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The Graphite-to-Diamond Transformation*

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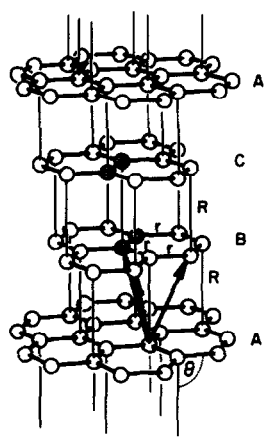
An orbital model for a solid state transformation, the graphite-to-diamond high-pressure reaction, is presented. Using solid state Walsh diagrams we relate this transformation to chemical reactions having orbital symmetry constraints. During the transformation the π-delocalization in the graphite planes is gradually lost, leading to buckling and in-plane bond length elongation as inter-plane bonds form. The pacing of the different components of the reaction coordinate is important. We show that the transformation passes through way points of metallic band structure, which may be related to symmetry dictated level crossings in the Walsh diagrams. © 1984 Academic Press, Inc.

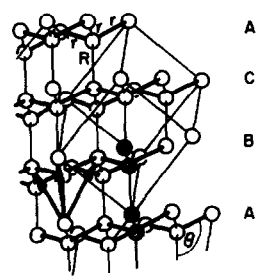
In what follows we shall describe an orbital model for a solid state transformation, in particular the reaction starting from graphite and leading to diamond. Aside from its intrinsic interest, it will turn out that this transformation bears resemblance to certain possibly concerted chemical reactions which have symmetry-related constraints (*1*). Burdett and Price (*2*) have elegantly applied the ideas of orbital correlation diagrams to solid state polymorphic transformations, and our analysis extends their work.

The basic geometries of the two allotropes related in this work, rhombohedral graphite and diamond, are shown in Schemes 1 and 2. Three coordinates define the structures and the reaction coordinate, the CC distance in the layer (r_G = 1.40, r_D = 1.54 Å), the CC distance between layers (R_G = 3.35, R_D = 1.54 Å), the angle θ between the perpendicular to the layers and a CC bond within a layer (θ_G = 90°, θ_D = 109.47°).

All three coordinates change continuously during a hypothetical concerted transformation, but it is R which is most changed, and causes the large reduction in volume. Choosing then R as an indepen-



SCHEME 1



SCHEME 2

* This paper is dedicated to our friend and colleague, Mike Sienko.

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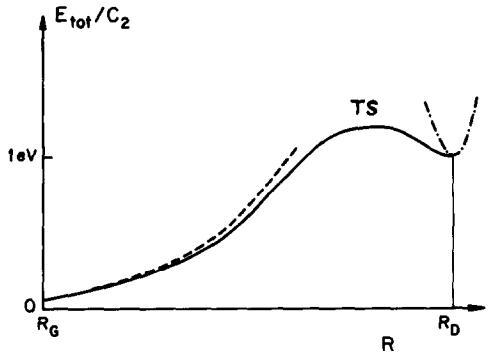


FIG. 1. Total energy per 2C units during the graphite to diamond transformation. —, Fully optimized; ---, rigid approach of graphite layers with fixed in-plane bond distances, -·-·-, energy curve of diamond, as function of the C–C distance. TS indicates the position of the transition state.

dent variable, we have optimized the other two parameters, r and θ, along the reaction path, using extended Hückel band calculations (*3*). Rhombohedral symmetry was maintained along the reaction path.

The computed energy profile is indicated in Fig. 1, and the evolution of the dependent geometrical parameters r and θ with R in Fig. 2. The extended Hückel method is not reliable for absolute energies, especially when bond distance changes are involved. In the case at hand the instability of diamond relative to graphite is much exaggerated. Nevertheless we have substantial ex-

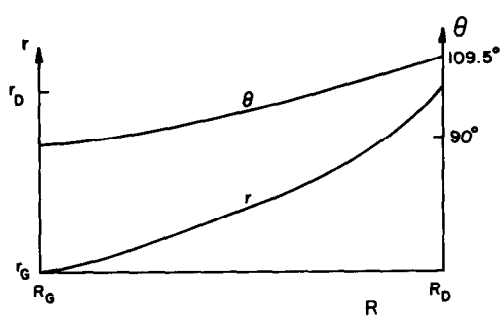
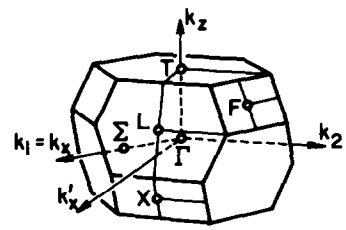


FIG. 2. Dependence of the shorter C–C distance (r) and the angle θ on the interplane distance, R, during the graphite-to-diamond transformation.



SCHEME 3

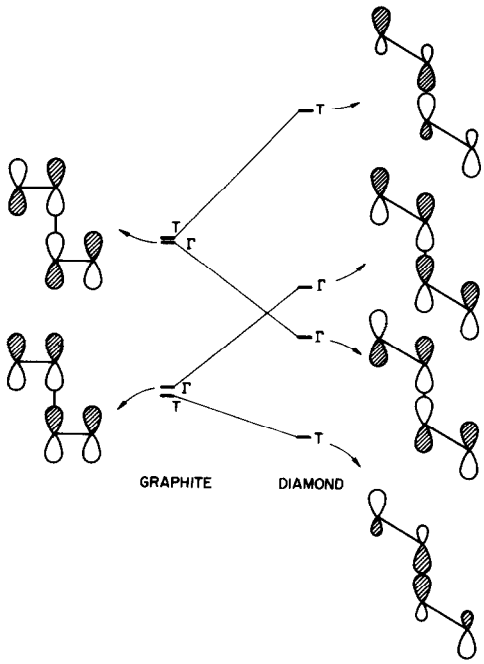
perience with extracting reliable orbital and symmetry arguments from the method, and it is in this sense that we will eventually use the computations.

Let us examine some features of the computed reaction path. The dashed line in Fig. 1 corresponds to the total energy within the graphite structure with $\theta = 90°$ and $r = r_g$ fixed. For R close to R_G the two curves run close, thus the energy gain due to the relaxation of θ and r is not significant. This is in accordance with the small slope of both $r(R)$ and $\theta(R)$ curves in Fig. 2. An analysis of the experimental compressibility data of graphite and diamond indeed led to the conclusion that for low pressures the graphite planes do not buckle (*4*).

Nearing the transition state (TS), the other two coordinates become very much involved. The calculations give a transition state for this reaction in which the pyramidalization is almost complete, the in-plane bonds have almost reached their diamond values, only the interplane bonds are very long and different from those in diamond. The graphite π-delocalization is completely lost.

The total energy is an average over the symmetric unit cell of the reciprocal space, the Brillouin zone, BZ (Scheme 3) just as the total energy in a molecule is a sum of the one-electron orbital energies.[1] The symmetry of orbitals in solids is tied to their k-vectors, and even in highly symmetrical

[1] For the Brillouin zone of diamond (fcc) the rectangles become squares, all the hexagons become regular and identical, see Ref. (*5*).



SCHEME 4

solids only a few points, lines or planes carry exact symmetries. However, as in the case of molecules, the nodal structure of the wave function is preserved to a great extent, even in quasisymmetrical cases. Thus, even off the high symmetry points or lines and planes of the BZ, but in their vicinity, the consequences of the symmetry are felt strongly. Therefore, these high symmetry points carry measurable weights in the averages over the BZ.

For the Γ point of diamond there is full s–p separation, (*5*) due to the tetragonal symmetry. One of the triply degenerate sets ($2p_z$) has the orbital diagram depicted in Scheme 4, together with the π and π^* orbitals in graphite.[2] Also included are the related orbitals at T.

A referee has made the following useful comment concerning this transformation: "Since the bonding p_z orbital in rhombohedral graphite plane involves an antibonding interaction between the sheets in the z direction at Γ, moving the atoms together in the transformation involves a level crossing at Γ, but not at T (0,0,½) where there is a phase change along z. The crossing at Γ, but not at T, is symmetry-imposed, (cf. the linear chain example of Burdett and Price (*2*)), and so this illustrates and broadens their suggestions as to situations where one could expect bond breaking and remaking transformations to result in level crossings at certain high symmetry k."

The symmetry correlation in Scheme 4 is such that along the reaction coordinate the levels cross somewhere. A series of actual calculations for intermediate geometries leads to the two curves shown in Fig. 3, which could be considered as the Walsh diagram at the Γ point of the BZ.

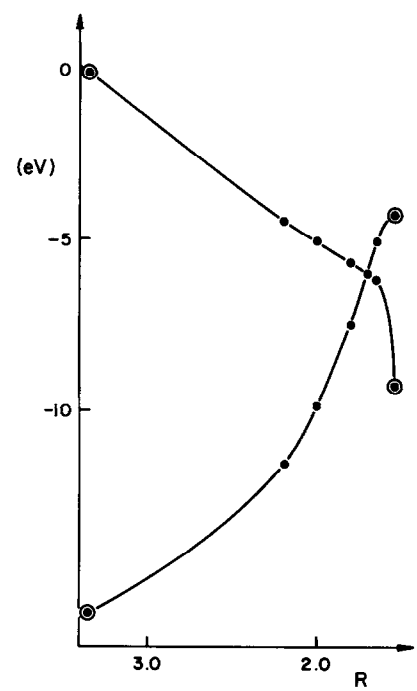


FIG. 3. Walsh diagram in the Γ point for the two frontier orbitals shown in Scheme 4 in text. ((⊙) refers to the fully optimized structures, (·) to a rigid intermediate approach at which $\theta = 75°$ and $r = 1.5$ Å, only R is varied.)

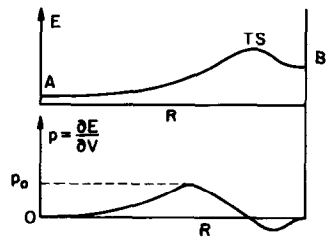
[2] Since the interlayer interaction in graphite is small, the s–p mixing is negligible.

While there are many similarities between level correlations and curve crossings in discrete molecules and similar phenomena in extended structures, there are important differences to note. First of all, the two curves on Fig. 3 *does not* correspond to the highest occupied (HO), or lowest unoccupied (LU) levels. Those HO or LU levels are dependent on the band structure as a whole, and they are even not necessarily at the zone edges or high symmetry points. This leads to the second important difference: the transition state, as well as a range of states on either side of TS corresponds to partly filled, thus *metallic* band structures. This is illustrated in Fig. 4 through the changes of the densities of states as the reaction proceeds. If we were to draw Walsh-type diagrams for many k points in the BZ, we could see how the changes of the densities of states come about. But we do not think this is necessary here. Due to the very strong perturbations of the p states in Scheme 4 the Γ point of the band structure is moved so strongly[3] that the filling has to become partial, leading necessarily to a metallic band structure.

The present work accounts for the reversible decrease of resistivity, followed by an irreversible increase in the same observable as the pressure is raised in graphite (*7*).

We have mentioned above the important work of Burdett and Price (*2*) on orbital theories of solid state transformations. Our analysis extends this by (a) making predictions about the metallic nature of the intermediate states; (b) analyzing the coupling of the different geometrical parameters during the transformation; (c) explaining the high stability of the metastable diamond phase.

The last point is quite general: after high pressure has put a system over the (symmetry related) barrier, it would require negative stress in the z direction to reverse the transition. This follows from the general shape of the energy curve, as illustrated schematically in Scheme 5. Reaching critical pressure, p_0, starting from structure A, the system collapses into structure B. The lower curve is only schematic, as the reaction coordinate R is not precisely proportional to the volume.



SCHEME 5

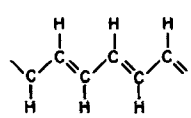
It is customary to relate different solid state structures by studies of hypothetical, sometimes unstable structural models. A well-known example of this kind is the rationalization of bond length alternation in polyacetylene (Scheme 6), which is believed to have an alternating structure (Scheme 6), because the most symmetrical (metallic) one (Scheme 7) is unstable electronically.[4] This instability is an application of Peierls' theorem on the nonexistence of one-dimensional metals (*9*).

Other examples for unstable hypothetical structures relating solids to each other may be found, for instance, in Burdett's paper (*10*) on the AB solids, which he derives as Peierls' distorted structures starting from a simple cubic arrangement.

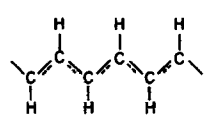
The fact that the TS structure is unstable,

[3] Large changes of energy band structures upon high pressure are well-known experimentally, see, e.g., Ref. (*6*).

[4] Notable examples include the distortion of quasi-one-dimensional systems as polyacetylene and transition metal layer compound, see, e.g., Ref. (*8*).



SCHEME 6



SCHEME 7

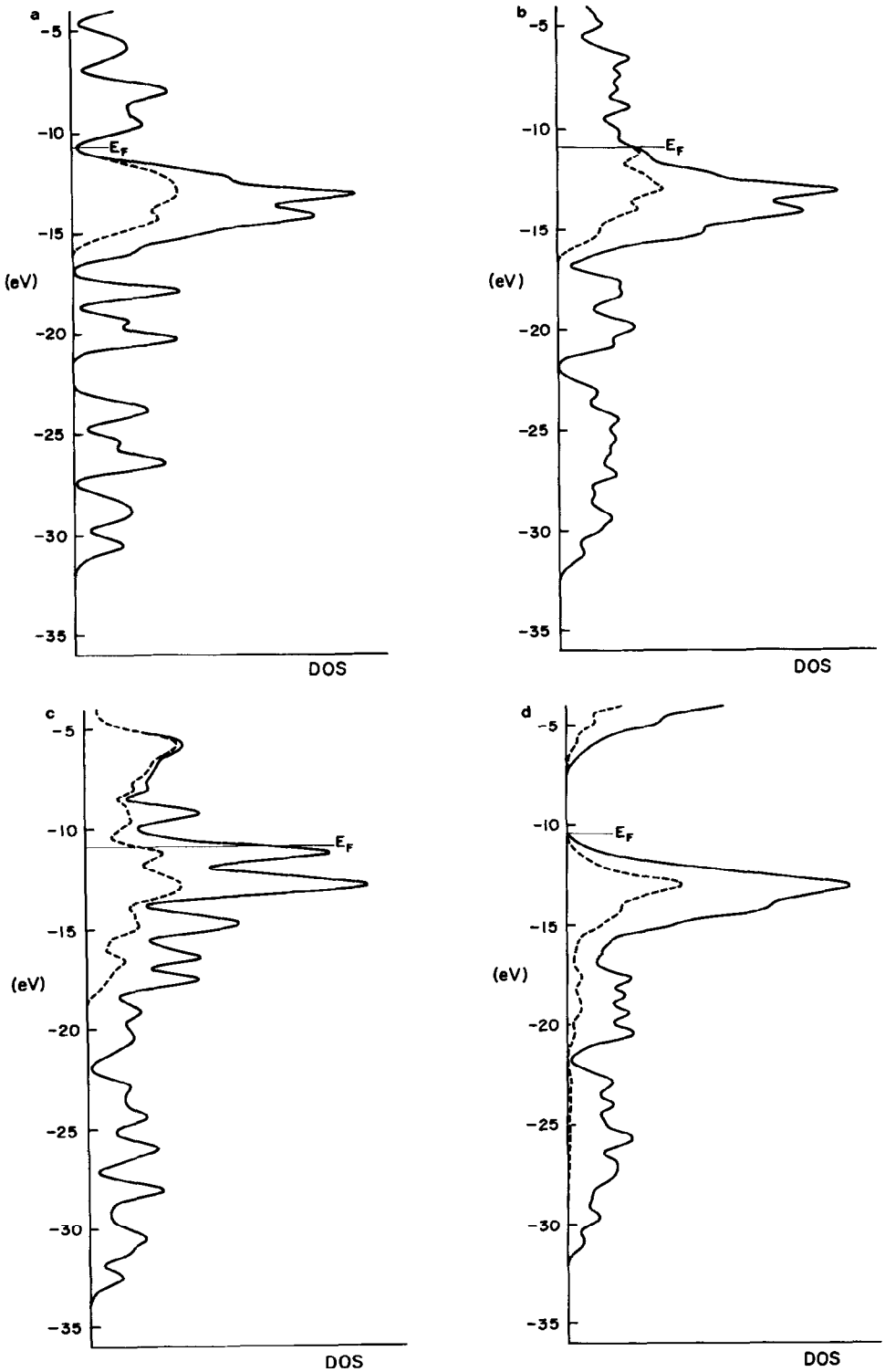
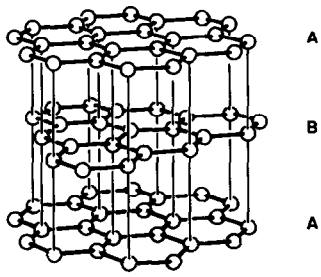


FIG. 4. Valence electron densities of states (DOS) along the graphite-to-diamond transformation: (a) graphite; (b) graphite, compressed, $R = 2.67$ Å; (c) at the computed transition state, TS; (d) diamond. The dashed projections are for $2p_z$ orbitals. Note that (b) and (c) have large DOS at the Fermi energy, E_F.

and that it is metallic, could possibly imply that its distortion to the insulating diamond, or to the semimetallic graphite, is in some way related to a Peierls-like effect. This is not so, because the degeneracy in the Peierls case is related to symmetry, whereas here it is an accidental degeneracy originating from a level crossing. This is in analogy with molecular transition states, which also are geometrically unstable, but not in the Jahn–Teller sense (*1*).

The actual mechanism of the high-pressure transformation of graphite to diamond (*11*) is certainly much more complex than the model we have studied. First of all, rhombohedral graphite is rare, and is always found together with hexagonal graphite (*11*). Hexagonal graphite, however, cannot yield a diamond structure, as illustrated on Scheme 8, unless the approach of the graphite planes is coupled to some in-plane slip in some of these planes. For instance, slipping leading to AA packing will lead to hexagonal diamond. A more complicated slip pattern leading to ABC packing (effectively rhombohedral) can then lead to cubic diamond. A further complication is that catalysts and heat treatment change the transformation appreciably (*11c*). The fact that if shear is applied in addition to high pressure the minimal temperature and pressure required for the transformation is lowered (*11f*) fits into the present picture.

The interconversion of graphite and diamond may also involve nucleation and growth (*2, 11g, 12*). These could be thought of as solid state analogs of nonconcerted or step-wise processes, which we know intervene in the molecular case when orbital symmetry barriers are imposed.



SCHEME 8

Nevertheless there is utility in thinking about the concerted bulk transformation. The region over which the transformation takes place synchronously, even if not extending over the whole crystal, may be modeled by a synchronous bulk transformation.

Applications of these ideas to transformations of boron nitride (*3*), are planned.

Acknowledgments

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