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Computational search for the real tetragonal B_{50}

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Using an expansion of ~12 700 plane waves, we calculate the lattice constants and heat of formation of tetragonal B_{50}, $B_{48}C_2$ $(B_{50}C_2)_\alpha$, $(B_{50}C_2)_\beta$, $(B_{52}C_2)_\alpha$, and $(B_{52}C_2)_\beta$. Of these only $(B_{50}C_2)_\beta$ has both a and c within 1% of their x-ray values as well as having, by far, the least negative heat of formation.

In 1943, Laubengayer *et al.*[1] prepared crystals which they believed to be pure boron with D_{4h} symmetry. In 1951 Hoard, Geller, and Hughes[2] determined that the crystal was tetragonal B_{50} with space group $P4_2/nnm$ consisting of two individual atoms[3] at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and four B_{12} icosahedra centered at $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$, $(\frac{3}{4}\frac{3}{4}\frac{1}{4})$, $(\frac{1}{4}\frac{3}{4}\frac{3}{4})$, and $(\frac{3}{4}\frac{1}{4}\frac{3}{4})$. In 1955 Longuet-Higgins and Roberts[4] (LHR) claimed that B_{50} had ten too few electrons per unit cell to fill all its covalent bonds and therefore could not exist. Hoard, Hughes, and Sands[5] presented a detailed study in 1958 in which they confirmed their earlier results and disputed the LHR theory. In 1976 Will and Kossobutzki[6] (WK) found that although it was impossible to crystallize B_{50}, both $B_{50}C_2$ and $B_{50}N_2$ would crystallize in the tetragonal structure but with the space group $P\bar{4}2m$. Belief in the existence of B_{50} apparently is not dead, however, as its electronic structure has very recently been calculated.[7]

In order to determine whether B_{50} can exist, we have calculated the lattice constants, atomic positions, cohesive energy, and heat of formation of B_{50}, $B_{48}C_2$, and two different structures of both $B_{50}C_2$ and $B_{52}C_2$. Since disorder, defects, electronic localization, and atomic relaxations are central features of the boron carbides, the value of energy-band calculations on nominal structures may be questioned. Aselage and Emin[8] (AE) would conclude that our results in Refs. 9 and 10 are at odds with the width of the single-phase regime (9–19 % carbon) and the carbon locations that are deduced experimentally. For example, we find the most stable boron carbide is B_4C, although AE say that all modern efforts find that this stoichiometry does not even exist. AE also claim that $B_{13}C_2$ consists of $B_{11}C$ icosahedra and BBC interstitial chains whereas we,[10] both from a comparison of calculated lattice constants and atomic positions with experiment and free-energy considerations, conclude it should be B_{12} icosahedra and CBC chains. On the other hand, Kirkpatrick *et al.*[11] apparently not only think they have made B_4C, but they also think it is the most ordered composition. From their nuclear-magnetic-resonance (NMR) data they conclude that only 10% of the $B_{13}C_2$ icosahedra are $B_{11}C$. It seems highly likely that there is a large potential barrier for a carbon, once captured by an icosahedron, to leave that icosahedron. Thus we feel 10 mol % $B_{11}C$ content in the best samples is consistent with no $B_{11}C$ icosahedra in ideal $B_{13}C_2$. Our structural calculations are in excellent agreement with x-ray data not only for[12,9,10] B_{12}, $B_{12}C_3$, and $B_{13}C_2$ but also for[13] $B_{12}O_2$ and[14] $B_{12}As_2$. While it is true that our calculations could not account for the stability of $B_{12+x}C_{3-x}$ with $x > 1$, we assumed these crystals would contain both CBC and BBC chains. In fact, there is some experimental evidence[15] that they contain interstitial clusters of four or more borons instead of BBC chains so that our calculated instability of boron carbide containing BBC chains may be correct. It has long been known[16] that density-functional calculations can account for the structure of the transition-metal monoxides without being able to predict their transport properties. We believe the same is true for the boron carbides.

We use our iterative plane-wave expansion method,[9] expanding in all plane waves with $k^2 < 44.005$ Ry as we did[12] for B_{12} but which here requires about 12 700 plane waves. The Kohn-Sham[17] exchange and the Wigner[18]

TABLE I. Lattice constants (with percent deviation from experiment), cohesive energy per atom, and heat of formation per unit cell of tetragonal B_{50}, $B_{48}C_2$, $(B_{50}C_2)_\alpha$, $(B_{52}C_2)_\alpha$, $(B_{52}C_2)_\beta$, and $(B_{50}C_2)_\beta$ with a 16 **k**-point BZ sample and $(B_{50}C_2)_\beta^*$ with a 96 **k**-point BZ sample.

	c (bohr)	a (bohr)	E_{coh} (eV)	H (eV)
Exp	9.6244	16.5408		
B_{50}	9.2752(−3.63%)	16.7005(0.97%)	6.7448	−4.770
$B_{48}C_2$	9.3230(−3.13%)	16.5312(−0.06%)	6.8465	−2.784
$(B_{50}C_2)_\alpha$	9.5582(−0.69%)	16.2871(−1.53%)	6.8036	−5.002
$(B_{52}C_2)_\alpha$	9.6481(0.25%)	16.3615(−1.08%)	6.7725	−6.754
$(B_{52}C_2)_\beta$	9.7680(1.49%)	16.3620(−1.08%)	6.7533	−7.791
$(B_{50}C_2)_\beta$	9.5689(−0.58%)	16.3891(−0.92%)	6.8974	−0.124
$(B_{50}C_2)_\beta^*$	9.5740(−0.52%)	16.3888(−0.92%)	6.8963	−0.181

correlation and the same pseudopotentials that were used in our previous calculations of boron[12] and its carbides[9,10] are used here. We sample the Brillouin zone (BZ) at $(\frac{1}{4}\frac{1}{4}\frac{1}{8})$ and $(\frac{1}{4}\frac{1}{4}\frac{3}{8})$ in the $\frac{1}{16}$th irreducible wedge which, because of the large unit cell, is a denser sampling than the standard 10 **k**-point sampling for diamond.

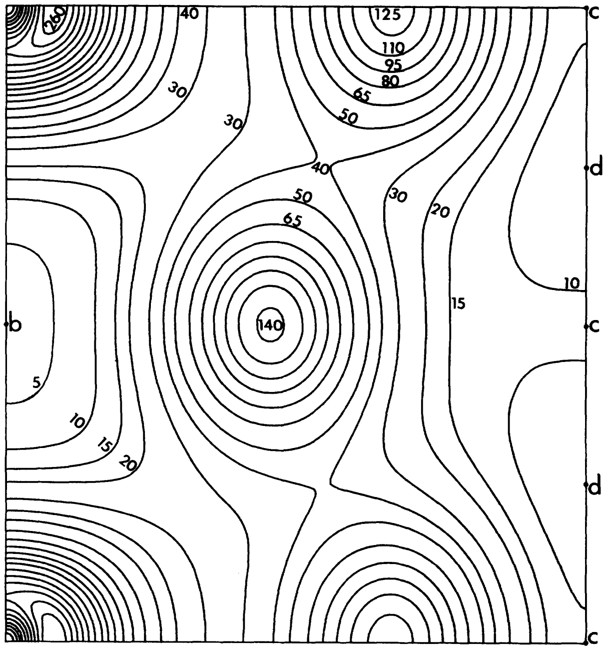

FIG. 1. Contours of constant charge density (in millielectrons per cubic bohr) plotted in half of the (100) face of the $B_{48}C_2$ unit cell.

In the first row of Table I we list the experimental values[6] of the (presumably) $B_{50}C_2$ lattice constants. Hoard, Hughes, and Sands,[5] who thought they were measuring B_{50} but might have been measuring $B_{50}C_2$, obtained the same value for c but an a 0.65% smaller. Since our previous calculations of boron and its carbides resulted in lattice constants within 0.5% of the experimental values, we here reject any structure with a discrepancy $>1\%$. In the second row we see that B_{50} has c 3.63% too small and a, if compared with Hoard, Hughes, and Sands,[5] 1.62% too large. It also has a heat of formation of -4.770 eV where $H(B_nC_m)=(n+m)E_{\mathrm{coh}}(B_nC_m)-nE_{\mathrm{coh}}(B_{12})-mE_{\mathrm{coh}}(C)$, where the E_{coh} of B_{12} and C are[10] 6.8402 and 8.3895 Ry/atom, respectively. Thus we conclude it highly unlikely that B_{50} exists. The most obvious thing to try next is to replace the two fourfold-coordinated borons with carbons. In spite of the large value of $E_{\mathrm{coh}}(C)$ this increases H to -2.784 eV but only improves the discrepancy in c slightly and thus we conclude $B_{48}C_2$ does not exist. In Fig. 1 we plot contours of constant charge density in units of ζ=millielectrons/bohr^3 in the (100) face of the $B_{48}C_2$ unit cell. Using Wyckoff notation for $P4_2/nnm$ we label $b=(00\frac{1}{2}),(\frac{1}{2}\frac{1}{2}0)$; $c=(0\frac{1}{2}0),(\frac{1}{2}00),(\frac{1}{2}0\frac{1}{2}),(0\frac{1}{2}\frac{1}{2})$; and $d=(0\frac{1}{2}\frac{1}{4}),(0\frac{1}{2}\frac{3}{4}),(\frac{1}{2}0\frac{1}{4}),(\frac{1}{2}0\frac{3}{4})$. If we add two borons at b we maintain $P4_2/nnm$; if we put them at either the first or last two c sites, the symmetry is reduced[19] to $P\bar{4}2m$; if we put them on either the first or last two d sites the symmetry is reduced to $P\bar{4}$, which is inconsistent with the x-ray data.[6] The charge density at these points is $\rho(b)=3.52\zeta$, $\rho(c)=10.42\zeta$, and $\rho(d)=6.91\zeta$. We first tried adding two borons to the sites with lowest charge density, b. This led to the highly unsatisfactory results listed in Table I under $(B_{50}C_2)_\alpha$. Because the chemical analysis of $B_{50}C_2$ showed[6] it was $B_{50}C_{1.9}$, which is consistent with $B_{52}C_2$, we tried two such configurations, α with the b and two of the c sites occupied and β with all four d sites occupied,[20] and obtained the most negative heats of formation yet. This convinced us that $(B_{52}C_2)_\gamma$ with all four c sites occupied could not be correct and so we tried $(B_{50}C_2)_\beta$ with a pair of c sites occupied. This satisfies our lattice constant criterion and yields by far the least negative heat of formation of any structure we have tried. Because $(B_{50}C_2)_\beta$ is metallic (as is B_{50}), we repeated its calculation using a 96 **k**-point BZ sample[21] with the very small changes shown in the last row of Table I. Although $(B_{50}C_2)_\beta$ is almost stable against decomposing into B and C, it is only the negligible mobility of the icosahedra that impedes

$$(B_{50}C_2)^*_\beta \rightarrow B_{13}C_2+\tfrac{37}{12}B_{12}+1.597\ \mathrm{eV}\ .$$

Although they found $P\bar{4}2m$ symmetry, consistent with our $(B_{50}C_2)_\beta$, WK (Ref. 6) assumed $P4_2/nnm$ when assigning atomic positions. They found 0.64 of the ten nonicosahedral boron electrons on each of the two b sites and 8.4 electrons centered on 16 different sites surrounding the four c sites. The small occupation of the b sites is consistent with our rejection of $(B_{50}C_2)_\alpha$ and the large random occupation of sites surrounding c is not inconsistent with our calculations provided (as indicated by

TABLE II. Positions of icosahedral boron atoms relative to the $\frac{1}{4}\frac{1}{4}\frac{1}{4}$ point. The reflection interchanging x and y yields the last four sites. The values in parentheses are those of Ref. 6, which assumes inversion symmetry through $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$.

$x(a)$	$y(a)$	$z(c)$
−0.004 63(−0.0026)	−0.004 63(−0.0026)	−0.334 51(−0.3349)
0.002 29(0.0026)	0.002 29(0.0026)	0.331 91(0.3349)
−0.129 36(−0.1273)	−0.129 36(−0.1273)	−0.129 39(−0.1298)
0.130 10(0.1273)	0.130 10(0.1273)	0.125 94(0.1298)
0.167 94(0.1694)	0.021 58(0.0240)	−0.166 18(−0.1627)
−0.170 15(−0.1694)	−0.024 23(−0.0240)	0.160 56(0.1627)
−0.165 57(−0.1610)	0.075 14(0.0759)	−0.157 13(−0.1490)
0.157 16(0.1610)	−0.077 11(−0.0759)	0.140 54(0.1490)

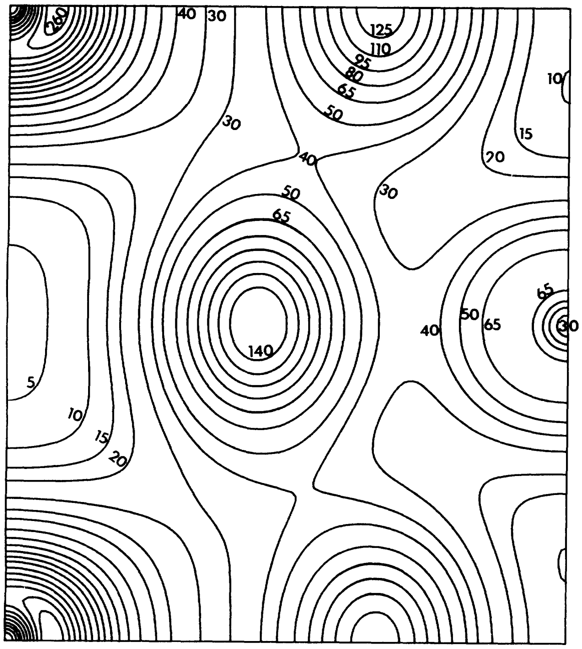

FIG. 2. Contours of constant charge density (in millielectrons per cubic bohr) plotted in half of the (100) face of the $(B_{50}C_2)_\beta$ unit cell.

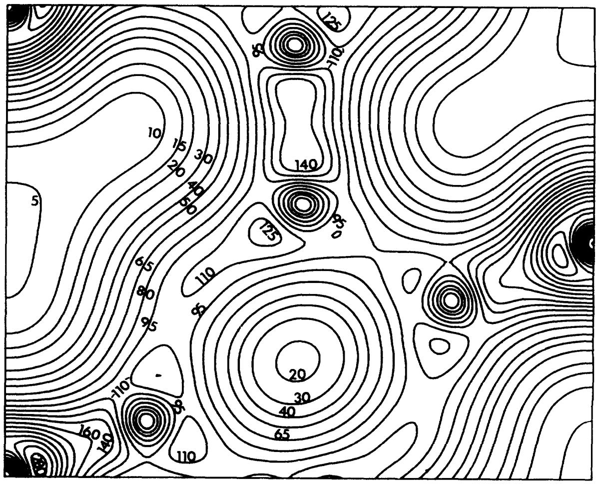

FIG. 3. Contours of constant charge density (in millielectrons per cubic bohr) in a (110) plane of $(B_{50}C_2)_\beta$).

our $B_{52}C_2$ calculations) that the probability of nearby sites being occupied is small. In Table II we compare the positions of the $(B_{50}C_2)^*_\beta$ icosahedral atoms relative to the $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ center with those of WK,[6,3] whose assumed symmetry results in a false inversion center. The agreement is much better than we expected. From Table II and the values of *c* and *a* for $(B_{50}C_2)^*_\beta$ all bond lengths can be calculated. For example, the bonds to the carbons at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ are 3.2475 and 3.0252 bohr, respectively, and to the icosahedra directly above or below are 3.1977 bohr. The 140 contour in Fig. 2 is near the center of the bond between atoms at (0.0799,0.2258,0.4106) and (−0.0821,0.2716,0.5838) on the $(\frac{1}{4}\frac{1}{4}\frac{1}{4})$ and $(\frac{\bar{1}}{4}\frac{1}{4}\frac{3}{4})$ icosahedra and is 3.2190 bohr long. These lengths span the range found in other carbides.[9,10]

Figures 2 and 3 are $(B_{50}C_2)^*_\beta$ contour plots in (100) and (110) planes. Intraicosahedral bonds as well as bonds to the carbons at (000) and $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ and to the icosahedron directly above are easily observed in Fig. 3. Comparing Figs. 1 and 2 we find that the borons added at *c* not only increase the charge between *c* and *d* but also in the intraicosahedral bond; however, they have a negligible effect on the charge at *b* or the empty *c* sites. We have calculated the electronic energy levels at six symmetry points in addition to the nine BZ points sampled in total-energy calculations. The 79th band at Γ lies 0.368 eV above the 80th band at *Z*, which suggests that if the disorder inherent in the boron carbides could be suppressed, $(B_{50}C_2)_\beta$ would either be metallic or a Mott-Hubbard insulator. There is a 0.476-eV gap between the 80th band at *A* and the 81st at *Z* so that if the rigid band approximation is valid, $(B_{50}N_2)_\beta$ is a semiconductor. That together with the difference between the C and N cohesive energies should result in it being stable rather than metastable.

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[19] Because of time reversal there is no reduction of the BZ symmetry.

[20] A slight dimerization occurred with $z = \frac{1}{4}$ and $\frac{3}{4}$ becoming 0.251 45 and 0.748 55.

[21] This corresponds to the nine points in the irreducible wedge $(\frac{1}{8}\frac{1}{8}z)$, $(\frac{1}{8}\frac{3}{8}z)$, and $(\frac{3}{8}\frac{3}{8}z)$ with $z = \frac{1}{12}, \frac{3}{12}$, and $\frac{5}{12}$.