

## *Ab initio* studies of the structural and electronic properties of solid cubane

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In this paper, we report *ab initio* calculation of the structural and electronic properties of solid cubane ( $s\text{-C}_8\text{H}_8$ ) in the local-density approximation. By using an *ab initio* constant pressure extended molecular dynamics method with variable cell shape proposed by Wentzcovitch, Martins, and Price, we compute a lattice parameter  $a$  and a bond angle  $\alpha$  for the rhombohedral Bravais lattice and compare it with experimental x-ray data. We obtain bond lengths for the mononuclear  $\text{C}_8\text{H}_8$  unit of basis atoms, as well as a density of states and heat of formation. [S0163-1829(98)02944-0]

While there has been an enormous amount of experimental and theoretical interest in the structural, electronic, and vibrational properties of the fullerenes,<sup>1</sup> there exists an even simpler carbon-based structure that has cagelike properties analogous to the fullerenes, namely, the hydrocarbon solid, cubane ( $s\text{-C}_8\text{H}_8$ ). Cubane was first synthesized by Eaton and Cole<sup>2</sup> and its crystalline structure was determined by Fleischer<sup>3</sup> to be rhombohedral with one molecule of cubane ( $s\text{-C}_8\text{H}_8$ ) per conventional unit cell (cf. Figs. 1 and 2). Its interesting dynamics has been recently investigated by Yildirim *et al.*<sup>4</sup> and Detken *et al.*<sup>5</sup> There is a significant amount of strain in the molecule due to the deviation from the normal C-C tetrahedral bond angle of  $109.5^\circ$  in the  $sp^3$  hybridized form of carbon, which exists in methane or ethane, to the highly strained C-C bond angles of  $90^\circ$ , which exist for the eight  $sp^3$  hybridized carbon atoms in the cubic molecular structure. Obviously, this strain in the molecule is the source of the highly energetic properties of cubane in the solid-state phase. In fact, nitro-substituted forms of cubane (e.g., 1,7-dinitrocubane) have also been synthesized, which are suitable candidates for energetic or explosive materials.

Despite the numerous molecular orbital calculations on the structural and electronic properties of the cubane molecule itself<sup>6-8</sup> there has been, to our knowledge, no theoretical work in the literature on the structural and electronic properties of the solid-state or crystalline form of cubane ( $s\text{-C}_8\text{H}_8$ ). As a first step towards our goal of computing the structural, electronic, and vibrational properties of solid cubane, we report in this paper the use of *ab initio* total energy methods to obtain an optimized structure for  $s\text{-C}_8\text{H}_8$  and evaluate the electronic properties of the material, such as the local density of states and heat of formation, within the local density approximation (LDA).

It is experimentally known that solid cubane has a rhombohedral Bravais lattice with a monomolecular unit of 16 basis atoms.<sup>3</sup> Thus, we would expect to see in our calculations some distortion of these monomolecular units from their cubic form in the isolated molecule due to the crystal-field effects of the rhombohedral Bravais lattice. We believe

that such calculations are important not only from a fundamental point of understanding cubane and its derivatives in the solid-state phase, but that they also offer another test case for applying the tools of first-principles electronic structure theory, which have been successfully applied to other carbon-based molecular solids like fullerite,<sup>9-14</sup> which is also bound by van der Waals interactions.

We used the plane-wave local-density formalism<sup>15</sup> to solve the Kohn-Sham (KS) equations of density functional theory using LDA in momentum space<sup>16,17</sup> with the Ceperley and Alder<sup>18</sup> form of exchange correlation as parametrized by Perdew and Zunger.<sup>19</sup> The first principles nonlocal norm-conserving pseudopotential for the carbon atoms was generated by a scheme developed by Troullier and Martins<sup>20</sup> using the separable form of Kleinman and Bylander,<sup>21</sup> and such soft pseudopotentials have been shown to be computationally efficient when they are used to solve the KS equations with a plane-wave basis in the iterative dual space formalism.<sup>22</sup> Furthermore, these Troullier-Martins pseudopotentials have been well tested for a number of second-row elements such as carbon.<sup>9,10</sup>

A  $1/r$  potential was used for the hydrogen atoms in our calculations. The structural optimizations were performed

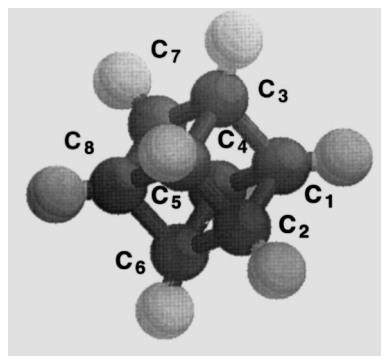


FIG. 1. Sketch of monomolecular unit of  $\text{C}_8\text{H}_8$  in solid cubane ( $s\text{-C}_8\text{H}_8$ ). Numeration scheme for carbon basis atoms is illustrated with members for hydrogen not shown for clarification.

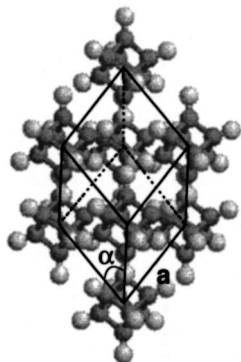


FIG. 2. Sketch of rhombohedral Bravais lattice of solid cubane ( $s\text{-C}_8\text{H}_8$ ). Here  $a$  is the lattice parameter of the crystal and  $\alpha$  is the bond angle. Note that monomolecular units of  $\text{C}_8\text{H}_8$  constitute a set of basis atoms at the corners of the rhomboderon.

using an *ab initio* constant pressure extended molecular dynamics method with variable cell shape developed by Wentzcovitch, Martins, and Price,<sup>23</sup> which was utilized for efficient structural optimizations for a member of the perovskite family of crystalline solids,  $\text{MgSiO}_3$ .

In particular, we used an energy plane-wave cutoff of 64 Ry ( $\approx 5371$  total plane waves) for our converged carbon pseudopotential and in our structural optimizations the forces were converged to within  $5 \times 10^{-4}$  hartrees/bohr<sup>3</sup> while the pressures were converged to within  $2 \times 10^{-4}$  hartrees/bohr<sup>3</sup>. The potential is converged to within  $10^{-5}$  Ry.

The results of our LDA optimized structure for solid cubane are shown in Tables I and II. The LDA optimized C-C and C-H bond lengths for the sixteen basis atoms of solid cubane are shown in Table I where the comparison between theory and experiment is quite good, as should be expected from an LDA calculation involving covalent bonds. We obtained the same results independent of the choice of the gamma point or two special k points for our total energy calculations. Thus, our calculations clearly show the distortion of the C-H and C-C bond lengths from their values in the isolated molecule due to the crystal-field effects of the rhombohedral Bravais lattice.

The comparison between the experimental and theoretical values for the lattice constant and the bond angle  $\alpha$  of the rhombohedral Bravais lattice of solid cubane are shown in Table II. Here, two special k points were used in our total energy studies. The agreement between theory and experiment reflects the difficulty that LDA has in determining structural properties for materials in which van der Waals

TABLE I. Comparison of experimental and theoretical C-C and C-H bond lengths for monomolecular  $\text{C}_8\text{H}_8$  cubane unit as shown in Fig. 1. Symmetry about  $\text{C}_7\text{-C}_2$  axis of Fig. 1 is exploited to show only the simplest bond lengths.

Bond lengths	Experimental ( $\text{\AA}$ )	Theoretical ( $\text{\AA}$ )
$\text{C}_3\text{-C}_4$	$1.549 \pm 0.003$	1.59
$\text{C}_4\text{-C}_2$	$1.553 \pm 0.003$	1.62
$\text{C}_3\text{-H}_3$	$1.11 \pm 0.05$	1.11
$\text{C}_4\text{-H}_4$	$1.01 \pm 0.05$	1.07

TABLE II. Comparison of experimental and theoretical lattice constants ( $a$ ) and bond angles ( $\alpha$ ) for solid cubane ( $s\text{-C}_8\text{H}_8$ ) which has rhombohedral crystal structure in solid form and is uniquely characterized by  $a$  and  $\alpha$ , as shown in Fig. 2.

	Experimental	Theoretical
Lattice constant ( $\text{\AA}$ )	5.34	4.87
Bond angle ( $\alpha$ )	72.3	75.2

bonding plays a dominant role, such as molecular crystals. For example, in selenium<sup>24</sup> the distance between van der Waals bound Se chains is 10% within the LDA. In the case of fullerite, which is also considered a van der Waals solid, lattice constants are well predicted by LDA,<sup>9-14</sup> but here we obtain results for the intermolecular distance in cubane that are not as good as the intramolecular distances calculated before, both according to the LDA. The equilibrium distance in van der Waals solids is achieved when the repulsive interaction between closed shell molecules due to the Pauli principle balances the attractive van der Waals interaction. In fullerite, as in graphite, this repulsion is due to the  $\pi$  electrons of the highest occupied molecular orbital, which has a dispersion of several tenths of an eV.<sup>10</sup> This indicates that there is already at the equilibrium intermolecular distance a chemical interaction that is not negligible and that is apparently well described within the LDA. In solid cubane we find that at the experimental intermolecular distance the dispersion of the highest occupied molecular orbital is even smaller, indicating a weak interaction. Cubane (cf. Fig. 3) has a larger band gap than fullerite<sup>10</sup> indicating again that it is chemically a less reactive species, but still a highly energetic material.

As far as energetics are concerned, our studies have determined the band gap to be 5.2 eV at the experimental lattice constant and 3.7 eV at the calculated lattice constant as shown in the calculated local density of states (LDOS) for solid cubane, which is illustrated in Fig. 3. This difference is to be expected because the effect of using the calculated LDA lattice constant is to squeeze the monomolecular  $\text{C}_8\text{H}_8$  units closer together thus causing a greater dispersion in the band structure of solid cubane. The spikes in the calculated LDOS using the experimental geometry are also not surprising as they are typically seen in other molecular crystals. In summary, we are seeing in our calculations the typical

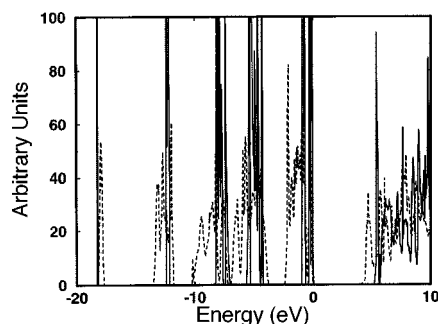


FIG. 3. Local density of states (LDOS) for solid cubane  $s\text{-C}_8\text{H}_8$ . The solid line is calculated for the experimental geometry while the dashed line is determined from the geometry computed within LDA.

overbinding that LDA gives for insulators and semiconductors, but this effect is further enhanced by the van der Waals nature of the bonding in solid cubane. This trend is also seen in molecular crystals like solid xenon and argon. We also estimate the heat of formation for  $s\text{-C}_8\text{H}_8$  at  $P=0$  and  $T=0$  to be  $-0.14$  Ry/molecular unit, which is consistent with the heat of formation for fullerite and smaller than the heat of formation for diamond. This trend makes sense considering the nature of the strong covalent bonding in diamond and the relatively weak bonding in a molecular crystal, like fullerite.<sup>25</sup>

In summary, we have completed the first LDA *ab initio* calculation for solid cubane and have obtained distorted C-C and C-H bond lengths, which compare well with experiment, but the lattice constant does not compare as well with experiment due to the treatment of van der Waals bonding between the monomolecular  $\text{C}_8\text{H}_8$  units using LDA. It is expected that improved schemes to treat the electronic exchange-correlation effects, which go beyond LDA (i.e., generalized gradient approximation and weighted-density approximation) will result in an improved structural optimization for solid cubane. We would nevertheless expect improved neu-

tron and x-ray scattering experiments to confirm our predictions of distortions in the C-C and C-H bond lengths within the  $\text{C}_8\text{H}_8$  units in cubane.

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