First-principles study of configurational disorder in icosahedral boron-rich solids

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This thesis is a theoretical study of configurationally disordered icosahedral boron-rich solids, in particular boron carbides, using density functional theory and alloy theory. The goal is to resolve discrepancies, regarding the properties of boron carbides, between experiments and previous theoretical calculations which have been a controversial issue in the field of icosahedral boron-rich solids. For instance, $B_{13}C_2$ is observed experimentally to be a semiconductor, meanwhile electronic band structure calculations reveal a metallic character of $B_{13}C_2$ due to its electron deficiency. In B_4C , on the other hand, the experimentally observed band gap is unexpectedly smaller, not the usual larger, than that of standard DFT calculations. Another example is given by the existence of a small structural distortion in B_4C , as predicted in theoretical calculations, which reduces the crystal symmetry from the experimentally observed rhombohedral ($R\bar{3}m$) to the based-centered monoclinic (Cm). Since boron carbide is stable as a single-phase over a broad composition range (~ 8 -20 at.% C), substitution of boron and carbon atoms for one another is conceivable. For this reason, the discrepancies have been speculated in the literature, without a proof, to originate from configurational disorder induced by substitutional defects. However, owing to its complex atomic structure, represented by 12-atom icosahedra and 3-atom intericosahedral chains, a practical alloy theory method for direct calculations of the properties of the relevant configurations of disordered boron carbides, as well as for a thermodynamic assessment of their stability has been missing.

In this thesis, a new approach, the superatom-special quasirandom structure (SA-SQS), has been developed. The approach allows one to model configurational disorder in boron carbide, induced by high concentrations of low-energy B/C substitutional defects. $B_{13}C_2$ and B_4C are the two stoichiometries, mainly considered in this study, as they are of particular importance and have been in focus in the literature. The results demonstrate that, from thermodynamic considerations, both $B_{13}C_2$ and B_4C configurationally disorder at high temperature. In the case of $B_{13}C_2$, the configurational disorder splits off some valence states into the band gap that in turn compensates the electron deficiency in ordered $B_{13}C_2$, thus resulting in a semiconducting character. As for B_4C , the configurational disorder eliminates the monoclinic distortion, thus resulting in the restoration of the higher rhombohedral symmetry. Configurational disorder can also account for an excel-

lent agreement on elastic moduli of boron carbide between theory and experiment. Thus, several of the previous discrepancies between theory and experiments are resolved.

Inspired by attempts to enhance the mechanical properties of boron suboxide by fabricating boron suboxide-boron carbide composites, as recently suggested in the literature, the SA-SQS approach is used for modeling mixtures of boron suboxide (B_6O) and boron carbide (B_{13}C_2), denoted by pseudo-binary $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloys. The knowledge of configurational disorder, gained from the previous studies of boron carbide, is applied to model the mixing alloys. By investigating the thermodynamics of mixing between B_6O and B_{13}C_2 , the phase diagram of the $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloys is outlined and it reveals the existence of a miscibility gap at all temperatures up to the melting point, indicating the coexistence of B_6O -rich and either ordered or disordered B_{13}C_2 -rich domains in $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloys under equilibrium condition. However, a limited intermixing of B_6O and B_{13}C_2 to form solid solutions at high temperature is predicted, e.g. a solid solution of $\sim 5\%$ B_{13}C_2 in B_6O and $\sim 20\%$ B_6O in B_{13}C_2 at 2000 K.

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1.1 Icosahedral boron-rich solids

Over the last few decades, icosahedral boron-rich solids have become attractive in a wide range of material science's research fields. Icosahedral boron-rich solids primarily comprise of clusters of boron atoms, i.e. 12-atom icosahedra, in which each boron atom is located on a vertex of an icosahedron. The simplest form of icosahedral boron-rich solids is given by elementary α -boron (B_{12}). Its structural unit can be represented by 12-atom icosahedra placed at vertices of a rhombohedral unitcell with $R\bar{3}m$ space group [1], as shown by Fig.1.1(a). Due to translational symmetry in the crystal lattice, the icosahedral unit loses its fivefold rotational axes, thus resulting in two different crystallographic sites, namely polar and equatorial, and each icosahedron links to the six neighboring icosahedra via the six polar atoms by forming direct inter-icosahedral bonds. Other icosahedral boron-rich solids, e.g. boron subpnictides ($B_{12}As_2$ and $B_{12}P_2$), boron carbide (B_4C), and boron suboxide (B_6O), can be seen as a modification of α -boron. In the case of boron carbide [1–4], a 3-atom chain composing either of boron or carbon is formed and the two chain-end atoms are connected to equatorial atoms residing on the six neighboring icosahedra (see Fig.1.1(b)). The chain unit is then aligning itself along the longest diagonal in the rhombohedron, i.e. in the $[111]$ direction of the rhombohedron. Rather than the 3-atom chain, a 2-atom chain of arsenic, and phosphorus is formed for $B_{12}As_2$, and $B_{12}P_2$, respectively, as illustrated in Fig.1.1(c). As for B_6O , a pair of oxygen atoms are residing in the interstices between the icosahedra, instead of the chain units, as shown in Fig.1.1(d). Apart from the examples given above, there exist other icosahedral boron-rich solids with even more complex crystal structures, e.g. (1) elementary β -boron, normally denoted by B_{105} , (2) elementary γ -boron (B_{28}), and (3) silicon hexaboride (SiB_6), *etc.* Even though β -boron

processes the same rhombohedral symmetry as does α -boron, the situation is far more complicated in which, apart from regular icosahedra, it can consists of larger clusters of boron atoms (B_{84}), deltahedra (B_{10}), and individual boron atoms [5, 6]. Due to its highly complex atomic structure, several structural models of β -boron have been proposed in the literature [7–9]. However, an issue, regarding both the number of boron atoms and the structure of boron clusters in the rhombohedron, is still being a debate among the community. On the other hand, γ -boron is found to be a high pressure phase of elementary boron. It consists of two B_{12} icosahedra and two B_2 dumbbells with a NaCl-type of arrangement in an orthorhombic unitcell [10, 11]. SiB_6 has also a rather complex atomic configuration. Within an orthorhombic cell, it contains not only regular icosahedra but also icosihexahedra, and isolated boron and silicon atoms [12].

Figure 1.1. Icosahedral structures of boron-rich solid: (a) α -boron, (b) boron carbide, (c) boron subpnictides, and (d) boron suboxide. Grey and black spheres represent atoms residing in the icosahedra and in the interstices between the icosahedra, respectively.

Chemical bonding of icosahedra in those icosahedral boron-rich solid is somewhat specific. It does not even follow the usual bonding criteria (two-center two-electron bond). Each boron atoms within an icosahedron, for instance in the case of α -boron, bonds to five neighboring boron atoms. Based on the regular bonding criteria, this is not possible since at least five electrons are required to satisfy their chemical bonding, meanwhile each boron atom can provide at most three electrons ($2s^2, 2p^1$) to the bonding process. To avoid the situation of electron deficiency and to form the icosahedral structure, the boron atoms, instead of two-center bonds, form three-center two-electron bonds in which each triangle face of the icosahedron, forming by three boron atoms, are sharing only two electrons and the electron density is peak around the center of the triangle [13]. Demonstrated by Longuet-Higgins and Roberts [14], twenty-six electrons are required to complete thirteen intra-icosahedral bonding orbitals. Consequently, six out of thirty-six electrons of the twelve boron atoms within the icosahedron are used in forming two-center inter-icosahedral bonds with the six neighboring icosahedra. Another twenty-six electrons are then filled in to complete the three-center intra-icosahedral bonds and

the rest four electrons are contributed to form the three-center inter-icosahedral bonds with neighboring icosahedra. Since all of the available electrons are used to fulfil the bonding, α -boron is a semiconductor. Similarly to α -boron, the concept of three-center bond can be applied to describe the bonding criteria of the other α -boron-based icosahedral boron-rich solids, e.g. $B_{12}As_2$, $B_{12}P_2$, and B_4C .

Due to their unusual crystal structures and the characteristic of the three-center bonding, these boron-rich solids come up with several outstanding properties, which are of importance in technological applications [13, 15], e.g. high hardness, low density, high melting point, low wear coefficient, high chemical stability. Such properties thus make icosahedral boron-rich solids useful as, for instance light weight armor, wear-resistant materials, cutting tool materials [16–19], candidate materials for high temperature electronic [15, 20] and thermoelectric devices [15, 21, 22], etc. Due to high absorption cross section for thermal neutron of the isotope ^{10}B , icosahedral boron-rich solids can be used as neutron absorbing materials in nuclear reactors [15, 16, 23, 24]. Note that naturally boron contains approximately 20 at.% of ^{10}B . Furthermore icosahedral boron-rich solids, especially B_4C , are recently of interest in neutron detector applications as a replacement of the commonly used 3He , which is running out of the world-wide supplies [25–27]. The advantage of B_4C over the other icosahedral boron-rich solids for a new types of neutron detectors is that it can be easily synthesized, using for example magnetron sputtering, in the form of thin solid films with high amount of ^{10}B [27]. In the following subsection, boron carbide, as a material under investigation in this thesis, will be discussed in detail.

1.2 Boron carbide

Boron carbide was discovered in 1858 [16]. Despite the fact that the compound has been known for more than 150 years, several issues, regarding its properties, remain ambiguous and has still been controversial in the field of icosahedral boron-rich solids. Confirmed by several independent experiments [16, 28], boron carbide is stable as a single-phase solid solution over a broad composition range. Even though a lot of B-C phase diagrams has been suggested from time to time in the literature [16, 29–32], they have been being argued among the community. It is however generally accepted that the single-phase region of boron carbide extends from 8 to 20 at.% C approximately. The proper stoichiometric formula of boron carbide is thus preferably given by $B_{1-x}C_x$, where $0.08 \lesssim x \lesssim 0.2$ corresponding to designations of $B_{10.5}C$ to B_4C . As mentioned in the previous subsection, x-ray and neutron diffraction measurements [1–4] reveal that boron carbide has the rhombohedral symmetry with $R\bar{3}m$ space group. The structural units are given by a 12-atom icosahedron connecting to a 3-atom chain, thus at least consisting of 15 atoms. Somehow, it is a formidable task to identify, at any specific at.% C, exact atomic positions of boron and carbon, owing to the similarities both of atomic form factor for x-ray diffraction [33] and nuclear scattering cross-sections (^{11}B and ^{12}C) for neutron diffraction [4, 34] between boron and carbon atoms. A lot of effort has so far been done in order to determine how boron and carbon

atoms are residing on the lattice sites, and how different atomic distributions of boron and carbon, as the at.% C changes within the single-phase region, alter the properties of boron carbide, which is considerably of importance for its technological applications. Up until now, several models of boron carbide, based on the crystal symmetry and the structural unit, have been suggested mainly focusing on $B_{12}C_3$ (B_4C) and $B_{13}C_2$ with 20 and 13.3 at.% C, respectively.

At the carbon-rich limit, a model of $B_{12}C_3$ or B_4C was firstly proposed by which the structural unit composes of 12-atom icosahedron of boron and 3-atom chain of carbon, denoted by $B_{12}(CCC)$ in order to preserve the $R\bar{3}m$ symmetry [2]. Later it was shown by nuclear magnetic resonance (NMR) studies [35–37], x-ray [1, 38] and neutron [39] diffractions that rather than $B_{12}(CCC)$, the structure unit of B_4C should be represented by $B_{11}C(CBC)$, in which one of the boron atoms in the icosahedron is substituted by the chain-center carbon atom, yielding a $B_{11}C$ icosahedron linking to a (CBC) chain. Demonstrated by *first-principles*-based theoretical calculations [40–44], the $B_{11}C^p(CBC)$ unit is most energetically favorable over the other B_4C units, i.e. $B_{11}C^e(CBC)$, $B_{12}(CCC)$, and $B_{11}C(CCB)$, where the superscript p and e denote the polar and equatorial sites of the icosahedron, respectively. The experimental findings are thus seemingly well-supported by the theoretical calculations. However, Swapping the chain-center carbon atom with a polar boron atoms to obtain the more favorable $B_{11}C^p(CBC)$ unit is theoretically found to reduce the crystal symmetry to base centered monoclinic (Cm) [43, 44]. Such symmetrical distortion, as a result, yields a discrepancy between experiments and theory. Additionally, inspecting theoretical NMR spectra of B_4C , and comparing them to the experiments suggest the existence of $B_{12}(CBC)$ and $B_{10}C_2(CBC)$ units [45]. Thus the assumption, that only the presumed $B_{11}C^p(CBC)$ unit represents the whole structure of B_4C , may not be always true.

As for $B_{13}C_2$, if the carbon concentration of $B_{1-x}C_x$ is deviating from 20 at.% C with the presumed $B_{11}C(CBC)$ unit toward 13.3 at.% C, the substitution of boron for carbon atoms can take place either within the icosahedra or within the chains. Substituting carbon atom within the icosahedra results in the $B_{12}(CBC)$ unit, meanwhile the $B_{11}C(BBC)$ unit will be achieved if the substitution takes place in the chains. Indicated by the *first-principles*-based total energy calculations [46–48], the model of $B_{12}(CBC)$ is shown to have considerably lower energy as compared to the $B_{11}C(BBC)$ unit, and thus often being discussed in the literature. The latter model is however consistent with the analyses of structural data from x-ray diffraction [49] and Raman spectra [50–52] of boron carbide at different at.% C in its single-phase region.

Not only the argument, regarding the representation of the structural units for $B_{1-x}C_x$, there is also a large discrepancy between theory and experiment in their electronic character. Experimentally, boron carbide is found to be a semiconductor throughout the single-phase region [53, 54]. The band gap of boron carbide reported so far fall into the range between 0.48 and 2.5 eV [55–58], depending on the stoichiometries and the qualities of boron carbide crystal. Based on the explanation of Longuet-Higgins and Roberts [14], forty-eight electrons are required in order to complete the valence band of boron carbide and thus yielding a semiconducting character. This condition is somehow satisfied only for B_4C , meanwhile

the other compositions, e.g. $B_{13}C_2$, should, in principle, have been metallic due to their electron deficiency as the number of electrons decreases from the substitution of boron for carbon atoms. Correspondingly, the theoretical calculation of electronic properties reveal $B_{12}(CBC)$ is metallic [40, 46, 59]. Unlike $B_{13}C_2$, B_4C does not suffer from the electron deficiency. Nevertheless an unusual situation still presents, since the calculated band gaps of B_4C are *overestimated*. Note that the band gaps, almost without exception, are underestimated in standard density functional theory calculations due to the approximation of the exchange-correlation functionals. The calculated band gaps of the presumed $B_{11}C^p(CBC)$, within the range from 2.6 up to 3.0 eV, are reported [5, 60, 61]. Note also that a smaller band gap of about 1.6 eV can be achieved from the high-energy $B_{12}(CCC)$ unit due to the appearance of the mid gap states [62].

The literature has suggested that the large discrepancies between experiments and theoretical calculations in boron carbide, given in the previous paragraphs, could be arising from B/C substitutional disorder [43, 63, 64]. However, due to the similar characteristics between boron and carbon atoms, experimentally identifying the exact atomic positions of boron and carbon is extremely difficult. On the other hand, including several types of B/C substitutional defects in theoretical modeling of configurationally disordered boron carbide is not a trivial task because of the complexity of the icosahedral network allowing a variety of substitutional disorders. In this thesis, *first-principles* calculations, based on the density functional theory (DFT), are mainly used to investigate configurationally disordered boron carbide. A new method, namely superatom-special quasirandom structure or SA-SQS, is proposed (Paper I) and used for modeling the disordered boron carbides with high concentrations of low-energy B/C substitutional defects. The method is based on the well-known special quasirandom structure approach [65] for random alloy modeling. Note that the investigations, in this thesis, are based on an assumption that such discrepancies in boron carbide are arising from configurational disorder due to substitutional defects. Thermodynamic stability and others, e.g. crystallographic, electronic, and elastic properties, of the disordered boron carbides obtained from SA-SQS approach are then considered (Paper I, Paper II, and Paper III). Special attention is paid to B_4C and $B_{13}C_2$.

1.3 Boron suboxide

Nowadays, superhard materials, with Vickers hardness (H_V) higher than 40 GPa, are highly desirable in many industrial applications, e.g. cutting tools and wear-resistant materials [66]. Diamond is known to be the hardest materials with H_V ranging between 70 and 100 GPa, followed by cubic boron nitride (cBN) with H_V of 45-50 GPa [67]. However, neither diamond nor cBN are indeed appropriate to the real applications as they require extreme conditions for their synthesis, resulting in extremely high cost of production and difficulty to obtain the materials with specific sizes and geometries [68]. Boron suboxide, often denoted by B_6O , is also a material of choice for a superhard material, as it is suspected to be the hardest

material after diamond and cBN [67]. Refined by the Rietveld method applied on x-ray powder diffraction data [69, 70], the crystal structure of boron suboxide can be derived from α -boron ($R\bar{3}m$), as already shown in Fig. 1.1(d). The structural unit for boron suboxide can be thus represented by twelve boron atoms, forming an icosahedron, and a pair of oxygen atoms, denoted by $B_{12}(OO)$.

Boron suboxide powder can be prepared, for example by the oxidation of boron with boron oxide (B_2O_3). Unlike boron carbide, boron suboxide is not commercially available yet due to some difficulty in fabricating the compound. The major problem is that it is difficult to densify boron suboxide even at high temperature without high-pressure sintering (PHS) process [68, 71], thus the as-synthesized boron suboxide is generally oxygen-deficient, given by B_6O_x , where $x < 0.9$, and has rather poor crystallinity with very small grain size ($\ll 1 \mu m$). Even though, boron suboxide, prepared by high-pressure techniques, has a good hardness, its fracture toughness is rather low ($1\text{--}2 \text{ MPa}\cdot\text{m}^{1/2}$) [72]. Attempts to enhance the mechanical properties of boron suboxide with high-pressure techniques have been made by fabricating boron suboxide-based composites with other materials, e.g. diamond [73], cBN [74], boron carbide [68, 75, 76], titanium diboride [77], and some metal oxide additives [78–80]. A significant improvement in the mechanical properties of boron suboxide-based composites have recently been highlighted by the work of Solodkyi *et al.* [68], in which they fabricated boron suboxide-boron carbide composites, using the spark plasma sintering (SPS) method. The composites have a good fracture toughness of $4.8 \text{ MPa}\cdot\text{m}^{1/2}$, while maintaining the high hardness of boron suboxide ($H_V \sim 40 \text{ GPa}$).

Motivated by the work of Solodkyi *et al.* [68] and previous experimental studies on boron suboxide-boron carbide composites [75, 76], in this thesis, the thermodynamics of mixing between $B_{13}C_2$ and B_6O , denoted by $(B_6O)_{1-x}(B_{13}C_2)_x$, as well as their elastic properties are investigated, using *first-principles* calculations (Paper III). Being considered as pseudo-binary alloys, different models for $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys are obtained from the SA-SQS approach. The knowledge of configurational disorder due to substitutional defects, gained from the previous studies of boron carbide (Paper I and Paper II), is applied to model the mixing alloys.

1.4 Outline

This chapter 1 is intended to provide a brief introduction of icosahedral boron-rich solids, an overview of boron carbide, in which the controversial issues in their properties, arising from discrepancies between experiments and theoretical calculations, as well as a short description of boron suboxide, are stated. The following chapter 2 provides a fundamental knowledge of density functional theory, which is mainly used to theoretically investigate properties of boron carbide-based materials. An approach for modeling configurationally disordered boron carbide-based materials, e.g. B_4C , $B_{13}C_2$, and $(B_6O)_{1-x}(B_{13}C_2)_x$, namely superatom-special quasirandom structure (SA-SQS) is given in chapter 3. Methods to determine the thermodynamic stability, and the elastic properties of configurationally disordered

boron carbide-based materials are given respectively in chapter 4 and 5. An outlook for future research is shortly given in chapter 6. The last chapter, chapter 7, presents the results, obtained from the investigations in this thesis, in the form of scientific papers.

2.1 Theoretical background

The advent of quantum mechanics with the concept of wave-particle duality allows one to describe the microscopic properties of condensed matters by solving the famous time-dependent Schrödinger equation (in Hartree atomic units);

$$i \frac{\partial \Psi}{\partial t} = \hat{H} \Psi \quad (2.1)$$

where Ψ is the wave function containing all the information of any system under consideration. Since all matter is composed of many microscopic particles, typically ions and electrons, interacting with each other, the Hamiltonian $\hat{H}$ of the system can be given by;

$$\hat{H} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 - \frac{1}{2} \sum_{I=1}^N \frac{1}{M_I} \nabla_I^2 - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2} \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_{I \neq J} \frac{Z_I Z_J}{|\mathbf{R}_I - \mathbf{R}_J|}. \quad (2.2)$$

The first two terms in Eq.(2.2) are the kinetic energy of electrons and of ions, respectively, where M_I denotes the mass of the ion at site I . Since both the ions and electrons are charged particles, the following three terms represent the potential energy due to the Coulomb interactions between electron-ion, electron-electron, and ion-ion, respectively. $\mathbf{r}_i$ is the electron-position at site i , meanwhile $\mathbf{R}_I$, and Z_I stand for the position and the charge number of the ion at site I , respectively.

Solving Eq.(2.1) for a general system of condensed matters is impractical at the moment, since a macroscopic system consists of a number of particles in the order of Avogadro's number. The wave function, describing the system, thus depends

on a huge number of degrees of freedom, and can be expressed by;

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \sigma_1, \sigma_2, \dots, \sigma_n, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N, t) \quad (2.3)$$

where σ_i denotes the spin of the electron at site i . To handle such difficulties, several approximations are involved in order to simplify the problem. Mostly, the stationary ground state properties of the system are of main interest. In this case, there is no explicit time dependence in the Hamiltonian. Therefore, only the time-independent Schrödinger equation alone is adequate to describe the system. The time-independent Schrödinger equation can be written as;

$$\hat{H}\Psi = E_{tot}\Psi. \quad (2.4)$$

The wave function Ψ is now time-independent;

$$\Psi = \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \sigma_1, \sigma_2, \dots, \sigma_n, \mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_N) \quad (2.5)$$

and is a set of solutions for the eigenvalue equation (Eq.(2.4)), which represents the stationary states of $\hat{H}$ with the corresponding total energy E_{tot} . The next simplification to the problem is the so-called *Born-Oppenheimer* approximation [81]. The approximation is based on the fact that the ions are moving much slower than the electrons because of their several orders of magnitude larger masses. One can assume, at this point, that the ions are fixed from the electrons' point of view. As a result, the kinetic term of the ions can be separated out, and the ion-ion interaction term in Eq.(2.2) becomes a constant (E_{II}), and can as well be taken care of separately. The problem now reduces to the system of interacting electrons, meanwhile the electron-ion interaction term is treated as an external field acting on the electrons. The eigenvalue equation of the electronic system is given by;

$$\hat{H}_{elec}\Psi_{elec} = E_{elec}\Psi_{elec}. \quad (2.6)$$

in which Ψ_{elec} is the wave function of the system of n -interacting electrons in the external field of the fixed ions;

$$\Psi_{elec} = \Psi_{elec}(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_n, \sigma_1, \sigma_2, \dots, \sigma_n) \quad (2.7)$$

and $\hat{H}_{elec}$ is the electronic Hamiltonian, given by;

$$\hat{H}_{elec} = -\frac{1}{2} \sum_{i=1}^n \nabla_i^2 + \sum_{i \neq j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,I} \frac{Z_I}{|\mathbf{r}_i - \mathbf{R}_I|}. \quad (2.8)$$

The eigenvalues E_{elec} represents the corresponding energies of the electronic system. The total energy (E_{tot}) of the system in Eq.(2.4) can thus be easily calculated from;

$$E_{tot} = E_{elec} + E_{II} - \frac{1}{2} \sum_{I=1}^N \frac{1}{M_I} \nabla_I^2 \quad (2.9)$$

The problem can be further simplified if the system under consideration is periodic, e.g. crystalline solids. Demonstrated by Bloch [82] that, due to the

periodicity of the crystal, it is sufficient to consider only the primitive unitcell consisting of a few particles, rather than taking into account a large number of particles in the macroscopic crystal. In this case, the wave functions Ψ_{elec} , as the solutions to Eq.(2.6), are taking the form;

$$\psi_{n\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{n\mathbf{k}}(\mathbf{r}) \quad (2.10)$$

where n is the *band index* and takes numbers $n = 1, 2, 3, \dots$ and $\mathbf{k}$ is a reciprocal vector, principally in the first Brillouin zone, $u_{n\mathbf{k}}(\mathbf{r})$ is a function with periodicity of the crystal lattice;

$$u_{n\mathbf{k}}(\mathbf{r} + \mathbf{R}) = u_{n\mathbf{k}}(\mathbf{r}), \quad (2.11)$$

and $e^{i\mathbf{k}\cdot\mathbf{r}}$ describes a plane wave. Even though the problem, at this point, is much simplified through the above approximations, it is still insufficient to directly solve Eq.(2.6). This is because solving the Schrödinger equation for a system containing more than a few particles is in fact practically formidable.

2.2 The Hohenberg-Kohn theorems

Instead of solving for the many-electron wave function Ψ_{elec} in Eq.(2.6), one preferably use the electron density $n(\mathbf{r})$ as a basic variable. For a system of n -interacting electrons, such a change of the variable reduces the number of spatial coordinates from $3n$ to 3 , thus substantially simplify the problem. The attempt to use $n(\mathbf{r})$ as a basic variable was first proposed in 1927 and is known as the Thomas-Fermi theory [83, 84]. Unfortunately, results calculated from the theory were inaccurate in most applications, since the many-particle interactions between the electrons, i.e. exchange and correlation, were completely neglected, and the kinetic energy were approximated far too much. In 1964, Hohenberg and Kohn formulated two theorems [85], based on $n(\mathbf{r})$, that has been seen as the starting point of modern density functional theory (DFT). The two theorems are stated [86] as follows;

Theorem I

For any system of interacting particles in an external potential $V_{ext}(\mathbf{r})$, the potential $V_{ext}(\mathbf{r})$ is determined uniquely, except for a constant, by the ground state particle density $n_0(\mathbf{r})$.

Theorem II

A universal function for the energy $E[n]$ in term of the density $n(\mathbf{r})$ can be defined, valid for any external potential $V_{ext}(\mathbf{r})$. For any particular $V_{ext}(\mathbf{r})$, the exact ground state energy of the system is the global minimum value of this functional, and the density $n(\mathbf{r})$ the minimizes the functional is the exact ground state density $n_0(\mathbf{r})$.

From the two theorems, it is clear that if the total energy functional $E[n]$ was known, all the ground state properties of any electronic system could be exactly determined by the ground state density $n_0(\mathbf{r})$. The total energy functional,

in principle, can be expressed;

$$E[n] = T[n] + E_{int}[n] + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{II}, \quad (2.12)$$

where the first term on the right-hand side is the kinetic energy of the interacting electrons, meanwhile the following three terms represent the potential energies due to the Coulomb interaction between the electrons, the Coulomb interaction of the electron density $n(\mathbf{r})$ with the external field $V_{ext}(\mathbf{r})$, and the interaction between the ions, respectively. However, the remaining problem to solve for the system of n -interacting electrons is that the exact forms of $T[n]$ and $E_{int}[n]$ are not known.

2.3 Kohn-Sham equations

In 1965, Kohn and Sham proposed a practical approach [87] to overcome the difficulties in solving for the ground state properties of the interacting many-particle problem. The main idea is to replace the real system of interacting particles (Eq.(2.6)) by an artificial system of non-interacting particles, having the same density $n(\mathbf{r})$ as does the real one. Rather than the external potential $V_{ext}(\mathbf{r})$, each non-interacting particle is subjected to the effective potential $V_{eff}(\mathbf{r})$, given by;

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + V_{xc}(\mathbf{r}). \quad (2.13)$$

The second term on the right-hand side of Eq.(2.13) is the so-called Hartree potential, describing the Coulomb interaction between the electrons, meanwhile the term $V_{xc}(\mathbf{r})$ is defined as the exchange-correlation potential, accounting for all the quantum many-particle interactions and can be calculated from the exchange-correlation energy functional $E_{xc}[n(\mathbf{r})]$ via;

$$V_{xc}(\mathbf{r}) = \frac{\partial E_{xc}[n(\mathbf{r})]}{\partial n(\mathbf{r})}. \quad (2.14)$$

Consequently, the non-interacting particles can be described by the so-called Kohn-Sham wave functions ψ_i , which are the eigenstates to the single-particle, Schrödinger like equation;

$$\left(-\frac{1}{2} \nabla^2 + V_{eff}(\mathbf{r})\right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}). \quad (2.15)$$

Eq.(2.15) is known as *Kohn-Sham equation*, and ϵ_i is the eigenvalue of the non-interacting single particle, corresponding to the Kohn-Sham eigenstate ψ_i . Within the Kohn-Sham scheme, the particle density $n(\mathbf{r})$ of a system with N non-interacting particles can be easily obtained as;

$$n(\mathbf{r}) = \sum_{i=1}^N |\psi_i(\mathbf{r})|^2. \quad (2.16)$$

The Kohn-Sham total energy functional is given by;

$$E_{KS}[n] = T_s[n] + \int d^3r V_{ext}(\mathbf{r})n(\mathbf{r}) + E_{Hartree}[n] + E_{xc}[n] + E_{II}, \quad (2.17)$$

where $T_s[n]$ is the kinetic energy functional of the non-interacting particles;

$$T_s[n] = -\frac{1}{2} \sum_{i=1}^N \langle \psi_i | \nabla^2 | \psi_i \rangle, \quad (2.18)$$

and $E_{Hartree}[n]$ is the classical Coulomb energy functional due to a particle-density $n(\mathbf{r})$, interacting with itself. The expression of the $E_{Hartree}[n]$ functional is given by;

$$E_{Hartree}[n] = \frac{1}{2} \int \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' \quad (2.19)$$

2.4 Exchange-correlation functional

The major problem to solve the Kohn-Sham equation (Eq.(2.15)) is that the form of the exchange-correlation functional $E_{xc}[n]$ is not known exactly. However, it is still possible to formulate the functional with some approximations. Several approaches to estimate $E_{xc}[n]$ have been proposed and constantly developed in order to improve the accuracy. Some are given as follows;

Local density approximation (LDA)

The local density approximation (LDA) is the simplest way to derive $E_{xc}[n]$. LDA was first suggested at the same time as the Kohn-Sham equation was formulated in 1965 [87]. In practice, LDA approximates $E_{xc}[n]$ by assuming that the exchange-correlation energy density $\epsilon_{xc}^{LDA}(n(\mathbf{r}))$ at each point $\mathbf{r}$ in space is of the same form as the homogeneous electron gas $\epsilon_{xc}^{hom}(n(\mathbf{r}))$, which has been well-studied using quantum Monte Carlo simulations [88]. The expression of $E_{xc}^{LDA}[n]$ is thus given by;

$$E_{xc}^{LDA}[n] = \int n(\mathbf{r})\epsilon_{xc}^{hom}(n(\mathbf{r}))d\mathbf{r} \quad (2.20)$$

At first, LDA was supposed to work well only for system with slowly varying density. Somehow it was found to be successful also for systems with high density gradients. The explanations to the relative success of LDA have been described elsewhere [86, 89].

Generalized gradient approximation (GGA)

Even though LDA has turned out to be successful in predicting the properties of solid materials, it in many cases underestimates the lattice spacing. The idea, to improve the accuracy by taking into account not only the density $n(\mathbf{r})$ but also the gradient of the density ∇n at the same point $\mathbf{r}$ to approximate $E_{xc}[n]$, were thus proposed [90–92] as an extension of LDA, which is a so-called *generalized gradient approximation* (GGA). Consequently,

$$E_{xc}^{GGA}[n] = \int n(\mathbf{r})\epsilon_{xc}^{GGA}(n(\mathbf{r}), \nabla n(\mathbf{r}))d\mathbf{r} \quad (2.21)$$

Most of the calculations in this thesis were performed using GGA in the form of Perdew *et al.* [92], also known as PBE96.

Hybrid functionals

In 1982, Perdew *et al.* [93] demonstrated, for a system of N -interacting electrons, the derivative discontinuities found in the curve of energy E as a function of the number of electrons N . The discontinuities, in principle, result in a jump by a positive constant of the exchange-correlation potential $V_{xc}(\mathbf{r})$, as the number of electrons changes by an integer. However, the approximation of $E_{xc}[n]$ using semi-local functionals, e.g. LDA and GGA, cannot display such features in the energy curve. As a result, electronic band gaps of solid materials, calculated within the Kohn-Sham scheme, are systematically underestimated with respect to experiment [94]. This problem can be partially corrected by mixing a portion of Hartree-Fock (HF) exchange with those of the semi-local functionals in calculating $E_{xc}[n]$. This concept thus becomes the basics of hybrid functionals. Up to now, several versions of hybrid functionals have been proposed, e.g. B3LYP [95, 96], PBE0 [97], and HSE [98, 99]. Note that by including the HF exchange, one ends up with an orbital (ψ_i)-dependent potential, which in turn drastically increases the computational demand, thus practically limiting the size of electronic systems possible to treat in the calculations. In this thesis, the hybrid functional HSE06 [99] were used in some calculations in order to investigate the electronic properties of the presumed $B_{11}C^p(CBC)$ and $B_{12}(CBC)$ units for B_4C and $B_{13}C_2$, respectively.

Modified Becke-Johnson (MBJ) exchange potential

Rather than the HF exchange, the modified Becke-Johnson (MBJ) exchange potential [100, 101] requires much less computational resources to perform the calculations, meanwhile the accuracies of electronic properties calculations, especially band gaps, are maintained at the same level as are the hybrid functionals. Although the MBJ exchange is a semi-local potential, similar to LDA and GGA, it is designed to mimic the behavior of those orbital-dependent potentials, i.e. the derivative discontinuities of the HF exchange potential. However, one needs to keep in mind that the MBJ functional exists only in the potential form $V_x(\mathbf{r})$, and there is no corresponding exchange energy functional $E_x[n]$. Therefore, the self-consistent calculations of the total energy $E_{KS}[n]$ will never be achieved with the MBJ potential. In this thesis, the MBJ exchange potential was used in combination with GGA-PBE96 correlation to calculate the electronic band gaps of configurationally disordered B_4C and $B_{13}C_2$.

2.5 Plane-wave basis sets

To numerically solve the Kohn-Sham equations in Eq.(2.15), the electron wave functions $\psi_i(\mathbf{r})$ need to be expanded in a basis set. Various choices of basis sets are available, e.g. atomic orbitals, Gaussians, and plane-waves. According to the Bloch's theorem [82], the plane-wave is considered as the first choice among the others, as he demonstrated that the wave functions of systems with periodicity, e.g. crystalline solids, can in principle be expanded in term of a plan-wave basis set, see Eq.(2.10). In practice, the basis set needs to be truncated at a finite cut-off energy. Based on the characteristic of the electron wave function, it may be

splitting in space into (1) an interstitial and (2) a core regions. In the interstitial region between the atoms, where the electrons are delocalized (valence electrons), the wave function is rather smooth and only a small number of plane-waves is already sufficient to well reproduce the wave function. On the other hand, a huge number of plane-waves with very high energy cutoff is required to accurately represent the rapidly oscillating wave function inside the core region due to the strong Coulomb interactions between the highly localized core electrons and the nucleus, thus resulting in an extremely high computational cost.

To implement the plane-wave basis sets in practice, one employs a pseudopotential (PP) approach, first suggested by Hellmann [102, 103]. The PP approach substitutes the real Coulomb potential by a smooth effective potential, specially designed in order to smoothen the rapidly oscillating part of the wave function within the core-region (a pseudo wave function), thus substantially reducing both the basis sets and the computational demand. Inspired by the fact that only the valence electrons in the interstitial region are taking part in the bonding formation, elimination of the oscillating part within the core region thus should not be affecting the bonding properties. Within the PP approach, the core region is determined by a certain cutoff radius from the nucleus. A few criteria to construct the pseudopotential is given as follows; (1) the pseudopotential need to reproduce the scattering properties of the core region. (2) outside the cutoff radius, the behavior of the pseudopotential and the pseudo wave function must be the same to the real ones. Among numerous developed versions of the pseudopotentials suggested in the literature, Norm-conserving [104] and Ultrasoft [105] pseudopotentials are most widely used PP in plane-wave basis set-based DFT calculations.

A generalization of the pseudopotential approach, also know as projector augmented wave method (PAW), were later proposed by Blöchl [106]. Instead of the pseudo wave function as obtained in the PP approach, the PAW method restores the full real electron wave function $\psi_i(\mathbf{r})$ at the end of the calculation. As the PAW method uses the smooth wave function within the core region, like the PP approach, the computational costs between these two approach are comparably cheap. At the same time, due to the restoration of the real wave function, the reliability and the accuracy of the PAW method are similar to those of all electron, and full potential Kohn-Sham approaches. All the calculations in this thesis were performed using the PAW method.

2.6 Solving the Kohn-Sham equations

To search for the ground state density $n_0(\mathbf{r})$, minimizing the Kohn-Sham total energy functional $E_{KS}[n]$ in Eq.(2.17), the Kohn-Sham equations, given by Eq.(2.15) must be solved self-consistently. Since the effective potential V_{eff} and the Kohn-Sham orbitals ψ_i in Eq.(2.15) are determined by the density $n(\mathbf{r})$, which is not known *a priori*, several iterative cycles of solving the Kohn-Sham equations must be performed as illustrated in Fig.2.1. The first step to solve the equation is to guess the initial density $n_{guess}(\mathbf{r})$ in order to construct V_{eff} , according to Eq.(2.13). After solving the Kohn-Sham equation, one obtains a set of ψ_i , which is in turn

used to calculate a new electron density $\tilde{n}_{k+1}(\mathbf{r})$. If the convergence criterion is not fulfilled, $\tilde{n}_{k+1}(\mathbf{r})$ will be mixed with the input electron density $n_k(\mathbf{r})$ using different numerical mixing schemes, e.g. the Anderson and the Broyden methods [86], to get $n_{k+1}(\mathbf{r})$ as a new input to construct a new V_{eff} , and then another iterative cycle of solving Kohn-Sham equation is performed. Such a process continues until the electron density converges and self-consistency is thus reached.

Figure 2.1. Flowchart showing the self-consistent loop for solving Kohn-Sham equations. After Martin [86].

Configurational disorder in boron carbide-based materials

3.1 Supercell approach

Instead of dealing with a large number of particles in the macroscopic crystal, the Bloch's theorem [82] allows one to consider only a small primitive unitcell consisting of a few particles due to the periodicity in the crystal. However, taking into account effects of configurational disorder in modeling substitutionally disordered alloys, for example, destroys the periodicity in the crystal, thus the Bloch's theorem is no longer valid. In this case, one can implement a supercell approach, consisting of several primitive unitcells. Depending on the supercell's size, one can introduce different degrees of configurational disorder, while the periodicity of the introduced configurational disorder is represented by the supercell.

3.2 Modeling of configurational disorder

In order to account for a contribution of configurational disorder in any crystalline material, e.g. random substitutionally disordered alloy, it is necessary to understand the concept of cluster expansion of the configurational part of the total energy for a given alloy, as developed by Sanchez, Ducastelle, and Gratias in 1984 for multicomponent alloy systems [107]. In this section, a brief introduction to the concept of cluster expansion will be given, based on the review article by Ruban and Abrikosov [108].

For simplicity, one consider a binary alloy, $A_{1-x}B_x$. The atomic configuration of the alloy, $A_{1-x}B_x$, is described by spin variables σ_i , where σ_i takes the values $+1$, or -1 if site i is occupied by A - or B -type atom, respectively. For an alloy system, consisting of N atomic sites, the atomic configuration of that alloy can be specified by the vector $\boldsymbol{\sigma} = \{\sigma_1, \sigma_2, \sigma_3, \dots, \sigma_N\}$. The product of spin variables

σ_i in turn determines a basis function for a given n -site cluster f , $\Phi_f^{(n)}(\sigma)$, given by;

$$\Phi_f^{(n)}(\sigma) = \prod_{i \in f} \sigma_i. \quad (3.1)$$

These functions form a complete and orthonormal set with the inner product between two functions, given by;

$$\langle \Phi_f^{(n)}(\sigma), \Phi_g^{(n)}(\sigma) \rangle = \frac{1}{2^n} \sum_{\sigma} \Phi_f^{(n)}(\sigma) \Phi_g^{(n)}(\sigma) = \delta_{f,g}. \quad (3.2)$$

The sum in Eq.(3.2) runs over all atomic configuration σ , and $\delta_{f,g}$ is the Kronecker's delta. The scalar product, obtained from Eq.(3.2), is thus equal to 1 only if $\Phi_f^{(n)}(\sigma)$ and $\Phi_g^{(n)}(\sigma)$ are specifying the exactly same n -site clusters in the crystal, while the product of any two clusters with different numbers of atoms is always equal to 0.

As the basis set is complete and orthonormal, one can expand any alloy's property $F(\sigma)$, which is a function of the configuration in this basis set:

$$F(\sigma) = \sum_f F_f^{(n)} \Phi_f^{(n)}(\sigma), \quad (3.3)$$

where the sum is running over all clusters in the considered alloy system. The expansion coefficients $F_f^{(n)}$ are obtained from the projections of $F(\sigma)$ on the basis functions:

$$F_f^{(n)} = \langle F(\sigma), \Phi_f^{(n)}(\sigma) \rangle. \quad (3.4)$$

In the case of configurational energy $E_{conf}(\sigma)$, the coefficients are so-called the n -site configurational interactions, given by;

$$V_f^{(n)} = \langle E_{conf}(\sigma), \Phi_f^{(n)}(\sigma) \rangle. \quad (3.5)$$

Due to the symmetry of the crystal lattice, one can define the n -site correlation function $\xi_f^{(n)}$ for the cluster f as the average value of the symmetrically equivalent $\Phi_f^{(n)}(\sigma)$ for a given configuration σ :

$$\xi_f^{(n)}(\sigma) = \langle \Phi_f^{(n)}(\sigma) \rangle. \quad (3.6)$$

Consequently, the configurational energy $E_{conf}(\sigma)$ for any atomic configuration σ can be expressed by;

$$E_{conf} = \sum_f V_f^{(n)} \xi_f^{(n)}. \quad (3.7)$$

In principle, one can create a supercell, representing the random substitutionally disordered alloy in the limit $V/T \rightarrow 0$, where V is the strongest configurational interaction in the system and T is the temperature. Such a supercell can be reasonably achieved using the special quasirandom structure (SQS) approach, suggested

by Zunger *et al.*[65]. In the case of completely random alloys, $\xi_f^{(n)}$ are zero for all clusters f and they are practically often defined by the Warren-Cowley short range order (SRO) parameters that represent the 2-site correlation functions [108]. For a binary alloy, $A_{1-x}B_x$, the SQS approach constructs a supercell by distributing A - and B -type atoms in a way that the SRO parameters between both kinds of atoms are zero, or close to zero for as many coordination shells as possible with focus on the short range shells in order to mimic the configuration, stable in the limit $V/T \rightarrow 0$. Since it is not practically possible, in most cases, to obtain zero value of the SRO parameters for all coordination shells due to the limitation of the supercell's size, the term E_{conf} does not vanish and could affect the alloy's properties in the calculations. For this reason, the properties, e.g. total energy, of the SQS structures need to be converged with respect to the supercell's size. In fact real alloys can display some degree of clustering and/or ordering at short-range scales. However, the SQS approach provides an unbiased starting point for modeling random substitutionally disordered alloys, for which their configurational entropy can be obtained analytically with a random-mimicking configuration (see Chapter 4).

3.3 Superatom-special quasirandom structure

Modeling of configurational disorder in materials, having complex crystal structures, such as boron carbide by using the complete mathematical apparatus of Sanchez, Ducastelle, and Gratias [107], as described in section 3.2, is often impractical. Owing to the complexity of the icosahedral structure, numerous kinds of B/C substitutional defects are conceivable. However, it might not be necessary to take into account them all in modeling configurationally disordered boron carbide, as many of them, resulting in high total energies, might be neglected. For this reason, one can try to reveal the important physics of the disordered boron carbide by focusing only on the modeling of low-energy disordered pattern. In principle, configurational disorder in boron carbide, induced by such defects, can be seen as a random distribution of different superatoms, each defined based on knowledge of low-energy dilute defects. This is a basic idea of a superatom-special quasirandom structure (SA-SQS) approach for modeling configurationally disordered boron carbide, filled with high concentrations of low-energy B/C substitutional defects (Paper I). In the SA-SQS approach, the configuration of the superatoms is mimicking a random alloy pattern, according to the SQS approach.

For B_4C , whose ground-state configuration is represented by $B_{11}C^p(CBC)$, there are two types of dilute B/C substitutional defects that are found to have distinctly lowest formation energy (Paper I). The first kind of low-energy defect originates from the site displacement of the icosahedral carbon (C^p) atom among the three polar-up sites, as labeled in Fig.3.1(a) by the numbers 1, 2, and 3, meanwhile the second is known as a bipolar defect, originating from the substitution of the C^p atom from one icosahedron for the B^p atom from a neighboring icosahedron forming $B_{10}C_2^p + B_{12}$, as shown in Fig.3.2. The first intuitive way to define the superatom basis is to identify the 15-atom structural unit of boron carbide, i.e. a 12-atom icosahedron and a 3-atom chain, as the superatom basis, namely Basis-1

Figure 3.1. Example of different superatom bases for modeling configurationally disordered boron carbide B_4C : (a) Basis-1, representing a whole 12-atom icosahedron with a 3-atom chain. (b) Basis-2, whose polar-down sites are replaced by the corresponding polar-down sites of neighboring icosahedra, bonded to it. Grey and black spheres are boron and carbon atoms, respectively. A set of numbers $\{1, 2, 3\}$ denotes the polar-up sites, meanwhile the set $\{4, 5, 6\}$ denotes the polar-down sites.

Figure 3.2. A bipolar defect involved with two icosahedra, i.e. $B_{10}C_2^p + B_{12}$. Numbers and colors denote the same crystallographic sites and types of atoms, as described in the caption of Fig.3.1. The 3-atom chains are not shown.

(see Fig.3.1(a)). The superatom types can be distinguished, for instance by the respective positions of the icosahedral carbon atom. Straightforwardly, the Basis-1's superatoms allow one to model a disordered configuration of B_4C in which the C^p atom in each icosahedron can substitute any of the three polar-up sites, which is a kind of low-energy B/C defect. However, Basis-1 alone is not sufficient to account for the bipolar defects. This is because, for the bipolar defect, not only the coexistence of $B_{10}C_2^p$ and B_{12} icosahedra, but their particular arrangements need to be taken into consideration. Therefore, in order to allow for the description of both the displacement of the C^p atoms among the three polar-up sites and the bipolar defects, one can define a new superatom basis, namely Basis-2, as shown in Fig.3.1(b). In this case, the polar-down sites from a single icosahedron are replaced by the corresponding polar-down sites of neighboring icosahedra with bonds to the original polar-up sites.

To create disordered configurations of superatoms, one firstly define different superatom types and then use the SQS approach to randomly distribute them in

a supercell in a way that mimics the configuration of the random alloy, stable in the limit $V/T \rightarrow 0$. For simplicity, one may assume equal concentrations for each superatom type. Fig.3.3 illustrates an example of a configurationally disordered B_4C , modeled by the SA-SQS approach in which the C^p atom in each icosahedron can substitute any of the three polar-up sites. Three superatom types from Basis-1 are defined with equal concentrations, i.e. $B_{11}C^{p(1)}$ (CBC), $B_{11}C^{p(2)}$ (CBC), and $B_{11}C^{p(3)}$ (CBC), where the numbers 1, 2, and 3 in the parentheses denote the atomic positions of the C^p atoms, corresponding to the notations labeled in Fig.3.1(a). In this case, the SRO parameters are zero for the first two coordination shells. By defining three more superatom types, i.e. $B_{11}C^{p(4)}$ (CBC), $B_{11}C^{p(5)}$ (CBC), and $B_{11}C^{p(6)}$ (CBC), and then including them in the supercell for modeling, one obtains a B_4C 's configuration, where the C^p atoms are configurationally disordered among the six polar sites.

Figure 3.3. Example of configurationally disordered B_4C in a $3 \times 3 \times 3$ supercell, represented in (a) normal-atom picture, and (b) superatom picture. The supercell consists of three superatom types: (1) $B_{11}C^{p(1)}$ (CBC), (2) $B_{11}C^{p(2)}$ (CBC), and (3) $B_{11}C^{p(3)}$ (CBC), where the numbers 1, 2, and 3 in the parentheses denote the atomic positions corresponding to the notations labeled in Fig.3.1(a). Grey and black spheres in (a) represent boron and carbon atoms, respectively, meanwhile black, white, and grey spheres in (b) stand for $B_{11}C^{p(1)}$ (CBC), $B_{11}C^{p(2)}$ (CBC), and $B_{11}C^{p(3)}$ (CBC) superatoms, respectively.

Instead of Basis-1, a configurationally disordered B_4C induced by the bipolar defects at high concentration can be easily modeled using Basis-2's superatoms by which two superatom types are included in this case; one with the C^p atom at position 1, and the other at position 4, as labeled in Fig.3.1(b). Highly configurationally disordered B_4C , where both types of the identified low-energy defects are taken into account, can also be achieved by including more Basis-2's superatom types (Paper I). Apart from the superatom basis, the types and the numbers of atoms, included in the superatoms are as well changeable. They can be assigned differently in order to model configurational disorder in boron carbide with other compositions as well as boron carbide-based materials in addition to B_4C , e.g. $B_{13}C_2$, and $(B_6O)_{1-x}(B_{13}C_2)_x$. For instance, if the C^p atom in the $B_{11}C^p$

superatom, given by Basis-1 (Fig.3.1(a)), is replaced by a boron atom, one obtains a $B_{12}(CBC)$ superatom, representing the presumed ground state of $B_{13}C_2$ (Fig.3.4(a)). If the CBC chain within the $B_{12}(CBC)$ superatom is in turn replaced by a pair of oxygen atoms, one obtains a $B_{12}(OO)$ superatom, which is the structural unit of B_6O (Fig.3.4(b)).

Figure 3.4. (a) $B_{12}(CBC)$ - and (b) $B_{12}(OO)$ -type superatoms in Basis-1. Grey, black, and white spheres represent boron, carbon, oxygen atoms, respectively.

For $B_{13}C_2$, the study of substitutional defects in the dilute limit (Paper II) indicates that a substitution of a chain-end carbon atom for a neighboring equatorial boron atom in the icosahedron by avoiding a formation of C-C bond between the chain unit and the icosahedron, denoted by $B_{11}C^e(BBC)$, gives the lowest defect formation energy. In this case, the superatom basis and the superatom types need to be chosen in a proper way in order to model configurationally disordered $B_{13}C_2$, which is not only dominated by $B_{12}(CBC)$ - and $B_{11}C^e(BBC)$ -superatom types, but the substitution of the chain-end carbon atoms for all six equatorial sites are also needed to consider. Some examples of superatom types in a new basis, namely Basis-3, for modeling such a disordered configuration of $B_{13}C_2$ is shown in Fig.3.5. Unlike those in Fig.3.1, Basis-3 is focused on the chain, in which the equatorial sites belonging to a single icosahedron within the basis are replaced by the corresponding equatorial sites of neighboring icosahedra, labeled by the numbers 2, 3, 4, 6, 7, and 8 in Fig.3.5, bonded to the original intericosahedral chain, corresponding to the numbers 1, and 5 in the same Figure. When defining the superatom types, one may also assign some constraints in order to avoid the C-C bond between the chain unit and the icosahedron within a superatom, e.g. the chain-end carbon atoms can swap their positions only with the neighboring equatorial boron atoms bonded to them and only one of the two chain-end atoms is allowed to swap within the single superatom. That is, the chain-end carbon atom at position 1 can swap its position either with the equatorial boron atom at position 2, 3, or 4 (Fig.3.5(b)), meanwhile the chain-end carbon atom at position 5 is allowed to swap its position with the equatorial boron atom at position 6, 7, or 8 (Fig.3.5(c)). Consequently, there can be as many as seven types of superatoms considered in modeling configurationally disordered $B_{13}C_2$, dominated by $B_{12}(CBC)$ and $B_{11}C^e(BBC)$.

The SA-SQS approach also allows for modeling boron carbide-based materials, e.g. $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$, which can be simply achieved by randomly distributing in a supercell two types of superatoms, i.e. $\text{B}_{12}(\text{CBC})$ and $\text{B}_{12}(\text{OO})$, as illustrated in Fig.3.4(a) and Fig.3.4(b), respectively. In this case, the model of $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ is only configurationally disordering between superatoms due to the use of SQS technique. However, if the effects of configurational disorder within superatoms, e.g. a substitution of oxygen atom for an icosahedral boron atom, are needed to be taken into account in modeling $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$, one can just define a new superatom basis, which can account for its corresponding low-energy defects (Paper III), as done for B_4C and B_{13}C_2 .

Figure 3.5. Example of chain-focused superatom types in Basis-3 for modeling configurationally disordered B_{13}C_2 . Grey and black spheres represent boron and carbon atoms, respectively. The set of numbers $\{1, 5\}$ and $\{2, 3, 4, 6, 7, 8\}$ denote, respectively, the chain-end and the equatorial sites. (a) a $\text{B}_{12}(\text{CBC})$ -type superatom. (b), and (c) are examples of $\text{B}_{11}\text{C}^e(\text{BBC})$ -type superatoms.

As demonstrated above, the SA-SQS approach can be effectively used for modeling configurational disorder in icosahedral boron-rich solids, in which high concentrations of low-energy substitutional defects are distributed in a random manner following the SQS technique. This approach however has a drawback. Since the SA-SQS technique is particularly designed in order to take into account effect of configurational disorder in icosahedral boron-rich solids, it may not be transferable to other materials systems with a different type of complex atomic structure. In some cases, where several types of superatoms are needed to be taken into account in modeling configurationally disordered boron carbide-based materials, an extremely huge supercell may be needed in order to obtain a reasonably disordered configuration of superatoms, thus resulting in extremely high computational costs. Additionally, unlike regular atoms, each superatom has an internal structure, which might break the symmetry of the lattice with the consequence of losing the commutative property. Consequently, an averaging procedure between different permutations of superatom types is conceivable, as they not only result in a different internal atomic configuration for each disordered configuration but also a different total energy, which in turn gives rise to an uncertainty in predicting the properties of the material, e.g. a configurationally ordered/disordered transition

temperature. Such an approximation is, however, not problematic in the present study, and the uncertainty in the predicted configurationally ordered/disordered transition temperature of boron carbide, caused by this approximation, is less than 20% (Paper II). The procedures to determine the thermodynamic stability of configurationally disordered boron carbide and $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ will be provided in the next chapter.

CHAPTER 4

Thermodynamic stability of boron carbide-based materials

It is important to investigate whether the substitutionally disordered configurations of boron carbide-based materials, e.g. boron carbides, and $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloys are stable from a theoretical thermodynamic point of view. Such analyses can answer to the question of which conditions, generally composition, pressure, and temperature, they will be thermodynamically stable, respecting to their competing phases. The thermodynamic stability of any system with a specified number of particles, in principle, can be described by a physical quantity, Gibbs free energy G ;

$$G(p, T) = E + pV - TS, \quad (4.1)$$

where E is the internal energy of a material, p is the pressure, V is the volume. T is the temperature, and S is the entropy. For a given condition, the thermodynamic equilibrium of a system will be reached by minimization of G . At $T = 0$ K, the temperature-dependent effects, e.g. lattice vibration, electronic excitation, and configurational disorder, might be neglected and thus, only the energy E and the pV -term remain. If the system is considered at its equilibrium volume, V_0 , E is minimized, and since at $V = V_0$ there is no pressure exerted on a system, the term pV in Eq.(4.1) vanishes. Consequently, the equilibrium condition of the system at 0 K, i.e. *ground state*, is determined by;

$$G(0, 0) = E_0 + E_{vib}(T = 0), \quad (4.2)$$

where E_0 denotes the total energy at 0 K of a material, directly obtained from the DFT calculations, and $E_{vib}(0)$ represents the vibrational energy at 0 K due to the zero-point motion of atoms, also known as the zero-point energy.

4.1 Convex hull and formation energy

A convenient starting point to evaluate the phase stability of any material system is to consider the system at $T = 0$ K and focus only on E_0 , the ground-state energy, since the zero-point energy $E_{vib}(0)$ is usually of minor importance. The phase stability of a multicomponent phase can then be analyzed by making a plot between the ground-state energies E_0 at all considered compositions, i.e. searching for the ground-state configurations determined by minimization of E_0 by allowing for decomposition into different fixed compositions. By drawing a set of tie lines, connecting E_0 for every studied compositions, one constructs a so-called *convex hull*. In order for a material to be stable, it needs to be favorable with respect to any possible decomposition into a set of competing phases, which is in fact a linear optimization problem. The stability of a binary compound or alloy with respect to competing pure elements is given by the formation energy;

$$\Delta E^{form}(A_mB_n) = \frac{E_0(A_mB_n) - (n \cdot E_0(A)) - (m \cdot E_0(B))}{m + n}, \quad (4.3)$$

where $\Delta E^{form}(A_mB_n)$ is the formation energy/atom for a binary compound A_mB_n , $E_0(A_mB_n)$ is the ground-state energy/formula unit of the compound, $E_0(A)$, and $E_0(B)$ are the ground-state energies/atom for the element A , and B , respectively. The considered compound is said to be stable with respect to its constituent atoms in their ground state, if the formation energy is negative. To visualize the relevant energy scale, rather than the ground-state energy, which depending on the definition can vary with thousands of eV, the formation energy with respect to pure phases is used, when plotting a convex hull.

Figure 4.1. Formation energies of boron carbides with respect to α -boron and diamond. Black circles at 0, 0.13, and 0.2 at.% C represent the formation energies of α -boron, ground-state $B_{13}C_2$, and ground-state B_4C , respectively. Black triangles and black squares stand, respectively, for configurationally disordered $B_{13}C_2$ and B_4C , modeled by the SA-SQS approach.

In the case of boron carbide, the ground state of $B_{13}C_2$, determined by the *first-principles*-based energy minimization, can be given by $B_{12}(CBC)$ [46–48], meanwhile it is $B_{11}C^p(CBC)$ for B_4C [40–44]. The convex hull of boron carbide, constructed based only on the two mentioned stoichiometries, is shown in Fig. 4.1. The formation energies, in this case, are calculated, respecting α -boron and diamond as the competing phases. Note that in fact the true ground states of boron and carbon are represented by β -boron and graphite, respectively. Somehow, due to the ambiguity in the crystal structure of β -boron, and van de Waals interactions between layers of graphite that cannot be accurately accounted for by general semi-local exchange-correlation functional, it is more straightforward to consider α -boron and diamond instead. Additionally, it is expectable that considering α -boron and diamond as the competing phases instead of β -boron and graphite would not result in a huge difference in determining the formation energy of boron carbide, since it is shown in the literature that the energy difference between diamond and graphite [109], and between α - and β -boron [8], are particularly small.

For binary compounds/alloys, the graphical solution is straightforward as demonstrated above. However, for ternary or multi-component compounds/alloys, all possible competing phases, i.e. both constituent elements and compounds, need to be taken into consideration in order to determine the stability of the ternary or multi-component compounds/alloys with respect to their constituents, and the convex hull must be carefully constructed by solving a linear optimization problem. As for $(B_6O)_{1-x} (B_{13}C_2)_x$ alloys, they can be treated as ternary B-C-O compounds. In this thesis, nine competing phases, as shown in Fig. 4.2, are taken into consideration in order to determine the stability of $(B_6O)_{1-x} (B_{13}C_2)_x$. It is found that, at 0 K, $(B_6O)_{1-x} (B_{13}C_2)_x$ alloys are unstable with respect to B_6O and $B_{13}C_2$, represented respectively by $B_{12}(OO)$, and $B_{12}(CBC)$, for a whole composition range (Paper III), while other stable phases, e.g. B_2O_3 and B_4C , do not come into play as competing phases. As a result, one can construct the convex hull for $(B_6O)_{1-x} (B_{13}C_2)_x$ alloys and consider their thermodynamic stability along the dashed-line, given in Fig. 4.2.

Figure 4.2. Sketch of ternary phase diagram for B-C-O system, labeled with nine considered competing phases. The dashed-line indicates two competing phases, i.e. B_6O and $B_{13}C_2$, which are stable against $(B_6O)_{1-x} (B_{13}C_2)_x$ alloys.

4.2 Configurational entropy and effects of configurational disorder on thermodynamic stability of boron carbide at a given composition

At non-zero temperature, the stability of a solid solution/compound at a fixed composition is not only determined by the ground-state energy E_0 . As mentioned above, vibrational, electronic, magnetic and configuration excitations contribute to the Gibbs free energy. For alloys, the configurational degree of freedom is often most important for understanding both the stability and the properties in the materials. For a given composition, there exists a number of way in which the atoms in the solid solution can be arranged, contributing to the configurational entropy S_{conf} . As a result, the Gibbs free energy in Eq.(4.2) is extended to;

$$G(0, T) = E_0 + E_{conf}(T) - TS_{conf}(T), \quad (4.4)$$

where $E_{conf}(T)$ is the configurational energy, given by Eq.(3.1), and is temperature-dependent. Since the entropy is generally a measure of randomness, the term $-TS_{conf}$ in Eq.(4.4) indicates a tendency of disorder as the temperature increases. Note that, apart from E_{conf} and S_{conf} , other contributions to the Gibbs free energy, e.g. lattice vibration, are also of importance. However, only the configurational parts are being considered in Eq.(4.4) as a starting point to determine the Gibbs free energy. To describe a configurational order/disorder transition, one calculates the Gibbs free energies both for the ordered and for the disordered states. From Eq.(4.4), the free energy for the ordered state G^{ord} and for the disordered state G^{dis} can be respectively given by;

$$G^{ord}(0, T) = E_0^{ord} + E_{conf}^{ord}(T) - TS_{conf}^{ord}(T), \quad (4.5)$$

and

$$G^{dis}(0, T) = E_0^{dis} + E_{conf}^{dis}(T) - TS_{conf}^{dis}(T), \quad (4.6)$$

where E_0^{ord} and E_0^{dis} represent the ground-state energies for the ordered and the disordered states, respectively. A good approximation is to assume the ordered state having the zero-temperature properties ($T = 0$ K), meanwhile the disordered state has the $T \rightarrow \infty$ properties, i.e. completely random. Eq.(4.5) and (4.6) thus respectively become;

$$G^{ord}(0, 0) = E_0^{ord}, \quad (4.7)$$

and

$$G^{dis}(0, T) = E_0^{dis} - TS_{conf}^{dis}. \quad (4.8)$$

The general expression of S_{conf}^{dis} is given by;

$$S_{conf}^{dis} = k_B \ln(\omega), \quad (4.9)$$

where ω is the number of distinguishable ways of arranging the atoms in the solution, and k_B is Boltzmann's constant. For a random alloy in the thermodynamic

limit, the configurational entropy S_{conf}^{dis} can be approximated using Stirling's approximation;

$$S_{conf}^{dis} = -k_B N \sum_i x_i \ln(x_i), \quad (4.10)$$

where N and x_i are defined as the number of lattice sites and the concentration of type i atoms. The disordered state is thermodynamically stable, with respect to the ordered state, if G^{dis} becomes lower than G^{ord} and the ordered/disordered transition temperature T_{trans} can be approximately obtained from;

$$T_{trans} = \frac{E_0^{dis} - E_0^{ord}}{S_{conf}^{dis}}. \quad (4.11)$$

In the case of boron carbide at a given composition, configurationally disordered boron carbides represent the disordered states, meanwhile the ordered state is given by the ground state at that composition. Since the disordered boron carbides as well as $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys are modeled using the SA-SQS approach, N and x_i in Eq.(4.10) denote instead the number of superatom sites and the concentration of type i superatoms, respectively. An illustration of configurationally ordered/disordered transitions in boron carbide, B_4C , is shown in Fig.4.3. The Plot in Fig.4.3 reveals two configurationally ordered/disordered transitions, taking place at 870 and 2325 K, respectively, in which the degree of disorder increases the temperature increases (Paper I).

Figure 4.3. Plot between Gibbs free energy and temperature of B_4C . The dashed-line represents the ordered state of B_4C , which is $B_{11}C^p(CBC)$. The solid lines represents a configurationally disordered state of B_4C , in which the icosahedral carbon atoms C^p are substitutionally disordered among the three polar up sites, meanwhile the dashed-dotted line represents a highly configurationally disordered B_4C . In the highly disordered state, the icosahedral carbon atoms C^p are substitutionally disordered at all six polar sites. According to this approximation, the transitions from the ordered to the disordered, and to the highly disordered B_4C take place at 870 and 2325 K, respectively.

Note that due to the use of the mean-field approximation to obtain S_{conf}^{dis} , given by Eq.(4.10), T_{trans} is generally overestimated by 20-30% [110], as the short-range ordering effects are being neglected within the approximation. In some cases, e.g. a modeling of configurational disorder in $B_{13}C_2$ (Paper II) and $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys (Paper III) using Basis-3 (see Fig.3.5), in which equally substituting the chain-end C atoms for only one, two, three, or for all six B^e atoms within the B_{12} icosahedra practically results in the same total energy, it is important to fully consider the multiplicity of apparently equivalent superatom types to approximate S_{conf}^{dis} , even if only a subset of superatom basis is used for SA-SQS modeling.

4.3 Thermodynamic stability of $(B_6O)_{1-x}(B_{13}C_2)_x$

In the case of alloys e.g. $(B_6O)_{1-x}(B_{13}C_2)_x$, where the composition (x) can be varied, the thermodynamic stability is determined by the mixing Gibbs free energy ΔG_{mix} , plotted as a function of x , by which ΔG_{mix} can be given by;

$$\Delta G_{mix}(x, T) = \Delta H_{mix} - T\Delta S_{mix}, \quad (4.12)$$

where ΔH_{mix} is defined as the mixing enthalpy. When $p = 0$ GPa, ΔH_{mix} is the same as ΔE , given in Eq. (4.3), if all of the energies E are calculated at equilibrium volume V_0 for each particular phase/composition. In this case, ΔE is defined as the difference in the ground-state energy E_0 between the mixing compounds $((B_6O)_{1-x}(B_{13}C_2)_x)$ and their constituents (B_6O and $B_{13}C_2$);

$$\Delta E = E_0((B_6O)_{1-x}(B_{13}C_2)_x) - [(1-x) \cdot E_0(B_6O)] - [x \cdot E_0(B_{13}C_2)]. \quad (4.13)$$

ΔS_{mix} denotes the mixing entropy, describing the difference in entropy before and after mixing. In this case, ΔS_{mix} is approximated within the mean-field approximation to be S_{conf}^{dis} , given by Eq.(4.10). If $\Delta G_{mix} < 0$, the $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys are stable with respect to their constituents, indicating a tendency of mixing between B_6O and $B_{13}C_2$. Meanwhile, $\Delta G_{mix} > 0$ indicates a tendency for the $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys to decompose into B_6O and $B_{13}C_2$, i.e. a phase separation. It is worth noting that the stability of any alloy for a given composition cannot be determined by its positive or negative values of ΔG_{mix} . In order to determine the stability of the alloy at any fixed composition, ΔG_{mix} of the alloy at all compositions must be considered. This can be done by applying common tangent construction to the ΔG_{mix} curves, which will be described in the following paragraphs.

Fig.4.4 illustrates a plot between the mixing Gibbs free energy ΔG_{mix} curves of $(B_6O)_{1-x}(B_{13}C_2)_x$ and the composition x at different absolute temperatures T . The $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys are modeled, using the SA-SQS approach, in which the $B_{12}(OO)$ and $B_{12}(CBC)$ units are defined as superatoms for B_6O and $B_{13}C_2$, respectively. At $T = 0$ K, $\Delta G_{mix} > 0$ for a whole composition range, and the $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys are likely to decompose into B_6O and $B_{13}C_2$. As the temperature T increases, the contribution from the mixing entropy ΔS_{mix} becomes larger, thus lowering the mixing Gibbs free energy ΔG_{mix} . At $T \gtrsim 1500$ K,

the ΔG_{mix} curves display two minima, and ΔG_{mix} of the $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloy at any composition between the two minima can be lowered, as it decomposes into two phases. The minimization of ΔG_{mix} is determined by a common tangent line, connecting between the two minima. As a result, the $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloy is most stable, in thermodynamic equilibrium, as a mixture of two phases, in which their compositions are also given by the common tangent.

Figure 4.4. Mixing Gibbs free energy of $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ as a function of composition x at different temperatures, respecting to B_6O and B_{13}C_2 given by the dashed line. A common tangent $\overline{AB}$ is given at 2000 K as an example.

As shown in Fig.4.4, the common tangent line $\overline{AB}$ is drawn at 2000 K for an example. At this temperature, the $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloy at any composition between x_α and x_β can lower its Gibbs free energy by decomposing into two phases - α and β for example. Once ΔG_{mix} lies on the common tangent $\overline{AB}$, e.g. point C for $x = 0.5$, the alloy is in thermodynamic equilibrium and stable as a mixture of α and β . The equilibrium compositions of α and β phases are given by x_α and x_β , respectively, and the relative amounts of the two phases can be obtained by the lever rule. The region where the two phases coexist is known as a miscibility gap. Either for $x < x_\alpha$ or for $x > x_\beta$, the minimum Gibbs free energy already lies on the ΔG_{mix} curve, and the $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloys within such composition regions are thermodynamically stable as a homogeneous single phase/solid solution. By constructing the common tangents to a set of ΔG_{mix} curves at different temperatures, one can sketch a phase diagram [111]. In this thesis, the pseudo-binary phase diagram of $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ is outlined in order to illustrate the stability of $(\text{B}_6\text{O})_{1-x}(\text{B}_{13}\text{C}_2)_x$ alloys (Paper III).

4.4 Effects of lattice vibration on thermodynamic stability of boron carbide-based materials

Apart from the configurational excitations, lattice vibration that contributes to the vibrational energy E_{vib} and the vibrational entropy S_{vib} , describing the number of ways in which vibrations can be set up in the solid, are also expected to play an important role to the stability of a system comprising of light elements, e.g. boron [112], as $T \geq 0$ K. However, for alloys, where configurational order/disorder or phase separation transitions are studied, it is possible that the vibrational degree of freedom acts similarly on all of the considered configurations and thus slightly contributes to their relative stability. A further investigation on the thermodynamic as well as the dynamical stabilities of configurationally disordered boron carbide and $(B_6O)_{1-x}(B_{13}C_2)_x$, in which the effects of lattice vibration are taken into account, can be done by performing phonon calculations within a harmonic [113] or a quasi-harmonic approximations [114] to the force constants.

Preliminary results of the effects of lattice vibration on the configurational order/disorder transition temperature, and the phonon density of states of B_4C are shown in Fig.4.5, and Fig.4.6, respectively. Fig.4.5 indicates that the transition temperature decreases from 870 K to 830 K and 750 K, when the effects of lattice vibration are taken into account within the harmonic and the quasi-harmonic approximation, respectively. The phonon density of states show no imaginary phonon frequency for both the ordered and the disordered configurations of B_4C , indicating their dynamical stability.

Note that, in this thesis, the vibrational contributions, i.e. zero-point motion and finite temperature effects, to the Gibbs free energy has been neglected. However, taking into account only the configurational entropy S_{conf} seems sufficient at this stage to qualitatively describe the tendency of configurational disorder in boron carbides and $(B_6O)_{1-x}(B_{13}C_2)_x$, as shown by the preliminary results in Fig.4.5, and Fig.4.6, as well as to provide the necessary starting point in term of candidate disordered configurations for future more elaborate investigations.

Figure 4.5. Plot between Gibbs free energy and temperature of configurationally disordered B_4C , in which the icosahedral carbon atoms configurationally disorder among the three polar-up sites. The Gibbs free energies are plot, relative to the ordered ground state (dashed-line). The solid line denotes the Gibbs free energy, calculated without taking into account the effects of lattice vibration, meanwhile the dotted- and the dashed-dotted lines represent the Gibbs free energies, whose vibrational contributions are obtained within the harmonic and the quasi-harmonic approximation, respectively.

Figure 4.6. Phonon density of states of the ordered ground state of B_4C (solid line) and the configurationally disordered B_4C (dashed-line), in which the icosahedral carbon atoms configurationally disorder among the three polar-up sites.

CHAPTER 5

Modeling elastic properties

Besides the crystallographic, and the electronic properties, it is as well of interest to explore the elastic properties of boron carbide-based materials, as they are candidates for being superhard materials. The elastic properties, generally determined by elastic constants, provide an important part of the information on the mechanical behavior, e.g. the mechanical stability and the stiffness, of materials, which is of great importance for technological applications, such as cutting tools and wear resistant materials. The other part, i.e. the plastic properties of materials, composes a formidable challenge for atomistic modeling, but it is indirectly related to the elastic properties. The elastic properties of boron carbide-based materials can be determined by applying strains ϵ with $\pm 1\%$ and $\pm 2\%$ distortions to their fully relaxed supercells without volume conservation. The elastic constants C_{ij} are then calculated by the numerical differentiation of the total energy of a material as a function of the imposed strains ϵ [115, 116];

$$C_{ij} = \frac{1}{V_0} \frac{\partial^2 E(\epsilon)}{\partial \epsilon_i \partial \epsilon_j} \Big|_{\epsilon=0}, \quad (5.1)$$

where Voigt's notation is used to describe the strain vector ϵ and the elastic tensor C [117, 118]. The strain vector ϵ is thus given by;

$$\epsilon = \{\epsilon_1, \epsilon_2, \epsilon_3, \epsilon_4, \epsilon_5, \epsilon_6\}, \quad (5.2)$$

meanwhile $E(\epsilon)$ is the total energy of the distorted supercell due to the corresponding applied strains, and can be expressed in term of a power series of the strains ϵ by [116];

$$E(\epsilon) = E(0) + V_0 \left(\sum_{i=1}^6 \tau_i \epsilon_i + \frac{1}{2} \sum_{i=1}^6 \sum_{j=1}^6 C_{ij} \epsilon_i \epsilon_j + O(\epsilon^3) \right), \quad (5.3)$$

where $E(0)$ and V_0 are the total energy and the equilibrium volume of the undistorted supercell, respectively. τ_i are the components of the stress vector $\boldsymbol{\tau}$, which vanishes if the undistorted supercell is stress free, as the derivatives in Eq.(5.1) are calculated at $\boldsymbol{\epsilon} = 0$.

Practically, one can obtain a strain-induced distorted supercell by applying the strains ϵ_i to the undistorted one via [119];

$$\begin{pmatrix} \mathbf{a}'_1 \\ \mathbf{a}'_2 \\ \mathbf{a}'_3 \end{pmatrix} = \begin{pmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \end{pmatrix} \cdot (I + \varepsilon), \quad (5.4)$$

where $\mathbf{a}'_i$ and $\mathbf{a}_i$ ($i = 1, 2, 3$) represent the lattice vectors of the distorted and the undistorted supercells, respectively. I is the unitary matrix, and ε is the strain tensor, which is related to the strain vector $\boldsymbol{\epsilon}$ in Eq.(5.2) by [119];

$$\varepsilon = \begin{pmatrix} \epsilon_1 & \frac{\epsilon_6}{2} & \frac{\epsilon_5}{2} \\ \frac{\epsilon_6}{2} & \epsilon_2 & \frac{\epsilon_4}{2} \\ \frac{\epsilon_5}{2} & \frac{\epsilon_4}{2} & \epsilon_3 \end{pmatrix}. \quad (5.5)$$

The second-order elastic stiffness tensor C can be represented by a (6x6) matrix and has in principle a maximum of 36 independent elements. As the (6x6) matrix representation of C is symmetric, i.e. $C_{ij} = C_{ji}$, the maximum number of the independent elastic constants C_{ij} reduces to 21. The elastic tensor C is thus represented by;

$$C = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & C_{15} & C_{16} \\ C_{12} & C_{22} & C_{23} & C_{24} & C_{25} & C_{26} \\ C_{13} & C_{23} & C_{33} & C_{34} & C_{35} & C_{36} \\ C_{14} & C_{24} & C_{34} & C_{44} & C_{45} & C_{46} \\ C_{15} & C_{25} & C_{35} & C_{45} & C_{55} & C_{56} \\ C_{16} & C_{26} & C_{36} & C_{46} & C_{56} & C_{66} \end{pmatrix}. \quad (5.6)$$

The number of independent elements for the elastic tensor C also depends on the crystal symmetry. In the case of boron carbide and boron suboxide, having the rhombohedral symmetry ($R\bar{3}m$), there are six independent elastic constants, i.e. C_{11} , C_{12} , C_{13} , C_{14} , C_{33} , C_{44} , and the elastic tensor C_{rhomb} is given by;

$$C_{rhomb} = \begin{pmatrix} C_{11} & C_{12} & C_{13} & C_{14} & 0 & 0 \\ C_{12} & C_{11} & C_{13} & -C_{14} & 0 & 0 \\ C_{13} & C_{13} & C_{33} & 0 & 0 & 0 \\ C_{14} & -C_{14} & 0 & C_{44} & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44} & C_{14} \\ 0 & 0 & 0 & 0 & C_{14} & C_{66} \end{pmatrix}, \quad (5.7)$$

where

$$C_{66} = \frac{1}{2}(C_{11} - C_{12}). \quad (5.8)$$

In this thesis, the effects of configurational disorder on the elastic properties of boron carbides and $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys, are investigated (Paper III). Note

that the SQS technique, in principle, breaks the point group symmetry. The projection technique, as introduced by Moakher *et al.* [120], is thus implemented in order to derive the closest elastic tensor with rhombohedral symmetry (C_{rhom}^*) for both configurationally disordered boron carbides and $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys, modeled by the SA-SQS approach. The obtained closest elastic tensor for the rhombohedral symmetry ($R\bar{3}m$), belonging to the trigonal crystal system, is thus given by;

$$C_{rhom}^* = \begin{pmatrix} C_{11}^* & C_{12}^* & C_{13}^* & C_{14}^* & 0 & 0 \\ C_{12}^* & C_{11}^* & C_{13}^* & -C_{14}^* & 0 & 0 \\ C_{13}^* & C_{13}^* & C_{33}^* & 0 & 0 & 0 \\ C_{14}^* & -C_{14}^* & 0 & C_{44}^* & 0 & 0 \\ 0 & 0 & 0 & 0 & C_{44}^* & C_{14}^* \\ 0 & 0 & 0 & 0 & C_{14}^* & C_{66}^* \end{pmatrix}, \quad (5.9)$$

where

$$C_{11}^* = \frac{3}{8}(C_{11} + C_{22}) + \frac{1}{4}C_{12} + \frac{1}{2}C_{66}, \quad (5.10a)$$

$$C_{12}^* = \frac{1}{8}(C_{11} + C_{22}) + \frac{3}{4}C_{12} - \frac{1}{2}C_{66}, \quad (5.10b)$$

$$C_{13}^* = \frac{1}{2}(C_{13} + C_{23}), \quad (5.10c)$$

$$C_{14}^* = \frac{1}{4}C_{14} - \frac{1}{4}C_{24} + \frac{1}{2}C_{56}, \quad (5.10d)$$

$$C_{33}^* = C_{33}, \quad (5.10e)$$

$$C_{44}^* = \frac{1}{2}C_{44} + C_{55}, \quad (5.10f)$$

$$C_{66}^* = \frac{1}{2}(C_{11}^* - C_{12}^*) = \frac{1}{8}(C_{11} + C_{22}) - \frac{1}{4}C_{12} + \frac{1}{2}C_{66}. \quad (5.10g)$$

Consequently, twelve independent elastic constants, i.e. C_{11} , C_{12} , C_{13} , C_{14} , C_{22} , C_{23} , C_{24} , C_{33} , C_{44} , C_{55} , C_{56} , and C_{66} , are needed to obtain C_{rhom}^* in Eq.(5.9). The elastic stability for configurationally disordered boron carbide-based materials is determined by the Born stability criteria [121]. For the rhombohedral structure, the criteria are given by;

$$C_{11}^* - |C_{12}^*| > 0, \quad (5.11a)$$

$$(C_{11}^* + C_{12}^*)C_{33}^* - 2(C_{13}^*)^2 > 0, \quad (5.11b)$$

$$(C_{11}^* - C_{12}^*)C_{44}^* - 2(C_{14}^*)^2 > 0, \quad (5.11c)$$

$$C_{44}^* > 0. \quad (5.11d)$$

The isotropic elastic moduli and the Poisson's ratio of configurationally disordered boron carbide-based materials are obtained using the Voigt-Reuss-Hill (VRH) approach [122] for calculating elastic properties of polycrystalline solids. The Voigt

method averages the elastic stiffness (C_{ij}) over all lattice orientations by assuming that strain is uniform throughout a grain. Two independent isotropic elastic moduli, i.e. bulk modulus B , and shear modulus G , given by the Voigt method, are;

$$B_V = \frac{(C_{11} + C_{22} + C_{33}) + 2(C_{12} + C_{13} + C_{23})}{9}, \quad (5.12a)$$

$$G_V = \frac{(C_{11} + C_{22} + C_{33}) - (C_{12} + C_{13} + C_{23}) + 3(C_{44} + C_{55} + C_{66})}{15}. \quad (5.12b)$$

The Reuss method averages the elastic compliances (S_{ij}) by assuming that stress is uniform throughout a grain. The elastic compliance tensor S is obtained by the inverse of the elastic stiffness tensor C , thus

$$S = C^{-1} = \begin{pmatrix} S_{11} & S_{12} & S_{13} & S_{14} & S_{15} & S_{16} \\ S_{12} & S_{22} & S_{23} & S_{24} & S_{25} & S_{26} \\ S_{13} & S_{23} & S_{33} & S_{34} & S_{35} & S_{36} \\ S_{14} & S_{24} & S_{34} & S_{44} & S_{45} & S_{46} \\ S_{15} & S_{25} & S_{35} & S_{45} & S_{55} & S_{56} \\ S_{16} & S_{26} & S_{36} & S_{46} & S_{56} & S_{66} \end{pmatrix}, \quad (5.13)$$

and the two independent elastic moduli within the Reuss method can be obtained as;

$$B_R = \frac{1}{(S_{11} + S_{22} + S_{33}) + 2(S_{12} + S_{13} + S_{23})}, \quad (5.14a)$$

$$G_R = \frac{15}{4(S_{11} + S_{22} + S_{33}) - 4(S_{12} + S_{13} + S_{23}) + 3(S_{44} + S_{55} + S_{66})}. \quad (5.14b)$$

In this thesis, the Voigt average elastic moduli, B_V , and G_V , for configurationally disordered boron carbide-based materials are obtained via Eq.(5.12), by which the elastic constants C_{ij} in the equations are replaced by the projected elastic constants C_{ij}^* , as determined by Eq.(5.10), while the Reuss average elastic moduli, B_R , and G_R , are obtained by replacing the elastic compliances S_{ij} in Eq.(5.14) with the projected elastic compliances S_{ij}^* , which are the elements of the compliance tensor S_{rhomb}^* . By using the relation between C and S , given in Eq.(5.13), the tensor S_{rhomb}^* can be directly obtained by the inverse of C_{rhomb}^* ;

$$S_{rhomb}^* = (C_{rhomb}^*)^{-1}. \quad (5.15)$$

Generally, the Voigt average gives the upper bound of elastic moduli, meanwhile the Reuss average gives the lower bound of elastic moduli. The Hill average is thus simply the arithmetic average of those obtained from the Voigt and Reuss averages;

$$B_H = \frac{B_V + B_R}{2}, \quad (5.16a)$$

$$G_H = \frac{G_V + G_R}{2}. \quad (5.16b)$$

The Young' modulus E and the Poisson's ratio ν for each average method can be obtained via the relationships between the different elastic moduli;

$$E = \frac{9BG}{3B + G}, \quad (5.17)$$

and

$$\nu = \frac{3B - 2G}{2(3B + G)}. \quad (5.18)$$

CHAPTER 6

Outlook

To use either the harmonic or the quasi-harmonic approximation to account for the lattice vibration in determining the stabilities of configurationally disordered B_4C , is methodologically a natural first step, as shown in section 4.4. However, one should be aware that, within these approximations, the potential energy surface of the atoms is extracted from the equilibrium atomic positions at 0 K. At very high temperature, where atoms are strongly vibrating and moving further away from their equilibrium positions, resulting in a system with strong anharmonicity, the two approximations become inaccurate and can fail to predict the thermal properties for such a highly anharmonic system [123]. To properly consider and fully take into account the effects of anharmonicity in determining the stabilities of configurationally disordered boron carbides at high temperature, it is worth trying to go beyond the harmonic and the quasi-harmonic approximations, by using a more accurate method, namely temperature dependent effective potential (TDEP) [124, 125], based on *ab initio* molecular dynamics (AIMD). This is motivated by the stabilities of a highly disordered state of B_4C (see Fig.4.3) and a semiconducting state of $B_{13}C_2$ (PAPER II) at high temperature, where the effects of anharmonicity are expected to be distinctively strong.

As mentioned in section 1.2, it is not trivial to use conventional diffraction techniques to verify the existence of configurational disorder in boron carbide due to the similar characteristics between boron and carbon atoms. However, one may try to calculate extended x-ray absorption fine structure (EXAFS) as well as core level shift (CLS) spectra, for both configurationally ordered and disordered boron carbides, using *first-principles* calculations, and use them as fingerprints to trace the presence of configurational disorder in boron carbide samples by comparing with experimentally measured spectra, focusing on C(1s) and B(1s) edges.

Even though boron carbide is extremely hard, its fracture toughness is fairly low due to the formation of local amorphous shear bands, when subjected to high-

velocity impact and high pressures [18, 28], thus limiting its usage in many engineering applications. A recent study has shown that a significant improvement in the mechanical properties of boron carbide can be achieved via silicon (Si) doping, in which the static pressure, required to induce amorphization, is approximately doubled [126]. It is thus of interest to investigate the thermodynamic stability of ternary B-C-Si alloys by using knowledge, accumulated from the previous studies to answer questions, regarding (1) a solubility of the silicon atoms in boron carbide to form solid solutions, followed by (2) candidates for the atomic configurations of the B-C-Si alloys, as demonstrated by an analysis of Raman spectra that silicon atoms can substitute into the 3-atom chains as well as the icosahedral units of boron carbide [127], and (3) influences of configurational disorder of B, C, and Si atoms, and of change in the alloy composition on the properties of the B-C-Si alloys.

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CHAPTER 7

Results and included papers

The results obtained from the investigations in this thesis are presented in the form of three scientific papers. The first two papers are published in *Physical Review B*, and the third one is given in the form of manuscript. The summaries of the three included papers and the papers are given in following pages;

PAPER I

First-principles study of configurational disorder in B_4C using a superatom-special quasirandom structure method

Physical Review B **90**, 024204 (2014)

Summary

Configurationally disordered boron carbide B_4C , whose ground-state is represented by the $B_{11}C^p(CBC)$ unit with monoclinic distortion, is studied using first-principles calculations. The results predict two configurationally ordered/disordered transitions at 870 and 2325 K, respectively. The first transition, in which the icosahedral carbon atoms configurationally disorder among the three polar-up sites, removes the distortion and the rhombohedral symmetry ($R\bar{3}m$) is restored. The second transition in turn reveals the random substitution of the icosahedral carbon atoms at all six polar sites, coexisting with bipolar defects ($B_{10}C_2^p+B_{12}$), yielding the full rhombohedral symmetry ($R\bar{3}m$). The restoration of the rhombohedral symmetry is in agreement with the experimental observations.

Author's contribution

I took part in planning, performed all the calculations, participated in the evaluation and interpretation of the results. I was responsible for writing the manuscript.

PAPER II

Configurational order-disorder induced metal-nonmetal transition in $B_{13}C_2$ studied with first-principles superatom-special quasirandom structure method

Physical Review B **92**, 014202 (2015)

Summary

First-principles calculations of boron carbide $B_{13}C_2$ reveal that as the temperature increases, the metallic-ordered state of $B_{13}C_2$, represented by $B_{12}(CBC)$, configurationally disorders, by which some of the $B_{12}(CBC)$ units turn into the $B_{11}C^e(BBC)$ units. The existence of the $B_{11}C^e(BBC)$ units in turn partially or fully compensate the electron deficiency in the $B_{12}(CBC)$ units, depending on their relative concentrations. As the concentration of the $B_{11}C^e(BBC)$ units increases with temperature under equilibrium condition, approaching 50%, the electron deficiency in $B_{13}C_2$, represented by a mixture of $B_{12}(CBC)$ and $B_{11}C^e(BBC)$, is gradually compensated until the completely semiconducting character is achieved, corresponding to the experimental observation that boron carbide is a semiconductor. The calculated band gap is also in fairly good agreement with the experiment.

Author's contribution

I took part in planning, performed all the calculations, participated in the evaluation and interpretation of the results. I was responsible for writing the manuscript.

PAPER III

Effects of configurational disorder on the elastic properties of icosahedral boron-rich alloys based on B_6O , $B_{13}C_2$, and B_4C , and their mixing thermodynamics

Manuscript in final preparation

Summary

This paper highlights effects of configurational disorder on the elastic properties of icosahedral boron-rich alloys based on B_6O , $B_{13}C_2$, and B_4C and their mixing thermodynamics. The results indicate that when configurational disorder of B and C atoms are taken into account, an excellent agreement on elastic moduli between theory and experiment is achieved for boron carbide. By investigating the thermodynamics of mixing between B_6O and $B_{13}C_2$, denoted by $(B_6O)_{1-x}(B_{13}C_2)_x$, the quasi-binary phase diagram of the $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys is outlined. The diagram reveals the existence of a miscibility gap at all temperatures up to the melting point, indicating the coexistence of B_6O -rich and $B_{13}C_2$ -rich domains in $(B_6O)_{1-x}(B_{13}C_2)_x$ alloys under equilibrium condition. At low temperature, B_6O -rich and $B_{13}C_2$ -rich regions are dominated, respectively, by $B_{12}(OO)$ and $B_{12}(CBC)$ structural units. As the temperature increases, a part of the C atoms in the CBC chains substitute for B atoms in B_{12} icosahedra, leading to an additional degree of configurational disorder in $(B_6O)_{1-x}(B_{13}C_2)_x$. Additionally, a limited but non-zero miscibility of B_6O and $B_{13}C_2$ to form solid solutions is predicted at high temperature.

Author's contribution

I took part in planning, performed all the calculations, participated in the evaluation and interpretation of the results. I was responsible for writing the manuscript.