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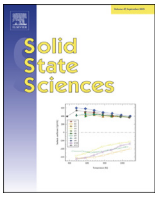

Phase transitions of boron carbide: Pair interaction model of high carbon limit

Sanxi Yao [a], W.P. Huhn [a, b], M. Widom [a, *]

[a] Department of Physics, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15232, United States
[b] Department of Mechanical Engineering and Materials Science, Duke University, Durham, NC 27708, United States

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Boron Carbide exhibits a broad composition range, implying a degree of intrinsic substitutional disorder. While the observed phase has rhombohedral symmetry (space group $R\bar{3}m$), the enthalpy minimizing structure has lower, monoclinic, symmetry (space group Cm). The crystallographic primitive cell consists of a 12-atom icosahedron placed at the vertex of a rhombohedral lattice, together with a 3-atom chain along the 3-fold axis. In the limit of high carbon content, approaching 20% carbon, the icosahedra are usually of type $B_{11}C^p$, where the p indicates the carbon resides on a polar site, while the chains are of type C–B–C. We establish an atomic interaction model for this composition limit, fit to density functional theory total energies, that allows us to investigate the substitutional disorder using Monte Carlo simulations augmented by multiple histogram analysis. We find that the low temperature monoclinic Cm structure disorders through a pair of phase transitions, first via a 3-state Potts-like transition to space group $R3m$, then via an Ising-like transition to the experimentally observed $R\bar{3}m$ symmetry. The $R3m$ and Cm phases are electrically polarized, while the high temperature $R\bar{3}m$ phase is nonpolar.

1. Introduction

The phase diagram of boron carbide is not precisely known, with both qualitative and quantitative discrepancies among the different research groups [1–7]. The most widely accepted diagram of Schwetz [4,5] displays a single boron carbide phase at temperature above 1000C, coexisting with elemental boron and graphite. The carbon concentration covers the range 9%–19.2% carbon, falling notably short of the 20% carbon fraction at which the electron count is believed to be optimal [8–10]. More interestingly, the nearly temperature independent behavior of the phase boundaries are thermodynamically improbable, and the broad composition range suggests substitutional disorder at 0 K, in apparent violation of the 3rd law. Since so much remains unknown, and experiment can only be assured of reaching equilibrium at high temperature, theoretical calculation offers hope for resolving the behavior at lower temperatures, in addition to interpreting the disorder at high temperatures.

As determined crystallographically [11–13], boron carbide has a 15-atom primitive cell, consisting of an icosahedron and 3-atom chain, in a rhombohedral lattice with symmetry $R\bar{3}m$. At 20% carbon a proposed B_4C structure featured pure boron icosahedra B_{12} with a C–C–C chain [14]. Although this structure exhibits $R\bar{3}m$ symmetry, later experimental work [13,15] suggested that the icosahedron should be $B_{11}C$ instead of B_{12} and the chain should be C–B–C instead of C–C–C. For other compositions, the icosahedra can be B_{12}, $B_{11}C$, or even $B_{10}C_2$ (the bi-polar defect [16]), and the chain can be C–B–C, C–B–B, B–B_2–B [17,18] or B–V–B (V means vacancy). Fig. 1 illustrates the rhombohedral cell, the C–B–C chain and the icosahedron. The 12 icosahedral sites are categorized into 2 classes: equatorial and polar. We further classify the polar sites into north and south. Icosahedra are connected along edges of the rhombohedral lattice, which pass through the polar sites.

Density functional theory studies of a large number of possible arrangements of boron and carbon atoms [16,19,20] identified four stable phases: pure β-Boron, rhombohedral $B_{13}C_2$, monoclinic B_4C, and graphite. The stable rhombohedral phase consists of B_{12} icosahedra with C–B–C chains, giving full rhombohedral symmetry $R\bar{3}m$, while the stable monoclinic phase has $B_{11}C^p$ icosahedra and C–B–C chains. Carbon occupies the same polar site (e.g. p_0) in every icosahedron, resulting in symmetry Cm. Introducing disorder in the occupation of polar sites (i.e. randomly choosing one polar site to

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* Corresponding author.
E-mail addresses: sanxiy@andrew.cmu.edu (S. Yao), wph@andrew.cmu.edu (W.P. Huhn), widom@andrew.cmu.edu (M. Widom).

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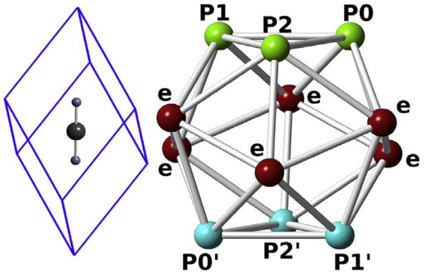

Fig. 1. Primitive cell of boron carbide showing C–B–C chain at center along the 3-fold axis. The icosahedron (not to scale) occupies the cell vertex. Equatorial sites of the icosahedron are shown in red, labeled "e", the north polar sites are shown in green and labeled p_0, p_1 and p_2, while the south polar sites are shown in cyan and labeled as p'_0, p'_1 and p'_2. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

occupy with carbon) can restore $R\overline{3}m$ symmetry. In general, we define site occupations m_i ($i = 0{,}1{,}2{,}0'{,}1'{,}2'$) corresponding to the mean occupation of the sites p_i. The experimentally observed phase has all $m_i = 1/6$. We call this orientational disorder. The stable monoclinic phase has one large order parameter (e.g. $m_0{\sim}1$) and the remaining $m_i{\sim}0$, which we call orientational order. Hence it was proposed [21] that a temperature-driven order-disorder phase transition is responsible for the high symmetry seen in experiments that are likely in equilibrium only at high temperature.

According to Landau's theory of phase transitions [22], the space groups of structures linked by continuous or at most weakly first order phase transitions should obey group-subgroup relationships. Additionally, the subgroup should be maximal, again provided the transition is continuous or at most weakly first order. Typically the high temperature phase possesses the higher symmetry, as this permits a higher entropy. In regard to boron carbide, the high temperature phase has space group $R\overline{3}m$ (group #166) and the low temperature phase has group Cm (group #8). However, Cm is not a maximal subgroup of $R\overline{3}m$, suggesting the possible existence of an intermediate phase. Two sequences of transitions obey the maximality requirement: $R\overline{3}m \rightarrow R3m \rightarrow Cm$ and $R\overline{3}m \rightarrow C2/m \rightarrow Cm$ [23]. The two corresponding intermediate symmetries $R3m$ and $C2/m$ have space group numbers #160 and #12, respectively.

In terms of the distribution of carbon atoms on icosahedra, $R3m$ breaks the inversion symmetry, and hence corresponds to occupying one pole (e.g. the north pole) more heavily than the other, so that $m_i{\sim}1/3$ ($i = 0{,}1{,}2$) with the remaining $m_i{\sim}0$. In contrast, $C2/m$ breaks the 3-fold rotational symmetry but preserves inversion. Thus the carbon atoms preferentially occupy a pair of diametrically opposite polar sites, e.g. $m_0 = m'_0 \sim 1/2$ while the remaining $m_i{\sim}0$.

Even though covalent bond is formed, carbon tends to draw electrons from surrounding borons, owing to its greater electronegativity. The phases that break inversion symmetry possess an electric dipole moment. Hence we name the $R3m$ state "polar". The possibility of a polar phase was independently suggested recently [24]. We name the Cm state "tilted polar" because the broken 3-fold symmetry creates a component of polarization in the xy plane. Although it lacks a net dipole moment, we name the $C2/m$ state "bipolar" because it is reminiscent of the bipolar defect [16]. Finally, we name the high symmetry phase $R\overline{3}m$ "nonpolar".

To identify phase transitions, and to determine which symmetry-breaking sequence occurs, we perform Monte Carlo simulations. Strictly speaking, phase transitions occur only in the thermodynamic limit of large system size, which is beyond the reach of density functional theory calculations. Hence we construct a classical interatomic interaction model, with parameters fit to density functional theory energies. For simplicity we consider only the high carbon limit where every icosahedron contains a single polar carbon (i.e. we essentially project the composition range onto the $x_C = 0.2$ line). We analyze our simulation results with the aid of the multiple histogram technique [25,26]. In the end we indeed discover a sequence of two phase transitions. One arises from the breaking of 3-fold symmetry linking Cm to $R3m$ that is first order, similar to the 3-state Potts model [27] in three dimensions. The other corresponds to the breaking of inversion symmetry linking $R3m$ to $R\overline{3}m$ that is in the Ising universality class.

2. Methods

2.1. Pair interaction model

Given that every primitive cell contains a $B_{11}C^p$ icosahedron and a C–B–C chain, the configuration can be uniquely specified by assigning a 6-state variable σ to each cell, corresponding to which of the six polar sites holds the carbon atom. The relaxed total energy of a specific configuration can be expressed through a cluster expansion in terms of pairwise, triplet and higher-order interactions [28,29] of these variables. As shown below, truncating at the level of pair interactions provides sufficient accuracy for present purposes. Further, we observe that symmetry–inequivalent pairs are in nearly one-to-one correspondence with the intercarbon separation $R_{ij} = |\mathbf{R}_i - \mathbf{R}_j|$ where the $\mathbf{R}_i$ are the initial positions prior to relaxation and belong to a discrete set of fixed possible values $\{R_k\}$, arranged in order of increasing length. Note that we need not concern ourselves with interactions of polar carbons with chain carbons, as the number of such pairwise interactions is conserved across configurations. Thus our total energy can be expressed as

$$E(N_1, \ldots, N_m) = E_0 + \sum_{i=1}^{m} a_k N_k \tag{1}$$

where N_k is the number of intercarbon separations of length R_k, and m is the number of such separations we choose to treat in our model.

We use the density functional theory-based Vienna ab initio simulation package (VASP) [30–33] to calculate the total energies within the projector augmented wave (PAW) [34,35] method utilizing the PBE generalized gradient approximation [36,37] as the exchange-correlation functional. We construct a variety of 2 × 2 × 2

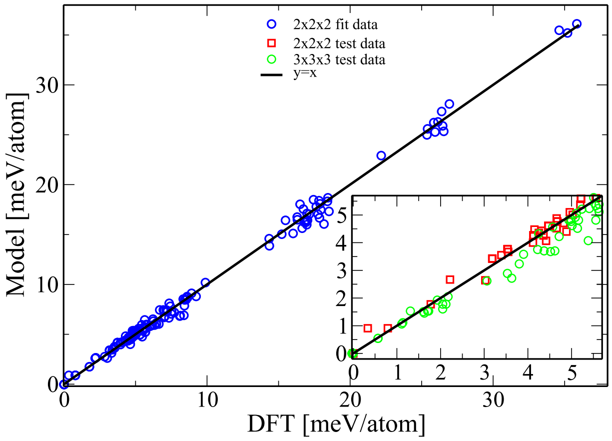

Fig. 2. Fit of bond interaction model to DFT-calculated total energies in 2 × 2 × 2 supercells. Inset shows cross validation check of 2 × 2 × 2 supercells transferability to 3 × 3 × 3 supercells.