

Band gaps in diamond-graphite hybrids

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The HOMO-LUMO gaps have been estimated in a graphite-like sp^2 carbon network with a progressive increase in the fraction of sp^3 carbons, taking into account several possible structural alternatives for each composition. The gap is shown to increase exponentially with the fraction of sp^3 carbons. Accordingly, the gap in a diamond-like sp^3 network decreases with the increase in the fraction of sp^2 carbons.

There is renewed interest in the different forms of carbon in the last few years. Besides structures involving mixtures of sp^2 and sp^3 carbons such as hydrogenated amorphous carbon ($a\text{-C:H}$) and diamond-like carbon,¹⁻³ there are other forms of carbon proposed on the basis of theoretical considerations. Thus, on the basis of topological considerations, Schwarzites involving 5, 6, 7, 8, and 9-membered rings have been proposed by Townsend *et al.*,⁴ while Hoffmann *et al.*⁵ have suggested a novel form of conducting carbon. We have studied the stability of structures of diamond-graphite hybrids with different sp^2/sp^3 atom ratios by employing the force field method.³ It is of considerable importance to explore whether such hybrids exhibit a range of band gaps between those of graphite and diamond. Balaban *et al.*⁶ have theoretically examined cubic or hexagonal diamond layers connected by graphitic strips and have predicted that the band gap should decrease with the increase in the strip width. Band gap estimates for the diamond-graphite hybrid structures with different fractions of sp^3 carbons, which take into account several possible structural alternatives, are, however, not available. Since the band gap in such hybrids would depend not only on the sp^2/sp^3 atom ratio but also on how the sp^3 (or sp^2) carbon atoms are distributed in a sp^2 (or sp^3) network, we have carried out a systematic study of the HOMO-LUMO gaps in diamond-graphite hybrids, with varying sp^2/sp^3 ratios, starting with a pure sp^2 layer at the graphite end and a three-dimensional sp^3 network at the diamond end.

In order to study the effect of incorporating sp^3 (or sp^2) carbons in a sp^2 (or sp^3) network, on the band (HOMO-LUMO) gap, we have started with large hydrocarbons containing either only sp^2 or sp^3 carbons and estimated the gaps by extended Huckel theory.⁷ It may be noted that for a series of related systems, the EHT method provides estimates of the HOMO-LUMO

gaps which follow the trend in experimental values.^{7,8} The atomic coordinates for the structures were obtained from force field minimization by using the molecular simulation program (Discover of Biosym Technologies, San Diego) described earlier.³ Extended Huckel calculations were performed by using the ICON version 8 (by R. Hoffmann) and were run in a VAX-88 machine. The program uses parameterized basis sets consisting of H 1s and C 2s and 2p orbitals for hydrocarbon molecules. The s/p electron exponent was 1.3 and 1.625, respectively, for H and C. The H(I, I) values for the s electron were -13.6 and -21.4 eV for H and C, and for p electron of C it was -11.4 .

Initial calculations on several hydrocarbon structures showed that the aromatic hydrocarbon $\text{C}_{110}\text{H}_{30}$ [Fig. 1(a)] containing only sp^2 carbons provides a good model for a graphitic sheet, with a very low HOMO-LUMO gap. Similarly, the hydrocarbon $\text{C}_{120}\text{H}_{92}$ [Fig. 2(a)] with a substantial band gap appears to be a good model for diamond. In what follows, we discuss the HOMO-LUMO gaps in $\text{C}_{110}\text{H}_{30}$ ($\text{C}_{120}\text{H}_{92}$) structure

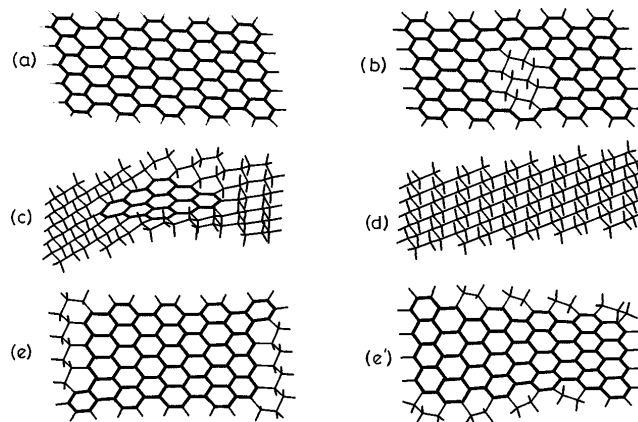


FIG. 1. Typical structures of the general composition C_{110}H_x : (a) $\text{C}_{110}\text{H}_{30}$ with only sp^2 carbons, (b) $\text{C}_{110}\text{H}_{40}$ with 9% sp^3 carbons, (c) $\text{C}_{110}\text{H}_{110}$ with 73% sp^3 carbons, (d) $\text{C}_{110}\text{H}_{140}$ with 100% sp^3 carbons, and (e) and (e') $\text{C}_{110}\text{H}_{48}$ with 16% sp^3 carbons.

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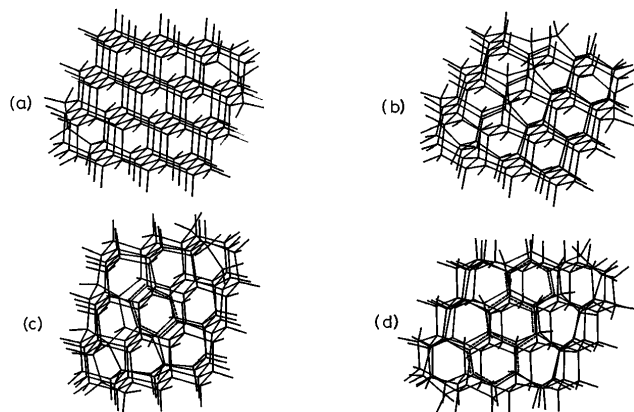


FIG. 2. Typical structures of the general composition $C_{120}H_x$: (a) $C_{120}H_{92}$ with only sp^3 carbons, (b) $C_{120}H_{98}$ with 5% sp^2 carbons, (c) $C_{120}H_{98}$ with 5% sp^2 carbons, and (d) $C_{120}H_{106}$ with 12% sp^2 carbons.

with the progressive increase in the proportion of sp^3 (sp^2) carbons.

$C_{110}H_{30}$ containing only sp^2 carbons [Fig. 1(a)] has a gap of 0.0009 eV. We have progressively increased the number of sp^3 carbons in this network, taking into account the different possible structures of such hybrids (see Fig. 1 for typical examples of such structures). Thus, the structure in Fig. 1(b) has 10 sp^3 carbon atoms. As we progressively increase the number of sp^3 carbons, we finally obtain the structure with only sp^3 carbons [Fig. 1(d)] with a high value of the gap (~ 9 eV). In Fig. 3 we have plotted the HOMO-LUMO gap, Δ , against the fraction of sp^3 carbons in the $C_{110}H_x$ system. (Note that the hydrogen content will also increase with the increase in the fraction of sp^3 carbons³). We see from Fig. 3 that the gap is in the 0.0–0.8 eV range up to a sp^3 fraction of ~ 0.4 and increases significantly when the sp^3 fraction is increased further. Structures with a high sp^3 fraction have gaps in the range 1.0–4.0 eV. When the sp^3 fraction is less than 0.4, we find a range of gaps (0.0–0.6 eV) for different structures with the same fraction of the sp^3 carbons because of the different ways of locating the sp^3 carbons in the sp^2 network. For example, the structures in Figs. 1(e) and 1(e') show gaps of around 0.0 and 0.6 eV, respectively, the main difference between the two structures being that the sp^3 carbons are along the zigzag edge in 1(e), whereas they are along the armchair edge in 1(e'). Such differences give rise to changes in the gap, but the changes are relatively small. When the sp^3 carbons cluster together to form cyclohexane, decalin, or the saturated forms of pyrene and coronene in the sp^2 layer, the gap becomes very small ($\sim 10^{-3}$ eV). Structures with a high sp^3 fraction (0.7–0.8) but low band gap (0.8 eV) are those where the sp^2 carbons form strips of fused benzene rings. It has been observed earlier⁹ that strips

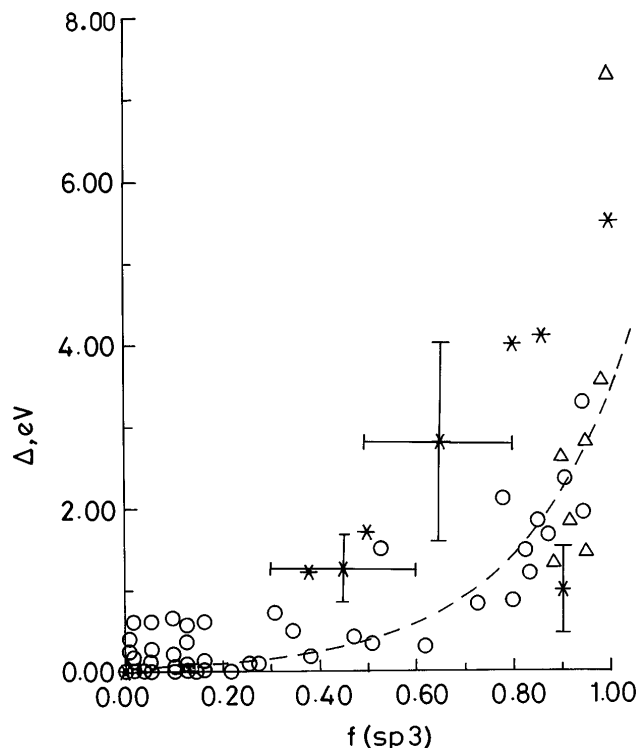


FIG. 3. Plot of the HOMO-LUMO gap, Δ , in $C_{110}H_x$ compositions (circles) against the fraction of sp^3 carbons, $f(sp^3)$. Triangles represent data on $C_{120}H_x$ compositions. Experimental values are shown by stars.

or rows of fused benzene rings lower the band gap due to their higher edge sites. Significant changes in the gap come about when we increase the number of sp^3 carbons not merely at the edges, but over the entire network as in Figs. 1(b) and 1(c).

The HOMO-LUMO gaps, Δ , in the hybrids of the general formula $C_{110}H_x$ are described satisfactorily by the expression,

$$\Delta \text{ (in eV)} = 0.04 \exp(4.34f),$$

where f is the fraction of sp^3 carbons. The broken curve in Fig. 3 is that predicted by the above expression. Experimental values of the optical gaps reported in the literature^{10,11} also show an exponential increase with the fraction of sp^3 carbons, although they tend to be somewhat higher than those predicted by the above expression.

We have studied the variation in the HOMO-LUMO gap in a diamond network with a progressive increase in the number of sp^2 carbons. The parent diamond network, $C_{120}H_{92}$, shown in Fig. 2(a) gives a gap of 7.22 eV. Although the experimental optical gap for diamond is 5.5 eV, theoretical values of 7–10 eV are considered to be good estimates.¹² We have calculated the gap of the $C_{120}H_x$ system by increasing the number of sp^2 carbons in the form of double bonds or aromatic rings as in diamond-like carbon.¹ Typical structures of $C_{120}H_x$ with

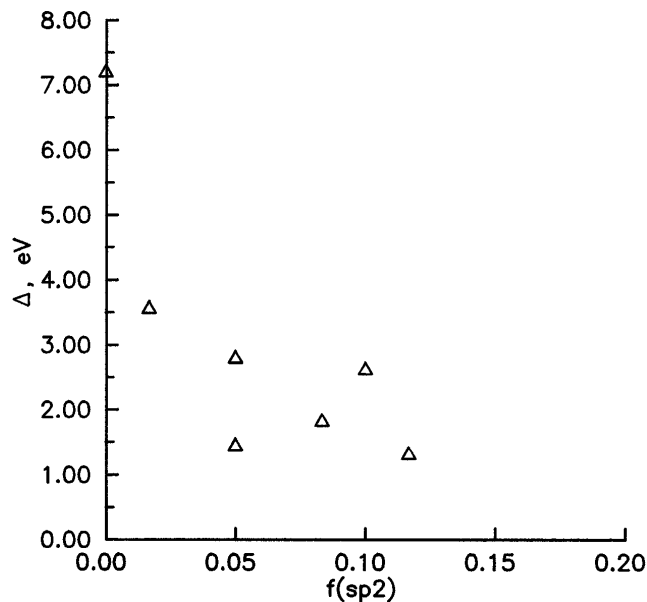


FIG. 4. Plot of the HOMO-LUMO gap, Δ , in $C_{120}H_x$ compositions against the fraction of sp^2 carbons.

sp^2 carbons are shown in Fig. 2. The calculated values of the gap are plotted against the fraction of sp^2 carbons in Fig. 4 to illustrate how it decreases progressively. The structures 2(b), 2(c), and 2(d) show gaps in the 1–3 eV range. For example, 2(c), which has a benzene ring in the sp^3 network, has a gap of 2.81 eV. The gap in pure benzene is, however, calculated to be 4.5 eV. Similarly, the gaps found in the structures containing isolated naphthalene and anthracene units [Fig. 2(d)]

are 1.84 eV and 1.34 eV, respectively, which are much lower than the gaps calculated for the pure hydrocarbons (2.8 eV and 1.8 eV, respectively). The data in Fig. 4 are also shown in the Δ vs $f(sp^3)$ plot in Fig. 3 (represented by triangles) to demonstrate that they are described reasonably well by the same expression. The experimental values of the gap with their uncertainties are also shown in Fig. 3 to illustrate that they are not far from the predicted trend.

The present study demonstrates how the HOMO-LUMO gap in diamond-graphite hybrids is a sensitive function of the sp^2/sp^3 ratio as well as the structure of the hybrid. The marked variation in the gap when the $f(sp^3)$ is between 0.4 and 1.0 is noteworthy.

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