

Comparison of electron bands of hexagonal and cubic diamond

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Using the local-density-theory and the linear-muffin-tin-orbitals method, we calculate the electron band structures of hexagonal (lonsdaleite) and cubic diamond. Even though the arrangement of atoms is very similar between the two crystal structures, we find significant differences in the electron bands, especially in the conduction bands. In particular, including estimated corrections on top of the local-density results, we find the lowest theoretical gap of hexagonal diamond to be 4.5 eV, i.e., a remarkable 1.1-eV drop as compared to that of cubic diamond. The lowest gap in the hexagonal structure is still indirect as in the cubic structure, but the gap is now from Γ to K . The reduction of the band gap should be observable in optical-absorption or reflectivity experiments.

I. INTRODUCTION

The beauty and rarity of diamond has made it an object of fascination since recorded history. Lately, industry has recognized the potential use of diamond and diamondlike carbon (DLC) in diverse applications such as high-power, high-temperature optoelectronic devices, efficient heat sinks, coating materials for tools used for drilling, etc. Currently, considerable effort is being made to prepare synthetic diamond using chemical-vapor deposition, dc plasma discharge, and other techniques.¹

Lonsdaleite or hexagonal diamond is a hexagonal modification of the cubic diamond structure. It has been found to occur in meteorites² and has also been synthesized in the laboratory using extreme conditions of pressure and temperature.³ Recently, in diamond and diamond-like-carbon films grown by chemical-vapor deposition, a high density of (111) microtwins and stacking faults have been observed, indicating that part of the deposited film might contain the hexagonal diamond phase.⁴ In the light of these current developments on diamond films, it is important to examine the properties of the hexagonal modification of diamond.

In this paper we present results of our local-density calculation of the electronic band structure of hexagonal diamond and compare the bands with those of cubic diamond. We predict significant differences in the band structures between the two forms of diamond.

II. METHOD

The crystal structures of the cubic and the hexagonal diamond are shown in Fig. 1. As seen from the figures, the local atomic arrangement is very similar between the two. Both structures have covalent tetrahedral bonds and contain only six-membered rings of bonds. Perhaps the difference between the two structures is best understood by considering the crystals to be constructed by stacking of (111) atomic planes. In both structures pairs of atomic layers (each pair designated by A , B , or C) are stacked on top of one another with successive pairs displaced sidewise. In cubic diamond, every fourth layer

pair is stacked on top without any sidewise displacement, giving rise to the stacking sequence $ABCABC\dots$, as seen in Fig. 1(a). The stacking sequence in hexagonal diamond, on the other hand, is of the type of $ABAB\dots$. All six-membered rings in cubic diamond are the so-called “chair” rings, where of the six atoms forming the ring, four lie on a plane and the remaining two occur on the *opposite* sides of this plane. In the hexagonal diamond, however, one has both the “chair” rings as well as the “boat” rings. In contrast to the “chair” rings, the “boat” rings have four atoms on a plane and the remaining two occur on the *same* side of this plane. Since the tetrahedral coordination preserves both the first as well as the second-nearest-neighbor distances, one expects little change in the bonding characteristics leading to, consistent with experiments, negligible change in the bond lengths and bond angles. We have in our calculation used the observed bond length of 1.545 Å for cubic diamond. This is consistent with the experimental values³ of $a = 2.52$ Å and $c = 4.12$ Å for hexagonal diamond.

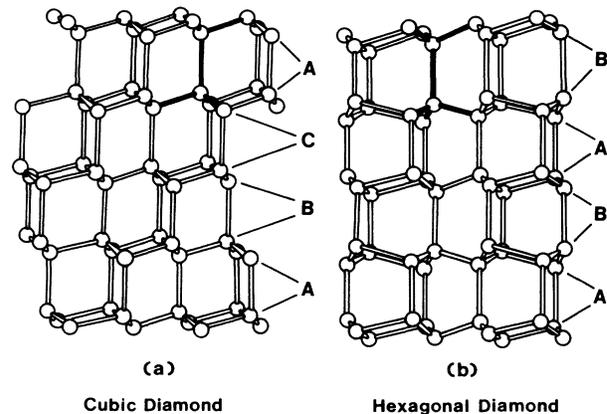


FIG. 1. Crystal structures of cubic and hexagonal diamonds. The difference in stacking sequence of (111) layer pairs in the two structures has been illustrated. Differences in the atom arrangements are highlighted by the darkened bonds.

TABLE I. Atom positions and the sphere radii used in our calculation for hexagonal diamond; E denotes the empty spheres and z denotes the internal position parameter. The atom positions refer to the tables of Henry and Lonsdale, space group No. 194 (Ref. 8).

Atom	Core	Atom positions	Sphere radii (Å)
C	[He]	$4f$ ($z = \frac{1}{16}$)	0.90
$E(1)$		$2b$	1.02
$E(2)$		$2d$	0.60

The band structures were calculated within the local-density approximation (LDA) to the density-functional theory.⁵ The von Barth–Hedin exchange correlation⁶ was used. We used the linear-muffin-tin-orbitals method⁷ in the atomic-sphere approximation (LMTO-ASA). Spin-orbit coupling was neglected. Since the atomic number of carbon is small, this would produce negligible effect. As is standard in the LMTO calculations, empty spheres were used to better describe electron charge density in the interstitial parts of the unit cell. The positions of the carbon atoms as well as of the empty spheres and the muffin-tin-sphere radii used in the calculation for the hexagonal structures are given in Table I. Carbon 1s electrons were treated as frozen-core electrons. Self-consistency was achieved by using 15 k points in the irreducible Brillouin zone (BZ). Muffin-tin orbitals with spd

angular momenta were retained on all atoms and empty spheres. The results of our calculation for the cubic structure are in excellent agreement with bands obtained by earlier authors.

The irreducible Brillouin zone of the hexagonal primitive lattice, relevant for the hexagonal diamond, is shown in Fig. 2. In this figure we have also shown the projection of a few symmetry points of the fcc BZ onto the hexagonal primitive BZ with the assumption that bond lengths and bond angles are preserved in going from the hexagonal to the cubic structure. With a similar assumption, this projection is also relevant for mapping of k points between the zinc-blende (cubic) and the wurtzite (hexagonal) forms of a compound, such as ZnS, SiC, and other binary semiconductors that exist in both forms. If the bond lengths are slightly different between the two forms, then the symmetry points of the fcc BZ will be mapped onto points on the hexagonal zone in the neighborhood of where they are shown in Fig. 2. Such a projection, as we shall see later, allows us to directly compare the electron band structures of the cubic and the hexagonal diamonds. After we obtained this projection, we became aware of an earlier work of Bergstresser and Cohen⁹ where a similar projection was obtained in connection with their study of the wurtzite semiconductors. Both results agree with each other. In addition to results shown in their paper, in Fig. 2 we have shown the mapping of the Δ and Λ lines which are important for the diamond structure.

The cubic diamond structure has two atoms in the unit

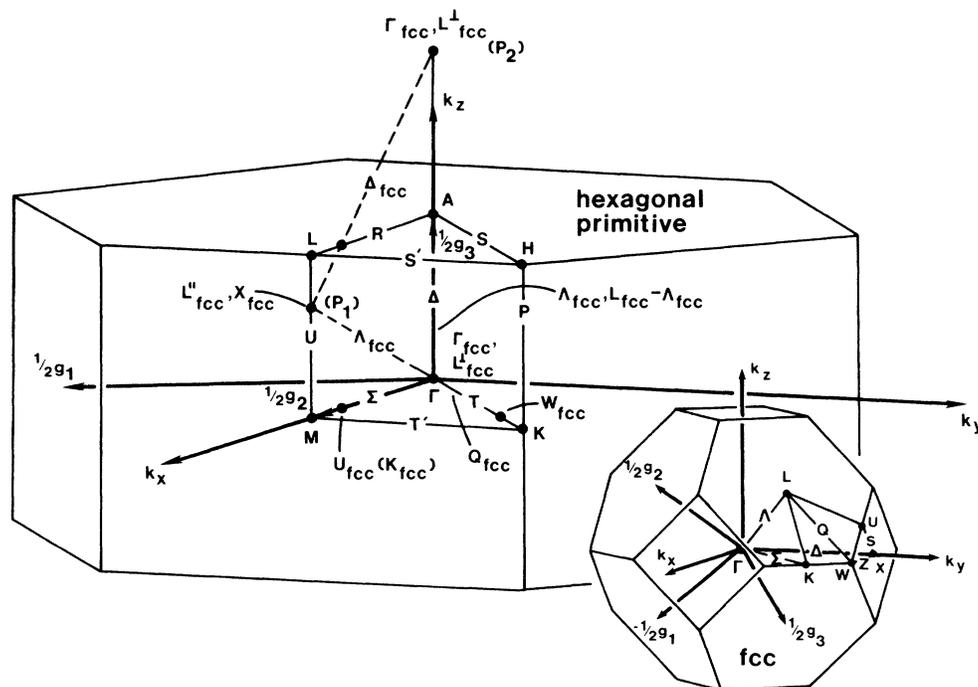


FIG. 2. Irreducible Brillouin zones (BZ) of the hexagonal primitive lattice and of the face-centered-cubic (fcc) lattice. Wave vectors of the irreducible fcc BZ corresponding to the cubic diamond structure (fcc) have been mapped onto the hexagonal BZ. Two k points of the fcc BZ are mapped onto each k point of the hexagonal zone, as discussed in the text. The two points denoted P_1 and P_2 refer to Fig. 3.

cell, while hexagonal diamond has four. The hexagonal structure, therefore, has twice as many bands as the cubic structure at any k point in the BZ. Consequently, there is a two-to-one mapping between the two BZ's. Two k points in the fcc zone are mapped onto the same k point in the hexagonal zone. For instance, both Γ_{fcc} and L_{fcc} are mapped onto the Γ point of the hexagonal zone. Similarly, both X_{fcc} and L_{fcc} are mapped onto a point on the line U of the hexagonal zone, two-thirds of the distance away from M , as shown in Fig. 2. We note, incidentally, that the eight equivalent L_{fcc} corresponding to wave vectors along the bond directions in cubic diamond are no longer equivalent in the hexagonal structure. The wave vectors k corresponding to L_{fcc} are along the bond directions. Two of these along the c axis, denoted L_{fcc}^{\parallel} , map onto the Γ point, whereas the rest (six) along other bond directions, denoted L_{fcc}^{\perp} , map onto a point on the line U . Notice also how the Δ_{fcc} line maps onto the hexagonal zone. This line is especially important since, as is well known, the conduction-band minimum of cubic diamond occurs along Δ_{fcc} close to the X_{fcc} point.

III. RESULTS

The calculated electronic band structures for the cubic and the hexagonal diamond are shown in Fig. 3. The cubic diamond bands have been "folded" into the hexagonal zone as discussed above. Our cubic diamond bands, although presented here in a nonconventional fashion for

direct comparison with the hexagonal bands, are in excellent agreement with those obtained by earlier authors.

The LDA band structure of cubic diamond has been calculated by earlier authors by using a variety of methods. The calculated valence-band width and the lowest gap are, respectively, 20.44 and 6.33 eV (LCAO),¹¹ 21.36 and 5.66 eV (LAPW),¹² 21.28 and 5.5 eV (LMTO-ASA),¹³ and 21.45 and 5.4 eV (plane-wave pseudopotential).¹⁴ These compare very well with our results of 21.2 and 5.5 eV, respectively, for the valence-band width and the lowest gap. The experimental values are 24.2 eV (Ref. 15) and 7.3 eV (Ref. 16), respectively. The discrepancy between the LDA results and the experimental values is typical of the local-density calculations.

Our calculated indirect Δ gap for cubic diamond is about 3.8 eV. In our calculation we have omitted the "combined-correction term," which would add about 0.3 eV (Refs. 13 and 17) to the Δ gap, making it equal to 4.1 eV, which is the correct local-density result. This term, which corrects for the errors introduced by the ASA as well as for the omission of the higher-angular-momentum orbitals in the basis set, is expected to be roughly the same for states in the gap region for the cubic and the hexagonal structures. Therefore omission of this term does not alter the key results presented in this paper.

There is a considerable similarity between the cubic and the hexagonal bands, as seen from Fig. 3. In the LMTO theory, the Hamiltonian H_k may be written in terms of the structure constants S_k and a k -independent

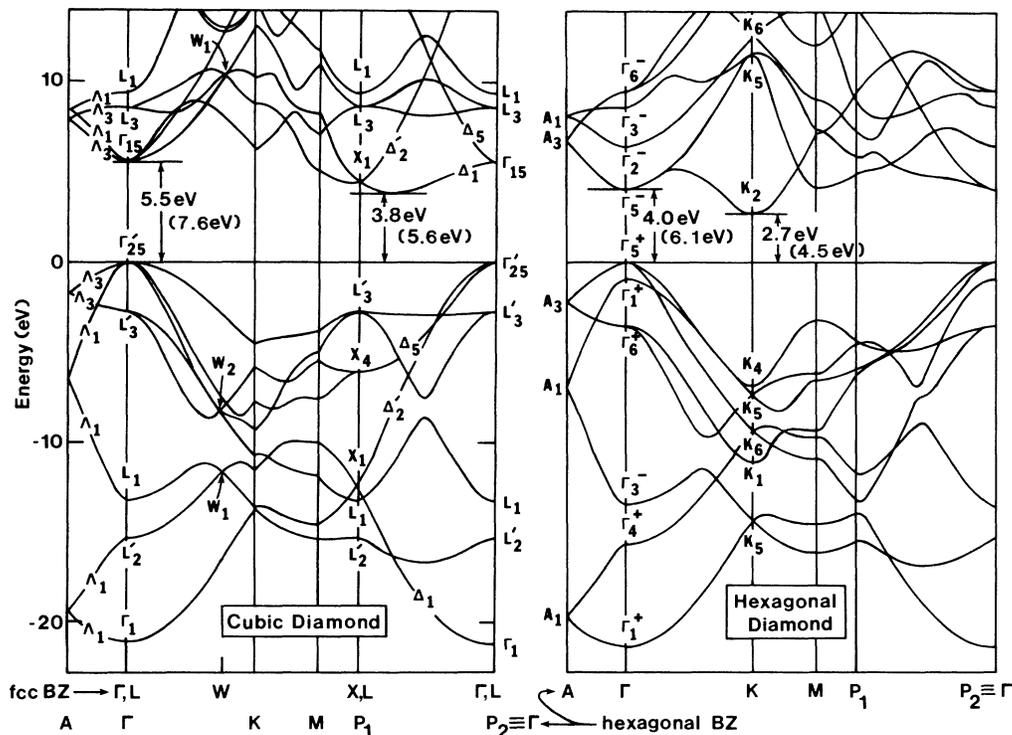


FIG. 3. Calculated electron bands for cubic diamond and hexagonal diamond. Note that the cubic diamond bands have been presented here in a nonconventional fashion for direct comparison with the hexagonal bands. We follow the symmetry conventions of Ref. 10 for hexagonal diamond. Even though there is a large similarity in the valence bands, there are important differences, especially in the conduction bands. A reduction of the lowest gap in the hexagonal structure by about 1.1 eV as compared to the cubic structure is predicted. The gap values in parentheses include estimated corrections to the calculated values, and these should be compared to experimental results.

potential parameter part:

$$H_k = C + \sqrt{\Delta} S_k (1 - \gamma S_k)^{-1} \sqrt{\Delta}, \quad (1)$$

where C , Δ , and γ are the band-center, bandwidth, and distortion parameters.⁷ The calculated self-consistent potentials, and therefore the potential parameters, are virtually the same for both structures. The primary differences in the bands are due to changes in the structure constants.

The valence-band widths are virtually the same: 21.4 eV in hexagonal diamond compared to 21.2 eV in cubic diamond. However, both the valence-band top and the conduction-band bottom of cubic diamond, of Γ_{25}' and Γ_{15} symmetries, respectively, are each split into a twofold (x, y) and a onefold (z) state by the hexagonal crystal field. The splitting is large, about 0.9 eV for the valence state and 2.4 eV for the conduction state, with the average energies more or less unchanged. Because of the crystal-field splitting the fundamental gap ($\Gamma_5^+ \rightarrow \Gamma_5^-$) in the hexagonal structure is reduced by about 1.5 eV as compared to the fundamental gap in cubic diamond.

It is well known that the local-density theory underestimates band gaps in semiconductors. In cubic diamond the correction to the LDA indirect gap has been calculated to be about 1.5 eV.¹⁸ If we add this to the LDA gap, the corrected gap becomes 5.6 eV, in good agreement with the observed indirect gap of 5.45 eV. Thus a net correction of 1.8 (0.3 eV for omission of the "combined-correction term" plus 1.5 eV for effects beyond the LDA) should be added to our calculated indirect gap of cubic diamond for comparison with experiments. This correction is a total of 2.1 eV (0.2 eV + 1.9 eV) for the direct Γ gap.

The nature of the wave functions remains virtually the same between the two forms, as seen from Table II, where the wave-function characters of a few relevant states in the gap region are given. The valence-band-top and conduction-band-bottom states are primarily of $C p$ character, while the conduction-band minima, at Δ and

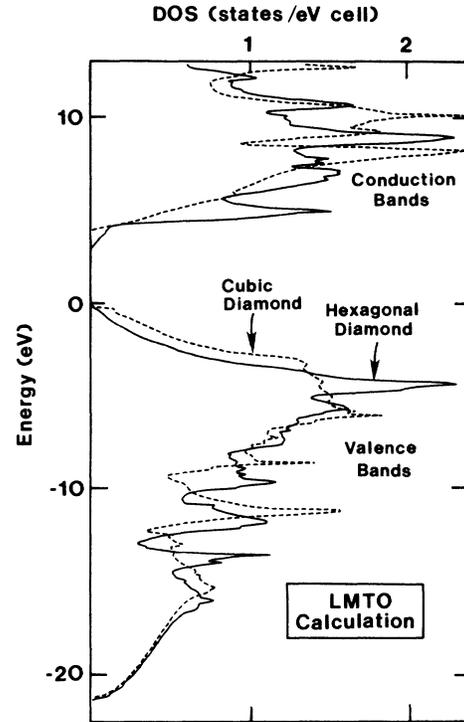


FIG. 4. Comparison of the one-electron DOS of cubic and hexagonal diamonds. The differences should be large enough for experimental observation.

K , respectively, for the cubic and hexagonal structures, have a large contribution from the interstitial empty spheres. Since the nature of wave functions is unchanged between the two structures, we expect the corrections to our calculated results to be very similar between the cubic and hexagonal structures. We should therefore add 1.8 eV to the calculated indirect gap and 2.1 eV to the direct gap of hexagonal diamond for comparison with experiments.

TABLE II. Calculated wave-function characters and energies of relevant electron states in the gap region of cubic and hexagonal diamonds.

Electron state	Symmetry	Energy ^a (eV)	Wave-function character ^b (%)					
			$C s$	$C p$	$C d$	$E s$	$E p$	$E d$
Cubic diamond								
Γ_v top	Γ_{25}'	0	0	87	8	0	1	5
Γ_c bottom	Γ_{15}	5.5 (7.6)	0	64	11	0	15	9
Δ_c min	Δ_1	3.8 (5.6)	23	20	16	31	1	10
Hexagonal diamond								
Γ_v top	Γ_5^+	0	0	91	8	0	0	1
Γ_c bottom	Γ_5^-	4.0 (6.1)	0	59	13	0	22	5
K_c min	K_2	2.7 (4.5)	0	30	17	48	3	2

^aThe energies in parentheses include estimated corrections due to the "combined-correction term" and effects beyond the LDA, as indicated in the text.

^b $C s, p$, and d refer to the components of the s, p , and d muffin-tin orbitals on the carbon atom, and $E s, p$, and d refer to those located on the interstitial empty spheres.

In hexagonal diamond the bottom of the conduction band corresponding to the Δ_{fcc} point has moved up above the Γ minimum. The lowest gap, nevertheless, remains indirect as the conduction-band minimum at the K point occurs well below the Γ minimum.¹⁹ Our calculation shows the lowest gap in the hexagonal structure to be about 4.5 eV (including corrections beyond the LDA), compared to the corresponding result of 5.6 eV in the cubic structure. This reduction of 1.1 eV is significant and should be observable in optical experiments.

We show in Fig. 4 the differences in the one-electron density of states (DOS) between the cubic and hexagonal structures. Apart from the band-gap reduction, the figure shows clear changes in the features in the DOS. In particular, the peaked structures near the gap in both valence and conduction bands of the hexagonal diamond should be experimentally detectable.

IV. CONCLUSIONS

In conclusion, by performing local-density calculations we have shown that there are significant changes in the bands of hexagonal diamond as compared to cubic diamond in spite of the similar tetrahedral atom coordination in the two structures. However, the lowest gap in the hexagonal structure is indirect, just as in the cubic structure. We find a dramatic reduction of both the direct Γ gap as well as the lowest indirect gap in the hexagonal diamond as compared to the gaps of cubic diamond.

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