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Mechanical properties of icosahedral boron carbide explained from first principles

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An exhaustive study of the neutral structural defects of icosahedral B_4C has been performed with the density functional theory. Vacancies have been determined to be boron vacancies in the C–B–C chains. Their presence is shown to yield a discontinuous variation of crystal volume upon increasing pressure, when the formation of a C–C bond occurs in the chains. The dynamical failure of shocked B_4C is attributed to the formation of these C–C bonds.

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I. INTRODUCTION

It would be highly desirable to use B_4C as a protective material for people and structures. It has the highest Hugoniot elastic limit (HEL) among ceramics ($\approx$17 GPa)[1] but, when impacted with a shock stress beyond the HEL, it shows a gradual loss of strength which is almost complete around 40 GPa. The failure of boron carbide under a shock compression is not understood, and the question whether the loss of strength of this brittle ceramics is mechanical in nature, or due to a phase transition, has been left open.[2] We are going to show that none of these hypotheses is confirmed by our calculations. Instead, we highlight the role of defects, and, in particular, vacancies, in the determination of the mechanical properties of B_4C. Futhermore, we show that the presence of vacancy defects in C–B–C chains can explain the failure of B_4C.

In favour of the first hypothesis mentionned above, the loss in strength of B_4C has been associated with a decrease in the shear strength leading to the mechanical instability and to a local amorphization.[3] This explanation has been contested in Ref. 4 by pointing out that only a very small fraction of the material had been damaged and that B_4C could elastically sustain loadings or unloadings from the shocked state, without any amorphization, thus proving capable of resisting high shear stresses in the shocked state.

The hypothesis of a phase transition could not be proved experimentally,[4] and the experiments involving a static loading in a diamond-anvil cell (DAC) did not clarify the question. Under a hydrostatic compression up to 36 GPa, no first-order phase transition has been detected.[5] Under (undefined) nonhydrostatic conditions, a local amorphization has been reported during the depressurization of the DAC from 50 GPa.[6] This was not the signature of a transition toward an amorphous state, as occurs in some other ceramics,[7] but the consequence of the formation of a metastable phase at the grain boundaries.[6] No relationship has been established so far between the observations under a static pressure[5,6] and the dynamical failure.[1,3,4]

However, during a high stress deformation, dislocations are mobile and dislocation jogs can follow the glide motion only by emitting or absorbing point defects.[8] This is known to give rise to clusters of vacancies,[9,10] but the role of such defects in the failure of materials has been totally ignored so far. As pointed out recently, the generation and motion of structural defects in a solid under severe external action is a complicated process, whose theory is still in its infancy.[11,12] In the following, vacancies are shown to be located in the C–B–C chains and to be boron vacancies only, C–V–C (Fig. 1). We show that, as pressure increases, a discontinuous variation of the crystal volume of $\approx$4 Å^3 *per* vacancy occurs when a C–C bond forms. The failure of B_4C is attributed to the formation of these C–C bonds. The computational method is detailed in Sec. II. Results are reported in Sec. III, and discussed in Sec. IV. The conclusion is drawn in Sec. V.

II. COMPUTATIONAL METHOD

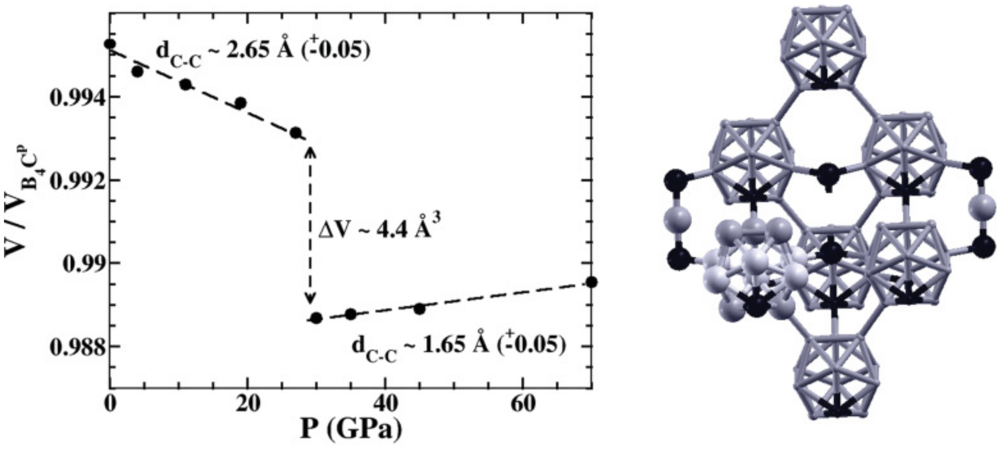
The defects of B_4C have been investigated within the local density approximation, using the density functional theory[16,17] for the energetics and the density functional perturbation theory for the lattice dynamics.[18] In this work, the investigation is restricted to the study of neutral defects. The pseudopotentials were as in Ref. 19 and the plane wave expansion has been limited with a cutoff energy of 80 Ry. Among the possible atomic structures, the lowest energy of formation with respect to its elemental constituents, solid boron + carbon, has been found for the *polar* model B_4C^p, i.e. $(B_{11}C^p)$C–B–C, and all of the defects presented in this work are metastable with respect to B_4C^p, but stable with respect to solid boron + carbon. Consequently, B_4C^p has been used as a matrix to isolate the defects. The enthalpy of formation of a neutral defect $\Delta\Omega_f$ depends on the conditions of pressure and stoichiometry:[20–22]

$$\Delta\Omega_f = \Delta H + \sum_{i=B,C} n_i \mu_i, \qquad (1)$$

where ΔH is the relative enthalpy of the defect. The last term of the right-hand side of Eq. (1) with $i = B$ (resp. $i = C$) represents the exchange of atoms with one reservoir of boron (resp. carbon) atoms. The number of exchanged atoms n_i is positive when the atom is transferred from the supercell to the reservoir, and μ_i is the excess chemical potential at which the exchange is performed.[23] ΔH is computed relatively to perfect B_4C^p from:

$$\Delta H = H(\text{defective } B_4C^p) - H(B_4C^p) + \sum_{i=B,C} n_i \mu_i^0, \qquad (2)$$

where the enthalpy $H = E + PV$ requires calculating the supercell total energy E and volume V at a fixed pressure P. The chemical potentials of the two reference states μ_B^0 and



(a) Volume relative to B_4C^p (b) Atomic struture

FIG. 1. *Defective* B_4C^p. Left panel: variation of the relative volume as a function of pressure for a 2 × 2 × 2 supercell of $(B_{11}C^p)$C–V–C. The supercell consisted of eight distorted icosahedra $(B_{11}C^p)$, of seven C–B–C chains,[13–15] and of one *defective* chain C–V–C shown at the center of the figure of the right panel, with a boron vacancy V. Black balls: carbon atoms in the polar site p of the icosahedron, C^p, and at the chain ends. Light grey balls: boron atoms in the polar site p and at the center of the chain. White balls: boron atoms in the equatorial site e of the icosahedron. Only part of the supercell is shown for clarity.

μ_C^0 have been taken to be the enthalpy H per atom of solid boron (α-boron) and of solid carbon (diamond).[23]

Perfect B_4C^p is formed from solid boron + carbon with the formation enthalpy ΔH_f. This fixes the relationship between the μ_B and μ_C, so that only one chemical potential is left as an independent variable:

$$3\mu_C + 12\mu_B = \Delta H_f(B_4C^p), \tag{3}$$

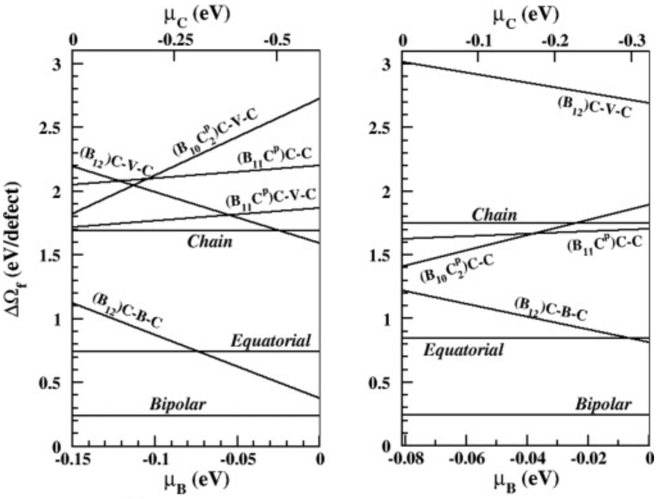
where $\Delta H_f(B_4C^p) = H(B_4C^p) - 3\mu_C^0 - 12\mu_B^0$. The values of μ_B and μ_C must be negative, pressure-dependent, and lie between the carbon-rich ($\mu_C = 0$) and the boron-rich ($\mu_B = 0$) limits. Finally, B_4C^p has four crystallographic sites [Fig. 1(b)], but only the polar site has substitutional disorder. The entropy of configuration induced by the substitutional disorder of the carbon atom in the polar site of the icosahedra has been left aside as it is expected to be identical for perfect B_4C^p and for defective one when the defect is in the chain.

The complex structure of B_4C^p offers numerous locations for a structural defect, and we have chosen the following criterium to select those having the lowest enthalpy of formation. We have first constructed 36 models with one defective unit-cell periodically repeated.[19] When the enthalpy of formation computed with Eq. (1) was smaller than 1.5 eV/defect at the carbon-rich limit $\mu_C = 0$, the defective unit-cell has been included into a 2 × 2 × 2 supercell of B_4C^p. The Brillouin zone (BZ) of the supercells has been sampled with a 2^3 Monkhorst-Pack (MP) mesh. When comparing the values of the formation energy of 1 × 2 × 2 and 2 × 2 × 2 supercells, finite-size effects turned out to be small. Moreover, the relative positions of $\Delta\Omega_f$ in Fig. 2 are marginally modified when computed for periodically repeated defects, showing that the supercells are large enough to weaken the interaction between the defects. This gave us confidence that we have studied *all* of the neutral defects having the lowest enthalpy of formation.

To compute the equilibrium concentration of vacancies in B_4C^p, we have followed the method of Ref. 24. The entropy of configuration reads:

$$S_{\mathrm{conf}} = k_B \ln\left[\frac{N!}{(N - n_v)!\, n_v!}\, n_d^{n_v}\right], \tag{4}$$

where n_v is the equilibrium concentration of vacancies, N is the number of chain center sites available for a vacancy, and



(a) $P = 0$ GPa. (b) $P = 30$ GPa.

FIG. 2. Enthalpy of formation of 2 × 2 × 2 supercells of defective B_4C^p with respect to perfect B_4C^p at low (left panel) and high (right panel) pressure, as a function of the excess chemical potential of boron μ_B or carbon μ_C (resp. lower or upper abscissa axis). The models $(B_{11}C^p)$C–V–C and $(B_{10}C_2^p)$C–V–C do not exist at high pressure, as a consequence of the C–C bond formation. All the models are dynamically stable.

n_d is the number of degenerate configurations per available site. In $2 \times 2 \times 2$ supercells, $N = 8$ and $n_d = 1$.

We have to minimize $\Delta G^{\text{solid}} = n_v \Delta H^v_{\text{tot}} - T S_{\text{conf}}$ with respect to n_v and we obtain the following expression of the equilibrium vacancy concentration:

$$n_v = N n_d \exp\left[-\frac{\Delta H^v_{\text{tot}}}{k_B T} \right], \tag{5}$$

where:

$$\begin{aligned} \Delta H^v_{\text{tot}} &= \Delta H + F_{\text{vib}}(\text{defective } \mathrm{B_4C}^p) \\ &\quad - F_{\text{vib}}(B_4C^p) + \frac{1}{12} F_{\text{vib}}(B_{12}) \end{aligned} \tag{6}$$

with ΔH as in Eq. (2).

To compute the vibrational contribution to the free energy, F_{vib}, the dynamical matrices of the defective supercell and of B_4C^p have been computed at both low and high presssure, at Γ with a 2^3 **k**-point MP mesh and interpolated on a 10^3 **q**-point mesh. For α-boron, the dynamical matrices have been computed with a 4^3 **q**-point mesh and interpolated to a 6^3 **q**-point mesh. The values of the phonon frequencies turned out to be particularly sensitive to the convergence criteria on the density and on its first-order variation with respect to the atomic displacements induced by the phonons.[18]

III. RESULTS

The formation enthalpies of *all* of the most stable defects in B_4C^p at low pressure are reported in Fig. 2(a). The defective structures having the lowest enthalpy of formation are native defects, i.e. defects formed during the material growth. They consist of the *bipolar* defect,[14] $(B_{10}C^p_2)$C–B–C + (B_{12})C–B–C + 6 formulas of B_4C^p, which is the result of the concerted exchange mechanism well-known in other semiconductors.[25,26] The *boron icosahedron* model (B_{12})C–B–C + 7 formulas of B_4C^p is also a *native* defect within the accuracy of our calculations. It forms only in the boron-rich domain ($\mu_B \approx 0$) at low pressure, and can be avoided by increasing the pressure during the material growth [Fig. 2(b)]. Finally, equilibrium properties of the *bipolar* defect, of the *boron icosahedron* defect and of B_4C^p are so similar that their equations of state cannot be distinguished (Fig. 3, insert), and are in extremely satisfactory agreement with experiments (Fig. 3, dashed line). As these defects turn out to decompose into solid boron + carbon at a pressure as high as ≈70 GPa, the failure of B_4C is not related to these native defects.

Most interestingly, all of the stable models with a vacancy have a boron vacancy located at the center of the chain [Fig. 2(a)], which is consistent with the observation that only boron atoms are evaporated from a heated surface of pure B_4C^p.[27] According to our calculations, the presence of a vacancy in the icosahedron or at the chain end is excluded. Furthermore, when we place a vacant hole at the center of the chain, i.e. C–V–C, the model $(B_{11}C^p)$C–V–C + 7 formulas of B_4C^p has the lowest formation energy among models with a vacancy [Fig. 2(a)]. The defect is characterized by the absence of electronic density at the center of the chain, and can also form when the icosahedron consists of boron atoms only, (B_{12})C–V–C, or when a double substitution occurs, $(B_{10}C^p_2)$C–V–C [Fig. 2(a)]. The metastability of such a chain vacancy is consistent with the fact that the boron atom at the center of the chain is known to be loosely bound,[28] and in agreement with the observations by the positron spectroscopy of chain vacancies in boron carbides with metallic impurities of zirconium or vanadium.[29]

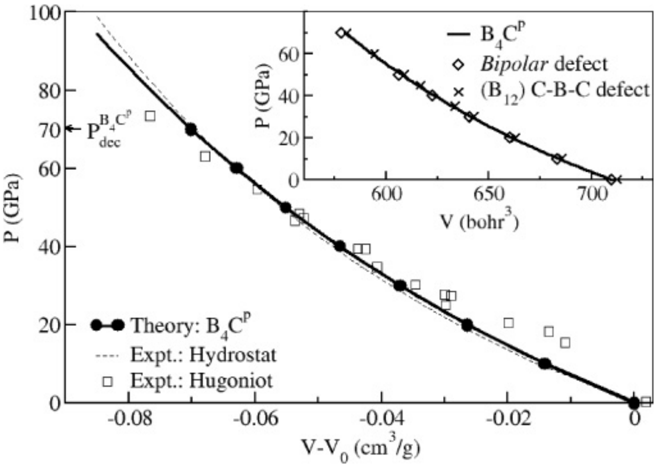


FIG. 3. Equation of state (EOS) of B_4C. Filled circles: theory for the *polar* model. Dashed line: Murnaghan's EOS extrapolated from ultrasonic measurements at ambient pressure.[30] Squares: Hugoniot points measured in a shock expt.[4] Solid line: fit of the theoretical data with Murnaghan's EOS. Insert: Murnaghan's EOS of perfect B_4C (solid line), *bipolar* model (diamonds), and *boron icosahedron* model (crosses).

The enthalpy of formation has also been computed at $P =$ 30 GPa [Fig. 2(b)]. Remarkably, the supercell $(B_{11}C^p)$C–V–C cannot exist any longer because a C–C bond is formed at high pressure, with a significant reduction in the distance between the carbon atoms. A sudden decrease in the C-C distance from ≈2.7 Å to ≈1.7 Å is observed at 28 GPa, and the model $(B_{11}C^p)$C–C + 7 formulas of B_4C^p is always formed.[33] We estimate the pressure to be underevaluated by 10 GPa because of our use of the local density approximation. As a consequence, the pressure at which the C–C bond forms in our calculations is very close to the pressure of 40 GPa at which the complete loss of mechanical strength is found experimentally.[4] The formation of C–C bonds yields the discontinuity observed in the variation of the volume [Fig. 1(a)] of 4 Å^3/vacancy, to which we attribute the failure of B_4C caused by the internal stresses. This volume variation is comparable to the one generated in phase transitions. For instance, the volume variation is about 3 Å^3/atom in the phase transition from *hexagonal* to *cubic* boron nitride.[34,35]

The frequencies of all the phonons modes turned out to be positive at both low and high pressures for $(B_{11}C^p)$C–V–C + 7 formulas of B_4C^p [Fig. 4(a)]. The model with C–C chains is also found to be dynamically stable at low pressure (not shown), and at high pressure up to at least 55 GPa. The dynamical stability is shown in Fig. 4(a) for $P = 35$ GPa. Thus, the energy as a function of the C–C distance is expected to have a double-well structure, with one minimum at $d_{\text{C-V-C}} \approx 2.7$ Å and one minimum at $d_{\text{C-C}} \approx 1.7$ Å. As pressure increases, under the influence of the PV term, the enthalpy H has only one minimum, corresponding to the shorter C–C distance. The transition from the C–V–C to the

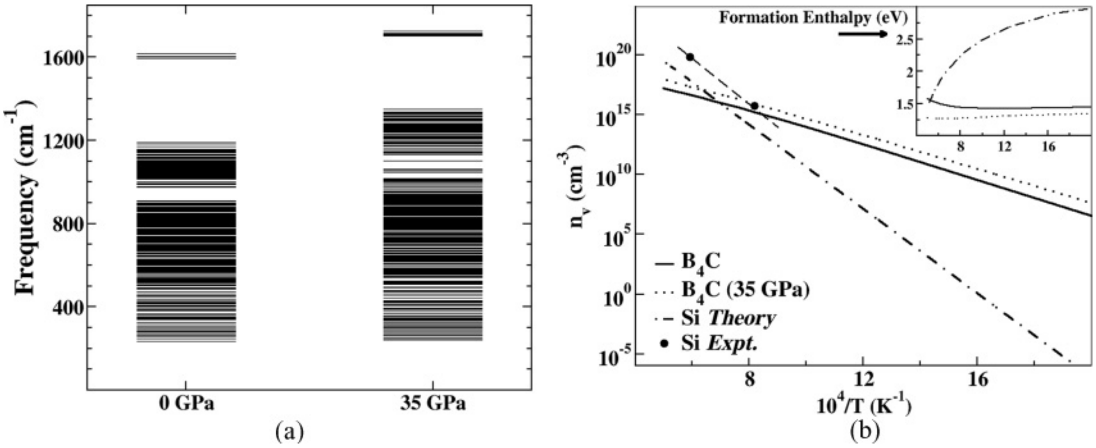


FIG. 4. *Defective* B_4C^p. Panel 4(a): theoretical phonon frequencies at $P = 0$ for $(B_{11}C^p)C-V-C + 7$ formulas of B_4C^p and $P = 35$ GPa, where the C–C bond is formed. Panel 4(b): vacancy concentration at thermodynamical equilibrium (n_v) *versus* the inverse temperature. Solid line: defective B_4C^p with C–V–C chains at $P = 0$ GPa; dotted line: defective B_4C^p with C–C chains at $P = 35$ GPa. Dash-dotted line: defective Si.[24] Symbols: Expt. for Si.[31,32] Dashed line: visual guide. Insert panel: formation free energy of defective B_4C (solid line: P = 0; dotted line = P = 35 GPa) and Si (Dash-dotted line).[24]

C–C well yields the large discontinuous variation of volume of Fig. 1(a).

IV. DISCUSSION

To estimate the concentration of vacancies, we have computed the free energy as in Ref. 24 [Fig. 4(b)]. At low pressure and 1000 K, the concentration of vacancies, 10^{14} cm^{-3}, is much higher than the concentration of 5.10^{10} cm^{-3} in silicon. However, this number is too small to modify the mechanical properties of B_4C, which is consistent with the fact that its hardness is preserved at high temperature.[36] The concentration increases at high pressure (6.10^{14} cm^{-3}) but remains insufficient to alter the mechanical properties of B_4C [Fig. 4(b), dotted line]. Therefore, if we invoked the increase in temperature and pressure as the sole cause which generates vacancies during the shock wave, we would reach the conclusion that the ratio of the number of vacancies to the total number of atoms is insufficient to greatly modify the mechanical properties.

However, another cause can yield the increase in the number of vacancies. Molecular dynamics simulations have suggested that dislocations are jagged.[37] Their motion is possible only by forming vacancies.[8] In shocked silicon, the number of vacancies is five orders of magnitude greater than the one at the thermodynamical equilibrium.[38] At variance with B_4C, the effect of these defects on the mechanical properties of silicon are masked by the occurrence of the phase transition toward the β-tin structure. We reach the conclusion that the number of vacancies is several orders of magnitude larger in shocked B_4C^p than the concentrations presented in Fig. 4(b). This conclusion calls for new experiments to quantify the number of vacancies in shocked B_4C^p. Theoretically, the generation and motion of defects in a solid under a shock wave should be computed out of equilibrium, for instance with methods as in Refs. 11 and 12.

Turning to the existing theoretical explanations for the failure of B_4C,[6,39] we are pointing out that (i) the tentative to explain the failure with the decomposition into solid boron + carbon of the *chain* model[39] is incorrect, because in our calculations, the *chain* model $(B_{12})C-C-C + 7$ formulas of B_4C^p is (meta)stable up to more than 30 GPa [Fig. 2(b)]. Neither the *chain* nor the *equatorial* model, $(B_{11}C^e)C-B-C +$ 7 formulas of B_4C^p, can be native defects of B_4C^p, and this confirms earlier calculations.[13,14] The absence of formation of the *chain* model has been reported independently.[40] (ii) By applying a uniaxial stress at a finite temperature during a quantum molecular dynamics simulation, a discontinuous variation of the volume has occurred.[6] We have found elsewhere[26] that this is the fingerprint of the formation of a carbon-carbon bond in presence of an interstitial boron. The value of the enthalpy barrier lies well outside the scale of Fig. 2 and invalidates the hypothesis of Ref. 6 as the cause of the dynamical failure.

V. CONCLUSION

In conclusion, under the Hugoniot elastic limit, native defects and vacancies are present in small numbers in B_4C and do not affect the mechanical properties. As pressure increases beyond the HEL however, the motion of dislocations leads to an increase in the number of vacancies. Formation of C–C bonds occurs in the chains at high pressure and the volume variation of ≈ 4 Å^3 *per* vacancy yielded by the bond formation is the reason for the loss in mechanical strength of the material. This is consistent with the observation that the hardness of B_4C is preserved at high temperature. We have shown that under thermodynamical conditions as those occurring in a diamond-anvil cell, the vacancy concentration is small, explaining why the material is able to resist a static loading. The change of paradigm resulting from this work involves paying more attention to the role of the generation of defects beyond the HELs, which has been ignored so far as the cause of mechanical failure. Our results are drawing attention to this yet unexplored topic and are calling for experimental studies about the generation of vacancies in plastically deformed ceramics.

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