an enormous computational simplification compared to the original highly dimensional wave equation. Surprisingly, this mapping is exact in principle.

2.3.1 The Hohenberg-Kohn theorems

In 1964, two theorems were first proven by Hohenberg and Kohn^{10,11}.

Theorem (1): For any system of interacting particles in an external potential

V_{ex} , the potential V_{ex} is determined uniquely, except for a constant, by the ground state density $n_0(r)$.

Theorem (2): For any external potential V_{ex} , a functional for the energy $E[n]$ in terms of the density $n(r)$ can be defined. Where $E[n]$ is such that the global minimum of $E[n]$ equals the ground state energy of the system, and the density at this minimum equals the ground state density $n_0(r)$ of the system.

2.3.2 The Kohn-Sham equations

Unfortunately, the exact density functional is not known. The above theorem in the previous section did not give any hint of how to deal with the correlation between the electrons. The difficulty of solving an inseparable problem is still left to deal with. The first solution was taken within the DFT formalism by Kohn and Sham in 1965, by mapping the interacting system onto a non-interacting reference system with same ground state density¹¹.

Conjecture: The ground state charge density $n(r)$ of a many electron system, can be represented with an auxiliary non-interacting system with an effect potential V_{ef} .

In the noninteracting electron system, the energy functional $E[n]$ has a kinetic contribution and a contribution from the external potential V_{ex}

$$E[n] = T[n] + \int d^3r \ n(r)V_{ex}(r). \quad (2.4)$$

By Varying the equation with respect to the density, we obtain

$$\frac{\delta T[n]}{\delta n(r)} + V_{ex}(r) = \lambda n(r) \quad (2.5)$$

Though the form of kinetic functional $T[n]$ is unknown, we know it does not depend on the external potential. The ground state energy and density of state can be gain by single-particle Schrödinger equation with spin-orbital Slater determination for the noninteracting electron system as

$$\begin{aligned} \left[-\frac{1}{2}\nabla^2 + V_{ex}(r)\right]\Phi_k(r) &= \epsilon_k \Phi_k(r) \ , \\ n(r) &= \sum_{k=1}^N |\Phi_k(r)|^2 \ . \end{aligned} \quad (2.6)$$

For the interacting electron system, the energy functional $E[n]$ can be written in the form

$$E[n] = T[n] + \int d^3r n(r) V_{ex}(r) + 1/2 \int d^3r \int d^3r' \frac{1}{|r - r'|} n(r') n(r) + E_{xc}[n], \quad (2.7)$$

where $T[n]$ is the kinetic energy functional of a system of noninteracting electron gas, the second and third terms are the external potential energy and the Hartree energy due to Coulombic interactions, and $E_{xc}[n]$ includes all other many-body contributions to the total energy, in particular the nonclassical contributions of electron-electron interaction (note that no approximations are made and the unknown correlations are moved into $E_{xc}[n]$).

By varying the equation with respect to the density, we obtain

$$\frac{\delta T[n]}{\delta n(r)} + \frac{\delta E_{xc}[n]}{\delta n(r)} + \int d^3r' n(r') \frac{1}{|r - r'|} + V_{ex}(r) = \lambda n(r). \quad (2.8)$$

If we write an effect potential V_{ef}

$$V_{ef}(r) = \frac{\delta E_{xc}[n]}{\delta n(r)} + \int d^3r' n(r') \frac{1}{|r - r'|} + V_{ex}(r). \quad (2.9)$$

The analogue of single-particle Schrödinger equation of noninteracting electron system now becomes

$$\left[-\frac{1}{2}\nabla^2 + V_{ef}(r)\right]\Phi_k(r) = \varepsilon_k \Phi_k(r). \quad (2.10)$$

Then we can gain the total energy as:

$$E[n] = \sum_{k=1}^N \varepsilon_k - \frac{1}{2} \int d^3r d^3r' \frac{1}{|r - r'|} n(r) n(r') + E_{xc}[n] - \int d^3r V_{xc}[n(r)] n(r), \quad (2.11)$$

$$V_{xc}[n(r)] = \frac{\delta E_{xc}[n]}{\delta n(r)}. \quad (2.12)$$

2.3.3 The local density approximation

The exact form of the exchange correlation potential is impossible to know. Up to this point, nothing has been said about how to find or approximate the exchange correlation functional E_{xc} . In the following, we give an introduction of the local

density approximation which is one of the widely used approximations.

In a homogeneous electron gas system, the electron density keeps constant by a uniformly distributed positive background charge. The exchange correlation energy density is independent of the spatial coordinates and only depends on the constant density. For a nonhomogeneous system, the value of the exchange correlation potential at the point r depends usually not only on the value of the density at r but also on its variation close to r . The local density approximation (LDA) assumes that that exchange-correlation potential only depends on the value of the density at r ,

$$E_{xc} = \int d^3r \varepsilon_{xc}[n(r)]n(r), \quad (2.13)$$

where $\varepsilon_{xc}[n]$ is the exchange correlation energy per electron of a homogeneous electron gas at the density $n(r)$.

Now we consider the exchange effect in Hartree-Fock formalism¹². In this formalism, the probability density of finding one electron with coordinate r_1 and another with r_2 can be expressed as

$$\rho(r_1, r_2) = \frac{1}{N(N-1)} \sum_{i,j} |\Phi_i(r_1)|^2 |\Phi_j(r_2)|^2 - \Phi_i^*(r_1) \Phi_i(r_2) \Phi_j^*(r_2) \Phi_j(r_1). \quad (2.14)$$

It can be seen that the opposite spin-orbitals are uncorrelated. In additional, the two terms cancel with each other for same spin-orbitals when $r_1=r_2$. It means that the electrons with parallel spin are kept apart and every electron is surrounded by an exchange hole. Thus, the exchange will result in the decrease of Coulomb interaction between the electrons. Considering the case of homogeneous electron gas¹¹, the electron gas is supposed to be with the density n and surrounded by a spherical exchange hole with radius r_c . The exchange contribution will be

$$E_x \approx -n^2 \int_0^{r_c} r^2 dr \frac{1}{r} \sim n^{4/3}. \quad (2.15)$$

So the exchange energy in density functional theory with LAD approximation can be expressed as,

$$\varepsilon_x[n(r)] = -const. \times n^{1/3}(r). \quad (2.16)$$

From open-shell system, the exchange energy can be expressed as¹³

$$E_x[n_\uparrow, n_\downarrow] = -const. \int d^3r [n_\downarrow^{4/3}(r) + n_\uparrow^{4/3}(r)]. \quad (2.17)$$

In the exchange-correlation functional, there is a contribution from the dynamic Coulomb correct effect, except the exchange effect. This dynamic correct effect represents the couplings between parallel and opposite spin pairs. Some parameterized forms of the correlation energy have been obtained successfully by quantum Monte Carlo simulations of the homogeneous electron gas^{14,15}.

2.3.4 The generalized gradient approximation

Though LDA has obtained some success in solid-state physics, the moderate accuracy of LDA is insufficient for many applications to some extent, especially that in chemistry. The logical first step in further development from LDA is to consider not only the charge density for the exchange-correlation functional, but also the gradient of charge density. In other word, if we interpret the LDA as the first term of Taylor expansion of the uniform density, better approximations of exchange correlation functional can be obtained by extending the series with the next lowest term¹⁶. However, such expansion does not guarantee to improve the accuracy, because the exchange-correlation hole in such the expansion has lost some important properties of the hole in LDA that made the LDA physically meaningful. In a brute way, some restrictions (such as the correct sum rule behavior and the negative behavior of hole everywhere) are added for the hole of beyond-LDA functionals. Based on the restrictions, the functionals that include the gradients of the charge density are collectively known as generalized gradient approximation (GGA) and can be written

$$\text{as: } E_{XC}^{GGA}[n_\alpha, n_\beta] = \int F(n_\alpha, n_\beta, \nabla n_\alpha, \nabla n_\beta) dr. \quad (2.18)$$

In practice, E_{XC}^{GGA} is usually split into two parts like LDA (the exchange and correlation contributions) and the approximations are sought individually. The exchange part E_X^{GGA} is written by Becke¹⁷ as:

$$E_X^{GGA} = E_X^{LDA} - \beta \sum_\sigma \int \frac{x_\sigma^2}{1 + 6\beta x_\sigma \sinh^{-1} x_\sigma} n_\sigma^{4/3}(r) dr, \quad (2.19)$$

where β is a constant and x_σ is a dimensionless ratio, $x_\sigma(r) = |\nabla n_\sigma(r)| / n_\sigma^{4/3}(r)$. There are also other forms of exchange function such as that in PBE¹⁸ and PW91¹⁹.

The corresponding gradient-corrected correlation functionals have even more complicated analytical forms. For example, in PBE, the gradient-correlated correlation functional is written as

$$E_C^{GGA}[n] = \int dr \ n [\varepsilon_C^{unif}(r_s, \zeta) + H(r_s, \zeta, t)], \quad (2.20)$$

where r_s is the local seitz radius ($n = 3 / 4\pi r_s^3 = k_F^3 / 3\pi^2$), $\zeta = (n_\uparrow - n_\downarrow) / n$ is relative spin polarization and $t = |\nabla n| / 2\phi k_s n$ is a dimensionless density gradient. Here, $\phi(\zeta) = [(1 + \zeta)^{2/3} + (1 - \zeta)^{2/3}] / 2$ is a spin-scaling factor, and $k_s = \sqrt{4k_F / \pi a_0}$ is the Thomas-Fermi screening wave number ($a_0 = \hbar^2 / me^2$). The gradient contribution H is constructed as

$$H(r_s, \zeta, t) = \frac{\gamma \phi^3}{a_0} \log \left[1 + \frac{\beta t^2}{\gamma} \left[\frac{1 + At^2}{1 + At^2 + A^2 t^4} \right] \right], \text{ with} \quad (2.21)$$

$$A = \frac{\beta}{\gamma} \left[\exp \left(\frac{-\varepsilon_C^{unif}}{\gamma \phi^3 / a_0} - 1 \right) \right], \quad (2.22)$$

where β and γ are constants.

2.3.5 Hybrid Functionals-B3LYP

Hybrid functionals are a class of approximations to the exchange correlation energy functional which incorporate a portion of exact exchange from Hartree-Fock theory with exchange and correlation from other sources (such as LDA, GGA). It is introduced by the adiabatic connection between non-interacting reference and real system with a coupling strength parameter.

In the framework of general Kohn-Shan theory, the exchange-correlation energy E_{xc} actually includes two parts: the difference between the kinetic energy of real system and that of the non-interaction reference system T_c and the nonclassical contributions to the potential energy due to the electron-electron interaction E_{ncl} . By the coupling strength parameter λ , we can fold T_c into E_{ncl} and get a new form of E_{xc}

as:

$$E_{xc} = \int_0^1 E_{ncl}^{\lambda} d\lambda, \quad (2.23)$$

where E_{ncl}^{λ} is the λ -dependent exchange-correlation potential energy, which is nothing else than the nonclassical contribution to the electron-electron interaction for different values of λ ¹⁶.

Now let us explore the nature of the integrand E_{ncl}^{λ} for two-end cases. At $\lambda=0$, we are dealing with the non-interaction reference system. Thus, $E_{ncl}^{\lambda=0}$ just represents the energy E_x^{HF} due to the antisymmetry of fermion wave function, which can be determined exactly by a Slater determinant. This means E_x^{HF} can be computed exactly if the KS orbitals are obtained. For $\lambda=1$, the system corresponds to the real interacting system and the interacting exchange-correlation energy $E_{ncl}^{\lambda=1}$ is not known. Nevertheless, there are some E_{xc} functionals that can approximate satisfactorily for it. However, we still need the intermediate values to this integral.

The first approximation introduced by Becke²⁰ is to assume that E_{ncl}^{λ} is a linear function of λ . This leads to

$$E_{xc}^{HH} = 1/2 E_x^{HF} + 1/2 E_{ncl}^{\lambda=1}, \quad (2.24)$$

This is called as half-and-half (HH) combination of ‘exact’ exchange and density functional exchange correlation. The next step will be to introduce semiempirical coefficients to determine the weights of the various components in this scheme. The most popular hybrid functional B3LYP actually is proposed based on this spirit by Stephens *et al.*²¹. This exchange correlation energy can be expressed as

$$E_{xc}^{B3LYP} = E_{xc}^{LDA} + a(E_x^{HF} - E_x^{LDA}) + b(E_x^{GGA} - E_x^{LDA}) + c(E_c^{GGA} - E_c^{LDA}), \quad (2.25)$$

where the three empirical parameters ($a=0.20$, $b=0.72$ and $c=0.81$) determined by fitting the predicted values to a set of total atomic energies, atomization energies, ionization potentials and proton affinities (the exchange functional with GGA is the B88 exchange functional¹⁷, the correlation functional with GGA is the LYP

correlation functional^{22,23} and the correlation functional with LDA is the VMN correlation functional²⁴).

2.4 Conclusion

In the past years, the density functional theory with the simple local density approximation/generalized gradient approximation has given the surprisingly accurate results for vast classes of materials and contributed to our understanding of the bonding and magnetism in materials. Nowadays, DFT codes, such as CPMD²⁵⁻²⁸, Dmol3^{29,30}, PWSCF³¹, CASTEP³², Guassian³³, WIEN2k^{34,35} and VASP³⁶⁻³⁸, are always married to the latest computer architectures, such as the computer cluster where several CPUs work in parallel for a given problem.

2.5 References

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Chapter 3

General Alloys theory

In this chapter, we give a brief introduction on the general alloy theory. An alloy system can exist as a single crystal phase or a mixture of several phases. A phase can be defined as a portion of the alloy system whose properties and composition are homogeneous. What are the phases of an alloy system (e.g. their structures and composition), and how does one phase change into a new phase or mixture phases in an alloy system? These are the core questions which the alloy theory needs to resolve. Firstly, we describe about the thermodynamics equilibrium of solid-state material system. Then, some theoretical models are introduced to analyze the binary alloy systems. Finally, we simply introduce the semiconductor alloy systems.

3.1 Thermodynamics equilibrium

In the phase space, there may be many phases that are stable, metastable or instable. How does one measure the phase stability and estimate the stability of a system? The answer is provided by thermodynamics¹. At fixed temperature and pressure, the relative stability of a system is determined by its Gibbs free energy G , $G=H-TS$, where H , S and T are the enthalpy, the entropy and the absolute temperature, respectively. Enthalpy H , as a measure of the heat content of the system, is given by the internal energy and the product of pressure and volume as the form $H=E+PV$. The internal energy E arises from the total kinetic and potential energies of the atoms. Kinetic energy can arise from atomic vibration in solids or liquids and from translational and rotational energies for the atoms and molecules within a liquid or gas. Potential energy arises from the interactions or bonds between atoms. Entropy S is a measure of the randomness of the system. The Gibbs free energy G is related with the Helmholtz free energy F through the formula $G-F=PV$. Usually, the pressure is one standard atmosphere pressure and the difference between G and F may be ignored in a solid or liquid. So Helmholtz free energy will be used to determine approximately the

stability of the alloy system.

A system is said to be in equilibrium when it usually is in the most stable state (named ground state)². This means the free energy of the system has the lowest possible value in this state. There could be other configurations that lie at a local minimum of the potential energy surface. Such configurations are called metastable equilibrium states. The unstable states, usually referred as the intermediate states, are such configurations that will rapidly rearrange its atomic positions and enter into the free energy minima under the thermal fluctuations. From the viewpoint of thermodynamics, any intermediate states and metastable states will make a phase transformation and become a ground state due to its lowest free energy. Of course, the metastable states in some systems can be short-lived and others may have very long life. For example, diamond is the metastable state at room temperature and pressure, but it is dynamically very stable. This is due to the presence of the large energy hump between the stable (graphite) and metastable (diamond) states. Solving the question such as transformation rates falls into the realm of kinetics.

3.2 The free energy of binary alloy system

Understanding the dependence of free energy on composition and temperature is a key step to understand the relation of phases in alloys³. For a binary alloy system $A_{1-x}B_x$ or a pseudo-binary alloy system $A_{1-x}B_xC$, the free energy, before mixing, can be expressed as

$$F_1(A+B) = (1-x)F_A + xF_B. \quad (3.1)$$

After mixing, the free energy can be expressed as

$$F_2(A_{1-x}B_x) = F_1(A+B) + \Delta F(A_{1-x}B_x), \quad (3.2)$$

where ΔF that is named as the mixing free energy or formation energy is the change of free energy caused by the mixing. ΔF should include the change of the internal energy ΔE (formation enthalpy) and the change of the entropy ΔS (formation entropy). Thus, the fixing free energy $\Delta F(x)$ can be expressed as

$$\Delta F(A_{1-x}B_x) = \Delta E(A_{1-x}B_x) + T\Delta S(A_{1-x}B_x). \quad (3.3)$$

3.2.1 Ideal solution model

In ideal solution model, it is assumed that there is no heat change in mixing and the formation enthalpy $\Delta E(x)$ is ignored. Thus, the mixing free energy $\Delta F(x)$ results from the additional entropy $\Delta S(x)$ which is the change in configuration entropy. Suppose that there are N lattice sites that will be hold by N_A A atoms and N_B B atoms and all configurations of A and B atoms are equally probable, the number of different arrangement is $N!/N_A!N_B!$. Using the Stirling approximation with $x=N_B/N$, the additional mixing entropy $\Delta S(x)$ becomes

$$\Delta S = -Nk[(1-x)\ln(1-x) + x\ln x]. \quad (3.4)$$

So for all x and T , the ideal solution model always gives a negative of $\Delta F(x)$ due to $\Delta F(x) = -T\Delta S$.

3.2.2 Regular solutions model

In practice, the mixing is endothermic or exothermic. The first strict-regular model named quasi-chemical model is proposed by Guggenheim (1952)⁴. In this model, the formation enthalpy (the heat of mixing) is attributed to the nearest-neighbor pair interaction only (the bond energies between adjacent atoms) and the formation entropy is with the same form as in ideal solution model.

Now assumed the coordination number is z , the total number of the nearest-neighbor pairs will be $M=zN/2$. Let M_{AA} , M_{BB} and M_{AB} be the number of pairs AA, BB and AB, respectively. The mixing energy is:

$$\Delta E = M_{AA}W_{AA} + M_{AB}W_{AB} + M_{BB}W_{BB} - (1-x)MW_{AA} - xMW_{BB}, \quad (3.5)$$

where W_{AA} , W_{AB} and W_{BB} are the pair interaction energies of AA, AB and BB, respectively. Now we define the pair probability of AB as $P_{AB} = P_r = M_{AB}/M$, then we can get the pair probabilities of AA ($P_{AA}=1-x-0.5P_r$) and of BB ($P_{BB}=x-0.5P_r$). So the mixing energy can be expressed as $\Delta E(x)=MP_rW$, where the excess energy per pair W is defined as $W=W_{AB}-(W_{AA}+W_{BB})/2$. For random alloy, the pair probability is given by $P_r=2(1-x)x$. Thus, the fixing free energy $\Delta F(x)$ is

$$\Delta F(x) = x(1-x)zNW + TNk[(1-x)\ln(1-x) + x\ln x]. \quad (3.6)$$

If $W < 0$, the internal energy of the alloy system is reduced by increasing the number of A - B bonds (i.e. by ordering the atoms). If $W > 0$, the internal energy can be reduced by increasing the number of A - A and B - B bonds (i.e. by the clustering of the atoms into A -rich and B -rich groups). However, the degree of ordering or clustering will decrease as temperature increases due to the increasing importance of entropy.

3.2.3 The questions of real alloy systems

In the actual alloy system, the arrangement of atoms to achieve the minimum free energy usually is a compromise between the configuration with the lowest internal energy and sufficient entropy and that with ideal random combination of A and B atoms. Therefore, the quasi-chemical model seems to be an oversimplification of reality and does not predict the correct dependence of $\Delta F(x)$ on composition and temperature.

In some alloy systems, there is a size difference between the atoms. The quasi-chemical model will underestimate the change in internal energy on mixing since no account is taken of the elastic strain fields that introduce a strain energy term into $\Delta F(x)$. In some alloy systems, two parents have the stable phases with different structures. The quasi-chemical model is obviously not sufficient to describe the system in which there is the structural phase transformation. In some alloy systems, there is strong chemical bonding between the atoms. There will be a tendency for the formation of intermetallic phases⁵. These intermetallic phases have a different crystal structure from the solutions based on the pure components and may be highly ordered. Generally, the real alloy system is so complicated that a simple model cannot give an accurate description.

3.3 The statistical theory of alloy system

In order to solve the questions in real alloy system, we need to analyze the phase space from the microscopic view. From statistical theory, we can relate the free energy

with the partition function and thus we need to know the internal energy of all the microstates. The number of the microstates will be astronomical, considering the change of lattice (all possible Bravais lattice), the change of configuration (the different substitution of the A and B atoms), the displacement of each atom away from its ideal lattice site, the free degree of electronic state (including spatial wave function and spin state)⁶. We need to grain coarsely the partition function into an effective Hamiltonian with some approximations.

3.3.1 Coarse graining of the partition function

The change of lattice usually occurs at the special concentration and temperature. This degree of free is considered usually by comparing with the different free energies that are constructed in the different lattices. Based on the same parent lattice, the free energy $F(N, V, T)$ at constant composition, volume and temperature is related to the canonical partition function $Z(N, V, T)$ by⁷:

$$F(N, V, T) = -\frac{1}{\beta} \ln Z(N, V, T) \quad \text{and} \quad (3.7)$$

$$Z(N, V, T) = \sum_j \exp(-\beta E_j(N, V, T)), \quad (3.8)$$

where N is a vector that specifies the number of atoms of all different chemical species and β has its usual meaning of $1/k_B T$. The free energy involves computation of the canonical partition function that incorporates a sum over all possible microstates.

What are these microstates? At zero temperature, all atoms occupy the well-defined sites (neglecting the zero point motion). For each site, we can assign an occupation variable σ_i which has the value +1 or -1 depending on the type of atom that is presented at that site. Together, these sites form the Ising lattice (note that the atomic positions do not need to coincide with a point of the Ising lattice). By this procedure, an alloy state is projected onto a configuration of the Ising lattice (note that the Ising lattice is a collection of possible atomic sites).

At non-zero temperature, all kinds of excited states are possible, such as vibrations around the average site, intra-atomic excitations and substitutional

excitations. Only the substitutional excitations in the alloy change the spin configuration on the Ising lattice that describes the alloy, and all other excitations keep the particular state of the Ising model unchanged. Substitutional excitations usually are long-time processes and can be separated, first. The microstates due to other excitations can project onto the same Ising model configuration⁶. Thus, we can partition all microstates of a real alloy into groups of state that have the same Ising lattice configuration such as

$$Z(N, V, T) = \sum_{\sigma} \Omega(\sigma), \quad (3.9)$$

$$\Omega(\sigma) = \sum_{v,e} \exp(-\beta E_{\sigma,v,e}), \quad (3.10)$$

where σ describes the configuration freedom of degree, v which denotes the displacement of each atom away from its ideal lattice site describes the vibration freedom of degree and e which is a particular electronic state (both the spatial wave function and spin state) presents the electronic freedom of degree.

Since many microstates of the alloy project onto the same configuration on the Ising lattice, this means an Ising model cannot specify an exact spatial arrangement of atoms. The Ising state is called as a state of colored connectivity (CC) by Geder *et al.*⁷, because it is a state of connectivity between the atoms in which the atom type is taken into account. Thus, $\Omega(\sigma)$ is the partition function of a new ensemble in which all microstates are in the same CC state. Now it is clear that the Ising model is just a formalism to label the possible atomic connectivity and has nothing to do with atoms sitted at fixed lattice sites. Actually, atomic displacements (relaxation) and vibrational energy contributions can be included in an Ising model through the partition function $\Omega(\sigma)$.

For the new ensemble based on a CC state, the characteristic function, free energy $H(\sigma)$, can be expressed as:

$$H(\sigma) = -\frac{1}{\beta} \ln \Omega(\sigma). \quad (3.11)$$

The canonical partition function then becomes

$$Z(N, V, T) = \sum_{\sigma} \exp(-\beta H(\sigma)) \quad (3.12)$$

and the alloy free energy $F(N, V, T)$ is:

$$F(N, V, T) = -\frac{1}{\beta} \ln \left[\sum_{\sigma} \exp(-\beta H(\sigma)) \right]. \quad (3.13)$$

The computation of the free energy of a binary alloy has been formally reduced to computing the free energy of an Ising model (an ensemble of the CC states). However, in practice, the free energy $H(\sigma)$ (Ising Hamiltonian) which is the value of the Hamiltonian of the Ising model will be further approximated.

3.3.2 Approximations for temperature-independent Ising Hamiltonian

The Ising Hamiltonian is still temperature dependent as it contains the integrated effect of all excitations apart from substitutional excitations. All practical *ab initio* computations should use a simple temperature-independent Ising Hamiltonian.

After decoupling the electronic and nuclear coordinates (Born-Oppenheimer)⁸, the Ising Hamiltonian can be written as

$$H(\sigma) = F_1(\sigma, N, V, T) + F_2(\sigma, N, V, T), \quad (3.14)$$

where $F_1(\sigma, N, V, T)$ is the lowest energy of the static configuration in the CC state (σ) (noted that the static configuration means the configuration with “frozen” nuclear coordinates) and $F_2(\sigma, N, V, T)$ contains the excitation part of the internal energy in the CC-ensemble due to atomic motion as well as the entropy of this ensemble. In practice, $F_1(\sigma, N, V, T)$ can be temperature dependent due to electronic excitations and $F_2(\sigma, N, V, T)$ is expected to be largely dominated by the vibrational free energy.

The first approximation:

At low temperature, by approximating the Fermi-Dirac distribution as a step function, $F_1(\sigma, N, V, T)$ is approximated as the temperature-independent function of the CC states $F_1(\sigma, N, V)$.

The second approximation:

$F_2(\sigma, N, V, T)$ is assumed to be independent of the configuration for each concentration $F_2(N, V, T)$.

In the case of coherent phase diagram computations (i.e. phase diagrams that consist solely of configurations on the same parent lattice), one usually makes an additional assumption that $F_2(\sigma, N, V, T)$ is a linear function of the composition as $F_2(N, V, T) = xF_{2,A}(N, T) + (1-x)F_{2,B}(N, T)$. Since $F_2(\sigma, N, V, T)$ is just a linear function of the composition, it can be left out completely for computing phase diagrams (noted that phase equilibrium are determined by chemical potentials and any linear function of the composition in the free energy just changes the chemical potentials by a constant). However, in the study of incoherent phase diagrams, $F_2(\sigma, N, V, T)$ cannot be omitted. For example, some *fcc-bcc* and *fcc-hcp* transitions in elemental solids are known to be driven by vibrational entropy.

Recently, van de Walle *et al.* reviewed the lattice vibration effect of binary alloy system⁹. They found that typical vibrational entropy differences between phases are of the order of 0.1 to $0.2k_B/\text{atom}$, which is comparable to the typical values of configurational entropy differences in binary alloys (at most $0.693k_B/\text{atom}$). So even in coherent alloy system, the vibrational entropy still has an important effect for alloy system.

3.4 Alloy calculation theory based first principle theory

The first-principles calculation is highly successful for the theoretical analysis of pure materials by calculating the small unit-cells. Nevertheless, for alloy system, searching some stable structures in the large configuration space (e.g. in a binary alloy system A_nB_m described by a unit cell with N sites, there are 2^N possible configurations), seems be impossible by the direct quantum-mechanical evaluation of the total energy. To treat these with first-principles accuracy, one need to build a ‘model Hamiltonian’ for all alloy states (Ising states).

3.4.1 The Ising Hamiltonian based on the cluster functions

In principle, one needs to know the ground state energies of the alloy corresponding to all configurations (Ising states) in the Ising lattice for computing the canonical partition function. Sanchez *et al.*¹⁰ showed that the Ising Hamiltonian for

the configurations can be expanded by a set of cluster functions (Ξ_α) as the expansion variables and the cluster interactions (J_α) as the expansion coefficients as

$$E(\vec{\sigma}) = J_0 + \sum_{\alpha} J_{\alpha} \Xi_{\alpha}(\vec{\sigma}). \quad (3.15)$$

Here one needs note that these cluster functions form an orthogonal basis set when the appropriate scalar product is defined.

For the expansion of the Ising-state energy of a binary alloy system with N lattice sites, there are 2^N cluster functions. Therefore, there are 2^N cluster interactions to be determined. Now we will analyze the space of cluster interaction (or the space of figures) and then use a set of effective cluster interaction (ECI) to expand approximately the Ising-state energy (formation energy of the configuration)¹¹⁻¹³. The lattice symmetry can reduce the number of the cluster interactions that must be determined¹⁴. Since the cluster interactions are independent of configuration, it follows that they should have the symmetry of the underlying lattice, which is generally higher than the symmetry of any configurations. For example, all lattice sites are equivalent for simple cubic, fcc, bcc, diamond and hexagonal lattices. So all the point interactions should be equivalent ($J_i = J_l$ for all sets i). For alloy $A_x B_{1-x}$, there are N sites occupied by A and B sites in a super-lattice. If we set “1” as the value of the variables σ_i for the sites i occupied by A and “-1” as the value for the sites by B , the one-body interaction part in the cluster interactions ($\sum_i N J_l \sigma_i$) can be reduced to $N J_l (2x - 1)$. Similarly, the reduced process can be used for other many-body interactions. For example, in the common lattices (sc, bcc, fcc, hexagonal, diamond, and so on), all the nearest-neighbor two body interaction should be equivalent, all the second-neighbor two body interaction should be equivalent, all the nearest-neighbor three body interaction should be equivalent, and so forth. In general, in the figures space on a crystal structure, the two figures (many-body interactions) should be equivalent if the one can be related to another by the space group symmetry of the underlying lattice. Now we define a correlation function GI_F for each class of symmetry-equivalent figures F as the average of the spin products over all figures which are related with each other by the symmetry as Lakes *et al.* shown¹⁴. A

correlation function GI can be expressed as

$$GI_F(\vec{\sigma}) = \frac{1}{D_F} \sum_f \Xi_f(\vec{\sigma}), \quad (3.16)$$

where f runs over D_F figures in class F . Now by symmetry-equivalent many-body interactions, Ising Hamiltonian can be expressed as

$$E(\vec{\sigma})/N = J_0 + J_1(2x-1) + \sum_i D_{2,i} J_{2,i} GI_{2,i}(\vec{\sigma}) + \sum_{m,k} D_{m,k} J_{m,k} GI_{m,k}(\vec{\sigma}), \quad (3.17)$$

where $D_{m,k}$ is the number of figures of class (m, k) per site (m for the number of sites in the figure and k for the k -th class of m -body interaction).

By the physics hypothesis, some classes of figures are considered intuitively to be not important and can be ignored in the expansion. The principles are the interactions that involve many sites are less important than interactions that involve fewer sites and the interactions between distant sites are less important than those between near sites. Thus, the number of figure classes need to be calculated should be smaller than 2^N and we have a simple model Hamiltonian that can be expanded by some limited classes of cluster functions.

3.4.2 Determination of ECI and Connolly-Williams method

Now the challenge is to determine the ECI interactions (J 's). There are three general approaches to compute these ECI's. The first method is a purely empirical fit of the J 's to known features of the phase diagram (some from the experimental data). This approach is simple and provides little new information about the properties of alloy. The second approach is the perturbation method based on the mean field theory. By either the coherent potential approximation (CPA)¹⁵⁻¹⁷ or the virtual crystal approximation (VCA)¹⁸, the random alloys are treated with tight-binding method¹⁹ or other band structure calculation method²⁰. Then the random state is considered as a reference state for the generalized perturbation method to gain the ECI interaction J 's. The third approach is the direct inversion method of Connolly and Williams¹¹. In this part, we will introduce how to use this method to determine the ECI interactions.

The effect of relaxations is very important in the alloy system in which the size

mismatch of the ions is large. The Connolly-Williams method can naturally incorporate these effects. In this method, some ordered structures (M_σ) in small unit cells are chosen and the total energies can be calculated by any electronic structure methods from simple classical approaches to complex quantum mechanical methods after optimizing of the structure. Then a set of ECI's (the number $N_f \leq M_\sigma$) is selected and the set of equations about J 's (the number is M_σ) can be solved by matrix inversion or by fitting the ECI's.

The formation of a configuration σ with compositions A_xB_{1-x} at volume V is defined by $\Delta E(\sigma, V) = E(\sigma, V) - xE(A, V_A) - (1-x)E(B, V_B)$, where $E(A, V_A)$ and $E(B, V_B)$ are the energies of parent A and B at their equilibrium volumes V_A and V_B . The calculated formation energy of the optimized structure is defined by $\Delta E_c(\sigma, V) = \min(V) \Delta E(\sigma, V)$. The ECI interactions can be fitted by the N_f correlation functions and the calculated energies of M_σ ordered structures. The procedure is to minimizing

$$\text{Min} \left\{ \sum_{\sigma}^{M_\sigma} w_{\sigma} \{ \Delta E_c(\vec{\sigma}, V) - N \sum_{m,k} D_{m,k} J_{m,k} G_{m,k}(\vec{\sigma}) \}^2 \right\} \quad (3.18)$$

with respect to the N_f values of ECI's, where w_{σ} are the weight of each ordered structure. The weight can be obtained by the degeneracy of the structure in configurations space which can be decided by the symmetry operation for the structure.

The above procedure doesn't indicate what clusters should be used to obtain a convergent cluster expansion. Since the degree of convergence is not known, the cluster-expanded energies should always be checked against the direct energies. Some of these directly calculated energies can be left out of the fit to be later compared with the predictions of the cluster expansion. More complex schemes can also be used to check the clusters chosen and the ECI's by carefully watching the effect of adding or taking out them during the fit. Another important issue is that the Connolly-Williams method is a fit to the absolute value of the formation energies. Most features in the phase diagram depend on subtle energetic differences. Furthermore, it can't guarantee that the true ground states can be predicted by the Ising model with the computed ECI's. Whenever there are close metastable structures, they can become stable during

the fit. Finally, there is no systematic way of truncating the expansion. These difficulties can be partly overcome by a linear programming technique recently developed²¹ in which not only the direct energies but also the ground-state line and the relative values of the formation energies are considered and by Evolutionary approach in which the effect many-body interactions be search by a genetic algorithm in a pool of many-body interaction types (MBITs)²².

3.5 Semiconductor alloy systems

Semiconductor materials have been used for a wide range of electronic, optoelectronic and spintronics devices. The application includes integrated circuits, lasers, light-emitting diodes laser, various light-detectors, solar cells, spin transistors, ultra-dense nonvolatile semiconductor memory, optical emitters with polarized output, and so on. Simple semiconductors usually include C, Si, Ge, GaAs, GaP, GaN, InAs, InP, AlAs, AlP, AlN, ZnTe, ZnSe, ZnS, CdTe, CdSe, CdS, BN and ZnO. Some have been the core materials of the applications and some have been widely studied as candidate materials. However, the existing number of simple semiconductors is small. They only provide a limited range of material properties (band gaps, carrier motilities, lattice constants)²³. Hence, the alloy phase A_xB_{1-x} of the parent compounds A and B has been regarded as candidates to obtain a larger range of material properties for technological application²⁴.

In semiconductor alloys, size mismatch between the atomic constituents usually leads to positive mixing enthalpy. The positive mixing enthalpy needs to be annihilated by the large entropy that is from the random arrangement of atoms (A and B) under high temperature. Under low temperature, the contribution of entropy ($-TS$) to the free energy is small and the random alloy will decompose into the binary constituents. It is believed that the isovalent semiconductor alloys (included IV-IV, III-V and II-VI) exist either as disordered solid solutions or as disproportionated products $A+B$ ²⁵.

In metal alloys, the prevailing paradigm was that positive mixing enthalpy means the existence of fundamentally repulsive interactions between the alloy constituents.

Since ordering requires attractive interactions, the possibility of ordering is excluded naturally. Whether does the positive mixing enthalpy reflect also repulsive interactions between the constituents? Then there are no being of the long-range ordered structures for isovalent semiconductor alloys. Zunger *et al.* found there are the structures with spontaneous long-range order in some size-mismatched semiconductor alloy²⁶. Thus, the semiconductor alloy seems to be dissatisfied to the paradigm in metal alloys. However, the long-range order is consistent with the positive mixing enthalpy, in principle. In semiconductor alloys, there is a distribution of many different local environments (named local clusters). The statistical average of these local clusters' energies (random alloy) is positive. This is major due to the strain of these local clusters. Now if one were to isolate a single cluster type and repeat it periodically in a strain-minimizing three-dimensional geometric arrangement, long-range order will be possible to exist. The reason is that the special ordered structure composed of the lower-energy cluster can remarkably minimize strain and maximize charge-transfer along some directions

3.6 References

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Chapter 4

Quasi-ordered Structure

Method and Color Bond Graph Theory

In this chapter, we build two new theoretical models for treating bulk semiconductor and cage-like alloy systems. Based on the consideration of the thermodynamics of the growth process of semiconductor alloy, the quasi-ordered structures are built by using the concept of factor group in group theory. In order to search the stable configurations in the huge configuration space of cage-like alloys, the color bond graph theory is built based on the concept of bond-counting rule and effect of local chemical environments.

4.1 Quasi-ordered structure method

4.1.1 Alloy semiconductor thin-films

In the modern optoelectronic and spin electronic devices, the active medium usually is in the form of thin film. For the growth of the thin-film alloys, there have two important effects need to be considered. Firstly, the substrate can help to stabilize the metastable phase of the epitaxial alloy film¹. The lattice confinement from the substrate can convert the bulk-phase metastable ordering of the alloy film into stable epitaxial one. In the bulk, the relaxed alloy constituents A+B are lower in energy than the ordered AB phase. But on a coherent substrate, the phase-separation of AB into A+B is discouraged because the coherently-matched alloy phase AB with low-energy ordered structures will have relative lower strain energy than the constituents (A and B) on the substrate. Therefore, the larger strain energy between epitaxial film of the constituents (A and B) and the substrate reduces the phase separation and stabilizes the local ordered alloy phase. Secondly, the thin film usually is grown under low temperature by advanced epitaxial growth techniques such as P-MBE^{2,3}. At this low-temperature nonequilibrium environment afforded by the epitaxial growth

techniques, the phase separation is kinetically limited. At the same time, the local stable alloy clusters with lower formation enthalpy will be formed. This is because the time the alloy needs to segregate into the parent lower-energy constitutions by lattice relaxation will be much longer than that of the epitaxial growth with a local single phase (local ordered alloy) due to the surface transfer of atoms or atomic clusters. In such conditions, the alloy films can be grown with local quasi-ordered structure for large range of the alloy concentration region.

4.1.2 Space group and crystal structure

For crystal structures, there are 14 different possible parallelepiped networks of points (14 Bravais lattices). Each one of the 14 Bravais lattices belongs to one of the 7 crystal systems (triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic symmetry) which are decided by the relations of the basis vectors of the unit cell (the angles between basis vectors and the values of the vectors). By the relation of the basis vectors and the point group, it is found there are 32 different point groups allowed by the crystal space structure. Since all lattice points are equivalent in a Bravais lattice, the point symmetry (rotations, inversion and reflections invariance) of any one of the 14 Bravais lattices should be described by some different point groups of the 32 point groups. However, the translation invariance of the Bravais lattices cannot be described by the point groups. By combining the translation operations (included the screw-axis and glide plane) with the point symmetry operations in 32 point groups, there are 230 groups named space groups⁴.

By the 230 space groups, the symmetry of any crystal structure based on the 14 Bravais lattices can be described completely. In nature, there are different crystal structures that are from the different stacking fashion of the elements due to the different chemical interactions of different elements (covalent bonds, ionic bonds, metal bonds and hydrogen bonds). There are some simple and familiar structures such as simple cubic (sc), face-centered cubic (fcc), body-centered cubic (bcc), hexagonal close-packed structures (hcp) and diamond structure. There are also complex structures based on simple space lattice. For examples, the sodium chloride (rocksalt)

structure can be considered as a NaCl molecule (Na on (0, 0, 0) point and Cl on (0, 0, 1/2) point) with fcc lattice. The perovskite structure can be considered as a BaTiO₃ molecule (Ba (0, 0, 0), Ti (1/2, 1/2, 1/2), O1 (1/2, 1/2, 0), O2 (1/2, 0, 1/2), O3 (0, 1/2, 1/2)) with sc lattice. The gallium arsenide structure can be considered as a GaAs molecule (Ga (0, 0, 0), As (1/4, 1/4, 1/4)) with fcc lattice. Generally, the crystal structure is considered as the combination of a group of atoms or molecules with some one of the Bravais lattices. Therefore, for any crystal structure, there is a space group corresponding to it. For an example, in the conventional cell with gallium arsenide structure, there are 8 atoms which are 4 As and 4 Ga atoms, respectively. The 4 crystal sets are occupied by 4 As atoms (or 4 Ga atoms) on a fcc lattice. The 4 crystal sets can be produced with each other and are equivalent, under the operation of the space group F-43M elements. So gallium arsenide structure has the symmetry of the space group F-43M.

4.1.3 Space group and quasi-ordered structure

For a binary alloy with N sites based on a fixed underlying Bravais lattice, there are $\sim 2^N$ candidate configurations. These are super-lattices, ordered structures, disordered structures, separated-phases, isolated- and clustered- impurity phases in the large configuration space, under the enough large number of lattice sites N . However, for small N (or small supercell), these configurations usually contain ordered structures, local-disordered structures and short-period super-lattices (named quasi-ordered structures by us). Under non-equilibrium growth condition, the mixed alloy phase can be obtained with these quasi-ordered structures in a lot of phase-separated alloy system. Therefore, the build of these quasi-ordered structures could be interesting.

Now we consider a supercell with small number of N under some crystal lattice. Here, a supercell is some structure that is the space extending of the conventional (or usual) unit cell. For an example, there is a $1 \times 1 \times 2$ supercell for GaAs material. It means the supercell is the double-extended structure of the conventional unit cell

along the $\bar{a}_3$ direction. For each supercell, there will be some lattice sets that are equivalent and should be produced by the operation of the space group element. However, the number of the space group elements is infinite in the theory due to the transition operation. Here we will use the concept of the quotient group to reduce the number of the symmetry operations to finite number of operation elements combined with the periodic boundary condition.

For a conventional unit cell with basis vectors $(\bar{a}_1, \bar{a}_2, \bar{a}_3)$ under some crystal structure, all the translation operations, $T = m_1\bar{a}_1 + m_2\bar{a}_2 + m_3\bar{a}_3$, form a group T . It is a normal subgroup of the space group of the crystal structure. As is well known in the theory of groups, a group can be decomposed into a sum of left (or right) cosets based on some subgroup. Therefore, the space group G can be decomposed into a sum of left cosets of the translation subgroup T like:

$$G = R_1T \cup R_2T \cup R_3T \cdots, \quad (4.1)$$

where R_i are coset representatives (pure point group operations, screw operations or glide operations with a minimal translation) and $\cup$ stands for a summation of two sets⁵.

Now we consider a supercell $(h \times l \times k)$ with basis vectors $(\bar{b}_1, \bar{b}_2, \bar{b}_3)$ (which equals to $(h\bar{a}_1, l\bar{a}_2, k\bar{a}_3)$) which is the space expansion of the conventional unit cell. The translation operations, $T' = m_1\bar{b}_1 + m_2\bar{b}_2 + m_3\bar{b}_3$, form a new translation group T' which is a normal subgroup of the translation group T . So the space group G can be decomposed into a sum of left cosets of the new translation subgroup T' like:

$$G = P_1T' \cup P_2T' \cup P_3T' \cdots, \quad (4.2)$$

where P_i are coset representatives which include all the pure point group operation of the space group, the screw and glide operations with a minimal translation for the basis vectors $(\bar{b}_1, \bar{b}_2, \bar{b}_3)$ (if the screw or glide operations are involved in the space group), and some finite number $(h \cdot l \cdot k)$ of translation operations (which is the

operations $T_s = m_1\bar{a}_1 + m_2\bar{a}_2 + m_3\bar{a}_3$ with $0 \leq m_1 < h$, $0 \leq m_2 < l$ and $0 \leq m_3 < k$). From the group theory, the set of cosets can form the factor group G/T' of the space group G about the new translation subgroup T' (which is operated based on the basis vectors $(\bar{b}_1, \bar{b}_2, \bar{b}_3)$) which is with finite number of operation elements. In the under text, we will show the symmetry of the supercell ($h \times l \times k$) can be described by the factor group G/T' with the periodic boundary condition.

By the periodic boundary condition, the space lattice sites are separated into each supercell. Whatever the lattices is occupied by the different atoms, each supercell is equivalent with each other. As shown in Fig. 4.1(A), the space expansion of a 1D supercell with 4 sites (which is labeled by a, b, c and d) can construct the entire lattice. By the translation operation T_s , such as left translating a site in Fig. 4.1(B), the entire lattice will be unchanged by choosing the supercell shown by the blue rectangle. This means the configuration in Fig. 4.1(A) is the same as that in Fig. 4.1(B). In the supercell, by the translation operation T_s with the periodic boundary condition (named as the period-limited translation operation T_{ps}), the entire lattice still can be build by the supercell like that chosen in Fig. 4.1(A). In Fig. 4.1(C), the period-limited translation operation T_{ps} is shown. It can be expressed as $T_{ps}(a, b, c, d) = (b, c, d, a)$. Since the translation operations, $T' = m_1\bar{b}_1 + m_2\bar{b}_2 + m_3\bar{b}_3$, do not change the supercell, the factor group G/T' with the period-limited operation can describe the symmetry of the supercell.

Fig. 4.1 (A) An one-dimensional lattice with 4-atom unit cell (B) To choose a new

4-atom unit cell shows the invariability of lattice after a translation operation (C) The translation operation in (B) can be completed by a the period-limited translation operation based on a 4-atom unit cell shown in (A).

Obviously, an appropriate group representation is important for the abstract factor group. Here we will use a permutation group of the vertexes (the lattice sets) as the representation of the factor group G/T' , since the integer representation of the vertexes can make the abstract group operation as a simple exchange of integer. To illustrate the permutation operation of the vertexes, a case of 2D supercell with simple cubic lattice is shown in Fig. 4.2 and the vertexes are labeled by the numbers 1-9. Obviously, the identity element g_e can be expressed as

$$g_e = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \end{pmatrix}. \quad (4.3)$$

Fig.4.2 A two-dimensional lattice with a 9-atom supercell in which the 9 atom-sits are labeled by the number (1-9).

It can be found the cubic supercell has rotational symmetry. For example, two rotation operations are to rotate an angle 180° and 90° round an axis that is perpendicular to the paper plane and through vertex 5, respectively. They can be expressed as

CHAPTER 4 Quasi-ordered Structure Method and Color Bond Graph Theory

$$g_2 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 9 & 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \end{pmatrix}, \text{ and}$$

$$g_4 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 7 & 4 & 1 & 8 & 5 & 2 & 9 & 6 & 3 \end{pmatrix}. \quad (4.4)$$

Now we show a simple period-limited translation operation which is to translate a site long x -axis. It can be expressed as:

$$g_{T_1} = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 2 & 3 & 1 & 5 & 6 & 4 & 8 & 9 & 7 \end{pmatrix}. \quad (4.5)$$

How does one get all the operation elements of the permutation group? First, we can follow the rule of closure of the group elements. If g_i and g_j are arbitrary elements of G , then

$g_i * g_j \in G$. For example:

$$g_2 * g_2 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 9 & 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 9 & 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \end{pmatrix} = g_e \quad (4.6)$$

$$g_4 * g_4 = \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 7 & 4 & 1 & 8 & 5 & 2 & 9 & 6 & 3 \end{pmatrix} \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 7 & 4 & 1 & 8 & 5 & 2 & 9 & 6 & 3 \end{pmatrix}$$

$$= \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 & 9 \\ 9 & 8 & 7 & 6 & 5 & 4 & 3 & 2 & 1 \end{pmatrix} = g_2 \quad (4.7)$$

Second, we can use the concept of the conjugacy class. In group theory, the elements of any group may be partitioned into conjugacy classes. An important theorem about conjugacy classes is the product of two classes $\mathcal{E}_i \mathcal{E}_j$ is constructed by some integrate class $\mathcal{E}_k$ as,

$$\mathcal{E}_i \mathcal{E}_j = \sum c_{ijk} \mathcal{E}_k, \quad (4.8)$$

where the parameters c_{ijk} equal to some integers. Thus, we just need to choose a small amount of elements from some group classes as the generators of the group elements.

Then all the group elements can be generated by these generators.

For a supercell ($h \times l \times k$) with $N = h \times l \times k \times M$ atoms (Assumed there are M equivalent sets in the conventional unit cell), we can be easy to get all the 2^N configurations for a binary alloy system. Then by the operation of the permutation group of the vertexes, we can get these quasi-ordered structures with the degeneracies.

4.2 Color bond graph theory

4.2.1 Color bond graph (CBG) theory for cage-like alloy clusters

We assume that the substitution between two different atoms will just change the local chemical environments of vertices due to the charge transfer and don't result in the change of the topology of structure. Based on the above hypothesis, the alloy question of cage-like cluster can be solved by constructing an Ising model. In the space of configurations, any configuration σ can be expressed by the arrangement of the atom sites (vertexes) as

$$\Gamma(\sigma) = \begin{pmatrix} 1 & 2 & \cdots & N \\ A & A & \cdots & B \end{pmatrix}, \quad (4.9)$$

where A is for atom A and B is for atom B . In term of the Ising model, $\Gamma(\sigma)$ is the set of spin-like variables σ_i which takes the value of 1 (or -1) for an A (or B) atom ($i=1$ to N). In other words, $\Gamma(\sigma)$ can be expressed as

$$\Gamma(\sigma) = (\sigma_1, \sigma_2, \cdots, \sigma_N). \quad (4.10)$$

For binary alloy cage with N atoms, there are 2^N configurations. Though we can enumerate all the configurations for first principle calculation, the search of the low-energy states can't be completed by the first principle calculation due to the very large space of configurations. For example, in a binary alloy cage system with 60 atoms, there are about 1.15×10^{18} configurations.

To treat the question with first-principles accuracy, a model Hamiltonian with proper parameters, which can be extracted from first principle calculation, is needed. It is well known that the rules of chemical bonding, such as the octet rule, the instability rule of appended bond with isolated single electron, the stability rule of

isolated electron pair, and so on, are important to analyze the stability of the chemical structure by intuition. Generally, counting the numbers of different chemical bonds (number of $A-A$ bonds, number of $B-B$ bonds and number $A-B$ bonds) for each configuration maybe distinguish the stability of configuration. Following the simple bond counting rules, the energy of any configuration (which is gained from the first principle calculation) can be expressed as:

$$E(\sigma) = E_o + \alpha_{A-A} N_{A-A} + \alpha_{B-B} N_{B-B} + \alpha_{A-B} N_{A-B}, \quad (4.11)$$

where α_{A-A} , α_{B-B} and α_{A-B} are for the strength densities of bonds $A-A$, $B-B$ and $A-B$, respectively. It is found that such a rule is so simple that it can not evaluate quantitatively the stability of an alloy cage structure.

Actually, counting the chemical bond is equivalence to consider the nearest -neighbor two-vertex interaction. It is well known that the local environments of the chemical bonds usually induce the charge transfer and thereby result in different local structural relaxation in different configurations. The local environment effects, such as the near-neighbor bond types, the angle between bonds, and so on, need to be considered for the stability of the structure. This means other two-vertex interactions and other many-vertex interactions need to be considered in the expression of energy for the prediction of the low-energy states. Thus, the energy of the alloy configurations can be recast in a general form

$$E(\sigma) = E_o + \sum_i \alpha_1^i C_1^i(\sigma) + \sum_{i,k} \alpha_{2,k}^i B_{2,k}^i(\sigma) + \sum_{i,k} \alpha_{3,k}^i A_{3,k}^i(\sigma) + \sum_{i,k} \alpha_{4,k}^i F_{4,k}^i(\sigma) + \dots, \quad (4.12)$$

where the parameters α 's represent the interaction energies, C_1 's are the energy of vertex i ($i=1$ to N), B_2 's, A_3 's and F_4 's are the generalized correlation functions for different types of "bonds" to include contributions from two-vertex (the B_2 's), three-vertex (the A_3 's) terms and four-vertex (the F_4 's). This means, for a structure or graph that are constructed by limited number of atoms or vertex, the physical properties of the configurations based on the structures or graph, such as the electronic total energy, can be expressed by the sum of the local interaction of vertexes. Therefore, we name the method based on the concept of bond as color bond graph theory.

4.2.2 Application of symmetry operation in high-symmetry topology structure

Since the parameters of the expression about energy of configurations need to be fitted by the total energy calculation of some configurations, the small number of parameters is expected in order to reduce the number of configurations that is calculated by first principle. Therefore, to class these interactions of vertexes will be important.

Firstly, we need to verdict the equivalence of these vertexes in the structure by the symmetry operations. For some clusters, the symmetry is very low and not all vertexes are equivalent after the optimization of structure. This makes all interaction nonequivalent. Fortunately, the cage structures usually have very high symmetry. This makes all the vertexes into a few of classes. In each class, the vertexes are equivalent with one another. For an example, C_{60} molecule consists of 60 carbon atoms, arranged as 12 pentagons and 20 hexagons. It has so high symmetry (there are 120 symmetry operations) that all vertex are equivalent under these symmetry operations. In some cases, we can even change properly the structure under unchanging the topology structure in order to obtain the high symmetry. Furthermore, we can consider two classes are approximately equivalent if the physics effects the two classes produced are not large difference. For an example, a cage structure C_{24} is constructed with 10 pentagons and 2 hexagons. There is a point group D_{6d} with 24 symmetry operations to describe the structure. However, it is found that there are 2 classes of vertex. One of classes is constitute with 12 vertexes from 2 hexagons and the other of classes is with residual 12 vertexes. Since each vertex has 3 bonds with other vertexes, it is considered roughly that the 2 classes are equivalent in first approximate calculation.

Secondly, we can consider the equivalence of different interactions of vertexes based on these equivalent vertexes. We can use the distance to estimate the equivalence of the interactions between vertexes. We can also consider the equivalence of the interactions of vertexes by symmetry operations. Now, we give a simple example to show how to decide the equivalence of the interactions of vertexes in a square structure shown as Fig 4.3. For this square structure, there is a symmetry

group with 8 group operations to describe the symmetry shown as Table 4.1. All the 4 vertexes are equivalent under the symmetry operations.

Fig.4.3 The sketch map of square structure in which the vertexes are labeled with the number (1-4).

Under operation of the group elements, the equivalent vertex interactions will transform with each other such as:

$$C_4^3 I(1,2) = I(4,1), \sigma_v I(1,2,3) = I(4,3,2). \quad (4.13)$$

Considering the nearest-neighbor two-vertex interactions (chemical bonds), all equivalent interactions enter a correlation function by symmetry operations as:

Group operations g_a	Vertex permutations
E	(1 2 3 4)
C_4^1	(2 3 4 1)
C_4^2	(3 4 1 2)
C_4^3	(4 1 2 3)
σ_v	(4 3 2 1)
$\sigma_{v'}$	(2 1 4 3)
σ_v'	(3 2 1 4)
$\sigma_{v''}$	(1 4 3 2)

Table 4.1 the operation elements of the point group and the vertex permutation presentation of the point group

$$\begin{aligned}
G_{21} &= \sum g_{\alpha} I(1,2) \\
&= I(1,2) + I(2,3) + I(3,4) + I(4,1) + I(4,3) + I(2,1) + I(3,2) + I(1,4) \\
&= 2[I(1,2) + I(2,3) + I(3,4) + I(4,1)]
\end{aligned} \tag{4.14}$$

where $I(i, j)$ is for two-vertex interaction between vertex i and vertex j (note that $I(i, j)=I(j, i)$ is hypothesized). Remove the prefactor, the correlation function about nearest-neighbor two-vertex interactions is get as

$$B_{21} = I(1,2) + I(2,3) + I(3,4) + I(4,1) . \tag{4.15}$$

The first three-vertex correlation function can be gained as:

$$\begin{aligned}
G_{31} &= \sum g_{\alpha} I(1,2,3) \\
&= I(1,2,3) + I(2,3,4) + I(3,4,1) + I(4,1,2) + I(4,3,2) + I(2,1,4) + I(3,2,1) + I(1,4,3) . \\
&= 2[I(1,2,3) + I(2,3,4) + I(3,4,1) + I(4,1,2)]
\end{aligned} \tag{4.16}$$

Remove the prefactor, the correlation function about nearest-neighbor two-vertex interactions is get as

$$A_{31} = I(1,2,3) + I(2,3,4) + I(3,4,1) + I(4,1,2) . \tag{4.17}$$

Here, it needs to be noted that we hypothesize the interaction of vertexes will not be changed, following the change of arranges of vertexes such as:

$$I(1,2,3) = I(1,3,2) = I(3,2,1) + I(3,1,2) = I(2,3,1) = I(3,2,1) . \tag{4.18}$$

After we gain the different classes about the interaction of vertexes, the colors of the bonds in each class can be added. For two-vertex interaction, there are 3 subclasses (AA , BB and AB) in each class. For three-vertex interaction, there are 4 subclasses (AAA , AAB , ABB and BBB) in each class. For n -vertex interaction, there are $n+1$ subclasses in each class. Thus, by the symmetry operation, we get an energy model with a few of parameters to predict the low-energy states in the space of configurations for cage-like alloy cluster.

4.3 References

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Chapter 5

A Direct First Principle Study

on the Structure and Electronic Properties of $\text{Be}_x\text{Zn}_{1-x}\text{O}$

In this chapter, we present a systematic study on the structural and electronic properties of all alloy configurations of $\text{Be}_x\text{Zn}_{1-x}\text{O}$ in a unit cell with 16 cations by using density functional theory (DFT) methods with quasi-ordered structures (QOS). The experimental structural and electronic properties of the bulk material are reasonably reproduced by the theoretical methods. The lattice constants of the alloy are found to follow Vegard's law and are comparable with the experimental values. The possible existence of three metastable ordered states is predicted by examining the formation enthalpies of all alloy configurations. The calculated band gaps of alloy $\text{Be}_x\text{Zn}_{1-x}\text{O}$ are compared with the experimental values and it is found that some alloy configurations with same concentration can have very different band gaps (~ 1.5 eV).

5.1 Introduction

ZnO is recognized as a next generation UV light emitting material due to its wide band gap (3.37eV at RT) and large exciton binding energy (60 meV)¹. The stable and reliable p-type ZnO semiconductor material can now be grown by doping with either nitrogen² or arsenic³. Another critical step in producing high-efficiency ZnO-based light emitting devices (LED) is the fabrication of quantum wells and super-lattices of ZnO-based semiconductor alloy by mixing with materials with even larger band gaps. $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, with MgO ($E_g=7.7\text{eV}$), has been studied extensively and this material can cover a range from blue to deep UV⁴. However, due to the different crystal structures between ZnO (B4) and MgO (B1), crystal phase segregation was theoretically predicted^{5, 6} and experimentally confirmed⁷ for $x \geq 1/3$.

From a material's point of view, BeO ($E_g=10.6\text{eV}$) is a better candidate for achieving even wider band gap modulation because both BeO and ZnO have

hexagonal wurtzite structure and their closer a -axis lattice constants (2.698 Å for BeO and 3.249 Å for ZnO) will reduce the degree of lattice mismatch. However, due to its toxicity, $\text{Be}_x\text{Zn}_{1-x}\text{O}$ alloy is under explored and only until recently Ryu *et al.* successfully synthesized $\text{Be}_x\text{Zn}_{1-x}\text{O}$ films by the hybrid beam deposition (HBD) method^{8,9}. Motivated by their work, one of our main goals is to investigate the detailed structural and electronic properties of $\text{Be}_x\text{Zn}_{1-x}\text{O}$ alloy by theoretical methods. For example, whether there exist ordered stoichiometric inter-semiconductor compounds $\text{Be}_x\text{Zn}_{1-x}\text{O}$ that can be thermodynamically more stable than the disorder states. If such ordered states exist, what are their electronic properties comparing to the random configurations?

5.2 Theory methods

In recent years, the first principle methods based on density functional theory (DFT) have become popular and been routinely for material simulation due to their increasing accuracy and efficiency. However, the major obstacle in studying $\text{Be}_n\text{Zn}_m\text{O}_{n+m}$ alloy is to deal with the 2^{n+m} possible configurations. One of the commonly used algorithms to deal with such the complexity is the cluster-expansion theory which can effectively maps the relative stability of the alloy configurations to an effective Hamiltonian.¹⁰ This effective Hamiltonian can then be used to explore the large (2^{n+m}) configuration space and study the thermal properties of the alloy. As a preliminary step toward a comprehensive study, our goal is to study the detailed structural and electronic properties of the all the configurations in a given unit cell. Here, we consider a supercell of $\text{Be}_x\text{Zn}_{1-x}\text{O}$ containing 32 atoms and if we simply consider the replacement of cations (Be and Zn) with each other, the total number of configurations will be $2^{16} = 65,536$. Direct calculation of such the large number of configurations is infeasible in practice. However, it is well known that the physical properties of a system will not be changed under the symmetry operations of the system. We employ this old wisdom to reduce the number of configurations in the above-mentioned unit cell. Thanks to the high-symmetry of the hexagonal wurtzite structure (symmetry group = $\text{P6}_3\text{mc}$), the number of symmetrically distinct

configurations is found to be 652. In short, by just utilizing the symmetry of the parent scaffold, we have reduced the amount of computation by 100 times.

The structural and electronic properties of these alloy configurations are examined directly by the DFT calculation in the local density approximation (LDA)¹¹ as implemented in the VASP program package¹². We have carried out tests on the k -space integral and plane-wave basis to ensure the total energy is converged at the 1 meV/cation level. We found that using a energy cut-off of $E_{\text{cut}}=1200$ eV and a $3\times3\times2$ Monkhorst-Pack type mesh in the first Brillouin zone¹³ is sufficient for the semiconductor alloy $\text{Be}_x\text{Zn}_{1-x}\text{O}$. The total energies were obtained after the geometrical optimization finished. It is important to note that, one must carefully relax not just the atomic positions but also the lattice constants of any alloy configurations to allow the configurations to reach their most stable conformations.

5.3 Results and discussion

A standard method to access the relative stability of an alloy configuration (σ) is to calculate the excess energy (the formation enthalpy) which is defined as the difference in energy between the alloy and the weighted sum of the constituents:

$$\Delta E(\sigma, x) = E(\sigma, \text{Be}_x\text{Zn}_{1-x}\text{O}) - x E(\text{BeO}) - (1-x) E(\text{ZnO}), \quad (5.1)$$

where $x(\sigma)$ is the concentration of configuration σ . The formation enthalpies of all 652 alloy configurations are depicted in Fig. 5.1. It is found that there is a concave feature which implies that random alloy configurations are instable with respect to the pure species. However, if we focus on the ground-state line, it can be found that there are three regions (at $x=0.25$, 0.50 and 0.75) with convexity. The convexity/concavity of a configuration (σ) can be accessed by calculating the local potential depth, Δ_σ , defined by Zunger *et al.*¹⁴:

$$\Delta_\sigma = \Delta E_\sigma - \frac{x(\sigma) - x(\alpha)}{x(\beta) - x(\alpha)} \Delta E(\beta) - \frac{x(\beta) - x(\sigma)}{x(\beta) - x(\alpha)} \Delta E(\alpha), \quad (5.2)$$

where α, β and σ are three configurations with concentrations in the order of $x(\alpha) < x(\sigma) < x(\beta)$. A local-stabled ground state will have $\Delta_\sigma < 0$. We found that when the

concentrations of Be are 0.25, 0.5 and 0.75, the local potential depths are -24.8meV/cation, -27.15meV/cation and -15.35meV/cation, respectively. These convex regions suggest the existence of ordered metastable structures. The formation of such ordered structures is possible when the Be concentration is between two vertexes and the alloy is likely to lower its energy by local decomposition.

Fig.5.1 Formation Enthalpy of all 652 symmetrical distinct $\text{Be}_x\text{Zn}_{1-x}\text{O}$ alloy configurations in a unit cell of 16 cations. The ground-state line is high-lined by a red line. The lattice structures of 3 meta-stable ordered states with Be concentrations of 25%, 50% and 75% are shown in the inset (red sphere for O atom, green sphere for Be atom and blue sphere for Zn atom).

The structures derived from our LDA calculations agree well with experiments. For the bulk materials, we got the following lattice constants: ZnO ($a=3.195\text{\AA}$ and $c=5.158\text{\AA}$) and BeO ($a=2.667$ and $c=4.333\text{\AA}$). These values are just slightly lower than the experimental values (ZnO ($a=3.249\text{\AA}$) and BeO ($a=2.698\text{\AA}$)) in literature¹⁵. The underestimate of the lattice constants by the LDA method is reasonable and can

be well understood by the thermal effects in the experimental samples.

In order to compare with the experimental work of Ryu *et al.*⁸ on the structures of the $\text{Be}_x\text{Zn}_{1-x}\text{O}$ alloy, we derive the lattice constants of the alloy configurations from their optimized super-cell size by fixing the a/c ratio at 1.619 (the averaged a/c of BeO and ZnO from our LDA calculations). The results of all 652 configurations are shown in Fig. 5.2(a). It is found that at each concentration the lattice constants of the ground state are generally smaller than the excited states. This observation is inline with the expectation that the ground state structures are those configurations with stronger bonding characters that will result in smaller volume. This notion is also confirmed by examining the dependence of the formation enthalpy and lattice constants at different Be concentrations as shown in Fig. 5.2(b) – which reminds us that lattice relaxation plays an important role in determining the relative stability of alloy configurations. The blue dot line in Fig. 5.2(a) is drawn to connect the lattice constants of the bulk material. It is obvious that the lattice constants of the ground states follow the Vegard's law¹⁶ closely, although notable deviation from the linear extrapolation is possible for some excited states.

Fig.5.2 (a) The lattice constants of $\text{Be}_x\text{Zn}_{1-x}\text{O}$ as a function of Be concentration is shown on the left. The lattice constant of the ground state at each concentration is highlighted by red sphere. The experimental values of reported in ref.8 are shown as black diamonds. Both lattice constants, especially the ground states follow the Vegard's laws. However, small deviation from the linear extrapolation is noticeable for some excited states. (b) It is clear from the right hand figures that there is a strong

correlation between the relative stability of an alloy configuration with its lattice constants.

Since both ZnO and BeO have direct band gaps, we estimated the band gaps of all the alloy configurations by calculating the band gaps at Γ -point with a self-consistent calculation that can generate a high quality charge density. The calculated band gap for ZnO and BeO are 0.905eV and 7.946eV, while the experimental values are 3.3eV and 10.6eV. This large error in the band gap is a well-known problem of the LDA method, which fails quantitatively in dealing with excited-state properties and tends to underestimate the band gap. However, the difference found between our calculated band gaps and the experimental ones will not affect our analyses that are mainly related to the relative value of band gaps.

Fig.5.3 (a) The Energy band gaps of $\text{Be}_x\text{Zn}_{1-x}\text{O}$ alloy at the Γ -point predicted by LDA method as a function of x are shown. The band gaps of the ground states are shown as red spheres. The band gaps of the [100] and [001] SLs are shown as green Δ and blue ∇ , respectively. (b) The “corrected” band gaps and the experimental band gaps from experiment from ref 8 are shown.

The band gaps of all the 652 alloy configurations calculated by the LDA method

is shown in Fig. 5.3(a). It is found that the band gaps of the ground states are larger than the excited states at the given concentrations. In order to compare with the experimental report⁸, the LDA band gaps are “corrected” by linear interpolation to fit the bulk values. The “corrected” band gaps are shown in Fig. 5.3(b). The experimental values are found to be smaller than the calculated value of the ordered states. This may be attributed to the errors in experimental measurements and/or the dominance of the disordered excited states existed in the sample that is due to the thermal effects of the growth process.

The structures of the three metastable states, shown in the bottom of Fig. 5.1, all have periodicity along the c -axis. Motivated by this observation, we have looked into whether the band-gaps are sensitive to directional decompositions. Since our supercell is not large enough to allow many general directions, we will focus only on the [100] and [001] supercells (SCs). It is clear from Fig. 5.3 that the [001] SCs have higher band gaps than the rest, and there is not systematic trend among the [100] SCs. One of the implications is that the [001] SCs of $\text{Be}_x\text{Zn}_{1-x}\text{O}$, if it can be grown, is expected to have larger and more consistent (due to the smaller deviations in the band-gaps among all the [001] SCs) band gaps than random decompositions.

5.4 Conclusion

In summary, we have demonstrated that using the symmetry of the parent structures can significantly reduce the complexity in studying alloy systems. Thanks to the high-symmetry of hexagonal wurtzite structure, we have gained a factor of 100 by reducing the 2^{16} possible alloy configurations to 652 symmetrically distinct configurations. This reduction in complexity enables us to examine the detailed structural and electronic properties of $\text{Be}_x\text{Zn}_{1-x}\text{O}$ by the first principle method.

We found that DFT methods could accurately reproduce the structure of the bulk materials. In the alloy configurations we found that the relative stability of a given alloy configuration has a linear dependence with its lattice constants. By examining the formation enthalpy profile, we found three convex regions which suggest the existence of metastable ordered states at concentration $x = 0.25, 0.50$ and 0.75 . These

results can be useful for designing the growth process and application of the electronic properties of alloy $\text{Be}_x\text{Zn}_{1-x}\text{O}$.

The electronic properties are found to be more sensitive to alloy configurations. We found that while the lattice constants of alloy configurations follow the Vegard's law with only a small deviation, their band gaps at Γ -point could be different by ~ 1.5 eV. Supercell structures along [001] are found to have larger band gap than the random configurations. A more comprehensive study on $\text{Be}_x\text{Zn}_{1-x}\text{O}$ is undergoing and we hope this systematic calculation and analyses of the structural and electronic properties of all alloy configurations reported here will provide useful information for the experimentalists and further stimulate more detailed and accurate investigations.

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Chapter 6

A first-principle analysis

on the phase stabilities, chemical bonds, and band gaps of wurtzite structure $A_x\text{Zn}_{1-x}\text{O}$ alloys: ($A=\text{Ca}, \text{Cd}, \text{Mg}$)

In this chapter, the phase stabilities, structural and electronic properties of three nonisostructural oxide alloys ($\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$) are studied by first-principle methods with quasi-ordered structures (QOS). We examine all the alloy configurations in three 16-atom supercells ($1\times1\times2$ $B1$ phase structure, $2\times2\times1$ and $2\times1\times2$ $B4$ phase structures) by using QOS methods. Taking into account of the contribution of the alloy statistics, we have drawn the regions of phase instability for $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ ($0.25 < x < 0.375$), $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($0.375 < x < 0.5$) and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ ($0.75 < x < 0.875$). We have also analyzed lattice constants, structural parameter u and the bond lengths in the wurtzite phases. It is found that the averaged lattice constants of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ do not follow the Vegard's rule and this is related to the degree of instability of the wurtzite MgO and CaO . Wurtzite CaO is an instable phase and turns into hexagonal CaO upon geometry optimization. The calculated band gaps are found to be consistent with the experimental values for alloys $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$. The bowing parameters for alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ are estimated to be 0.87 and 1.30 eV, respectively.

6.1 Introduction

Following the group-III nitrides (AlN , GaN , InN) and their alloys, ZnO has attracted much attention as a candidate material for light emitting devices (LEDs) and laser diodes (LDs) in the wavelength range from blue-green to ultraviolet due to its unique physical properties especially the large exciton binding energy (60 meV)¹⁻⁴. An important step toward the development of ZnO -based optoelectronic devices⁵ is the fabrication of ZnO -based alloy semiconductors with flexible band gap engineering that allows for the construction of quantum-well and superlattice⁶.

$\text{Be}_x\text{Zn}_{1-x}\text{O}$, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ are possible candidates to achieve wider band-gap modification. While a lot of experimental work about $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ⁷⁻²² have been carried out, the fabrication of $\text{Be}_x\text{Zn}_{1-x}\text{O}$ is hindered by the high degree of toxicity of BeO and it was reported only recently by Ryu *et al.*²³. In the theoretical community, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy^{24, 25} has also received more attention than $\text{Be}_x\text{Zn}_{1-x}\text{O}$. Our recent studies found the solubility of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ is still better than $\text{Be}_x\text{Zn}_{1-x}\text{O}$ in the Zn-rich region, although ZnO and BeO have the same wurtzite structure²⁶. $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ is another candidate to achieve wider band, but has remained under-explored. To gain ZnO-based optoelectronic materials in the whole visible-ultraviolet emission region from 1.8 to 3.3 eV⁶, Extensive experimental effects have been made on $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ for narrower band gap modification²⁷⁻³⁷. A lot of first-principle calculations on the properties of the parent compounds CaO ³⁸⁻⁴⁰, CdO ⁴¹⁻⁴³, MgO ^{44, 45} and ZnO ⁴⁶⁻⁴⁸ in the different structures (wurtzite and rocksalt) have appeared in the literatures⁴⁹⁻⁵⁴. However, as far as we know, the crystal structure and stability of these ternary alloys $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ still have been not well studied except for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy^{24, 25}.

Unlike III-N nitrides, which all assume the same wurtzite structures, thermodynamically stable II-O oxides can be either wurtzite structures (ZnO, BeO) or rocksalt structures (CaO, CdO and MgO)^{55, 56}. The ternary Zn-based oxide alloys ($\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$) are made from the nonisostructural components (rocksalt + wurtzite). Therefore, in Zn-based ternary oxide alloys, the structure phase separation will occur in some transition concentration. For example, both experimental⁵⁷ and theoretical^{24, 25} investigations have shown that the stability of alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ with wurtzite structure is up to $x \leq 1/3$. For wurtzite $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ alloy, different stability ranges were obtained with varying growth methods. So far, the maximal Cd concentration with stable wurtzite structural $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ phase is achieved by Ishihara *et al.* with $x \leq 0.69$ ³⁶. For $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ alloy, to our knowledge, there has been no experimental and theoretical analysis for the phase stability. One of our main motivations in this chapter is to engage the systematical first principle calculations to compare the stability of B4 phase (wurtzite structure) in the above-mentioned II-VI

oxide alloys. The results are expected to shed some light on the fundamental understanding of physical properties in these nonisostructural alloy systems and serve as references for future experimental analysis. Moreover, we have investigated chemical, structural and electronic properties in these alloys. These structural and electronic properties are crucial for the heterostructure design and optimized growth of the related quantum wells and superlattices.

This chapter is organized as follows. In the next section, the detailed calculation methods and the theoretical model for the construction and analysis of alloy structures used in our work are described. The main results of this work are presented in the section 6.3. Finally, a brief summary is given in section 6.4.

6.2 Computational methods and theoretical model

The effects of disorder on the stability and structure of alloys has gained considerable attention over the past few decades. Simple single-site theory, such as the coherent-potential approximation(CPA)⁵⁸, based on the average occupation of the substitution atoms often brings about some deviation from the actual physical properties. The importance of the local chemical environment such as charge transfer and local structural relaxation in different configurations for determining the thermodynamics and electronic properties of an alloy has been noted. Zunger *et al.*^{59, 60} has shown that the most important physical properties can be analyzed correctly just by considering the correlation of nearby neighbors. In order to include the local correlations, in this work, the calculation and analysis are carried out in several supercells with 16 atoms. For the *B1* phase (rocksalt structure) unit cell, with space group *FM-3M*, a $1\times 1\times 2$ supercell (shown in Fig. 6.1a) is used. For the *B4* phase unit cell, with space group *P6₃mc*, we have considered two supercells along [001] and [100] directions as shown in Fig. 6.1b and Fig. 6.1c.

The $2^8=256$ configurations in each of the three supercells have been simplified by eliminating the symmetrically equivalent ones. For the $1\times 1\times 2$ supercell of the *B1* phase, there are 27 symmetrically distinct configurations. For the *B4* phase, we found 22 and 34 symmetrically distinct configurations in the $2\times 2\times 1$ and $2\times 1\times 2$ supercells,

respectively. The degeneracy factors of all the above-mentioned configurations are detailed in Table 6.1.

Fig.6.1 Illustration of $1\times 1\times 2$ $B1$ phase supercell (a), $2\times 2\times 1$ $B4$ phase supercell (b) and $2\times 1\times 2$ $B4$ phase supercell (c). Red spheres represent the O atoms and grey spheres represent the Zn atoms.

The Helmholtz free energy in determining the stability of the system can be divided into two parts, namely the mixing energy (the formation enthalpy) ΔE and the mixing entropy ΔS by the formula⁶¹:

$$\Delta F(x, T) = \Delta E(x, T) - T\Delta S(x, T), \quad (6.1)$$

At zero temperature, the relative stability of an alloy configuration can be estimated by the calculation of the formation enthalpy that is defined as the difference in energy between the alloy and the weighted sum of the constituents. For the parents with the same phase (α), such as group-III nitrides alloys, the formation enthalpy of the alloy configuration (σ) can be shown by the formula:

$$\Delta E_\alpha(\sigma, x) = E_\alpha(\sigma, A_x B_{1-x} C) - x \cdot E_\alpha(\text{AC}) - (1-x) E_\alpha(\text{BC}), \quad (6.2)$$

where $x(\sigma)$ is the concentration of configuration σ . For nonisostructural compounds, with $E_\alpha(\text{AC}) < E_\beta(\text{AC})$ and $E_\beta(\text{BC}) < E_\alpha(\text{BC})$, the formation enthalpy is expressed as²⁵:

$$\Delta E_{\alpha,\beta}(\sigma, x) = E_\gamma(\sigma, A_x B_{1-x} C) - x \cdot E_\alpha(\text{AC}) - (1-x) E_\beta(\text{BC}) \quad (6.3)$$

where γ can be either α or β phase.

The averaged structural and electronic properties as a function of the concentrations can be analyzed by considering the contribution of all the alloy configurations with the same concentration and using the following formula:

$$\langle P(x) \rangle = \sum_{i=1, i \max} g_i P_i / \sum_{i=1, i \max} g_i \quad (6.4)$$

where P_i is the property of the i -th configuration and g_i is the degeneracy factor. Note that the summation in Equation 6.4 is limited to those configurations with concentration x .

In this work, the structural and electronic properties of all the alloy configurations described above are examined by the density functional theory (DFT) and the local density approximation (LDA)^{62, 63} along with the projector augmented wave (PAW) method^{64, 65} as implemented in the VASP program package⁶⁶⁻⁶⁸. The PAW potentials used for cadmium and zinc treat 4p electrons in the valence. The k -space integral and plane-wave basis, as detailed below, are tested to ensure the total energy is converged at the 1 meV/cation level. An energy cut-off of $E_{\text{cut}} = 1200$ eV is sufficient for the different supercells of the three alloy ($\text{Ca}_x \text{Zn}_{1-x}\text{O}$, $\text{Cd}_x \text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x \text{Zn}_{1-x}\text{O}$), while the different k points are chosen for the different supercells. For the $1 \times 1 \times 2$ supercell with the $B1$ phase, a $4 \times 4 \times 2$ Monkhorst-Pack type mesh⁶⁹ is chosen in the first Brillouin zone. With regard to the $B4$ phase, the $3 \times 3 \times 4$ and $3 \times 5 \times 3$ Monkhorst-Pack type mesh⁶⁹ is chosen for the $2 \times 2 \times 1$ and $2 \times 1 \times 2$ supercells, respectively. In order to enable the alloy configurations to converge to their most stable conformation, all atomic positions and the lattice constants are relaxed. The total energies are obtained after the geometrical optimizations are finished. The

Γ -point band gap is estimated after a self-consistent calculation that can generate high quality charge density is finished with the optimized geometrical structure.

1×1×2 Rocksalt			2×2×1 wurtzite			2×1×2 wurtzite		
No. #	(A)	g_j	No. #	(A)	g_j	No. #	(A)	g_j
0	0	1	0	0	1	0	0	1
1	1	8	1	1	8	1	1	8
2	2	4	2	2	12	2	2	4
3	2	4	3	2	12	3	2	4
4	2	16	4	2	4	4	2	8
5	2	4	5	3	8	5	2	4
6	3	8	6	3	24	6	2	8
7	3	16	7	3	24	7	3	8
8	3	16	8	4	2	8	3	16
9	3	16	9	4	6	9	3	8
10	4	32	10	4	8	10	3	16
11	4	4	11	4	24	11	3	8
12	4	8	12	4	6	12	4	16
13	4	8	13	4	24	13	4	16
14	4	6	14	5	24	14	4	2
15	4	8	15	5	8	15	4	4
16	4	4	16	5	24	16	4	8
17	5	16	17	6	12	17	4	2
18	5	16	18	6	12	18	4	4
19	5	8	19	6	4	19	4	8
20	5	16	20	7	8	20	4	2
21	6	4	21	8	1	21	4	8
22	6	4				22	5	8
23	6	4				23	5	16
24	6	16				24	5	8
25	7	8				25	5	8
26	8	1				26	5	16
						27	6	4
						28	6	4
						29	6	8
						30	6	4
						31	6	8
						32	7	8
						33	8	1

Table 6.1 All symmetrically distinct alloy configurations in 1×1×2 Rocksalt, 2×2×1 wurtzite, and 2×1×2 wurtzite supercells (defined in Fig. 1). # (A) indicates the

number of A atoms in the alloy configuration and g_j is the degeneracy factor defined in Equation 6.4.

6.3 Results and discussion

6.3.1 Structures of the parent compounds

Before handling the main steps of this work, let us analyze the basic properties of the pure bulk materials (CaO, CdO, MgO and ZnO). The wurtzite structure, which contains two formula units per primitive cell, requires three parameters to specify with space group $P6_3mc$. These parameters are the lattice constant a , c (or the c/a ratio) and the dimensionless internal structural parameter u which is defined as the ratio of the length of the bond parallel to the c axis to the lattice constant c . In the ideal wurtzite structure characterized by equal bond lengths, c/a and u are 1.6333 and $3/8$, respectively. For the rocksalt structure, the only one degree of freedom required is the lattice constant a , since anion and cation occupy two different fcc lattice sites, respectively.

Compound	a (Å)		c (Å) (c/a)		u		V (Å ³ /pair)
	LDA	Exp.	LDA	Exp.	LDA	Exp.	LDA
CaO(“wurtzite”)	3.8939		4.6755 (1.201)		0.4997		30.70
CaO(Rocksalt)	4.6942	4.81 ^a					25.86
CdO(wurtzite)	3.5817		5.6659 (1.582)		0.3849		31.47
CdO(Rocksalt)	4.6561	4.696 ^b					25.23
MgO(wurtzite)	3.2786		4.8736 (1.486)		0.4046		22.68
MgO(Rocksalt)	4.152	4.212 ^c					17.89
ZnO(wurtzite)	3.2032	3.283 ^d 3.258 ^e	5.1386 (1.604)	5.309 ^d 5.220 ^e	0.3814	0.3786 ^d 0.382 ^e	22.83
ZnO(Rocksalt)	4.2110	4.275 ^f , 4.278 ^g , 4.271 ^h , 4.283 ⁱ					18.67

^a Reference⁷⁷

^d Reference⁷⁸

^g Reference⁷⁸

^b Reference⁷⁹

^e Reference⁸⁰

^h Reference⁸⁰

^c Reference⁸¹

^f Reference⁸²

ⁱ Reference⁸³

Table 6.2 The LDA-optimized lattice constants a and c (c/a), internal dimensionless parameter u and volume percent anion-cation pair V of CaO, CdO, MgO and ZnO with wurtzite and rocksalt structures. The (c/a) and u values for a perfect wurtzite structure are 1.6333 and 0.375 respectively. Some experimental data in literature are

listed for comparison.

The calculated equilibrium structural parameters of wurtzite and rocksalt CaO , CdO , MgO and ZnO are listed in Table 6.2 along with some experimental values for comparison. For the rocksalt structures, all the calculated values agree with the experimental ones within 2%. Hence, it is expected that the lattice parameters of the alloys can be described with similar accuracy in our calculation method. For wurtzite structures, we found that the agreement between our calculation and extensive experimental measurements on ZnO is of the same accuracy as those in the rocksalt form.

While the wurtzite CaO , CdO and MgO have not been successfully synthesized yet, our calculations reveals an interesting trend that the stability of a wurtzite phase (that is $\text{ZnO} > \text{CdO} > \text{MgO} > \text{CaO}$) is correlated with its deviation from the ideal wurtzite values. Our calculations show that wurtzite CdO is stable, with u (0.385) and c/a ratio (1.582) sufficiently close to the ideal values. The instability of wurtzite MgO and the possibility of spontaneous relaxation to the h - MgO structure (a hexagonal form of MgO where puckered wurtzite (001) layers are leveled out, leading to $u=0.5$) was discussed in the literatures^{70, 71}. In our $2\times 2\times 1$ and $2\times 1\times 2$ unit cell, wurtzite MgO remain as a stable minimum with a small barrier that separate the wurtzite MgO and the h - MgO structure. Such instability of wurtzite MgO is consistent with the significant deviation of u (0.405) and c/a ratio (1.486) from the ideal values. In our calculation wurtzite CaO is unstable in both $2\times 2\times 1$ and $2\times 1\times 2$ unit cell, where the wurtzite CaO relaxes to h - CaO structure with $u=0.5$ spontaneously. We will come back to this issue in section 6.3.3, where we shall analyze the stability of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Ca}_x\text{Zn}_{1-x}\text{O}$.

6.3.2 Formation enthalpy and phase stability

It is found that fourfold-coordinated (CN4) $B4$ phase (wurtzite structure) configurations have lower energy than their sixfold-coordinated (CN6) analogs (rocksalt structure) in Zn-rich region and the reverse situation occurs in Mg(or Ca,

Cd)-rich region. Since structural phase separation should occur in these alloy systems with different parent crystal structures, the analysis of the phase transition point is an important issue. The crossover of the CN4-CN4 and CN6-CN6 lines is determined by the end-point energies near $x = 0.43, 0.46$ and 0.59 for alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, respectively. These crossover concentrations can be regarded as a rough estimate to define the maximum concentration at which wurtzite phases are stable (it would be exact if there is no deviation from the Vegard's rule⁷²). The crossover concentration points of alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ are smaller (0.43 and 0.46) than that of alloy $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ (0.59), which is consistent with the fact that wurtzite MgO and CaO have larger value for the internal parameter u reflecting the stability of wurtzite structure. Here we should note that the crossover concentration point of alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ (0.43) is smaller than that of $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, which is due to the use of h - CaO structure in the calculation (Noted that wurtzite CaO is not stable and easy to be relaxed to h - CaO).

Beyond the Vegard's rule, we have calculated the total energy of all alloy configurations in the $1\times1\times2$ supercell of the $B1$ phase, the $2\times2\times1$ and $2\times1\times2$ supercells of the $B4$ phase, respectively. Formation enthalpies of these alloy configurations for $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ are depicted in Fig.6.2. For $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, significant deviation from Vegards' rule with $\Delta E_{B1}>0$ and $\Delta E_{B4}>0$ is apparent. The positive formation (mixing) enthalpy can be well understood by large size mismatch between the atomic constituents (Zn^{2+} : $0.74 \text{ \AA}$, Ca^{2+} : $0.99 \text{ \AA}$, Cd^{2+} : $0.97 \text{ \AA}$). $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, on the other hand, has small and negative ΔE_{B1} and ΔE_{B4} , which is consistent with the theoretical calculations reported by Sanati *et al.*²⁵ and the commonly accepted notion that there is less volume deformation in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ because of compatible size of Mg (Mg^{2+} : $0.72 \text{ \AA}$) and Zn (Zn^{2+} : $0.74 \text{ \AA}$) ions.

Taking into account of these alloy configurations, we can draw a region of phase transition for three alloys (depicted by the arrows in Fig. 6.2). For alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, the region is approximately $0.375 < x < 0.5$ as shown in Fig. 6.2c. The lower limit ($x=0.375$) is consistent with the result of experiment and other theoretical calculations for the stable wurtzite structure^{24, 25, 57}. The calculated phase transition region is

consistent with the recent experimental mixing region of two phases ($0.34 < x < 0.65$) by Vashaei and coworkers¹⁹. For $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, the regions are approximately $0.75 < x < 0.875$ and $0.25 < x < 0.375$, as shown in Fig. 2b and 2a. The stable wurtzite $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ with $x \leq 0.69$ reported recently³⁶ by Ishihara *et al.*³⁶ are consistent with wurtzite stable region of the theoretical calculation here. The large stable region of wurtzite $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ seems to be understandable because pure crystal CdO has relative stable wurtzite structure, as shown in Table 6.2.

Fig. 6.2 Formation Enthalpy of all symmetrically distinct alloy configurations in $1 \times 1 \times 2$ B1 phase supercell (black “x”), $2 \times 2 \times 1$ B4 phase supercell (black square) and $2 \times 1 \times 2$ B4 phase supercell (red empty diamond). Three lines connect the ends for each

alloy system: two dash dot lines for AO ($A=\text{Ca}, \text{Cd}$ and Mg)-ZnO with B1 phase and B4 phase, one dot line for AO (B1)-ZnO (B4).

The enthalpies $\Delta E_{B1, B4}$ that are taken with respect to the most stable form of parents materials are all positive for the three alloy systems. This means the alloy systems are unstable at zero temperature. Since the effect of temperature need to be considered in the actual process of material synthesis, the mixing entropy should not be ignored in analyzing the stability of alloy system. In the nonmagnetic alloy system, the mixing entropy usually includes the parts of configuration, vibration and electron. Normally, electron excitation has very high characterization temperature, so the mixing entropy induced by electron excitation is small and can be ignored. The major part is the mixing entropy induced by the configurations. Considering the formation enthalpy is in the range of ~ 100 meV/cation at zero temperature, it will need the high temperature ($\sim 2000\text{K}$) to counteract the positive formation enthalpy by the mixing entropy induced by the configurations for the three alloy systems. Usually, the mixing entropy by the vibration will reduce the temperature of thermo-equilibrium state to $\sim 10\%$. Therefore, the high temperature needed by the thermo-equilibrium state implies the alloy system made from the nonisostructural components will be easy to experience phase separation and there will be the low solubility for each one of parent phases. For the alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, this has been confirmed by the observation of the low solubility limit of Mg in ZnO for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ⁷³. Actually, the success in fabricating the single-phase alloy with higher concentrations is based on today's epitaxial growth techniques (P-MBE, L-MBE, RP-MOCVD, and so on) that allow for the extremely non-equilibrium growth condition. For an example, in the process of the epitaxial growth of the oxide materials by P-MBE, the temperature of the substrate usually is in range of $\sim 400 - \sim 1000\text{K}$. In addition, under so low temperature of growth, the surface of the substrate will have an important effect for the lattice relaxation that phase separation need. As Andrei *et al.*⁷⁴ considered, the phase separation is kinetically limited⁷⁴. At the low temperature, the time that the alloy needs to segregate into the parent lower-energy constitutions by lattice relaxation will be much longer than that

of the epitaxial growth with a single phase due to the surface transfer of atoms or atomic clusters. Therefore, the local single alloy phase would be formed as the observation of the experiments.

6.3.3 Structural properties of the alloys in B4 phase

To obtain the statistic average of local environment effect, the structural properties will be analyzed in the $2\times 2\times 1$ and $2\times 1\times 2$ supercell for wurtzite structure. The lattice constants of all the alloy configurations and the averaged lattice constants calculated via Equation 6.4 for $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ are shown in the upper panels of Fig. 6.3 (a), (b) and (c), respectively. The agreements between theoretical calculations and the experimental results for alloys $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ are comparable with the results of the pure materials (in Table 6.2). The slight underestimate of the lattice constants by theoretical methods is inline with the well-known tendency for DFT/LDA to overbind. Furthermore, we should note that the lattice constants of different alloy configurations of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ can differ by $0.4 \text{ \AA}$ at $x = 50\%$. This is a reminder that sufficient alloy statistics must be included in order to faithfully reflect the structural properties.

Fig.6.3 Calculated lattice constants a (presented by $\triangleleft$) and c (presented by $\triangleright$) of all

the alloy configurations and averaged lattice constants (red line) for three alloy systems $A_xZn_{1-x}O$ ($A=Ca, Cd$ and Mg) are shown in the upper panels. Experimental data (different symbols) from ref. 22, 57, 5 and 36 ($Mg_xZn_{1-x}O$ ref.22, 57 and $Cd_xZn_{1-x}O$ ref. 5, 36) are shown for comparison. Lattice parameter u of alloy configurations (noted that black diamonds are for $2\times 2\times 1$, red one for $2\times 1\times 2$) and averaged lattice parameter (red line) are shown in the lower panels.

The averaged lattice constants of the three alloys are compared with linear behavior governed by Vegard's law⁷². For $Cd_xZn_{1-x}O$, we can see the averaged lattice constants of both a and c have a linear dependence with the concentration. Nevertheless, for alloy $Ca_xZn_{1-x}O$ and $Mg_xZn_{1-x}O$, significant deviation for Vegard's law is observed. In $Mg_xZn_{1-x}O$, the sudden increase in a (and decrease in c) at $x \sim 0.80$ indicates that the wurtzite $Mg_xZn_{1-x}O$ becomes unstable and has a tendency to form h - $Mg_xZn_{1-x}O$ (see discussion on the lattice parameter u latter). For alloy $Ca_xZn_{1-x}O$, dramatic change of lattice constant c is observed between $0.375 < x < 0.625$ which means that structural phase transition (from wurtzite to hexagonal) should occur in the region.

The averaged u for all alloy configurations are shown for the three alloys in the lower panel of Fig. 6.3. The concentration dependence of the mean value u has the same trends with that of the lattice constants. This trend is actually the reflection of phase stability as a function of the concentration of A (Ca, Mg, Cd) for wurtzite structure. For an example, the mean values u of $Ca_xZn_{1-x}O$ almost reaches 0.5 for $x > 0.5$. This result combined with the dramatic change of lattice constants c is a direct indicator that wurtzite CaO is not stable and the metastable form of pure crystal CaO should be a hexagonal phase. For each configuration of each concentration, the values of lattice parameter u have larger variations in alloys $Ca_xZn_{1-x}O$ and $Cd_xZn_{1-x}O$ than $Mg_xZn_{1-x}O$. This phenomenon is partly attributed to the larger ionic radius of Cd^{2+} and Ca^{2+} than that of Zn^{2+} and the close radius of Mg^{2+} to that of Zn^{2+} .

The calculated nearest-neighbor (NN) bond lengths d_{A-O} and d_{Zn-O} for all alloy configurations and the mean values (via Equation 6.4) are shown in Fig. 6.4. The individual NN bond lengths d_{A-O} and d_{Zn-O} in the alloy are found to be closer to the

pure bulk values than the concentration weighted average values for the three alloy systems.

Fig.6.4 Nearest-neighbor bond length (Δ for A-O and ∇ for Zn-O) of the alloy configurations and averaged bond length (red line) as a function of concentration x for three alloy systems $A_x\text{Zn}_{1-x}\text{O}$ ($A=\text{Ca}, \text{Cd}$ and Mg).

Here we note that the difference of bond length of Zn-O and that of Mg-O bonds is very small in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ that can be contributed to the similar size of Mg^{2+} radius and Zn^{2+} radius. This may be the important reason why the formation energy of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy is negative if we just consider the isostructural $B4$ phase and ignore

the metastability of $B4$ MgO. It is deduced that the ordered $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ alloy with wurtzite structure will be possible to be grown in rich-Zn region by epitaxial growth techniques. It is more interesting to note while the length of NN Mg-O bond in pure MgO is larger than that of NN Zn-O bond in pure ZnO, all the NN Mg-O bond lengths in alloys are shorter than that of NN Zn-O bonds in $\text{Mg}_x\text{Zn}_{1-x}\text{O}$. While the exact origin is not known, this unique feature implies that the Mg-O bonds are strengthened in the alloy configurations.

6.3.4 Band gap and bowing parameter

As a fundamental property of the optoelectronic materials, the fundamental energy gaps of the alloys are studied in this part. Since wurtzite CaO, MgO, CdO and ZnO all have the fundamental gaps with the $\Gamma_c(\text{min}) \rightarrow \Gamma_v(\text{max})$ energy transition, it is reasonable to expect that the three alloy systems with wurtzite structures would also have direct band gaps. So the LDA-calculated band gaps of each configuration in the $2 \times 2 \times 1$ and $2 \times 1 \times 2$ supercells are extracted by just analyzing the Γ point energy levels.

Compound	LDA	Experiment	‘Predicted’
CaO (“wurtzite”)	3.25		7.63*
(Rocksalt)	3.42	7.8 ^c	
CdO (wurtzite)	-0.34 ^a		0.91*
(Rocksalt)	1.03	2.28 ^b	
MgO (wurtzite)	3.53		6.34*
(Rocksalt)	5.09	7.9 ^c	
ZnO (wurtzite)	0.81	3.43 ^c	
(Rocksalt)	2.61		5.23*

^a Reference⁵²

^b Reference⁸⁴

^c Reference⁸⁵

Table 6.3 Band gaps of CaO, CdO, MgO and ZnO with wurtzite and rocksalt structures. First column shows the band gaps at Γ point calculated by LDA method (noted that the calculated value of wurtzite CdO from ref. 52). Experimental data in literature are listed in the second column for comparison. The “predicted” band gaps (shown in the third column) for those thermodynamically un-stable forms are obtained by shifting the LDA-calculated bandgaps at Γ -point by the difference between the LDA-calculated and experimental values of the same oxides in their thermodynamically stable phase.

The calculated Γ point band gap of the pure compounds CaO, MgO, CdO and ZnO are compared with the experimental values in Table 6.3. The large error in the band gap is a well-known problem of the LDA, which fails quantitatively in dealing with excited-state properties. For wurtzite MgO and CdO, the expected experimental values are obtained by using the same correction for both wurtzite and rocksalt structures as Anderson *et al.* assumed⁵². The same method is applied to yield the “predicted” (or expected experimental) values for rocksalt ZnO. These experimental and “predicted” band gaps of the bulk materials will be used to correct the band gaps of the alloy configurations.

Quasiparticle corrections for the band gap have been shown to vary almost linearly with the composition in ternary nitride alloys⁷⁵. It is reasonable to expect that the same correction relation is valid for ternary oxide alloys. We have therefore applied a linear shift in the band gap for alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ in order to match the experimental values for the band gaps of the parent materials. Since the credible band gaps of wurtzite and rocksalt CaO are not known, we have only shown the raw LDA-calculated value for $\text{Ca}_x\text{Zn}_{1-x}\text{O}$.

Fig.6.5 The band gaps as a function of concentration for three alloy systems $A_x\text{Zn}_{1-x}\text{O}$ ($A=\text{Ca}, \text{Cd}$ and Mg). LDA-calculated band gaps at the Γ -point are shown as empty

squares. The “corrected” band gaps (empty diamonds) and the average “corrected” band gaps of each concentration (red line) are compared to the experimental data (different black symbols) for alloy $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ (ref.57) and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ (ref.30). Note that the band gaps of $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ are not “corrected” due to the lack of reliable experimental value of the bulk wurtzite CaO .

The original calculated values, the corrected calculated values and the experimental values are illustrated in Fig.6.5. A small downward bowing of the band gaps for the calculated values and the experimental value is clearly seen, and we will elaborate on the bowing parameter later. The band gaps of different alloy configurations with the same concentration can be quite different, for example, the band gaps of $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{O}$ can differ by 1 eV. This observation signifies the importance of considering the alloy statistics when analyzing the electronic properties. From Fig. 5c, the corrected calculated band gaps of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ are generally larger than the experimental value. This trend is expected and can be attributed to the fact that experimental values were obtained at room temperature and the disordered excited states existed in the sample that is due to the thermal effect of the process of growth. From Fig. 6.5b, we can see that the experimental band gaps of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ can be greater than our calculated values. This may be due to the underestimate of the theoretical band gap of the pure crystal CdO , as well as the potential errors in experimental measurements.

Because of the importance of fundamental band gap for device design, its nonlinear dependence on the concentration needs further qualitative understanding and quantitative analysis. Through the simple theory analysis such as the perturbation scattering theory, it is considered that a quadratic function of the concentration can be used to describe the downward shift of the band gap of the alloy from the linear average, by defining a bowing coefficient b as⁷⁶:

$$E_g(A_xB_{1-x}C) = x \cdot E_{AC}(a_{AC}) + (1-x)E_{BC}(a_{BC}) - b \cdot x(1-x). \quad (6.5)$$

In order to deduce the bowing parameters b_{MgZnO} and b_{CdZnO} , we first calculated the averaged band gaps as a function of the concentration based on Equation 6.4. It is

apparent that the averaged band gaps of “wurtzite” $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, does not follow a simple quadratic form. This strange trend is linked to instability of bulk wurtzite CaO and we found that in Ca-rich region the dominating structures are closer to h - CaO rather than the wurtzite phase.

The averaged band gaps of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ can be well fitted with formula 6.5 and we found the bowing parameters are $0.87\pm 0.03\text{eV}$ and $1.03\pm 0.05\text{eV}$ for alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, respectively.

6.4 Conclusions

In summary, we have presented systematical studies of phase stability, structural and electronic properties of three zinc-based oxide alloy systems ($\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$) by first-principles calculations. In order to consider the importance of the alloy statistics, the phase stabilities of the isovalent alloy with nonisostructural compounds are analyzed by examining all alloy configurations in three different 8-cation supercells ($1\times 1\times 2$ $B1$ phase structure, $2\times 2\times 1$ and $2\times 1\times 2$ $B4$ phase structure). We have used the symmetry of the bulk materials to reduce the 2^8 complexities to about 20 to 30 distinct alloy configurations for each supercell.

The overall mixing energies of these alloys are positive which indicates that the alloy phases with either wurtzite or rocksalt are not stable with respect to their parent materials. This suggests that the successful fabrication of alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ with broad composition ranges should be attributed to the non-equilibrium growth condition offered by the today’s epitaxial growth techniques that kinetically limits the phase separation process. $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ is found to be problematic partially due to the instability of the wurtzite CaO . Taking into account of the alloy statistics, we have drawn the regions of phase stability for $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($0.375 < x < 0.5$) and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ ($0.75 < x < 0.875$). These regions are inline with the experimental works of Vashaei *et al.*¹⁹ and Ishihara *et al.*³⁶.

The structures of the three alloys in $B4$ phase were analyzed by examining their lattice constants and averaged structure parameters (u). We found that the lattice constants of $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ follow the Vegard’s rule, while that of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and

$\text{Ca}_x\text{Zn}_{1-x}\text{O}$ have notable deviation for $x > 70\%$ and $x > 50\%$ respectively. Inspecting the structure parameters (u), we found that the significant deviation from Vegards' rule in $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ is associated with the instability of the wurtzite CaO .

For alloy $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, the calculated band gaps are generally consistent with the experimental values, considering the error of experimental measurement and the veracity of the LDA correction. The bowing parameters are calculated and found to be 0.87eV and 1.03eV for alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, respectively.

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Chapter 7

A Comprehensive Theoretical

Study of Thermal Stability and Electronic Properties of Wurtzite and Zincblende $\text{ZnO}_x\text{S}_{1-x}$

In this chapter, a comprehensive theoretical study on the thermodynamic stability and electronic properties of wurtzite (WZ) and zincblende (ZB) $\text{ZnO}_x\text{S}_{1-x}$ as been carried out with first-principles methods with special quasi-random structures (SQS) and quasi-ordered structures (QOS). SQS are employed to model the random alloys and from the calculated phase diagram, it is clear that the solubility limits in mother lattices (sulfur-doped WZ-ZnO and oxygen-doped ZB-ZnS) are very small for both WZ and ZB phases. Detailed electronic and structural properties of QOS were investigated by examining alloy configurations in different supercells. It is found that the concentration dependence of the band gap is highly nonlinear and the large bowing coefficients are also sensitive to the composition. The intriguing difference in band gaps and bowing coefficient between WZ- and ZB- $\text{ZnO}_{1-x}\text{S}_x$ is evident. This result predicts that the band gap bowing with the WZ structure can be quite different from that with the ZB structure in some semiconductor alloys and deserves further experimental investigations for verification.

7.1 Introduction

ZnO is a promising candidate for optoelectronic and spintronics devices due to its unique physical properties, such as the large exciton binding energy (60 meV)¹⁻³. Two important issues toward the development of ZnO-based ultraviolet optoelectronic technologies are (1) to engineer the band gap^{4,5} and (2) to obtain the stable *p*-type conductivity⁶. For band gap engineering, band structure can be modified by substitution of isoelectronic anions or cations in ZnO. While a lot of experimental and theoretical work on cations-substituted alloys, such as $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and

$\text{Be}_x\text{Zn}_{1-x}\text{O}$ has been carried out⁷⁻¹², relatively less attention has been paid to anion doping. One of problems in the process of alloying $\text{ZnO}_x\text{S}_{1-x}$ originates from the significant difference between the stability of ZnS and ZnO at film growth temperature¹³⁻¹⁵. On the other hand, the large difference in the electronegativity between O and S is likely to result in a larger bowing parameter in $\text{ZnO}_x\text{S}_{1-x}$ ¹⁵. Thus, it would be a possibility to achieve wide band gap modulation with low fraction of S in ZnO.

In spite of on-going efforts, obtaining stable *p*-type ZnO is still a challenging task^{6,16,17}. Ashrafi *et al.*¹⁸ suggest that Zincblende (ZB) ZnO phase is expected to solve this long standing problem. However, few reports were found on ZB ZnO epitaxial growth to date, due to the lack of suitable substrates¹⁹⁻²². It was proposed that ZB ZnOS/ZnS thin alloy layers can be used as the interlayer and/or nucleation layers for the ZB ZnO film epitaxy^{19,20,22}. Furthermore, ZnOS alloy layer can be used to improve ZnO device performances. For example, it has been shown that the use of ZnOS buffer layer can effectively enhance the conversion efficiency of Cu(In,Ga)Se₂ based thin film solar cells²³. Pt contacts on S treated *n*-type ZnO results in Schottky behavior in contrast to the Ohmic interface of untreated Pt/ZnO²⁴. Recently, the valence-band offset bowing of $\text{ZnO}_{1-x}\text{S}_x$ was reported to enhance *p*-type nitrogen doping of ZnO-like alloys²⁵. Previous theoretical calculations of ZnSO alloy mainly focused on ZB $\text{ZnO}_{1-x}\text{S}_x$ alloy^{15,26,27}. For example, Ito *et al.* studied the phase stability of ZB $\text{ZnO}_{1-x}\text{S}_x$ alloy with valence force field (VFF) method²⁶. Moon *et al.* studied the electronic properties of ZB $\text{ZnO}_{1-x}\text{S}_x$ alloy by combining special quasi-random structures (SQS) with first-principles calculation¹⁵. To our knowledge, there isn't any theoretical study about the ZB/WZ phase stability of ZnOS alloy by following the change of compositions (oxygen and sulphur).

The special role of $\text{ZnO}_{1-x}\text{S}_x$ alloy in further developments of ZnO-based optoelectronics provides essential motivation for this work. We engaged systematic first-principles calculations to compare the thermal stability between wurtzite and zincblende structures. In particular, the composition-temperature (*x-T*) phase diagram is obtained to shed new lights to the growth process of $\text{ZnO}_x\text{S}_{1-x}$. Moreover, we have

also investigated the structural and electronic properties of the alloys with different phases. These fundamental physical properties will be important for designing and optimizing the growth of the related quantum wells and superlattices.

The remainder of this chapter is structured as follows. In Sec. 7.2, we will discuss the methodology used. In Sec. 7.3, we will first show the calculated x - T diagram and compare our results with recent experimental works. Second, we will discuss formation energy, lattice constants and the electronic structures of alloy configurations in different supercells, in particular, the bowing parameter is found to be quite different for the wurtzite and zincblende structures. This chapter concludes with a short summary.

7.2 Computational methods and theoretical model

The importance of the local chemical environment such as charge transfer and local structural relaxation in determining the thermodynamic and electronic properties of alloy has received considerable attention over the past few decades. It has been shown that the effects of disorder and local correlation of the atomic arrangements on the stability and structure of alloys can be modeled with a moderate-sized supercell, because the most important physical properties can be analyzed correctly by considering the correlation of nearby neighbors²⁸. The SQS method, developed by Zunger *et al.*²⁹ in which the short and intermediate range correlations are considered can be used to efficiently study the random alloy systems. In this work, SQS with 32 atoms is employed for modeling the thermodynamics properties of WZ and ZB $\text{ZnO}_{1-x}\text{S}_x$ alloys. The SQS of this size was found to be effective when dealing with other alloy systems such as $\text{In}_x\text{Ga}_{1-x}\text{N}$ ³⁰.

Modern epitaxial growth techniques (P-MBE, LMBE, RP-MOCVD) usually operate at non-equilibrium conditions. Therefore, samples grown are not able to reach thermal equilibrium and are likely to results in short range ordering. To study these alloy structures with quasi-ordering, we begin by constructing all configurations in three different 16-atom supercells. For the zincblende structure, a $1\times 1\times 2$ supercell (shown in Fig. 7.1a) is used. For the wurtzite structure, we have considered $2\times 2\times 1$

and $2 \times 1 \times 2$ supercells (shown in Fig. 7.1b and 7.1c). The $2^8=256$ alloy configurations in each of the three supercells have been simplified by eliminating the symmetrically equivalent ones¹⁰. We found there are 27, 22, and 34 symmetrically distinct configurations in ZB- $1 \times 1 \times 2$, WZ- $2 \times 2 \times 1$ and WZ- $2 \times 1 \times 2$ supercells respectively. The averaged electronic properties of these quasi-ordered structures can be analyzed by including the contribution of all the alloy configurations with the same concentration and using the following formula:

$$\langle P(x) \rangle = \sum_{i=1, i_{\max}} g_i P_i / \sum_{i=1, i_{\max}} g_i, \quad (7.1)$$

where P_i is the property of the i -th configuration, g_i is the degeneracy factor arising from the symmetry of the i -th configuration, and $i_{\max}$ is the number of symmetrically distinct configurations at the concentration x . Noted that the summation is limited to those configurations with concentration x .

Fig.7.1 Illustration of $1 \times 1 \times 2$ B3 phase supercell (a), $2 \times 2 \times 1$ B4 phase supercell (b) and $2 \times 1 \times 2$ B4 phase supercell (c). Red spheres represent the O atoms and grey spheres represent the Zn atoms.

1×1×2 ZB			2×2×1 WZ			2×1×2 WZ		
No. # (O)	g_j		No. # (O)	g_j		No. # (O)	g_j	
0	0	1	0	0	1	0	0	1
1	1	8	1	1	8	1	1	8
2	2	4	2	2	12	2	2	4
3	2	4	3	2	12	3	2	4
4	2	16	4	2	4	4	2	8
5	3	16	5	3	8	5	2	4
6	4	4	6	3	24	6	2	8
7	3	16	7	3	24	7	3	8
8	4	8	8	4	2	8	3	16
9	2	4	9	4	6	9	3	8
10	3	8	10	4	8	10	3	16
11	4	6	11	4	24	11	3	8
12	3	16	12	4	6	12	4	16
13	4	8	13	4	24	13	4	16
14	4	8	14	5	24	14	4	2
15	4	32	15	5	8	15	4	4
16	5	16	16	5	24	16	4	8
17	5	16	17	6	12	17	4	2
18	5	8	18	6	12	18	4	4
19	6	4	19	6	4	19	4	8
20	6	4	20	7	8	20	4	2
21	4	4	21	8	1	21	4	8
22	5	16				22	5	8
23	6	16				23	5	16
24	6	4				24	5	8
25	7	8				25	5	8
26	8	1				26	5	16
						27	6	4
						28	6	4
						29	6	8
						30	6	4
						31	6	8
						32	7	8
						33	8	1

Table 7.3 All symmetrically distinct alloy configurations in 1×1×2 Rocksalt, 2×2×1 wurtzite, and 2×1×2 wurtzite supercells (defined in Fig. 7.1). #(O) indicates the number of O atoms in the alloy configuration and g_j is the degeneracy factor defined in Equation 7.1.

In this work, the structural and electronic properties of all the alloy configurations described above are examined by the density functional theory (DFT) under local density approximation (LDA)³⁰⁻³² along with the projector augmented wave (PAW) method³³⁻³⁵ as implemented in the VASP program package^{36,37}. The PAW potentials used for Zn treat $4p$ electrons in the valence. The k -space integral and plane-wave basis, as detailed below, are tested to ensure the total energy is converged at the 1 meV/cation level. the kinetic energy cutoff of 600 eV for the plane wave expansion is found to be sufficient, while different Monkhorst-Pack type³⁸ k -point meshes are chosen for the different supercells. For the ZB- $1\times 1\times 2$ supercell, a $5\times 5\times 3$ Monkhorst-Pack type mesh is chosen in the first Brillouin zone. With regard to the wurtzite structures, the $3\times 3\times 4$ and $3\times 5\times 3$ Monkhorst-Pack type mesh are chosen for the WZ- $2\times 2\times 1$ and WZ- $2\times 1\times 2$ supercells. In order to enable the alloy configurations to converge to their most stable conformation, all atomic positions and the lattice constants are fully relaxed. The total energies are obtained after the energy minimization is finished. The band gap at Γ -point is estimated after a self-consistent calculation that can generate high quality charge density is finished with the optimized geometrical structure.

7.3 Results

7.3.1 Basic Properties of the Parent Materials

The LDA-calculated structural parameters of WZ and ZB ZnO and ZnS are listed in Table 7.1. All calculated values agree with the experimental ones within 2%. Hence, it is reasonable to expect that the lattice parameters of the alloys can be described with similar accuracy in our calculations. Usually, the larger ionicity will induce the smaller c/a ratio in the WZ structures¹⁸. From the calculated c/a ratio, Zn-O bond have more ionic characteristic than Zn-S bond. It is well known that compounds with stronger polar bonds will have a tendency to crystallize in structures with larger Madelung constants. Since the Madelung constant ($\text{MC}_{\text{WZ}}=1.641$) of wurtzite structure is greater than that of zincblende structure ($\text{MC}_{\text{ZB}}=1.638$), it is reasonable that

ZnO prefer to crystallize in WZ structure, and ZnS prefer to crystallize in ZB structure.

We found that WZ ZnO is more stable than ZB ZnO by 14.87 meV/cation and the reverse situation occurs for ZnS (ZB ZnS is more stable than WZ ZnS by 11.16 meV/cation). The small differences of the total energy between WZ and ZB forms of ZnO and ZnS are due to the subtle differences between wurtzite and zincblende structure. This is reasonable as ideal wurtzite and zincblende structures are quite similar and only differ from the third-nearest neighbor onward.

Compound	a (Å)		c (Å) (c/a)		U	
	LDA	Exp.	LDA	Exp.	LDA	Exp.
ZnO(wurtzite)	3.205	3.258 ^a	5.149 (1.606)	5.220(1.602) ^a	0.381	0.382 ^a
	3.283 ^b			5.309(1.617) ^b		0.379 ^b
ZnO(zincblende)	4.501	4.570 ^c				
		4.595 ^{e,f}				
ZnS(wurtzite)	3.744	3.820 ^d	6.148 (1.642)	6.260(1.639) ^d	0.374	
ZnS(zincblende)	5.302	5.405 ^c				

^a Reference⁴⁸

^b Reference⁴⁹

^c Reference⁴⁴

^d Reference⁵⁰

^e Reference²¹

^f Reference¹⁸

Table 7.1 The LDA-optimized lattice constants a and c (c/a), internal dimensionless parameter u for $B4$ phase (ZnO and ZnS) and lattice constant a for $B3$ phase (ZnO and ZnS). c/a and u values for a perfect wurtzite structure are 1.633 and 0.375 respectively. Some Experimental data in literature are listed for comparison.

7.3.2 Composition-temperature diagram

For alloy materials with non-isostructural parent compounds, the formation enthalpies of these SQS structures with different phases can be expressed as:

$$\Delta H_{B3,B4}(\sigma, x) = E_{\gamma}(\sigma, \text{ZnO}_x\text{S}_{1-x}) - x \cdot E_{B4}(\text{ZnO}) - (1-x) E_{B3}(\text{ZnS}), \quad (7.2)$$

where γ can be either WZ or ZB. The formation enthalpies of the SQSs are shown in Fig. 7.2. We fit the data of the zincblende structures to the form $\Delta H = (\alpha + \beta x) \cdot x \cdot (1-x) +$

$14.87x$ and obtain $\alpha=0.689$ eV/cation and $\beta=0.007$ eV/cation. For the wurtzite structures, we found to $\Delta H = (0.681 - 0.043x) \cdot x \cdot (1-x) + 11.16 \cdot (1-x)$. From the crossover of two curves (shown in Fig. 6.2), we can roughly estimate that the phase transition point should be around $x=0.25$. In addition, it can be found from the Fig. that the formation enthalpy curve of the ZB ZnOS alloy is more symmetric than that its WZ counterpart.

Fig.7.2 Formation Enthalpy of wurtzite (WZ) and zincblende (ZB) random alloy $\text{ZnO}_x\text{S}_{1-x}$ (SQS-16) as a function of composition x . The solid curve is a fit to the calculated values.

At finite temperature, the thermal stability of the solid state system is determined by the Helmholtz free energy³⁹, $\Delta F(x,T) = \Delta H(x,T) - T\Delta S(x,T)$, where ΔH is the mixing energy (formation enthalpy) and ΔS is the mixing entropy. Within the mean-field approximation, the entropy is given by $\Delta S(x) = k_B [x \ln x + (1-x) \ln(1-x)]$, where k_B is the Boltzmann constant. The binodal curve, which indicates equilibrium solubility limits as a function of temperature, can be calculated by the common tangent approach from the Helmholtz free energy. As shown in Fig. 7.3, the critical temperatures, above which complete miscibility is possible for some concentration, are 4018 K and 3831 K for ZB and WZ phases, respectively. These high critical

temperatures reveal that it will be difficult to mix randomly ZnO and ZnS whether the alloy is synthesized as ZB or WZ structure. For example, the solubility limit is less than 2% at growth temperature of ~ 1000 K.

Fig. 7.3 The x - T phase diagram of random alloy $\text{ZnO}_x\text{S}_{1-x}$ (SQS-16) with $B3$ (ZB) and $B4$ (WZ) phases. (Solid line for ZB binodal curves and dashed line for WZ binodal curves. Circles for WZ spinodal curves and cross for ZB spinodal curves.)

With the spinodal curve, we can draw out the region of metastability. On the O-rich side, the ranges of metastable region are relatively larger for $B4$ (WZ) phase than for $B3$ (ZB) phase. In S-rich side, the reverse situation occurs. The concentration is more than 92% in O-rich region for $B4$ phase and the limit of phase separation is 7% in S-rich region for $B3$ phase at growth temperature 1000 K. The values are consistent with recent experimental results where the author achieves the zincblende structure $\text{ZnO}_x\text{S}_{1-x}$ for $0 \leq x \leq 0.4$ and the wurtzite structure $\text{ZnO}_x\text{S}_{1-x}$ for $95\% \leq x \leq 1$ in bulk crystal⁴⁰. Therefore, combining SQS structure with mean-field approximations, we can obtain properly the concentration-temperature phase diagram of ZnOS with $B3$ or $B4$ phase in the condition of thermodynamic equilibrium. Here, we should point it out that the contribution of phonon to the free energy is not included in the calculations due to the large computational costs. According to a previous study on

the phonon entropy in InGaN^{30} , the critical temperature should be reduced to $\sim 20\% \sim 30\%$ after the lattice vibration is taken into account. This will result in that the experiment result fall in the vicinity of the stable region from the calculations and make the theoretical calculation is more consistent with the experimental data. Additional, it is found that the critical temperature still remain high for $\text{ZnO}_x\text{S}_{1-x}$ alloys. This means the random mixing of ZnO and ZnS for all the composition range is actually difficult under the thermal equilibrium conditions, whatever with WZ and ZB structure.

7.3.3 Quasi-ordered structures

In the modern optoelectronic devices, the active mediums usually have the form of thin film grown by various epitaxial techniques. The non-equilibrium environments offered by these techniques will result in a wider range of the alloy concentration. As Yoo *et al.*¹³ reported, the range of concentration is $0.85 < x < 1$ for the $\text{ZnO}_x\text{S}_{1-x}$ films by pulsed laser deposition. By RF reactive sputtering, Meyer *et al.*⁴¹ even extend the composition range to $0 \leq x \leq 1$ in the temperature ~ 620 K. The increase of the composition range can be attributed to the existence of the quasi-ordered structure induced by the non-equilibrium conditions.

In Fig. 7.4a, we show the formation energy of all quasi-ordered configurations in the three supercells shown in Fig. 7.1. For ZB $\text{ZnO}_x\text{S}_{1-x}$, the metastable ground states are at the concentration 25% with Famatinite structure and at concentration 50% with Chalcopyrite structure. Both of these two structures are layer structures oriented along the (201) crystallographic direction. This finding is consistent with the report by Liu *et al.*⁴² in which they have shown that isovalent zincblende alloys can exhibit ordered coherent, tetrahedral networks characterized by alternate atomic bilayers along the (201) direction. For WZ $\text{ZnO}_x\text{S}_{1-x}$, we find that the alloy configurations in the WZ- $2 \times 2 \times 1$ supercell are in general more stable than that in WZ- $2 \times 1 \times 2$ supercell and this appears to be a general trends in cation-substituted II-VI alloys¹⁰. The metastable ground states are at concentration 25%, 50% and 75%, respectively.

Compared these quasi-ordered structures to the random SQS structures, it is clear

that some of quasi-ordered ground states have relatively lower formation energy, and therefore they are more likely to exist in samples prepared by epitaxial growth. At the concentration of 50%, the energy of the ZB Chalcopyrite structure is lower than the wurtzite ground state. This means, at the range of $0 \leq x \leq 0.5$, the alloy film will tend to form in zincblende structure under the highly non-equilibrium epitaxial conditions. Our finding here is inline with the idea of using ZB $\text{ZnO}_x\text{S}_{1-x}$ alloy as the nucleation layers for the ZB ZnO film growth, since it is easy to grow ZB $\text{ZnO}_x\text{S}_{1-x}$ in low temperature.

Fig.7.4 (a) Formation Enthalpy of all symmetrically distinct alloy configurations in $1 \times 1 \times 2$ $B3$ phase supercell (red crosses), $2 \times 2 \times 1$ $B4$ phase supercell (blue diamonds) and $2 \times 1 \times 2$ $B4$ phase supercell (violet circles). (b) The lattice constants of $\text{ZnO}_x\text{S}_{1-x}$ as a function of O concentration are shown. Note that red triangle for the configurations

in $2 \times 2 \times 1$ $B4$ phase supercell and violet triangle for the configurations in $2 \times 1 \times 2$ $B4$ phase supercell.

In addition, the lattice constants of all quasi-ordered ordered configurations are calculated and shown in Fig. 7.4b. The lattice constants of $\text{ZnO}_x\text{S}_{1-x}$ alloy with WZ or ZB vary linearly with the change of the oxygen concentration as indicated by the XRD experiment results⁴¹. This linear behavior governed by Vegard's rule shows both phases will be structural stable in all the range of concentration and therefore further supports that using ZB $\text{ZnO}_x\text{S}_{1-x}$ alloy as the nucleation layer will be beneficial to the growth of ZB ZnO film.

7.3.4 Electronic properties

As an optoelectronic material, the fundamental energy gaps of $\text{ZnO}_x\text{S}_{1-x}$ alloys deserve a more detailed investigation. The LDA-calculated band gaps of the binary constituents (ZnS and ZnO) with WZ and ZB structures are tabulated and compared with the experimental values in Table 7.2. The systematic underestimation of the LDA-calculated band gap is a well known problem of the LDA^{43,44}, which fails quantitatively in dealing with excited-state properties. In order to compare with the experimental report, the LDA band gaps are “corrected” by linear interpolation to fit the bulk values of WZ-ZnO and ZB-ZnS to yield the “predicted” values as suggested by Janotti *et al.*⁴⁵. The ‘predicted’ values of ZB-ZnO and WZ-ZnS by the above procedure are comparable with the values obtained in experiments.

compounds	LDA	experiment	“predicted”
ZnO (wurtzite)	0.81	3.43	
ZnO (zincblende)	0.71	3.30	3.33
ZnS (wurtzite)	2.24	3.91	3.94
ZnS (zincblende)	2.14	3.84	

Table 7.2 Band gaps of ZnO and ZnS with zincblende and wurtzite structures. First column shows the band gaps at Γ point calculated by LDA method. The “predicted” band gaps (shown in the third column) for those meta-stable forms are obtained by shifting the LDA-calculated band gaps by the difference between the LDA-calculated and experimental values of the oxides in their stable phases. Experimental data (ref. 47) are listed in the second column for comparison.

Fig.7.5 The band gaps as a function of concentration for structure-ordered alloy $\text{ZnO}_x\text{S}_{1-x}$ with $B3$ and $B4$ phases. (a) LDA-calculated band gaps and the averaged band gaps for each concentration (b) the “corrected” averaged band gap (read diamonds and blue squares), the fitted gap-composition curves (solid curves) and the experimental data (magenta squares)

Since both ZnS and ZnO have the fundamental energy gaps with the direct

$\Gamma_c(\text{min}) \rightarrow \Gamma_v(\text{max})$ transition, the LDA-calculated band gaps of each configuration are extracted by analyzing the Γ -point energy levels. The original LDA calculated values are shown in Fig. 7.5a. The band gaps of the ZB configurations are consistently larger than that of WZ configurations. This may be a result of the crystal-field splitting in WZ structure due to its relatively lower symmetry. The band gaps of different alloy configurations with the same concentration can be quite different, for an example, the band gaps of $\text{ZnO}_{0.5}\text{S}_{0.5}$ can differ by more than 1 eV. This diversity in the band gap of alloy configurations signifies the importance of taking the alloy statistics into account when analyzing the electronic properties. Here, by considering the degeneracy factor of each calculated configuration in a supercell (shown in Table 7.3) with the formula 7.1, the averaged band gap is obtained as a function of concentration as shown in Fig. 7.5a.

The band gaps of the parent materials will be used to correct the LDA-calculated band gaps of the alloy configurations. Quasiparticle corrections for the band gap have been shown to vary almost linearly with the composition in ternary nitride alloys⁴⁶. It is therefore reasonable to expect that the same correction relation is valid for ternary oxide alloys. In order to match the experimental values for the band gap of the parent materials, we have therefore applied a linear shift in the band gap for alloy $\text{ZnO}_x\text{S}_{1-x}$. The corrected averaged band gaps and the experimental values are illustrated in Fig. 7.5b. The corrected calculated band gaps of WZ- $\text{ZnO}_x\text{S}_{1-x}$ are consistent with the experimental values⁴¹, except at very low oxygen concentrations. At this diluted O-doped limit, the bowing of band gap is very large from experiment data. This may be due to the large size and chemical mismatch of oxygen and sulfur. It should be noted that similar huge bowing of the band gaps have been observed in As-rich impurity limit of $\text{GaN}_x\text{As}_{1-x}$ alloy as well.

Because of the importance of the fundamental band gap for device design, its nonlinear dependence on the concentration deserves further qualitative understanding and quantitative analysis. The linear behavior of the averaged lattice shown in Fig. 7.4b is due to the relaxation effect of the localized Zn-O and Zn-S bonds. At the same time, this relaxation effect will result in positional disorder of constituent atoms (Zn, S

and O) due to the shift of atomic positions away from the sites of parent lattice (WZ or ZB). Both the volume deformation and positional disorder due to the relaxation effect will change the electronic structure. Furthermore, the compositional disorder will also result in the change of electronic structure. If we consider the effects of relaxation and compositional disorder as a weak potential fluctuation, the change of electronic structure can be evaluated by solving the self-energy equation associated with the scattering potential and it can be found that the change of fundamental band gap will include a quadratic term $bx(1-x)$ with positional bowing coefficient b ³⁹. So a quadratic function of the concentration is typically used to describe the downward shift of the band gap of isovalent semiconductor alloys with a constant bowing coefficient b as the fomula⁴⁷:

$$E_g(\text{ZnO}_x\text{S}_{1-x}) = xE_g(\text{ZnO}) + (1-x)E_g(\text{ZnS}) - bx(1-x) \quad (7.3)$$

Fig. 7.6. Lattice parameters u of all the symmetrically distinct alloy configurations in WZ- $2 \times 2 \times 1$ supercell (presented by ∇) and WZ- $2 \times 1 \times 2$ supercell (presented by Δ). Note that blue triangles stand for the parameter u from Zn-S bonds, black triangles represent that from Zn-O bonds, red triangles depict the averaged parameter u for each configuration. The solid lines are the statistical averages obtained from Equation 7.1.

Both the calculated values and the experimental band gaps of alloy $\text{ZnO}_x\text{S}_{1-x}$, as

shown in Fig. 7.5b, indicate a very significant downward bowing of the band gaps. A constant bowing parameter is clearly not sufficient to describe the band gap. The nonlinearity of the bowing coefficient has, therefore, been fitted to the corrected averaged band gaps by $b(x) = P_0 + P_1x + P_2x^2 + P_3x^3$ and shown in the insert of Fig. 7.5b. For both WZ and ZB structures, the bowing parameters are relatively low in the center of composition range and are largest for both phases in S-rich limit. Furthermore, we found that the bowing parameter of WZ structures is systematically larger than that of ZB structures. While the electronic properties of ZB- $\text{ZnO}_x\text{S}_{1-x}$ have not been determined by experiments, it is clear from Fig. 7b that the electronic properties of ZB- $\text{ZnO}_x\text{S}_{1-x}$ are different from that of the WZ- $\text{ZnO}_x\text{S}_{1-x}$. This result from first-principles calculations predicts that the band gap bowing with WZ structure can be quite different from that with ZB structure in some semiconductor alloys.

To shed some lights on these puzzling results, we consider the structural properties of the $\text{ZnO}_x\text{S}_{1-x}$ alloy based on the configurations in ZB- $1\times 1\times 2$, WZ- $2\times 2\times 1$ and WZ- $2\times 1\times 2$ supercells. As shown in Fig. 7.6, the average internal parameter u just has small change, following the change of concentration of sulfur. This confirms that the WZ phase can be structural stable in all the range of concentration, as the demonstration of the lattice constants. Nevertheless, the lattice parameter u from Zn-O bond is very different from that from Zn-S bond for each concentration. This means the diversity of the sizes of oxygen and sulfur ions can make a very big difference between the localized chemical environment of Zn-O bond and that of Zn-S bond and result in a strong potential fluctuation, though the local strain due to the difference of size has been eliminated by charge transfer and structural relaxation. This may be the reason that bowing coefficient b will change by following the variety of composition, whatever with ZB and WZ structures. The bond lengths of Zn-O and Zn-S bonds with ZB and WZ structures are plotted in Fig. 7.7a. The individual Zn-O and Zn-S bonds in the $\text{ZnO}_x\text{S}_{1-x}$ alloy are closer to the values of their pure crystal counterparts (ZnO and ZnS) than the concentration weighted average value, as the other semiconductor alloys, such as CdZnO. It is also found that the difference of the Zn-O (or Zn-S) bond

length in both WZ and ZB crystal lattice is very small and is impossible to induce the obvious difference of bowing coefficient b of $\text{ZnO}_x\text{S}_{1-x}$ alloy with WZ and that with ZB structure. The Zn-O and Zn-S bond lengths along $\langle 0001 \rangle$ direction and that in (0001) plane with WZ structure are shown in Fig. 7.7b. It is found that the difference of the bond lengths of Zn-O (or Zn-S) bonds along $\langle 0001 \rangle$ direction and that in (0001) plane in $\text{ZnO}_x\text{S}_{1-x}$ alloy is more than that in pure crystals ZnO (or ZnS). This means the anisotropic crystal-field splitting ($\langle 0001 \rangle$ direction and (0001) plane) is larger in alloy than in pure crystals with WZ structure. So the difference of band gap bowing with WZ and that with ZB structure may be attributed to the larger anisotropic crystal-field splitting with the large chemical mismatch of oxygen and sulfur in $\text{ZnO}_x\text{S}_{1-x}$ alloy.

Fig. 7.7. (a) Bond lengths of Zn-O and Zn-S of all the symmetrically distinct alloy

configurations in WZ- $2 \times 2 \times 1$ (presented by ∇), WZ- $2 \times 1 \times 2$ supercell (presented by Δ) and ZB- $1 \times 1 \times 2$ (presented by square) supercell. (b) Bond lengths of Zn-O and Zn-S along $\langle 0001 \rangle$ direction and in (0001) plane of the configurations in WZ- $2 \times 2 \times 1$ (presented by ∇) and WZ- $2 \times 1 \times 2$ supercell (presented by Δ). Note that dot and dash lines are used for the statistical averaged values of each concentration x for Zn-S and Zn-O bonds, respectively.

7.4 Summary

We have performed first-principle density-functional calculations to study the thermodynamic stability and material properties of semiconductor alloy $\text{ZnO}_x\text{S}_{1-x}$ with both ZB and WZ structures. The disordered alloy was modeled using the special quasirandom structure (SQS) approach and the formation enthalpy of the SQSs shows that the structural phase transition would occurred at $x \sim 0.25$ due to the difference of the stable phases of parent (WZ-ZnO and ZB-ZnS). The large miscibility gap in the calculated x - T phase diagram suggests that at the typical growth temperature ($\sim 1000\text{K}$), the solid solubility limits in mother lattices are very small (less than 2%) from both sides (sulfur-doped ZnO and oxygen-doped ZnS).

The quasi-ordered structures, likely to exist in epitaxial grown samples, are investigated by constructing all the alloy configurations in three distinct 16-atom supercells. We found that some ordered structures are more stable than the random phase. In particular, ZB- $\text{ZnO}_x\text{S}_{1-x}$ structures are systematically more stable on the S-rich side that implies that under epitaxial conditions, ZB- $\text{ZnO}_x\text{S}_{1-x}$ alloy can be used as a good nucleation layer for the epitaxy of the zincblende ZnO film.

The electronic properties of the alloy $\text{ZnO}_x\text{S}_{1-x}$ are studied by analyzing the quasi-ordered alloy configurations. In both WZ and ZB forms, large bowing parameters are found to be asymmetric and composition dependent due to the large size and chemical mismatch. It is intriguing to note that both the band gaps and the bowing coefficient of WZ- $\text{ZnO}_x\text{S}_{1-x}$ are significantly different from that of ZB- $\text{ZnO}_x\text{S}_{1-x}$. Our prediction on the disparity between the electronic properties of the semiconductor alloys with WZ and ZB structures calls for further experiments for verifications.

7.5 References

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Chapter 8

A First Principles

Study on High-density Pseudo-cubic BC_2N

In this chapter, the structural stability and hardness of cubic BC_2N (c - BC_2N) has systematically studied by first-principle calculations with bond counting rules. In this work, all the distinct supercells with less or equal to 12 atoms are considered with the help of the point group of the Bravais lattice. By considering that the configurations of high-density phase BC_2N should be free of the low-energy bonds B-B and N-N, the configuration space of the ternary alloy is reduced to a configuration space that is the direct product of two configuration spaces (fcc spaces) of binary alloy. With bond counting rules, ~200 configurations are chosen and calculated by DFT methods. The correlation between the stability of the alloy configuration and its hardness is found. It is also found that there are many high-density alloy configurations with the formation energies in the order of 100–200 meV/atom in the configuration space. This result suggests that a mixture of high-density alloy configurations in the experimental samples is likely to occur due to the high temperature and nonequilibrium conditions offered by modern growth techniques. Theoretical analysis on elastic stiffness and Vickers hardness confirms that these stable high-density c - BC_2N alloy configurations are indeed harder than BN.

8.1 Introduction

Diamond is the hardest substance ever known based on the intrinsic perfect three-dimensional network, which is composed of short, highly-directional covalent bonds with four-coordinate symmetry ($Fd-3m$)¹. It is used as an excellent material in various applications such as cutting, polishing tools and high-pressure devices. However, diamond has its limitations, for example, it reacts with iron and can not be used for cutting steel². In order to overcome the major drawbacks of diamond¹, cubic

boron nitride (*c*-BN) with zincblende structure (F-43m) which is the second hardest material has been successfully synthesized. Is it possible to make any other materials that match or exceed hardness of these two hardest materials known³? The ternary alloy of these two excellent materials, cubic BC₂N (*c*-BC₂N), is naturally considered as an ideal candidate^{4, 5}. Recently, by using high-pressure and high-temperature techniques, several successful syntheses of *c*-BC₂N compounds have been reported⁶⁻¹¹. However, different experimental conditions, (such as temperature, pressure and starting materials) seem to yield different products. The products (*c*-BC₂N) with same chemical composition and percentage seem to have different structures, resulting in different lattice constants and hardness under different experimental conditions.

The experimental results are generally divided into two categories: high-density phase and low-density phase. For high-density *c*-BC₂N phase, lattice constant (~ 3.60 Å) roughly follows the Vegard's law, while bulk modulus (~345-355 GPa) is found to be slightly lower than that of *c*-BN (~369-400 GPa)^{7, 10, 11}. For low-density *c*-BC₂N phase, lattice constant (3.642 Å) and bulk modulus (282 GPa) are different from high-density counterpart, as reported by Solozhenko *et al*⁹. Nevertheless, these experiments share two common characteristics. First, the synthesis processes were carried out at high temperature (~2000 – 3000 K). Second, absence of the (002) peak in *X*-ray diffraction measurement suggested the presence of pseudo-diamond and/or pseudo-zincblende in the sample.

Several theoretical studies on the structure of this fascinating ternary superhard material have also been reported¹²⁻²². After several initial theoretical efforts, Sun *et al.*¹⁸ focused on a 8-atoms cubic supercell (SC) and reduced all possible configurations (C₈⁴C₄²) to seven symmetrically distinct configurations. The hardness of these seven configurations were examined in great details²³⁻²⁵. Chen *et al.*²² took a different approach and carried out a bond-counting-rule-based search in different SCs. They founded a series of short period (111) superlattices (SL) structures have lower total energy and larger bulk modulus than that of the structures in the 8-atoms cubic SC. By calculating the hardness, they found these (111) SL structures are harder than *c*-BN. Thus, there have been active debates on whether bulk BC_xN would have

intermediate hardness between diamond and *c*-BN. Moreover, among the theoretical calculations carried out so far, it is found that many of the mechanical and electronic properties of BC_xN are sensitive to the atomic arrangements and substitution patterns.

In this chapter, our main goal is to carry out systematical first-principle calculations of BC_2N alloy configurations in different unit cells to look for low-energy structures. Furthermore, we also hope to find out the correlation between the mechanical and electronic properties, the atomic arrangements and substitution patterns from this systematic search. Our strategy is to exhaustively search for distinct SCs of different shapes and sizes, then enumerate alloy configurations within these SCs.

8.2 Methodology

Theoretical examination of the structure of BC_2N is hindered by the astronomical number of alloy configurations. For an example, there are $\sim 2 \times 10^4$ configurations in a 12-atom SC for alloy BC_2N . To reduce the complexity of the alloy configurations, we employ two methods in this work. Firstly, we transform the ternary alloy (BC_2N) to an effective binary system based on distinct bonding characters of B–B and N–N. The method is to begin with the zincblende *c*-BN structure. Half of the B atoms in an fcc lattice are replaced by C atoms and the remaining half of the C atoms is replaced by the N atoms on the other fcc lattice. By the use of this approach, all the alloy configurations generated are guaranteed to be free of B–B and N–N bonds and the configuration space of BC_2N is equivalent to a direct product of the two fcc spaces. Secondly, we further reduce the number of the structures by the use of bond-counting rule. Based on the relative stability of different chemical bonds, the stability of a configuration is evaluated by counting the numbers of different bonds. In the case of BC_2N , the configurations are chosen by counting the numbers of relative stable C–C and B–N bonds.

To avoid artificial constraints in small unit cells, we adopt a divided-conquer method. With the help of the point group of the Bravais lattice^{26, 27}, all the distinct

supercells with less or equal to 12 atoms are considered. The smallest unit cell for BC₂N is a 4-atoms unit cell. For other larger SCs, we found that there are 7 distinct 8-atoms SCs and 10 non-equivalent 12-atoms SCs. Within these SCs, we found that there are 126 configurations in the 8-atoms SCs and 2000 configurations in the 12-atoms SCs. We have included all 126 configurations in the 8-atoms SCs for further first-principle analysis. For 12-atoms SCs, we selected only 55 configurations. These configurations have maximum number of C-C and B-N bonds in each SC. Furthermore, in light of the previous discussions on the (111) SL structures²², we have also included 47 alloy configurations that are SL structures along the <111> direction with relatively large number of C-C and B-N bonds.

All these selected alloy configurations are examined by density functional theory (DFT). The local density approximation (LDA)^{28, 29} and the projector augmented wave (PAW) method³⁰ were used throughout and all DFT calculations reported here were carried out with VASP program package³¹⁻³³. The *k*-space integral and plane-wave basis, as detailed below, are tested to ensure that total energy converges at the 0.2 meV/4-atoms level for the same structure in different SCs. The cutoff energy for plane-wave basis at 500 eV is used and a 9×9×9 Monkhorst-Pack type mesh³⁴ is chosen to sample the Brillouin zone. In order to enable the configurations to converge to their most stable conformations, all atomic positions and the lattice constants are relaxed. The total energies are obtained after the geometrical optimization is finished.

8.3 Results and Discussions

8.3.1 stabilities and structures of the alloy configurations

A standard method to access the relative stability of an alloy configuration (σ) is to calculate the formation energy, which is defined as the energy difference between the alloy and the weighted sum of constituents²⁶:

$$\Delta E(\sigma, x) = E(\sigma, B_x C_{2(1-x)} N_x) - x E(BN) - (1-x) E(C_2) \quad (8.1)$$

where $x(\sigma)$ is the concentration of configuration σ . We found all the *c*-BC₂N structures examined to have positive formation energies. This indicates that all the *c*-BC₂N

structures are metastable, and they tend to separate into diamond and *c*-BN phase structure at low temperature if thermal equilibrium can be reached.

Fig.8.1 The correlation between number of C-C bonds and formation energy of all calculated structures is shown in the upper panel (A). The correlation between volume and formation energy of all calculated structures is shown in the lower panel (B). black triangles are the 126 configurations in seven nonequivalent 8-atoms SCs. Red circles represent the 55 low-energy configurations chosen from ten 12-atoms SCs. Blue crosses indicates the 47 (111) SL configurations. Note that 5 low-density unstable structures with volumes more than $24.00 \text{ \AA}^3/4\text{-atoms}$ are removed here.

The correlation between number of C-C bond and formation energy is shown in Fig.8.1(A). It is clear that there is a trend for the formation energy to increase when the number of C-C bonds increases. We should note here that for all the alloy configurations constructed here (by avoiding B-B and N-N bonds), the number of C-C

bonds is always equal to that of B-N bonds and the number of B-C bonds equals to that of N-C bonds. Therefore, the same dependence of formation energy with respect to number of B-N is also expected. These trends are clear evidence that simple concept of bond counting works well in identifying low-energy configurations. However, simple bond counting rules is not accurate enough to predict the precise energetics of alloy configurations. For an example, among all the configurations with 3 C-C bonds, their formation energies range from 0.7 to 1.7 eV/4-atoms. Similarly, all configurations with 2 C-C bonds can have their formation energies differed by more than 1 eV/4-atoms as depicted in Fig. 8.1(A).

Volumes of all calculated structures as a function of formation energies are shown in Fig.8.1 (B). It is clear that the volume has an approximately linear relation with the formation energy. This observation is inline with the general notion that the strength of chemical bonds is proportional to a certain power of the inverse length of the bonds and stronger bonding will often result in a smaller volume³⁵. Furthermore, it is found that the volumes of all structures are larger than the ideal mixing volume of diamond and *c*-BN. This tendency observed in the volume is consistent with the fact that all the alloy structures BC₂N have positive formation energies and prefer to have phase segregation at lower temperature. This can be assigned that the presence of nonbonding and antibonding states of N-C bond³⁶. The first-principle calculations by Zhang, Sun, and Chen³⁷ also suggested that the strength of previously predicted hardest C₃N₄ phase is lower compared not only to diamond but also cubic boron nitride by a surprisingly large amount. All of these indicated that the excessive electrons on the N atoms play a key role in determining the high elasticity and low hardness.

8.3.2 Low-energy configurations

In the pioneering work by Sun *et al.*¹⁸, the two most stable structures (shown as BC₂N-1 and BC₂N-2 in Fig. 8.2), found in a cubic 8-atoms unit cell, have formation energies of 1.749 and 1.768 eV/4-atoms. From our exhaustive search of alloy configurations in all 8-atoms SCs, we found that there were many alloy configurations

that were more stable than those considered by Sun *et al.*¹⁸, as shown in Fig. 8.1. This cautioned us the importance of a systematic search of alloy configurations beyond those in some conventional unit cells.

Fig.8.2 Crystal structures of selected low-energy configurations (grey spheres represent C atoms, blue spheres represent N atoms and red spheres represent B atoms). BC_2N -1 and BC_2N -2 are the most stable forms from ref. 18. Some short period (111) SL structures (denoted as 3+3, 2+2 and 1+1 for $(C_2)_n(BN)_n$ with $n=1, 2, 3$ and 2+1 for $(C_2)_2(BN)_2(C_2)_1(BN)_1$) are shown in the middle. The $\langle 110 \rangle$ “sandwich” structure (denoted as PMM2) is shown on the right.

In a series of work by Chen *et al.*^{22, 38}, the (111) SL structures have been considered as candidates for low-energy configurations. Our systematic search confirmed that these short-period (111) SL structures were among the most stable alloy configurations (see the caption in Fig. 1). We found that some low energy (111) SL were missing in the previous search²². For example, the “2+1” SL structure, shown in Fig. 8.2, has a formation energy between that of “1+1” and “2+2” SL structures. Over all, all these (111) SL structures seem to follow certain monotonic trends when the periodicity increases. Furthermore, we should note here that structures, other than the (111) SL, could be quite stable as well. For example, we found a “sandwich” structure with the carbon layer and the BN layer along $\langle 110 \rangle$ direction (as shown in the right panel of Fig. 8.2.) has a low formation energy (0.581 eV/4-atoms) that is

comparable to the “1+1” and “2+1” SL along $\langle 111 \rangle$ direction.

Although all the configurations have positive formation energies for the alloy BC_2N , it is anticipated that some low-energy metastable structures (with formation energy of ~ 100 to 200 meV per atom) can be stable at experimental conditions with high temperature T ($\sim 2000 - 3000$ K). If we use these thermal energies ($k_B T \sim 172$ meV – 258 meV) as a gauge, another six new structures with higher-density and lower formation energy can be found. The structures of these six c - BC_2N are shown in Fig. 8.3. These structures have the same number of C-C bond with the 1+1 (111) SL and the formation energy of the 1+1 (111) SL is just $0.09\text{eV}/4\text{-atoms}$ lower than that of these structures.

Fig.8.3 Crystal structures of six new structures whose formation energies are slightly lower than that of 1+1 (111) SL (shown in Fig.8.2). The same convention used in Fig.8. 2 representing the atoms are adapted here.

8.3.3 Theoretical estimation of hardness

The elastic stiffness is an important index to estimate the hardness. The elastic

stiffness constants are obtained by calculating the stresses of each *c*-BC₂N structure when small strains are applied to each relaxed structure. The bulk modulus *B* and isotropic shear modulus *G*_{ISO} of each structure are extracted from the elastic stiffness constants. Considering the slight distortion of each relaxed structure, the bulk modulus and isotropic shear modulus³⁹ are given by

$$B = (1/9)[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})], \quad (8.2)$$

$$G_{ISO} = (1/15)[(C_{11} + C_{22} + C_{33}) + 3(C_{44} + C_{55} + C_{66}) - (C_{12} + C_{13} + C_{23})], \quad (8.3)$$

where *C_{ij}*'s are elastic stiffness constants of the lattice. In Table 8.1, we summarized the calculated volumes, formation energies, number of C-C bond, bulk modulus and isotropic shear modulus for diamond, *c*-BN, and the low-energy BC₂N structures listed in Fig. 8.2 and Fig. 8.3.

Structures	V (Å ³ /4-atoms)	ΔE (eV/4-atoms)	No. C-C bond (#/4-atoms)	B (GPa)	G _v (GPa)
Diamond	22.111	0.00	...	463.4	532.10
<i>c</i> -BN	22.99	0.00	...	403.4	405.54
BC ₂ N-2(P2221)	22.83	1.768	2.00	409.2	448.90
BC ₂ N-1(PMM2)	22.88	1.769	2.00	403.8	439.80
<111>1+1	22.73	0.738	3.00	423.0	457.44
<111>2+1	22.70	0.566	3.33	423.8	459.94
<111>2+2	22.67	0.479	3.50	425.8	458.72
<111>3+3	22.64	0.380	3.67	426.9	462.46
<110>"sandwich"	22.69	0.581	3.33	424.1	461.62
New-1(CM)	22.75	0.770	3.00	420.4	460.40
New-2(PMN21)	22.73	0.782	3.00	421.9	457.27
New-3(CM)	22.75	0.811	3.00	420.4	458.83
New-4(PM)	22.75	0.817	3.00	429.2	457.86
New-5(CM)	22.72	0.823	3.00	421.6	460.20
New-6(PM)	22.73	0.828	3.00	432.3	456.00

Table 8.1 Calculated volume (*V*), formation energy (ΔE), bulk modulus (*B*) and shear modulus (*G_v*) for diamond, *c*-BN, and some of low-energy BC₂N structures in the paper. BC₂N-1 and BC₂N-2 in ref. 18, some short period (111) SL, the (110) sandwich structure and six new metastable BC₂N structures with 3 C-C bonds per 4-atoms in the paper.

The bulk modulus and isotropic shear modulus of all the low-energy structures

(except BC₂N-1 and BC₂N-2) are larger than that of *c*-BN. They are only slightly lower than the ideal mixing bulk modulus (433.3 GPa) and isotropic shear modulus (468.82 GPa) of diamond and *c*-BN. Since the hardness have the correlation with elastic stiffness, especially the shear modules which reflects the ability of resisting to scratch or indent a material by a small elastic shear changes, these low-energy BC₂N alloy structures are expected to be harder than *c*-BN. Furthermore, it is more interesting to note that the six structures (shown in Fig. 8.3) with 3 C-C bonds/4-atoms have comparable bulk modulus and isotropic shear modulus, with that of the 1+1 (111) SL. It is reasonable to expect that these new low-energy structures could also be harder than *c*-BN.

To further estimate the hardness and to compare with the experimental results, we looked into the microscopic model⁴⁰ which was deduced based on the bond length, valence charge density and ionicity of chemical bonds to access the Vickers hardness of the alloy structures. In this model, the Vickers hardness can be calculated by

$$H_V = \left[\prod_u (H_V^u)^{n^u} \right]^{1/\sum n^u}, \text{ with } H_V^u = 350(N_e^u)^{2/3} e^{-1.191 f_i^u / (d^u)^{2.5}} \quad (8.4)$$

Where H_V^u , n^u , d^u , and N_e^u and f_i^u are the hardness, bond number, bond length, effective valence electron density and the Phillips ionicity of *u*-type bond, respectively. The effective valence electron density of *u*-type bond N_e^u can be calculated by the formula

$$N_e^u = [Z_X^u / N_X + Z_Y^u / N_Y] [\sum_u n^u (d^u)^3] / [V (d^u)^3], \quad (8.5)$$

where Z_X^u (Z_Y^u) is the effective valence electron number of the *X* (*Y*) atom forming the *u*-type bond, N_X (N_Y) is the nearest coordination number of the *X* (*Y*) atom and V is the volume of the unit cell. The Phillips ionicity of the *u*-type bond f_i^u can be obtained by the formula

$$f_i^u = \left[1 - e^{-|P_c - P^u| / P^u} \right]^{0.735}, \quad (8.6)$$

where P^u and P_c are the Mulliken's overlap population of the *u*-type bond and the overlap population of bond in a specified pure covalent crystal (here $P_c=0.75$ for zincblende structure). In this work, DFT calculations implemented in CASTEP code

were carried out within the local density approximation and ultrasoft pseudopotential to access the above-mentioned parameters. The cutoff energy of 800 eV and $8 \times 8 \times 6$ Monkhorst-Pack type k-points mesh were used to ensure that total the charge density can be converged.

In Table 8.2, Vickers hardness of diamond, c -BN, and five low-energy BC_2N structures from the microscopic model is tabulated. The calculated values of diamond and c -BN bear comparison with the experiment values that insures the validity of the above-mentioned microscopic model. The calculated hardness of all the five low-energy structures is consistently higher than that of c -BN, therefore, we are confident that the high density configurations with low formation energies should be harder than c -BN. Furthermore, the calculated hardness of c - BC_2N is slightly above the experimental value. Since the samples are obtained under the high temperature and nonequilibrium conditions in the experiment, it is considered that a mixture of high-density alloy configurations will be possible to occur and then reduce slightly the hardness of the experimental samples. However, It is obvious that the hardness of c - BC_2N is larger than that of c -BN.

Structure	$H_v^{\text{cal.}}$	$H_v^{\text{exp.}}$
Diamond	98.52	96 ± 5
c -BN	69.61	63 ± 5
$\langle 111 \rangle 1+1$	77.24	76
$\langle 111 \rangle 2+1$	78.19	
$\langle 110 \rangle$ “sandwich”	78.64	
$\langle 111 \rangle 2+2$	78.80	
$\langle 111 \rangle 3+3$	79.70	

Table 8.2 Calculated Vickers hardness $H_v^{\text{cal.}}$ for diamond c -BN and five low-energy c - BC_2N configuration and the experimental Vickers hardness $H_v^{\text{exp.}}$ of diamond, c -BN and ZB- BC_2N ^{9,41}.

8.4 Conclusions

In summary, the c - BC_2N structures are systematically analyzed by searching through all alloy configurations in all nonequivalent 8-atoms and 12-atoms unit cells.

It is found that the stability of an alloy configuration is correlated with its density and hardness. High-density phase configurations that have larger bulk modulus and isotropic shear modulus are more stable and hard. Other than the (111) SL structures, there exists many low-energy structures with high density. These low-energy structures have very high shear modulus and will be expected to be harder than c -BN as the short period (111) SL.

Although all the alloy configurations have positive mixing energies, meaning that the c - BC_2N is energetically more favorable to separate phase, the high-density low-energy configurations have low formation energies in the order of 100 to 200 meV per atom. Our results suggested that high-density c - BC_2N could be synthesized at the high growth temperature and non-equilibrium experimental conditions offered by the modern growth techniques. Another implication of high growth temperature in the synthesis process is that different configurations with close energies are likely to co-exist in samples and mixing of the different configurations may result in the reduction of hardness. The calculated Vickers hardness of the lower-energy structures indicates the mixed alloy pseudo-cubic BC_2N with high-density is still possible to be harder than c -BN.

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Chapter 9

On the use of Bond Counting Rules in Predicting the Stability of $C_{12}B_6N_6$ Fullerene

In this chapter, the stability and the BN-substitution pattern of $C_{12}B_6N_6$ fullerene have been investigated by bond-counting rules (BCR) with first-principle calculations. It is found that the simple BCR by only including the nearest-neighbor terms can serve as an effective guide to look for the low-energy alloy configurations in the configuration space of cage-like alloy. However, for the quantitative description of the stability of the alloy configuration, a model Hamiltonian should include the contributions of other two-body interactions and many-body interactions. With the study of the structures of the low-energy configurations, the substitutions of BN units in the cage seem to follow a “continuity” pattern. However, all the alloy configurations have positive mixing energy, the low-energy isomers are quite stable (less than 150 meV/atom). We expect that these fullerene structures can be synthesized under the high temperature and nonequilibrium experimental conditions offered by the modern growth techniques such as laser ablation, direct-current arc, and chemical vapor deposition.

9.1 Introduction

Recent success in studying hybrid materials of carbon and boron nitride (BN) has opened a new window into the field of this multicomponent system $(BC_xN)^{1-5}$. It is generally expected that the hybrid materials would inherit the properties of the parent materials⁶⁻⁸. However, recently there have been active debates on whether bulk BC_xN would have intermediate hardness between diamond and *c*-BN⁹⁻¹¹. Among the theoretical calculations carried out so far, it is found that the stabilities of the alloy structures are sensitive to the atomic arrangements and substitution patterns^{9, 12, 13}.

Since the discovery of buckminsterfullerene C_{60} ¹⁴⁻¹⁶, carbon fullerenes have been an active area of research¹⁷⁻¹⁹ due to the potential technological importance in

electrochemistry^{20, 21}, ferromagnetism²² and superconductivity²³⁻²⁶. $(BN)_n$ fullerenes, the iso-electronic analogues to carbon fullerenes²⁷⁻³¹, has also attracted considerable attention for its special electronic, optical and magnetic properties³²⁻⁵⁵. Comparing to bulk materials, BC_xN fullerenes has received relatively less attention despite that both carbon and BN fullerenes have been thoroughly studied⁵⁶⁻⁶⁴. In this work, we carry out a systematic theoretical study to investigate effects of atomic arrangements on the stability of BC_xN fullerenes. In particular, we also test the applicability of simple bond counting rules (BCR) to predict the stability and locate low-energy minima.

The small $(BC_2N)_n$ clusters such as dimer and trimer have been studied at the Hartree-Fock (HF) and Møller-Plesset perturbation (MPn) levels with various basis sets up to 6-311G(p)^{65, 66}. Larger fullerenes C_n ($n=20, 24, 28, 32, 36$ and 40) with mono-BN-replacement are investigated by semi-empirical (MNDO and AM1) and Density Functional Theory (DFT) with small basis set (such as 3-21G)⁶⁷. For even larger clusters, Zhao *et al.* studied the BN-substituted fullerenes by considering $C_{60-2x}(BN)_x$ and $C_{70-2x}(BN)_x$ ($x=1-3$)^{68, 69}. Further investigations by Pattanayak *et al.* have extended to substitution by as many as seven BN pairs⁵⁹ and they have also examined the relative stability of some isomers by semi-empirical MNDO and density functional theory (B3LYP/3-21G) and concluded some rules for the BN-substitution in BCN-fullerene⁷⁰. Such kind of *ad hoc* methods may be useful to identify low-energy isomers; it is not possible to draw a comprehensive picture on the over-all dependence of the binding characters on the atomic arrangements.

In this chapter, we will focus on the cluster structures with 24-atoms for several reasons. First, these medium-sized fullerenes allow us to systematically explore the configurational complexity ($\sim 3^N$). Furthermore, the 24-mer fullerenes also have a few unique features among the fullerenes. For example, $B_{12}N_{12}$ with 4- and 6-member rings (shown as BN-4⁶8 in Fig. 9.1) is found to be the smallest stable BN fullerenes^{39, 42, 45, 47, 55}. C_{24} with different structural isomers such as monocyclic ring, graphite-like, bowl-like and cage-like structures have been examined by different calculation methods⁷¹⁻⁷³. While there is no general consensus on the most stable form, the cage structure with hexagonal rings (shown as C_{24} -5¹²6² Fig. 9.1) has been proved to exist

by the mass spectrum⁷⁴ and is considered to be stable under cool clustering conditions and very gentle ionization⁷⁵. Therefore, the cage structure with D_6 symmetry is at least a meta-stable form for C_{24} . The unique co-existence of 4, 5 and 6-member ring in 24-mer allows us to explore richer BN-substitution patterns among the different rings.

9.2 Methodologies

9.2.1 Method of quantum calculations

Previous investigations on BN/BCN/C systems have shown electron correlation is important for the structure and stability^{65, 66, 76}. In this sense, the DFT method is preferred over HF method. Though DFT method^{77, 78} is less accurate than more extensive correlated methods such as CCSD, with appropriate exchange correlation functional and moderate basis functions it will be more efficient than any other methods that include electron correlation for systems with large numbers of atoms. Here, for the calculation of ground state energies and structures, the three-parameter empirical formulation B3LYP is employed, since it is most widely used in the calculation of molecular electronic structure⁷⁹⁻⁸¹. Geometry optimization was carried out with the standard 6-31G* basis set since such a basis set has been found quite adequate for present systems. All *ab initio* calculations reported in this work were performed with the GAUSSIAN 03 package⁸².

9.2.2 Enumeration and selection of configurations

For both 4^66^8 and $5^{12}6^2$ structures, the configuration space is very large ($\sim 2.5 \times 10^9$). While it is possible to use the symmetry of fullerenes ($5^{12}6^2$ has O_h symmetry and 4^66^8 with D_{6d} symmetry) to reduce the alloy configuration space and leaving only “chemically distinct” isomers, the size of the latter ($\sim 1 \times 10^8$) is still too huge for a direct first principle study. We have therefore begin with the simple “bond counting rules” (BCR) and further divided all the distinct structures into different sets and each set would include all configurations with the same number of chemical bonds (that is the same number of C-C, N-N, B-B, C-N, C-B and B-N bonds). If the energy of an alloy configuration strictly follows the simple BCR, all configurations

within each set would be iso-energetic and the energy of each alloy configuration would have the following form:

$$E(\sigma) = E_o + \alpha_{C-C}N_{C-C} + \alpha_{B-B}N_{B-B} + \alpha_{N-N}N_{N-N} + \alpha_{B-N}N_{B-N} + \alpha_{C-B}N_{C-B} + \alpha_{C-N}N_{C-N} \quad (9.1).$$

If one focuses on the low-energy configurations, the above-mentioned BCR can be used as a guiding rule to choose the low-energy configurations. It is generally accepted that C-C and B-N bonds are stronger and B-B and N-N bonds tends to be the weakest among the 6 kinds of bonds within this ternary system. In this work, there are ~300 configurations chosen as low-energy candidates for each structure by maximizing the number of C-C and B-N bond and minimizing the number of B-B and N-N bond.

This idea of BCR can be further generalized and the energy of the alloy configurations can be recast in a more sophisticated form:

$$E(\sigma) = E_o + \sum_{i,k} \alpha_{2,k}^i B_{2,k}^i(\sigma) + \sum_{i,k} \alpha_{3,k}^i A_{3,k}^i(\sigma) \quad (9.2)$$

where the parameters α 's represent the interaction energies, B_2 's and A_3 's are generalized correlation functions for other types of "bonds" to include contributions from other two-body (the B_2 's) and three-body (the A_3 's) terms. In this work, on top of ~ 300 configurations chosen in the previous step, we have included ~ 200 randomly chosen to be used configurations to train and test the generalized BCR (GBCR) model. In principle, the size of the train set can continue to grow until reaching self-consistency. It is found the result is quite satisfactory after the first run.

9.3 Results and discussions

9.3.1 Energy of parent structures

The structures of the cage isomer of parent (carbon and boron nitride) are shown in Fig. 9.1. The energies are calculated after geometry optimization and are tabulated in Table 9.1. For the two carbon cages, we found that $C_{24}-5^{12}6^2$ cage is more stable than $C_{24}-4^66^8$ by about 23 kcal/mol. The stability of $C_{24}-5^{12}6^2$ over $C_{24}-4^66^8$ is considered to be connected with the large surface curvature induced by 4-member

ring in $C_{24}-4^66^8$. This notion is not valid in BN-fullerene as the $B_{12}N_{12}-4^66^8$ can avoid formation of weak B-B and N-N bonds and in $B_{12}N_{12}-5^{12}6^2$ B-B or N-N will be formed on the 5-member ring. Among all the possible $B_{12}N_{12}-5^{12}6^2$ fullerenes, we found that there are five symmetrically distinct configurations with lowest number of B-B and N-N bonds and these five configurations (shown in Fig. 9.1) can be regarded as the low-energy candidates. According to the calculated relative energy and bonding energy, the $B_{12}N_{12}-4^66^8$ is more stable than $B_{12}N_{12}-5^{12}6^2$ by at least 200 kcal/mol. In our following discussion on the stability of alloy BCN fullerene, the energy of $C_{24}-5^{12}6^2$ and $B_{12}N_{12}-4^66^8$ are used as the energy of the parent structures.

Fig.9.1 Structures of the two possible 24-mer fullerenes of carbon C_{24} and boron nitride $B_{12}N_{12}$. Black spheres for C atoms, blue spheres for N atoms and green spheres for B atoms. Five symmetrically distinct $BN-5^{12}6^2$ configurations with lowest number of B-B and N-N bonds are listed as $BN-5^{12}6^2A$ to $BN-5^{12}6^2E$.

Isomer stru.	Energy (a.u.)	Relative energy (kcal/mol)	Bonding energy (eV/atom)
$C_{24}-5^{12}6^2$	-913.83976	0.00	-8.178
$C_{24}-4^66^8$	-913.80247	23.40	-8.135
$B_{12}N_{12}-4^66^8$	-956.14499	0.00	-7.438
$B_{12}N_{12}-5^{12}6^2-A$	-955.82375	201.58	-7.074
$B_{12}N_{12}-5^{12}6^2-B$	-955.81451	207.38	-7.064
$B_{12}N_{12}-5^{12}6^2-C$	-955.80748	211.79	-7.056
$B_{12}N_{12}-5^{12}6^2-D$	-955.80365	214.19	-7.052
$B_{12}N_{12}-5^{12}6^2-E$	-955.80276	214.75	-7.050

Table 9.1 Calculated energy (in hartree), relative energy (in kcal/mol) and bonding

energy (in eV/atom) of the cage isomers of carbon C_{24} and boron nitride $B_{12}N_{12}$

9.3.2 Energy of different configurations from two cage structures

While the relative stability of the parent fullerene is simple, the existence of carbon can avoid the formation of B-B and N-N bonds in 5-member ring complicates the analysis. For the above-mentioned reason, it can not be determined immediately that whether the most stable $C_{12}B_6N_6$ cage should be $5^{12}6^2$ or 4^66^8 . Again, we start to look for structures with maximum number of C-C and B-N bonds and minimum number of B-B and N-N bonds. All configurations with no more than two B-B and N-N bonds are chosen as candidates for low-energy configurations. All these configurations are categorized and sorted into different groups according to their chemical bonds and the results are tabulated in Table 9.2 and Table 9.3 for 4^66^8 and $5^{12}6^2$ respectively.

The structure and energies of these ~ 600 alloy configurations are fully examined by DFT methods and their calculated energies are shown in Fig. 9.2. For the cage 4^66^8 , the two most stable configurations are indeed those with the largest number of C-C and B-N bonds. For the cage $5^{12}6^2$, the most stable configuration is also a configuration without B-B and N-N bond and with 12 C-C and B-N bonds. We should note that the most stable configurations of cage 4^66^8 and cage $5^{12}6^2$ are very close in energy (differed by only 4.3 kcal/mol). This small difference is surprising as the energy difference between carbon and BN fullerenes are roughly 20 or 200 kcal/mol respectively. This means the simple notion that the strain induced by the surface curvature results in the increase of the energy will become invalid in the BCN alloy system, even in the absence of the B-B and N-N bonds.

The energies of all 4^66^8 configurations, as shown in the left panel of Fig. 9.2, seem to roughly follow the number of B-B and N-N bonds (the x -axis of Fig 9.2 follow the increasing number of B-B and N-N bonds). The energies of all $5^{12}6^2$ configurations, however, reveal very different diverse energetics as shown in the right panel of Fig. 9.2. For example, among the 201 configurations without B-B and N-N bonds, the energies can differ by as much as 60 kcal/mol. It is well known that the

local environments of the chemical bonds will induce different charge transfer and result in different local structural relaxation in different configurations. This large amount of energy difference should be connected with the environment effect of the bond such as the near- neighbor bond type, the angle between bonds, and so on. It is speculated that the electronic properties such as total energy can be systematically parameterized as shown by Equation 9.2 (GBCR model).

No.\#of bond	C-C	B-N	C-B	C-N	B-B	N-N	# of stru.
$C_{12}B_6N_6-4^66^8-1$	15	15	3	3	0	0	2
$C_{12}B_6N_6-4^66^8-2$	14	14	4	4	0	0	25
$C_{12}B_6N_6-4^66^8-3$	13	13	5	5	0	0	227
$C_{12}B_6N_6-4^66^8-4$	14	13	3	5	1	0	13
$C_{12}B_6N_6-4^66^8-5$	14	13	5	3	0	1	13
$C_{12}B_6N_6-4^66^8-6$	15	13	3	3	1	1	3
$C_{12}B_6N_6-4^66^8-7$	14	12	2	6	2	0	29
$C_{12}B_6N_6-4^66^8-8$	14	12	6	2	0	2	29

Table 9.2 All symmetrically distinct $C_{12}B_6N_6-4^66^8$ configurations having less or equal to two B-B and N-N bonds. All these configurations classified into eight groups by the number of different chemical bonds. These groups are arranged in the order of increasing number of weak B-B and N-N bonds.

No.\#of bond	C-C	B-N	C-B	C-N	B-B	N-N	# of stru.
$C_{12}B_6N_6-5^{12}6^2-1$	12	12	6	6	0	0	201
$C_{12}B_6N_6-5^{12}6^2-2$	14	13	3	5	1	0	3
$C_{12}B_6N_6-5^{12}6^2-3$	14	13	5	3	0	1	3
$C_{12}B_6N_6-5^{12}6^2-4$	15	13	3	3	1	1	2
$C_{12}B_6N_6-5^{12}6^2-5$	14	12	2	6	2	0	32
$C_{12}B_6N_6-5^{12}6^2-6$	14	12	6	2	0	2	32

Table 9.3 All symmetrically distinct $C_{12}B_6N_6-5^{12}6^2$ configurations having less or equal to two B-B and N-N bonds. All these configurations classified into six groups by the number of different chemical bonds. These groups are arranged in the order of increasing number of weak B-B and N-N bonds.

For each structure, about 40 parameters are used to fit the energies of ~300

configurations chosen by BCR and ~200 configurations by random choosing. The ability of the parameterized model (GBCR) to capture the trends in energy for cage 24-(4, 6) and cage 24-(5, 6) is confirmed in Fig.9.3. The root-mean-squared deviation of the model fit from the calculated energy is ~5 kcal/mol. Compared to a range of ~400 kcal/mol between least and most stable isomers, the ratio of the error is just 1.25 %. Then we can use the model with the fitted parameters to predict the energy of any alloy configuration. For each structure, we choose randomly 100,000 configurations to predict by the model. As fig.9.4 shown, it confirms further that BCR will be valid when choosing the low energy configurations.

Fig.9.2 Calculated energies of all the alloy configurations listed in Table 9.2 (left panel) and Table 9.3 (right panel) for $C_{12}B_6N_6-4^66^8$ and $C_{12}B_6N_6-5^{12}6^2$ respectively. The x -axis follows the group number in the respective tables and both of them roughly follow the increasing number of B-B and N-N bonds (from left to right).

9.3.3 Structure and nature of bonding of the low energy configurations

For each cage, 8 configurations with the lowest energies are chosen to analyze in detail. The calculated energies, relative energies and bonding energies are tabulated in Table 9.4. The bonding energies are between the pure cage-structure carbon and boron nitride. This means the ternary alloy cage structure is relatively stable like the parent

(carbon and boron nitride) fullerenes. For further evaluation of the relative stability of the alloy cage, we will use the notion of mixing energy (ΔE_{mix}) which is defined as

$$\Delta E_{\text{mix}}(\sigma, (BN)_n(C_2)_m) = [E(\sigma, (BN)_n(C_2)_m) - \frac{n}{n+m} E(BN_{n+m}) - \frac{m}{n+m} E(C_{2n+2m})] / (2n+2m), \quad (9.3)$$

where $E(BN_{n+m})$ and $E(C_{2n+2m})$ are the energy of the parent cages. In this work, the energy of $C_{24}-5^{12}6^2$ and $B_{12}N_{12}-4^66^8$ are used as the energy of the parent structures.

Fig.9.3 The effectiveness of using the GBCR model: $C_{12}B_6N_6-4^66^8$ configurations are shown in the left panel and $C_{12}B_6N_6-5^{12}6^2$ configurations in the right panel. The x-axis is the calculated energy of the configurations by DFT and the y-axis is the result of a least squares fit to these energies using the GBCR model (Equation 9.2). The low-energy alloy configurations, tabulated in Table 9.2 and Table 9.3, are shown as solid black circles and the randomly chosen configurations (~ 200 for each fullerene) are shown in open red circles.

The mixing energy corresponds to the change in the energy in constructing the alloy cage from the parent cages and a negative value of ΔE_{mix} means the alloy cages are stable with respect to pure parent cages. The mixing energies of the eight lowest energies configurations for each cage are tabulated in Table 9.4. We find all the configurations calculated have positive mixing energies. This indicates that all the alloy cages are just metastable structures and tend to separate into pure parent cage

structure at low temperature – which is similar to the case of bulk c -BCN alloy.

Fig.9.4 The distribution of the predicted energies based on Equation 9. 2. The low-energy configurations chosen based on simple BCR are shown in red. Furthermore, we have calculated the predicted energy of 100,000 randomly chosen configurations in gray as a rough representative of the over all alloy space. It is clear that simple BCR is very effective in locating low-energy structures.

In experiments, the fullerenes can usually be obtained by laser ablation, direct-current arc and chemical vapor deposition methods. These methods offer a high temperature and highly nonequilibrium environment. If the synthesis processes were to carry out at high temperature (~ 2000 - 3000 K), the thermal energy $k_B T$ (172 meV –

258 meV) will allow the formation of these alloy cages since the mixing energy (~ 140 meV/atom) of these configurations of the alloy cage are in the range of the thermal energy. From the calculated relative energies, the energies of the chosen 16 configurations are comparable which means the different configurations in both with the two 4^66^8 and $5^{12}6^2$ structures are likely to co-exist in the experimental productions.

Configurations	Energy (a.u.)	Relative energy (kcal/mol)	Bonding energy (eV/atom)	Mixing energy (mev/atom)
$C_{12}B_6N_6-4^66^8-1$	-934.87369	0.00	-7.673	134.511
$C_{12}B_6N_6-4^66^8-2$	-934.87101	1.68	-7.670	137.546
$C_{12}B_6N_6-4^66^8-3$	-934.84752	16.42	-7.644	164.169
$C_{12}B_6N_6-4^66^8-4$	-934.84713	16.67	-7.643	164.613
$C_{12}B_6N_6-4^66^8-5$	-934.84663	16.98	-7.643	165.179
$C_{12}B_6N_6-4^66^8-6$	-934.84602	17.36	-7.642	165.869
$C_{12}B_6N_6-4^66^8-7$	-934.84445	18.35	-7.640	167.653
$C_{12}B_6N_6-4^66^8-8$	-934.84367	18.84	-7.639	168.531
$C_{12}B_6N_6-5^{12}6^2-1$	-934.86683	4.31	-7.666	142.287
$C_{12}B_6N_6-5^{12}6^2-2$	-934.86460	5.70	-7.663	144.807
$C_{12}B_6N_6-5^{12}6^2-3$	-934.85841	9.59	-7.656	151.824
$C_{12}B_6N_6-5^{12}6^2-4$	-934.85599	11.10	-7.653	154.567
$C_{12}B_6N_6-5^{12}6^2-5$	-934.85523	11.59	-7.653	155.436
$C_{12}B_6N_6-5^{12}6^2-6$	-934.85422	12.22	-7.651	156.577
$C_{12}B_6N_6-5^{12}6^2-7$	-934.84625	17.22	-7.642	165.610
$C_{12}B_6N_6-5^{12}6^2-8$	-934.84301	19.25	-7.639	169.276

Table 9.4 Energies of the eight most stable alloy configurations of $C_{12}B_6N_6-4^66^8$ and $C_{12}B_6N_6-5^{12}6^2$ fullerenes. Though all the configurations listed here have positive mixing energy, the value of the mixing energy of the most stable configuration is comparable to $k_B T$ at $T \sim 2000$ K.

By examining the low-energy alloy configurations shown in Fig. 9.5, it is found that B and N atoms always form BN pairs to replace C-C units and the substitutions of these BN units always connect to one another. This is referred as the “continuity” rule by Pattanayak *et al.* in their analysis of buckminsterfullerene BCN⁷⁰. The continuity rule is consistent with the concept of simple BCR, because the connected substitutions of BN units will reduce the boundary of carbon and boron nitride. Noted that all

low-energy configurations are free of B-B and N-N, therefore, maximization of C-C and N-N bonds is equivalent to minimization of C-B and C-N bonds. Another implication of the continuity rule is carbon and boron nitride prefers to be separated which is in agreement with the positive mixing energy we observed.

Fig.9.5 Structure of the eight most stable alloy configurations of $C_{12}B_6N_6-4^66^8$ and $C_{12}B_6N_6-5^{12}6^2$ fullerenes. Their energies are reported in Table 9.4.

In order to study the bonding characteristic of the alloy $C_{12}B_6N_6$ cages further, Mulliken charge population is analyzed for the parent structures and the lower-energy configurations. In each structure, the mean values and root mean square deviation of Mulliken charges of nitrogen, boron and carbon are extracted as listed in Table 9.5. The charges of all the 9.5 cage isomers of $B_{12}N_{12}-5^{12}6^2$ are smaller than that of $B_{12}N_{12}-4^66^8$ due to the being of the B-B and N-N bonds in $B_{12}N_{12}-5^{12}6^2$ structure. In

the lower-energy configurations of alloy $C_{12}B_6N_6-5^{12}6^2$, the Mulliken charges of nitrogen become relative larger compared to that of the mother structures $B_{12}N_{12}-5^{12}6^2$ are considered to be due to the annihilation of B-B and N-N bonds by carbon doping. However, the charges of boron of the lower-energy configurations in alloy $C_{12}B_6N_6-5^{12}6^2$ and $C_{12}B_6N_6-4^66^8$ are found to be smaller than that of $B_{12}N_{12}-4^66^8$.

Isomer stru./ Config.	HOMO-LUMO Gaps (eV)	Mulliken charges		
		N	B	C
$C_{24}-5^{12}6^{12}$	0.911	—	—	0.000
$C_{24}-4^66^8$	1.260	—	—	0.000
$B_{12}N_{12}-4^66^8$	3.427	-0.441±0.000	0.441±0.000	—
$B_{12}N_{12}-5^{12}6^2$ -A	2.524	-0.419±0.068	0.419±0.059	—
$B_{12}N_{12}-5^{12}6^2$ -B	2.361	-0.414±0.065	0.414±0.074	—
$B_{12}N_{12}-5^{12}6^2$ -C	2.315	-0.410±0.060	0.410±0.081	—
$B_{12}N_{12}-5^{12}6^2$ -D	2.213	-0.408±0.061	0.408±0.085	—
$B_{12}N_{12}-5^{12}6^2$ -E	2.480	-0.409±0.052	0.409±0.086	—
$C_{12}B_6N_6-4^66^8$ -1	1.571	-0.439±0.010	0.420±0.056	0.009±0.067
$C_{12}B_6N_6-4^66^8$ -2	1.769	-0.446±0.010	0.405±0.077	0.021±0.073
$C_{12}B_6N_6-4^66^8$ -3	1.507	-0.438±0.016	0.403±0.087	0.018±0.082
$C_{12}B_6N_6-4^66^8$ -4	1.659	-0.442±0.010	0.389±0.104	0.026±0.089
$C_{12}B_6N_6-4^66^8$ -5	1.825	-0.438±0.016	0.418±0.082	0.010±0.085
$C_{12}B_6N_6-4^66^8$ -6	1.640	-0.439±0.013	0.420±0.039	0.010±0.070
$C_{12}B_6N_6-4^66^8$ -7	1.546	-0.440±0.012	0.393±0.065	0.024±0.088
$C_{12}B_6N_6-4^66^8$ -8	1.585	-0.440±0.014	0.397±0.103	0.021±0.096
$C_{12}B_6N_6-5^{12}6^2$ -1	1.631	-0.449±0.010	0.418±0.075	0.015±0.084
$C_{12}B_6N_6-5^{12}6^2$ -2	1.760	-0.450±0.009	0.419±0.019	0.015±0.088
$C_{12}B_6N_6-5^{12}6^2$ -3	1.421	-0.450±0.008	0.417±0.101	0.017±0.071
$C_{12}B_6N_6-5^{12}6^2$ -4	1.605	-0.446±0.000	0.437±0.001	0.004±0.098
$C_{12}B_6N_6-5^{12}6^2$ -5	1.398	-0.451±0.007	0.418±0.068	0.016±0.075
$C_{12}B_6N_6-5^{12}6^2$ -6	1.356	-0.450±0.008	0.417±0.066	0.016±0.074
$C_{12}B_6N_6-5^{12}6^2$ -7	1.382	-0.451±0.005	0.416±0.095	0.017±0.060
$C_{12}B_6N_6-5^{12}6^2$ -8	1.361	-0.458±0.006	0.409±0.069	0.024±0.080

Table 9.5 the HOMO-LUMO gaps and Mulliken charges of the cage isomers of carbon C_{24} and boron nitride $B_{12}N_{12}$ and the eight most stable alloy configurations of $C_{12}B_6N_6-4^66^8$ and $C_{12}B_6N_6-5^{12}6^2$ fullerenes

From the Table 9.5, though the root mean square deviation of the charge of

carbon is very large (it means some carbon atoms have small positive charges and the charges of some atoms are negative due to the different chemical environment such as near nitrogen- or boron- neighbor), the mean values of charges of carbon are positive. Therefore, some positive charges have been transferred from boron to carbon in alloy $C_{12}B_6N_6$. In Table 9.5, we also tabulate the energy gap of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of each structure. For the parent structures, the energy gap of $B_{12}N_{12}$ - 4^66^8 and C_{24} - 4^66^8 are larger than that of $B_{12}N_{12}$ - $5^{12}6^2$ and C_{24} - $5^{12}6^2$, respectively. This may be attributed to the different surface curvature induced by 4- and 5-member ring. Although the energy gaps (HOMO-LUMO) are sensitive to the configurations and no obvious trend is found, the lower-energy alloy cages $C_{12}B_6N_6$ have gaps between the parent structures in general (carbon cage structures and boron nitride cage structures). This can be attributed to the interaction between atomic orbit of carbon and that of boron nitride in these lower-energy configurations of alloy $C_{12}B_6N_6$.

9.4 Conclusion

Both C_{24} and $B_{12}N_{12}$ fullerenes are considered to be the smallest and stable cage-like structures. With these two cages as mother structures, the alloy $C_{12}B_6N_6$ is expected to be a good candidate of the smallest alloy cage. We have therefore attempted to tackle the very large alloy configuration space ($\sim 2.5 \times 10^9$ configurations) and examine the stability of $C_{12}B_6N_6$ with first principle methods coupled with BCR.

It is confirmed that the simple BCR rule plays an instructive role in the search of the most stable configurations. The stable alloy cage structures are usually formed with maximum number of C–C and B–N bonds and avoidance of the B–B and N–N bond. However, the stability of the configurations can't be accurately determined by the simple BCR rule and the environment effects beyond the nearest neighbor and two-body interaction must be accounted for. The GBCR with about 40 parameters seems to give a rational description on the energy landscape of the BCN fullerenes. It is considered that the model will be still effective in the prediction of the most stable structure of other cages since there are not other restricting conditions in the model.

It was found that the substitutions of BN units in the cage follow a “continuity” rule in both of the two cage structures. This phenomenon actually has been also found in the cage-like $(BN)_n C_{60-2n}^{60}$ and bulk alloys $c\text{-BCN}^9$. This is because the C-C and B-N bond are more stable than the C-B and C-N bonds. Maximization of the number of both C–C and B–N bonds will be inevitable to lead to the continuity of the B-N substitutions in the stable structures.

The bonding energies of the low-energy BCN fullerenes are between the pure cage-structure carbon and boron nitride meaning that this ternary alloy cage structures is relative stable. Though all the configurations calculated have positive mixing energy, the value of the mixing energy of the most stable configuration is comparable to $k_B T$ at $T \sim 2000K$. In the high temperature and non-equilibrium environment offered by the modern techniques such as laser ablation, direct-current arc and chemical vapor deposition³⁴, these small alloy fullerene are likely to be synthesized.

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Chapter 10

Theoretical Study on Structural Stability of $\text{Si}_n\text{C}_{60-n}$ ($0 \leq n \leq 30$) Heterofullerenes

In this chapter, the color bond graph (CBG) model is constructed to address the problem of complexity in alloy cages due to the different combinatorial possibilities. Using $\text{C}_{60-n}\text{Si}_n$ as a paradigm, the validity of the parameterized CBG model is demonstrated. With genetic algorithms (GA) method, the parameterized CBG Hamiltonian can quickly explore the large configuration space of alloy and identify the low-energy region. By integrating density functional calculations and the CBG model, the structural stability and Si-substitution pattern in fullerene cage of $\text{C}_{60-n}\text{Si}_n$ have been investigated. The low-energy (stable) structures are obtained from the configuration space ($\sim 1.15 \times 10^{18}$) for each concentration ($1 \leq n \leq 30$) by the CBG model with about 40 parameters. It is found that silicon atoms have the tendency of aggregation for all the low-energy alloy structures. However, these low-energy alloy cages are found to have small positive mixing energies (~ 35 meV/atom) and are expected to synthesize in experiment.

10.1 Introduction

Nano-sized clusters have gained considerable attention for the peculiar optical, electronic, magnetic and catalytic properties that originated from their special geometric structures¹⁻⁴. As a special case of nanocluster, cage-like carbon fullerenes have rapidly become an active area of research⁵⁻¹⁰, since the discovery of fullerene C_{60} ¹¹⁻¹³. Due to the stability of hybridized carbon sp^2 bonds, these cage-like molecules have been considered as a potential building block for new nano-structured materials with novel properties^{9,12,14,15}. The exohedral and endohedral doping of metal atoms on C_{60} have led to the well known superconductivity of fullerenes^{16,17}. The substitutional doping is also expected to enable tailoring and functionalizing of the fullerene

molecules¹⁸⁻²⁴. Recently, doping carbon cages with silicon has been actively explored^{21,25-28}. Although having the same number of valence electron as carbon, silicon is known to prefer sp^3 -hybridization. If silicon atoms can be substitutionally doped in the carbon cages, the reactivity of Si sites will offer a new path toward the polymerization of fullerenes²¹. So far, successful synthesis of $\text{C}_{60-n}\text{Si}_n$ ($n=1, 3$) has been reported^{21,25,29,30}. While it was speculated from photofragmentation experiments^{31,32} that up to 12 silicon atoms can be substituted in a fullerene without destroying its structure, clear experimental evidence for $\text{C}_{2N-n}\text{Si}_n$ ($n>3$) is elusive²⁸. Thus, systematic theoretical study on this new multi-component system will be helpful and timely to answer the fundamental questions such as the stability, morphology, electronic behavior, and basic features of chemical bonding.

For the study of alloy clusters, the first challenge is to determine the ground state and low-energy structures. In the case of binary alloy clusters (A_nB_m), the number of combinatorial possibilities² (2^{n+m}) due to different arrangement of A- and B- type atoms increases exponentially with the size of alloy clusters. This makes the finding of lowest energy structures of alloy cluster with high-level quantum calculation impossible. For $\text{C}_{60-n}\text{Si}_n$ cage structures in rich carbon region, searching systematically the ground states in the space of alloy configurations is still a formidable task, even though the geometric structures are assumed to establish. By intuitively and experientially choosing the configurations, the structure and electronic properties of some “low-energy” states with different number of substitutional atoms (silicon) have been studied in a series of density function theory calculations^{27,33-38}. However, the absence of an effective method makes the theoretical study blindfold to some extent and we can't draw a comprehensive picture on the binding characters between silicon and carbon atoms on the cage structures.

In this chapter, we intended to fill up the gaps in the existing theoretical framework for treating cage-like alloy structures. Using the alloy fullerene $\text{C}_{60-n}\text{Si}_n$ as a paradigm, the complexity of the question was illustrated. A parameterized model Hamiltonian based on first-principles calculations was established based on a few randomly chosen structures. Then initial Hamiltonian was used to guide a systematic

search powered by genetic algorithms. Low-energy structures were identified to improve the accuracy of the model Hamiltonian. This procedure was reiterated a few times to assure the validity of our predictions. Selected low-energy states of $\text{C}_{60-n}\text{Si}_n$ were examined in details to understand their structural stability and electronic properties.

10.2 Methods

10.2.1 Complexity of question and purposed method

The simplest prototype C_{58}Si_2 ²⁸ was considered to be difficult to perform by first-principles calculation due to numerous isomers ($\text{C}_{60}^2=1770$). Billas *et al.* constructed 9 isomers based on the distance between two silicon atoms and studied their stability with quantum calculations³³. We revisited this issue and found that C_{58}Si_2 cage can be simulated. Thanks to the very high symmetry (symmetry group= I_h) of fullerene cage, there are just 23 symmetrically distinct configurations after the operation of symmetry. However, following the increase in the number of substitutional Si atoms, the complexity quickly increases. There are 303 symmetrically distinct configurations in C_{57}Si_3 . For $\text{C}_{30}\text{Si}_{30}$, there are about 1.2×10^{17} (C_{60}^{30}) isomers. In total, there are about 6.3×10^{17} configurations for $0 \leq n \leq 30$. Even using the symmetry group to eliminate repeated configurations, there are still about 5.2×10^{15} configurations. It is obvious that this enormous task can't be completed by direct application of quantum calculations.

To solve the problem of having so many configurations with first-principles accuracy, a model Hamiltonian with proper parameters is needed. From the view of chemical bonds, it is normal anticipated that the stability of the chemical bonds is directly linked to the stability of the molecule structure. The rules of chemical bonding, such as the octet rule, are very important for analyzing the stability of the chemical structure by intuition. The stability of the alloy configurations can be studied by counting the number of different bonds. Actually, we have proposed that bond counting rules (BCR) can be considered as an effective guide in identifying the low-energy configurations in cage-like $\text{C}_{12}\text{B}_6\text{N}_6$ ³⁹. However, such a rule is so simple

that it cannot evaluate quantitatively the stability of an alloy structure.

The same chemical bonds are well known to have different strength intensity and bond length depending on the chemical environments. For example, different environments (such as the near- neighbor bond type, the angle between bonds) can induce different amount of charge transfer and thereby result in different local structural relaxation. It is therefore reasonable to assume that total energy should be correlated with the chemical bonds and its nearby local chemical environments. Thus, we generalized the idea of BCR to a new method named color bond graph (CBG) theory. In CBG, the energy of the alloy configurations is recast in a general form:

$$E(\sigma) = E_0 + \sum_i \alpha_1^i C_1^i(\sigma) + \sum_{i,k} \alpha_{2,k}^i B_{2,k}^i(\sigma) + \sum_{i,k} \alpha_{3,k}^i A_{3,k}^i(\sigma) + \sum_{i,k} \alpha_{4,k}^i F_{4,k}^i(\sigma) + \dots (10.1)$$

where the parameters α 's represent the interaction energies, C_1 's are the energy of vertex i ($i=1$ to N), B_2 's, A_3 's and F_4 's are the generalized correlation functions for different types of "bonds" to include contributions from two-vertex (the B_2 's), three-vertex (the A_3 's) terms and four-vertex (the F_4 's). In this work, the vertices are sorted as 2 classes (carbon and silicon) and we include all two-vertex correlation functions, one three-vertex and one forth-vertex correlation functions. In total, there are about 40 parameters (α 's) that were fitted to the first principle calculations.

After the effective Hamiltonian with fitted parameters is obtained, we can tackle the selection of potential ground states by different algorithms methods, such as directly searching for each composition, Monte Carlo simulations⁴⁰ and genetic algorithms (GA)^{41,42} which mimic the idea of Darwinian biological evolution. Here, the GA method which is a powerful paradigm for global optimization⁴³⁻⁴⁵ is used to quickly search the low-energy region for each concentration.

Inspired by the power of natural evolution, GA conducts global search by maintaining a population of candidate solutions and evolving the population by subjecting the solutions to selection, crossover, and mutation⁴². Firstly, an initial population of candidate configurations (randomly chosen $\text{C}_{60-n}\text{Si}_n$ with different concentration of silicon) is created randomly to ensure a uniform sampling throughout the search space. Each candidate configuration is represented by a string

(‘chromosome’) of m integers (‘genes’) with each integer indicating the localization of a silicon atom at the corresponding vertex. The length of the chromosome, m , is determined by the concentration of Si atoms. Secondly, the fitness of each chromosome is then evaluated using Equation 10.1. Two parent chromosomes are selected based on the fitness values so that the lower the energy of a chromosome the more likely it will be selected. Thirdly, new chromosomes, generated from previous ones by crossover and mutations, are then used to generate the next generation. Using uniform crossover, two new child chromosomes are generated from parent 1 and parent 2. Then the child chromosomes undergo random mutations. Finally, the new child chromosomes are added to the new population and the best chromosome from previous generation is guaranteed to survive in the new population.

10.2.2 Quantum chemistry method

All the initial structures of Si-doped fullerenes are from the geometrical configuration of C_{60} . Preliminary investigations were carried out using semi-empirical method MNDO. Geometries of all systems were fully optimized without any symmetry constraints at this level. Vibrational analyses were also carried out to ensure the optimized structures are true minimum in their energy landscapes. However, previous investigations on carbon cage systems have shown electron correlation is important for the stability of structure^{46,47}. Though DFT method⁴⁸⁻⁵⁰ is less accurate than more extensive correlated methods such as CCSD, with appropriate exchange correlation functional and moderate basis functions it will be more efficient than any other methods that include electron correlation for systems with large numbers of atoms. The three-parameter empirical formulation B3LYP is employed, since it is most widely used in the calculation of molecular electronic structure⁵¹⁻⁵³. All the structures optimized by MNDO method are optimized further by DFT method with 3-21G basis set without any symmetry constraints. All *ab initio* calculations reported in this work were performed with the GAUSSIAN 03 package⁵⁴.

10.3 Results and Discussions

10.3.1 Parent structures and isomers with low Si concentration

We began our study by structural optimization of the pure fullerene C_{60} and Si_{60} . The hybridized quasi- sp^2 bond of carbon makes the structure very stable with high binding energy (tabulated in Table 10.1). Bonding of silicon prefers sp^3 hybridization that leads to the distorted fullerene cage (as shown in Fig. 10.1) and smaller binding energy. Furthermore, Sun *et al.*⁵⁵ examined other form of Si_{60} and found that stuffed fullerene (SF) $\text{Si}_{20}@\text{Si}_{40}$ is more stable than Si_{60} fullerene cage. In this work, we will focus on substitution in rich-carbon region ($1 \leq n \leq 30$).

Fig. 10.1: Structures of C_{60} , Si_{60} , C_{59}Si_1 and the low-energy isomers of C_{59}Si_2 . Black spheres for C atoms, yellow spheres for Si atoms.

Fullerene cage structure has very high symmetry (I_h) and all sites in C_{60} are equivalent. For C_{59}Si_1 , there is only one unique isomer. The relaxed structure has an energy gain about 8.59 eV and is 0.09 eV/atom smaller than the binding energy of C_{60} . The modifications of the bond lengths are mainly confined to Si-C bonds and relative long Si-C bonds make Si atom raised on the cage structure in the structure of C_{59}Si_1 as shown in Fig. 10.1. For C_{58}Si_2 , the structures of all the 23 symmetrically distinct configurations are optimized. The 3 most stable structures are found to have similar characters which is two Si atoms occupying in the same ring (hexagon or pentagon)

shown in Fig. 10.1. In the most stable isomer $\text{C}_{58}\text{Si}_2\text{-A}$, two Si atoms are arranged on para-sites (the third nearest-neighbor positions) of a hexagonal ring which is consistent with the previous study and their experimental findings for disilabenzene complexes²¹. It should be noted here that the energetic difference ($\sim 4\text{meV/atom}$) among three most stable structures are very small thus making the confirmation of the most stable structure non-trivial²⁸.

Isomer stru.	Energy (Hartree)	Binding energy (eV/atom)	Formation energy (meV/atom)	Relative energy (eV/60-atoms)
C_{60}	-2273.5216	8.684	0.000	-----
Si_{60}	-17278.9600	4.321	0.000	-----
C_{59}Si_1	-2523.5679	8.591	20.104	-----
$\text{C}_{58}\text{Si}_2\text{-A}$	-2773.6392	8.509	28.872	0.000
$\text{C}_{58}\text{Si}_2\text{-B}$	-2773.6334	8.507	31.506	0.158
$\text{C}_{58}\text{Si}_2\text{-C}$	-2773.6287	8.505	33.619	0.284

Table 10.1: Calculated energy, Binding energy, Formation energy and Relative energy of the parents cage structures (C_{60} and Si_{60}), C_{59}Si_1 and three low-energy isomers of C_{59}Si_2

For the three most stable isomers of C_{58}Si_2 , two Si atoms sitting in same ring can reduce the strain energy of structure. Two Si atoms avoiding the nearest-neighbor positions can be attributed to that the Si-C bond is more stable than Si-Si bond. For further evaluation of the relative stability of alloy cage, we will use the notion of formation energy (ΔE_{form}) which is defined as

$$\Delta E_{\text{form}}(\sigma, \text{C}_{60-n}\text{Si}_n) = [E(\sigma, \text{C}_{60-n}\text{Si}_n) - \frac{60-n}{60} E(\text{C}_{60}) - \frac{n}{60} E(\text{Si}_{60})] / 60, \quad (10.2)$$

where $E(\text{C}_{60})$ and $E(\text{Si}_{60})$ are the energy of C_{60} and Si_{60} fullerene cage that are used as the parent structures. The formation energy corresponds to the change of energy when constructing the alloy cage from the parent cages. A negative value of ΔE_{form} means the alloy cages are stable with respect to pure parent cages. The formation energies of C_{59}Si_1 and some isomers of C_{58}Si_2 are tabulated in Table 10.1. The positive mixing

energies of these isomers indicate that these isomers are metastable structures and will be thermodynamically instable at low temperature.

10.3.2 Searching low-energy isomers with high Si concentration

Fig. 10.2. The effectiveness of CBG model: the x -axis is the DFT-calculated formation energies and the y -axis is the predicted formation energies from CBG model. Two hundred randomly chosen configurations are shown in open black circles. The solid blue circles are the predicted low-energy configurations (~ 140) in the first run by CBG model with GA in which the parameters are fitted to the DFT energies of 200 randomly-chosen configurations.

Following the increased concentration, existence of numerous isomers makes the systematic search for low-energy structures a challenging task. For each concentration n ($\text{C}_{60-n}\text{Si}_n$), there are $60!/n!(60-n)!$ configurations. Here we rely on the CBG theory to predict the low-energy structures. In order to obtain the parameters (α 's) in Equation 10.1 from the first-principles calculation, we randomly choose 6-8 configurations for each concentration. There are about 200 configurations chosen in the range of concentration $2 \leq n \leq 30$ for first-principles structural optimization. The formation energies are extracted from the calculated total energies and are used for the

fitting of Equation 10.1. The ability of the parameterized model (CBG) to capture the trends in energy of $\text{C}_{60-n}\text{Si}_n$ is confirmed in Fig. 10.2. The root-mean-squared deviation of the model that is fitted from the extracted formation energy is ~ 8 meV/atom. Compared to the range of ~ 280 meV/atom (estimated from random-chosen structures), the ratio is just 2.8%. Thus, we can use the model with fitted parameters to predict the low-energy structures for each concentration.

Fig.10.3. The effectiveness of prediction in low-energy region (the same convention as Fig. 10.2 is adapted here). Low-energy isomers from first run (see Fig. 10.2) were split into two groups: The blue diamonds (~ 80 configurations) were used to reparameterize Equation 10.1 and the magenta diamonds (~ 60 configurations) were used as test set to verify the effectiveness of the CBG. Their rms errors are 3.4 and 4.0 meV/atom respectively. The red spheres are the new low-energy isomers from the revised CBG model in which the parameters are fitted by the calculated energies of the low-energy configurations.

The GA method is integrated with CBG model for searching the low-energy structures in the space of the enormous configurations. For each concentration, about 5 isomers with low-energies were identified. We found that the formation energies of all configurations are in the region of $\sim 25\text{--}75$ meV/atom. In order to evaluate the validity of CBG theory in the region of low formation energies, all the ~ 140

configurations are examined by first-principles calculation. It is found that the parameters from the first run to be very effective in differentiating high- and low-energy region, but the accuracy needs further improvement. With the aim to improve our description on ground-state structures, we use the data from low-formation energy region (~ 140 configurations) to fit of Equation 10.1. A training set of 80 configurations is chosen to re-parameterize Equation 10.1. The root-mean-squared deviation of the fitting has gone down to ~ 3.4 meV/atom. The formation energies of other ~ 60 configurations (used as test set) are found to have a root-mean-squared error of ~ 4.0 meV/atom. Then the newly parameterized model is used to explore the low-energy structures again. New low-energy isomers for each concentration (shown as red sphere in Fig. 10.3 and 10.4) are found.

Fig. 10.4: Formation energies of all the structures as the function of the concentration. It is obvious that the CBG model when integrated with genetic algorithm can predict the low-energy ground states starting from the randomly chosen configurations. We find that formation energy of low-energy configurations shows very little dependency on the concentration of Si.

In Fig. 10.4, the formation energies from first-principle calculations of all the structures are shown as the function of the concentration. It is obvious that the CBG model when integrated with genetic algorithm can predict the low-energy ground states starting from the randomly chosen configurations. The formation energy of low-energy configurations shows very little dependency on the concentration of Si. This means the alloy with cage structure in each concentration ($2 \leq n \leq 30$) have same structural stability based on the stability of the structures of two parents (fullerene cage C_{60} and Si_{60}). However, fullerene cage Si_{60} is a metastable state and is not the ground state of Si_{60} . Therefore, the stability of the alloy cage structure is likely to be reduced as the concentration of silicon increases. In the literature, the upper limit of 12-Si doping in the cage are speculated based on mass spectrometry and photofragmentation studies,^{31,32}. In another work, an upper limit is expended to 24-Si dopant by the analysis of dynamical instability²⁷.

10.3.3 Properties of the low-energy configurations

Ten lowest-energy states of some concentrations are chosen to analyze their properties in detail. The calculated energies, binding energies and formation energies are tabulated in Table 10.2. The binding energies are between that of the pure cage C_{60} and Si_{60} . This means the alloy cage structure is relatively stable like the parent cage structure. All these low-energy structures have positive formation energy at the temperature 0 K. From the energetic point of view, all the alloy cages are metastable structures and tend to separate into pure parent cage structures at low temperature. Fortunately, the value of positive formation energies of these alloy structures is not very large ($\sim 35\text{meV}$). The thermal energy induced by several hundred degree of temperature can counteracted the effect of positive formation energy. In the range of

concentration of silicon ($1 \leq n \leq 30$), the alloy cages are not difficult to be produced by recent experiment technique, such as laser ablation or vaporization.

Structure	Energy (Hartree)	Binding energy (eV/atom)	Formation energy (meV/atom)
C_{55}Si_5	-3523.8958	8.284	35.827
C_{54}Si_6	-3773.9877	8.212	35.247
$\text{C}_{50}\text{Si}_{10}$	-4774.3518	7.922	34.556
$\text{C}_{48}\text{Si}_{12}$	-5274.5425	7.781	30.278
$\text{C}_{46}\text{Si}_{14}$	-5774.7309	7.639	27.061
$\text{C}_{42}\text{Si}_{18}$	-6775.0738	7.339	35.986
$\text{C}_{38}\text{Si}_{22}$	-7775.4464	7.053	31.400
$\text{C}_{36}\text{Si}_{24}$	-8275.6284	6.908	31.095
$\text{C}_{34}\text{Si}_{26}$	-8775.7966	6.756	37.038
$\text{C}_{30}\text{Si}_{30}$	-9776.1649	6.468	35.827

Table 10.2: Energy of ten most-stable cage alloy structures chosen for different concentration of silicon (structures are shown in Fig. 10.5).

Fig. 10.5: Structure of the ten most-stable cage alloy structures with different concentration of silicon. Their energies are reported in Table 10.2.

The structures of these low-energy alloy configurations are depicted in Fig. 10.5. An obvious result is all the low-energy alloy configurations are at phase-separated states and the chemical ordering rule of bulk SiC don't exist in fullerene cage with 60

atoms. In bulk SiC, the existent of chemical ordering means sp^3 -hybridized Si-C bond are more stable than the average of Si-Si and C-C bonds. However, this is not true for quasi- sp^2 hybridized Si-C bonds in the fullerene cage. This can be attributed to the tendency of the sp^3 -hybridization of Si bonds and the strain-induced cage distortion due to the large size of Si atoms. Aggregation of Si atoms in the cage structure can reduce the strain energy by changing the position in a larger local space of the cage structure.

In order to analyze the electronic properties of the cage-like cluster $\text{Si}_n\text{C}_{60-n}$ ($0 \leq n \leq 30$), the HOMO-LUMO gaps of the low-energy configurations were calculated. As shown in Fig. 10.6, we can find the gaps quickly reduce to a value that is near the gap of Si_{60} , following the increase of the concentration of Si. This can be explained by the analysis of the spatial distribution of HOMO and LUMO. From the HOMOs and LUMOs of some low-energy configurations shown in Fig. 10.6, we can find that the HOMO/LUMO orbitals mainly distribute on Si atoms of the cage. This means the gaps of alloy clusters are more similar to that of Si_{60} . Another finding is that the gap is sensitive to the change of concentrations and different substitutional positions. For example, the gaps of three low-energy structures of Si_2C_{58} are 1.63 eV, 2.21 eV and 2.13 eV, respectively. This means there should be a distribution of gaps in experiment, even for single substitutional concentration due to the co-existence of different substitutional patterns.

10.4 Conclusion

The size change, shape difference and combinatorial possibilities of different arrangement make the theoretical simulation of the alloy clusters complicated. Especially, combinatorial possibilities have resulted in a very large configurational space (2^{n+m}). Using the alloy fullerene $\text{C}_{60-n}\text{Si}_n$ as a paradigm, we attempt to tackle the large alloy configuration space ($\sim 1.15 \times 10^{18}$) by the combination of first principle calculation with genetic algorithms (GA). Based on the CBG theory, a model Hamiltonian has been built for predicting the total energy of the alloy cage. Based on the results from first-principles calculations, the parameters in the model Hamiltonian

are established. Then the validity of the parameterized Hamiltonian are confirmed. With GA method, the model Hamiltonian can efficiently guide GA to locate the low-energy region for cage structures. By optimizing the parameters in the model farther in low-energy region, the low-energy stable states can be obtained for each concentration.

Fig. 10.6: Molecular orbitals (HOMO and LUMO) of C_{58}Si_2 -A, C_{58}Si_2 -B, C_{58}Si_2 -C, C_{54}Si_6 , $\text{C}_{46}\text{Si}_{14}$, $\text{C}_{36}\text{Si}_{24}$, $\text{C}_{30}\text{Si}_{30}$. It is obvious that the spatial distribution of both HOMO and LUMO are concentrated on Si atoms. This spatial preference can explain

that HOMO-LUMO gaps of stable low-energy configurations (shown in the bottom) quickly reduce to a value very close to Si_{60} .

For fullerene cage $\text{C}_{60-n}\text{Si}_n$, all the alloy cages are studied systematically in the C-rich region. In all concentrations ($2 < n \leq 30$), silicon atoms have the tendency of aggregation and the chemical ordering doesn't exist in fullerene cage with 60 atoms. Very small positive mixing energy (~ 35 meV/atom) can be easily counteracted by the thermal effect of temperature and we expect the alloy cages can be produced in experiment.

10.5 References

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Chapter 11

Conclusion and Future Work

This thesis contains two parts: First, quasi-ordered structure method (QOS) is made in order to study the binary semiconductor alloys. Then the structural stability and electronic properties of ZnO-based alloys including $\text{Be}_x\text{Zn}_{1-x}\text{O}$, $\text{Ca}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{ZnO}_x\text{S}_{1-x}$ are investigated based on QOS method with first principle calculation. Second, the color bond graph (CBG) theory is built by expanding the idea of bond counting rule (BCR) for the study of alloy clusters. The BCR rule has been applied the bulk alloy system BC_2N for choosing stable/metastable ground states. The CBG theory has been test in alloy cage-like cluster $(\text{BN})_6\text{C}_{12}$ and $\text{C}_{60-n}\text{Si}_n$.

11.1 Quasi-ordered structure method and ZnO-based semiconductor alloy

Special quasi-random structure (SQS) method is usually used to study the properties of the semiconductor alloys. This is because size mismatch between the atomic constituents usually leads to phase separation due to the positive mixing enthalpy and the high growth temperature needed result in the random alloy configuration in bulk semiconductor alloys. By the advanced epitaxial growth techniques like P-MBE, LMBE and RP-MOCVD, the alloy films can be synthesized for large range of the alloy concentration region. The process of phase separation is considered to be kinetically limited and the local stable alloy clusters with lower formation enthalpy will be possibly formed. Based on the above consideration, we make the quasi-ordered structure (QOS) method. In this method, all the quasi-ordered structures in a supercell can be constructed by the application of space group theory. By this method, the first principle calculations combined with statistical mechanics are used to study the properties of the ZnO-based semiconductor alloy films.

For isostructural phase alloys $\text{Be}_x\text{Zn}_{1-x}\text{O}$, a systematic study on the structural and electronic properties is carried out by first principle methods. QOS are constructed in

a unit cell with 32 atoms. The structures and electronic properties obtained by the DFT methods are found to be consistent with the experimental results, considered the error of experimental values. The structures that have the same periods along the [0001] direction as the parents are found to be relatively more stable. Three metastable ordered states are suggested to exist possibly by examining the formation enthalpy of all alloy configurations. The lattice constants of the alloy are found to follow the Vegard's law and are comparably with the experimental values. The calculated band gap of the $\text{Be}_x\text{Zn}_{1-x}\text{O}$ is also compared with the experimental measurements and we find that some alloy configurations with the same concentration can have band gaps differed by ~ 1.5 eV.

For the nonisostructural phase alloys $\text{Cd}_x\text{Zn}_{1-x}\text{O}$, $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$, the phase stabilities, structural and electronic properties are investigated by first-principle methods. QOS are constructed in three 16-atom supercells ($1\times 1\times 2$ B1 phase structure, $2\times 2\times 1$ and $2\times 1\times 2$ B4 phase structure). Taking into account the contribution of the alloy statistics, we have drawn the mixing regions of phases for $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ ($0.25 < x < 0.375$), $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ ($0.375 < x < 0.5$), and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ ($0.75 < x < 0.875$). The averaged lattice constants of $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Ca}_x\text{Zn}_{1-x}\text{O}$ with wurtzite structure are found to don't follow the Vegards' rule and this is related to the degree of instability of the wurtzite MgO and CaO. Wurtzite CaO is found to be instable and turns into hexagonal CaO. The calculated band gaps are found to be consistent with the experimental values for alloy $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ and $\text{Mg}_x\text{Zn}_{1-x}\text{O}$. The bowing parameters for alloys $\text{Mg}_x\text{Zn}_{1-x}\text{O}$ and $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ are estimated to be 0.87 eV and 1.30 eV, respectively.

For the nonisostructural phase alloys $\text{ZnO}_x\text{S}_{1-x}$, the thermodynamic stability and electronic properties are studied. SQS are used to model the random phases and QOS are used to model the quasi-ordered states. The solubility limits in mother lattice (sulfur-doped ZnO and oxygen-doped ZnS) are found to be very small for both phases from calculated phase diagram. However, under the nonequilibrium thermodynamics condition, the local stabled single-phase $\text{ZnO}_{1-x}\text{S}_x$ alloy with zincblende structure can be obtained at the range of concentration $0 \leq x \leq 0.5$. The concentration dependence of

the band gap is found to be very nonlinear and the large bowing coefficients sensitively depend on the composition. Furthermore, the bowing coefficient for wurtzite structure is very different from that for zincblende structure in alloy $\text{ZnO}_{1-x}\text{S}_x$.

11.2 Color bond graph (CBG) theory

In order to tackle the 2^N question about configurations in alloy clusters, a method named color bond graph (CBG) theory are constructed. The stability of a structure can be evaluated by the stability of the chemical bonds in the structure. Based on this idea, bond-counting rules can be used for search the configuration of 2^N configurations. However, such a rule is so simple that it cannot evaluate quantitatively the stability of an alloy structure. Considering the local environments of the chemical bonds, the interaction of many-body interaction and long-ranged two-body interaction are included in a model Hamiltonian. It is speculated that the electronic properties such as total energy which be used to estimate accurately the stability of a structure should have relation with the chemical bonds with its local chemical environments in the structure. With the first-principles calculation, the parameterized Hamiltonian can be used to predict the stable ground states.

11.3 BC_2N superhard material and $\text{C}_{12}\text{B}_6\text{N}_6$ and $\text{C}_{60-n}\text{Si}_n$ Fullerene

By combining simple bond counting rules (BCR) and first principle methods, a systematic search for the low-energy alloy configurations of BC_2N in different unit cells are carried out. The stability of an alloy configuration is found to be correlated with its density and hardness. It is also found that there are many low-energy configurations with high density to exist. These high-density pseudo-cubic BC_2N alloy configurations all have a large ratio of B-N and C-C bonds; their formation energies are in the order of 100 ~ 200 meV/atom. At high temperature and nonequilibrium experimental conditions offered by the modern growth techniques, our calculated results suggest that a mixture of different high-density alloy configurations is likely and this may result in the reduction of hardness.

By BCR and CBG theory, the stability and the BN-substitution pattern of $C_{12}B_6N_6$ fullerene have been investigated theoretically. The simple BCR is provided to can serve as an effective guide to look for the low-energy alloy configurations. The CBG theory is tested to can describe quantitatively the stability of the alloy structure. The substitutions of BN units in the cage are found to follow a “continuity” pattern in the low-energy configurations. Though all the alloy configurations have positive mixing energy, the low-energy isomers are found to be quite stable (less than 150 meV/atom). We expect these fullerene structures can be synthesized under the high temperature and nonequilibrium experimental conditions offered by the modern growth techniques such as laser ablation, direct-current arc and chemical vapor deposition.

With genetic algorithms (GA), the CBG theory is also applied to study the structural stability of $C_{60-n}Si_n$ ($1 < n \leq 30$). It is found that silicon atoms have the tendency of aggregation and the chemical ordering doesn't exist in fullerene cage with 60 atoms. Very small positive mixing energy (~ 35 meV/atom) can be easily counteracted by the thermal effect of temperature and it is expected that the alloy cages can be produced in experiment.

11.4 Future work

The quasi-ordered structure (QOS) method is expected to be used for other alloy system. The cluster expansion (CE) method is expected to be related with the QOS method. Then the other alloy systems are expected to study by this method. The pattern of alloy surface on some substrate is interested and worth to study for exploring the surface/interface effect of epitaxial growth. Furthermore, the electron properties of the alloy need to be explored in detail for some applied study such as solar cell and optical detectors. The high-pressure simulation of alloy phase can also be carried out for phase transition.

Si-doping substitutionally in carbon cage structure will be possible to offer a path towards the polymerization of fullerenes due to the reactivity of Si sites. The color bond graph (CBG) theory has used to study systematically the substitutional pattern of

Si in C_{60} . In order to obtain the low-energy ground states, Algorithms such as the Monte Carlo (MC) method and genetic algorithm (GA) has been found to can explore effectively the space of configurations. Excepted for the alloy cage $C_{60-n}Si_n$, there are many related alloy cage-like structures ($C_{60-n}B_n$, $C_{60-n}N_n$, $C_{60-n}X_n$ ($X=Fe$, Co and Ni), $C_{m-n}X_n$, $C_{60}Y_n$, ($Y=H$, F , $CH_4...$)) to need to study for exploring novel properties such as optical-electron, electro-chemistry, ferromagnetism and storage of hydrogen.

The CBG theory needs to be developed further. How to choose the different many-body interactions will make the method more effective for predicting the stability of the structures. Can it be used for other form of cluster except the cage-like structure? Metal clusters with large active surface still have being studied extensively for catalyst with high catalytic efficiency. The study of metal alloy clusters with large size is still in its infancy and there is not an effective method to exist (though there are some semi-empirical embedded atom potentials methods to can be used). With first principle method, CBG theory is expected to can explore the metal alloy cluster.