PHYSICAL REVIEW B VOLUME 57, NUMBER 10 1 MARCH 1998-II

Possible high-pressure phase of diamond

S. Serra,* G. Benedek, M. Facchinetti, and L. Miglio
Istituto Nazionale per la Fisica della Materia, Dipartimento di Scienza dei Materiali dell'Università, via Einaudi 15,
I-20126 Milano, Italy

(Received 22 August 1997)

We theoretically investigate a hypothetical sp^3 form of diamond carbon with 16 atoms per unit cell. It contains fivefold rings as a possible result of fullerene transformation under pressure and could be a stable phase of diamond at high pressure. We have calculated the ground-state structure, the cohesive energy, the bulk modulus, and the electronic density of states by means of tight-binding molecular-dynamics and density-functional total-energy calculations. Finally we have compared the phonon spectra at Γ and the Raman spectra to existing Raman data for a possible noncubic phase of diamond. [S0163-1829(98)02109-2]

I. INTRODUCTION

The progress made in growing diamond films and diamondlike films has renewed interest in the identification of novel possible allotropes of carbon. This research aims at improving our knowledge of the carbon phase diagram, and favoring the determination of new structures and phases which may appear in the synthesis of diamondlike films. Since the calculations of Fahy and Louie,[1] it became clear that these allotropes should be found only in threefold- and fourfold-coordinated structures even at pressures of the order of 10–20 Mbar, any higher coordination having a too low stability. These first studies[1,2] have shown a remarkably different behavior of carbon with respect to silicon and germanium, because of the large difference in the enthalpy of fourfold- and threefold-coordinated networks with respect to those with sixfold, eightfold, and 12-fold coordination. They are found to be 2.5, 4.5, and 5 eV/atom less stable than diamond, respectively. As a consequence only fourfold-coordinated phases (bc-8, st-12, $R8$, cubic diamond, and hexagonal lonsdaleite) have been predicted at pressures <20 Mbar, while metallic sixfold-coordinated phases (such as simple cubic) should appear only at larger pressures (20–30 Mbar).

The unique bonding strength of diamond makes it a material of extreme properties with technological applications of enormous importance. Among them, particularly interesting for this context is the development of diamond anvil cells (DAC's) capable of sustaining megabar pressures.[3] In this work we address the problem of the behavior of carbon at pressures <20 Mbar, which is still a matter of discussion, lacking reliable experimental data. The present limit to the pressure experimentally attainable in hydrostatic conditions approaches 4.5 Mbar. Unfortunately, this value is still too far away from the calculated stability limit of diamond in the aforementioned conditions, so that the theoretical predictions cannot be directly verified. The theoretical attempts to determine an upper bound on the stability limit of carbon have focused on the determination of phase transitions from total-energy calculations of different crystalline structures like β-Sn, face-centered-cubic, body-centered-cubic, hexagonal-close-packed, simple cubic, and several fourfold-coordinated networks. From these calculations the simple cubic structure is found to be the most stable structure in the high-pressure part of carbon phase diagram for pressures higher than 30 Mbar.[1,2] At lower pressures the results are still a matter of debate. By analogy with silicon and germanium, bc-8 (a body-centered-cubic structure with eight molecules per unit cell) has been proposed by Fahy and Louie[1] to be the stable phase of carbon in the intermediate region, where it becomes more stable than diamond for pressures as large as 11 Mbar. Further studies, by Clark *et al.*,[4] have lowered the transition pressure to 6 Mbar, in particular from diamond to a rhombohedral $R8$ structure (a rhombohedral structure with eight atoms per unit cell), which seems to be stable from pressure of 6 Mbar up to 30 Mbar. Anyhow, the question is far from being solved; new phases may lower the limit further, and changes in the transition pressures of $R8$ may be obtained using more accurate calculations (Clark *et al.* have used only 30 Ry for the energy cutoff). The st-12 (simple tetragonal with 12 atoms per unit cell) is always less stable than diamond.[1]

Recent *ab initio* simulations[5] making use of the variable-cell method[6] have questioned this argument, as the diamond to bc-8 transition or to any other proposed sp^3 carbon network has not been observed; on the contrary a sudden transition to a new metallic phase, called sc-4, has been found, which turns out to be only metastable with respect to bc-8. Although also this approach suffers some limitations due to the brief simulation times and small size of the simulation box (which can induce an overestimation of the transition pressures), it indicates the presence of high energetic barriers which make the transformation to bc-8 or R-8 very unlikely. Moreover, it was already pointed out by Fahy and Louie that bc-8 should not be a metastable phase of carbon at low pressures, in contrast with the case of silicon, since the reconversion into graphite would proceed with no energy barrier. Similar arguments can be applied also to $R8$, being much less stable than diamond at low pressure. These considerations suggest that bc-8 may not be the high-pressure fourfold-coordinated allotrope of carbon and stimulated us to search for a possible alternative. Concerning the experimental data, they clearly show that diamond is stable up to the pressures reachable, which are unfortunately much lower than the theoretically determined limit.

So far we have considered only the case of hydrostatic

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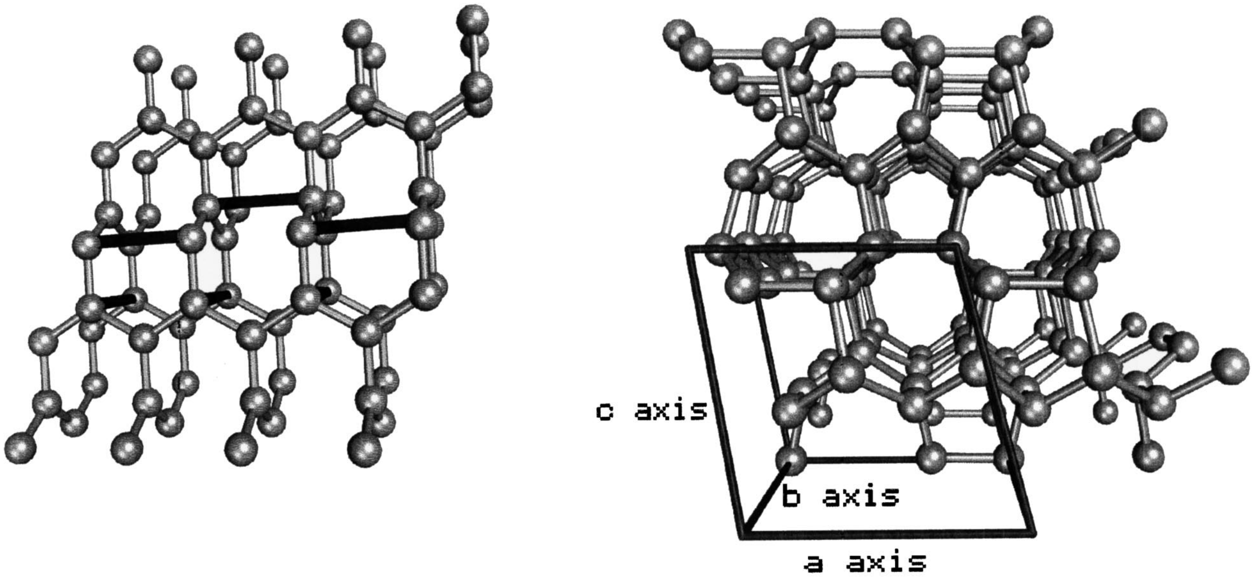

FIG. 1. Left panel: bct-4 crystal structure with the additional bonds (in black) considered in the rebonding procedure. Right panel: resulting crystal structure of tcl-16.

compression. Experimentally diamond is known to undergo changes in the bonding properties under uniaxial stress at much lower pressure (~ 2 Mbar), where the Raman response changes and fluorescence emission is observed. This has been demonstrated by Mao and Hemley[7,8] and Liu and Vohra.[9] In particular they have shown that these transformations occur in diamond by a tetragonal distortion (compression along the $\langle 001 \rangle$ axis) of the unit cell. The nature of these changes is not still clear, but it may indicate a structural transformation of diamond under uniaxial compression. The structures $R8$ and bc-8 do not seem to be good candidates for such transformations as they are much less stable (0.9 and 0.7 eV/atom, respectively) than diamond at low pressures ($<$ 1 Mbar), and alternative phases must be found also in this important case, where the stability limit of diamond is much smaller.

Our search has been biased by the conjecture that the presence of fivefold rings in an sp^3 network may increase the stiffness of diamondlike materials, resulting in a material harder than diamond. Moreover, such a structure may give an alternative and more favorable way of reconverting fullerite under moderate pressure, involving a relatively straightforward atomic rearrangement. Thus, we have predicted a possible sp^3 triclinic form of diamond with 16 atoms for the unit cell, which we have named tcl-16. This phase is characterized by periodic arrays of fivefold, sevenfold, and sixfold rings (Fig. 1, right panel). We have calculated the structural and electronic properties of this phase by means of tight-binding molecular dynamics (TBMD), based on a very flexible potential that we have previously developed.[10] Then, we have refined our predictions by a state-of-the-art *ab initio* approach. We have found that tcl-16 has a high stability and a large bulk modulus, comparable to body-centered (bc-8), $R8$, and simple tetragonal (st-12) phases,[1] both features pointing it out as an interesting and competitive hypothetical material.

The paper is organized as follows: In Sec. II we present the topological properties of tcl-16; in Sec. III we give some computational details on the methods, along with the structural and electronic properties of this new phase, its bulk modulus, and transition pressure. In Sec. IV we present the phonon and the Raman spectra of tcl-16 at Γ as calculated by TBMD. Comparison to recent spectroscopic results and conclusions are found in Sec. V.

II. TOPOLOGY OF THE tcl-16 PHASE

The tcl-16 phase can be generated through the rebonding of the bct-4 phase. The bct-4 phase is an all sp^2 structure proposed by Hoffman *et al.*[11] and quantitatively studied by Liu and Cohen,[12] who found it relatively stable (0.3 eV above diamond). The bct-4 crystal consists of buckled layers of carbon chains joined by bonds parallel to the c axis (see Fig. 1, left panel) and displays a body-centered tetragonal unit cell with four atoms per unit cell. It has been predicted to be mechanically stable with respect to the transformation into diamond, at variance with a similar phase of hexagonal symmetry, named H-6.[13] The basal planes of H-6 and bct-4 are very similar to the (111) and (100) diamond surfaces, respectively. As a consequence it was suggested that it would be possible to grow a bct-4 carbon crystal as a pseudomorphic phase on the diamond (100) surface. As can be seen from Fig. 1, bct-4 is constituted by large rings of ten atoms. Such rings can be unstable towards rebonding, even at low pressures, which leads to smaller rings.

In Fig. 1 (left panel) we show a possible rebonding process which generates tcl-16 from bct-4. A compression along a and b axes directly leads to the closure of the large ten-membered rings, giving pentagons and heptagons along the two crystallographic directions and hexagons along the third one. This transformation involves continuous deformations without any bond breaking, so that this transformation path should have a comparatively low barrier and might occur even at low temperature. The resulting sp^3 structure has a triclinic symmetry and has 16 atoms per unit cell (Fig. 1, right panel).

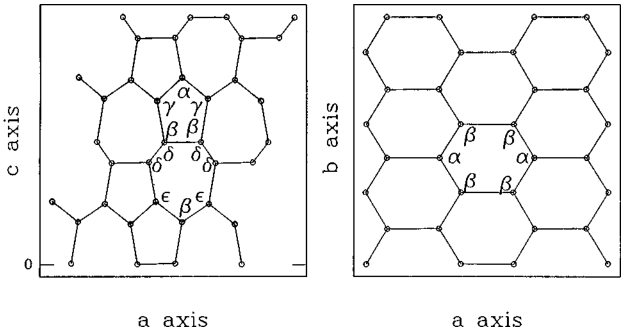

FIG. 2. Two-dimensional representation of tcl-16 structure along a, b, and c axes.

In Fig. 2 we show a two-dimensional projection of the tcl-16 unit cell along two different crystallographic directions, which shows the characteristic periodic array of five-fold and sevenfold rings along the a and b axes and sixfold rings along the c axis. From a topological point of view bct-4 is a platonic three-fold-connected net $(10^3)_4$,[14] while tcl-16 is a four-fold-connected net $(6^3 5^2 7)_{16}$. This means that two of the six shortest rings per atom are five-fold rings against only one seven-fold ring. The conjecture about a large stiffness of tcl-16 relies on this topological argument.

It is interesting to note that tcl-16 can be seen as a set of buckled hexagonal layers stacked along the c axis in $a\ldots ABCD\ldots$ sequence and joined by pentagons and heptagons. This would suggest that tcl-16 could spontaneously appear from diamond or lonsdaleite simply by sliding the buckled hexagonal layers, which are present also in those structures. In particular this may happen at high pressure, during the process of carbon metallization.

There is an important difference between diamond, lonsdaleite, bc-8, and our tcl-16, since in the latter the hexagonal rings are stacked in planes which are progressively rotated by 30°. The resulting misorientation is accommodated by the presence of pentagons and heptagons with bonds of different lengths and angles.

Incidentally, this peculiarity may stabilize tcl-16 with respect to the reconversion into graphite, contrarily to bc-8. In the latter case an elongation of the bonds along the c axis leads directly into graphite, while in tcl-16 it would give rise to misoriented graphite planes, making this path unrealistic. Therefore, reconversion into graphite should take a different and more complicated path, involving atomic rearrangements at a larger extent, probably with a higher-energy barrier. These qualitative considerations suggest that the tcl-16 may be a metastable phase of carbon even at low pressure.

III. STRUCTURAL AND ELECTRONIC PROPERTIES OF THE tcl-16 PHASE

Both the actual equilibrium configuration of the atoms within the unit cell and the sides of unit cell have been determined by minimizing the total energy with tight-binding molecular dynamics based on the Serra-Molteni-Miglio (SMM) carbon potential.[10] This potential has been fitted to the *ab initio* calculations of the band structure and total energies of diamond, graphite, and linear chain. Thanks to the inclusion of a many-body part in the repulsive part of the potential, it is able to reproduce very well the phase diagram of carbon even for the high-pressure phases of carbon (simple cubic, body-centered cubic, face-centered cubic). The TBMD method makes use of the TB potentials to calculate the ionic interactions in molecular-dynamics simulations. Due to the explicit inclusion of the electronic degrees of freedom in the calculation, it has been proved to have a reliability and transferability much higher than totally empirical potential and comparable to the *ab initio* simulations. TBMD is particularly efficient in performing structural relaxation or for studying structural transformations or simply to calculate phonons even in disordered systems. As a matter of fact we used TBMD to determine the liquid and amorphous carbon structure, finding good agreement with the experimental data of their structural properties. A detailed description of this potential and its performances concerning phonons, stability, and equilibrium properties of many different carbon politypes twofold-, threefold-, and fourfold-coordinated (always within few percent of the correspondent experimental or *ab initio* results) has been given elsewhere.[10] On the basis of these previous calculations we expect our potential be able to work well for the structural properties, stabilities, and phonons of carbon polytypes, in particular for threefold- and fourfold-coordinated networks even at high pressure.

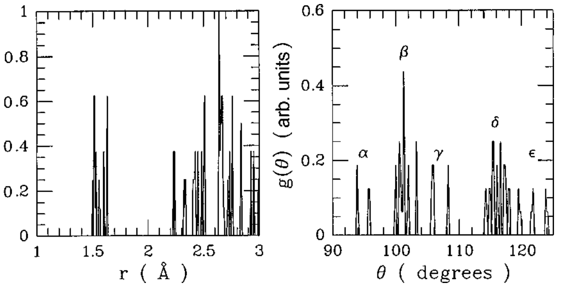

FIG. 3. Bond length distribution of tcl-16 (left panel) and bond angle distribution (right panel).

The computational scheme that we have adopted is the following: We first fix the cell parameters a and c/a and let the atoms freely relax to their ground state by a simulated annealing (SA) technique. Then, starting from these atomic positions, we slightly adjust the values of a and c/a and iterate the SA run. We have repeated this procedure for several unit cell parameters until the global minimum was found. In Fig. 3 we show the resulting bond length and bond angle distributions. As for the bc-8 structure,[1] tcl-16 does not display a perfectly tetrahedral site symmetry, albeit four coordinated. Owing to the low symmetry, the number of unequivalent bonds is quite large, resulting in a sensible spread of the bond length and bond angles.

These results have been checked and further refined by *ab initio* calculations in the local density approximation (LDA), using a state-of-the-art pseudopotential description of the electron-ion interaction. Besides we have adopted gradient corrections in the exchange and correlation functional, within the generalized gradient approximation (GGA),[15] which are known to have an important influence on the transition pressure.

All the calculations have been done with 32 points in the irreducible Brillouin zone of tcl-16 (125 for diamond) and with an energy cutoff of 40 Ry in the plane wave basis set.

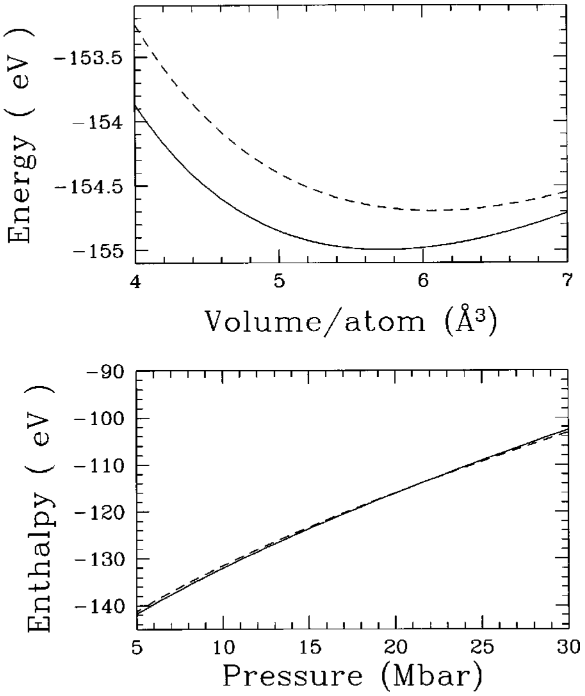

FIG. 4. *Ab initio* LDA results for total energy vs atomic volume (upper panel) and enthalpy vs pressure (lower panel) for tcl-16 and diamond (solid line).

This ensures good convergence in our calculations. The total-energy curve has been calculated for different volumes with a constant energy cutoff. For each volume we have minimized the ionic positions by a standard gradient-conjugated algorithm and found the strain-free configuration of the cell (no off-diagonal elements in the stress tensor).

We have obtained the most stable configuration having unit vectors of the crystal lattice a, b, and c equal to $(d,0,0)$, $(0,d,0)$, and (u,u,f), respectively, with $d=4.717$ Å, $f=4.6768$ Å, and $u=1.144$ Å. Actually, the TB calculations are within 2% of the LDA ones. The total energy versus volume was also obtained within the same tight-binding scheme, and the bulk modulus was calculated by fitting the total-energy curve by the Murnaghan equation of state.[16] Taking full advantage of the relatively low computational cost of the semiempirical TB scheme, we used a very high number of k points in the Brillouin zone (8000 points). The cohesive energy turns out to be only 0.23 eV above that of diamond against 0.3 eV for the bct-4 structure, while the LDA calculation gives 0.30 eV. Moreover, the bulk modulus is found to be 413 GPa by the TB scheme, and 408 GPa by the LDA, which represents, to our knowledge, the stiffest phase of carbon after the hexagonal (lonsdaleite) and cubic diamond forms.[17]

In order to confirm the conjecture that tcl-16 could be a metastable phase of carbon at low pressure ($<$ 1 Mbar), we have calculated the energy barrier for the reconversion of tcl-16 into graphiticlike planes. Following Fahy, Louie, and Cohen,[18] this is possible by only breaking one bond per atom by a progressive elongation of the c axis with a relaxation of the atomic positions. Along this path, which transforms tcl-16 into a graphiticlike structure with misoriented graphitic planes, we have found an energy barrier of 0.21 eV per atom. Looking to the topology of tcl-16 it seems likely that this is the path which transforms tcl-16 into a graphitic structure with the lowest-energy barrier. This result suggests that tcl-16 is a metastable phase of carbon at low pressure.

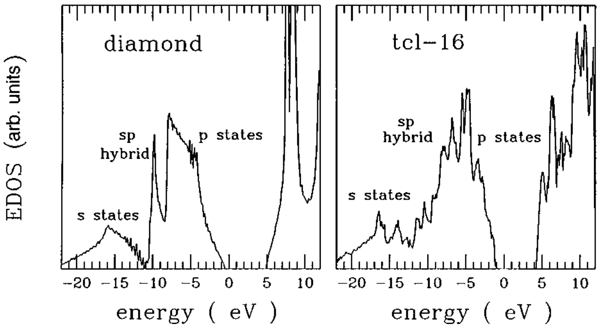

FIG. 5. Electronic density of states of diamond (left panel) and tcl-16 (right panel) in comparison.

In Fig. 4 we show the total energy and enthalpy versus atomic volume of tcl-16 and diamond. A remarkable feature is the high density of this new phase, slightly smaller than that of diamond and consistent with the high stability and bulk modulus. In particular, the smaller value of the bulk modulus with respect to diamond is due to the elongation of the bonds on the c axis of the unit cell, which produces an increase in the mean bond length and in turn a decrease in the density. Concerning this point, we recall that the bulk modulus B, as it has been shown by Cohen,[19] is inversely proportional to the bond length. Unfortunately this effect overcompensates the stiffening of the bonds induced by pentagons and yields an overall softening of the bulk modulus. From these data it has been possible to calculate the transition pressure from cubic to tcl-16 diamond, by simply finding the common tangent to their energy curves. We have found the value of 18 Mbar (12 Mbar with the TB scheme), which is in the expected range of pressure and comparable to the one for the diamond–bc-8 transition. This confirms that our tcl-16 is in competition with bc-8 and $R8$ in this range of pressure. Even if both bc-8 and $R8$ have a lower transition pressure for hydrostatic compression, tcl-16 may have a lower transition barrier in the uniaxial load case, being much more stable than bc-8 and $R8$ at lower pressure. Consequently it could be easier to obtain it with a transition in the uniaxial load case. Concerning this point, we want to point out that a compression along the (001) direction, as in the previously mentioned experiment of Mao and Hemley, may lead to a sliding of the (111) hexagonal planes, giving rise to a phase transformation compatible with the tcl-16 structure. Investigations along this direction are now in progress.

In Fig. 5 we show the electronic density of states (EDOS) of tcl-16 and diamond, along with the main character of the electronic states. It can be seen that the gap is only slightly increased (5.55 eV instead of 5.5 eV). The s band at lower energy is wider with respect to diamond while the p band becomes more localized, resulting in a lack of the sp hybrid peak, which is characteristic of diamond.

It is interesting to note that the tendency to become metallic by an increasing of pressure in fourfold-coordinated structures seems to be related to the presence of tetrahedral bonds in the eclipsed configuration. Indeed the fourfold-coordinated nets bc-8, hex-4 (lonsdaleite), and tcl-16 display this behavior, unlike diamond, which is the only fourfold-

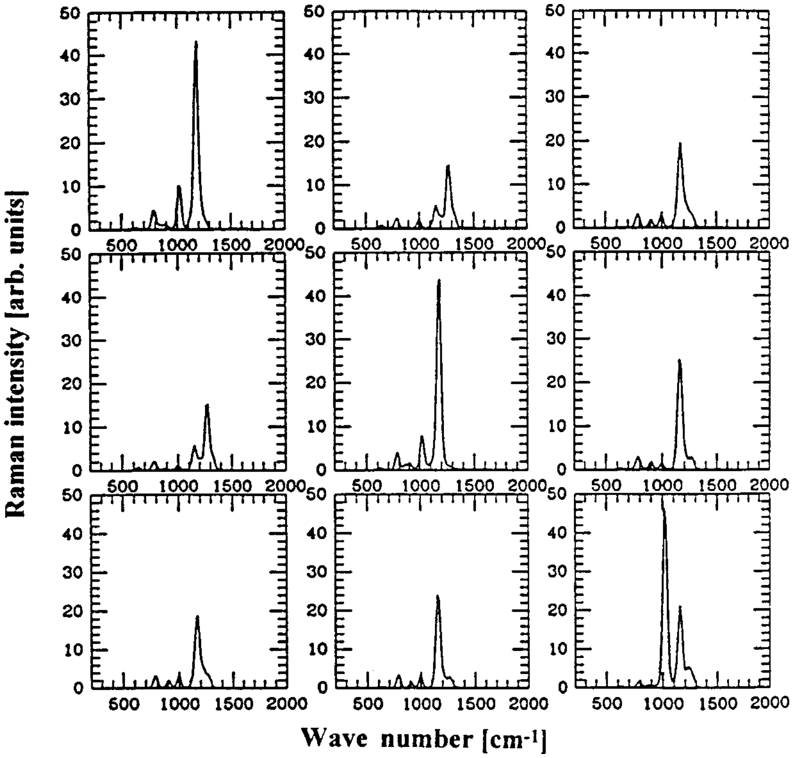

FIG. 6. Raman spectra of tcl-16 obtained from a TBMD simulation.

coordinated net with bonds only in the staggered configuration. This can be understood from simple geometric considerations, based on the fact that the eclipsed configuration increases the π coupling between second neighbors, resulting in a spectral broadening of antibonding states, which shrinks the gap.

It is our opinion that metallization of carbon proceeds first by partial reconversion of tetrahedral bonds from a staggered to eclipsed configuration. This can be achieved by sliding the hexagonal planes, possibly leading to bc-8, $R8$, or tcl-16: By increasing pressure, the presence of eclipsed bonds should favor the reconversion into the final simple cubic lattice. The latter mechanism is due to the fact that the eclipsed configuration promotes the closure of bonds between second neighbors, forming the squared rings of the simple cubic network. We believe that the negative results of Scandolo *et al.*[5] may be related to the relatively short period of time accessible by computer simulations, along with the stiffness of carbon bonds. As a matter of fact, it is clearly stated in that paper that bc-4 is only a metastable state of carbon at high pressures with higher enthalpy with respect to bc-8.

IV. CALCULATED RAMAN SPECTRA OF tcl-16

In order to characterize new phases which may occur in artificial diamondlike materials and thin films, it is very useful to know their vibrational spectra and in particular their Raman spectra. Comparison to the experimental data provides indications on the nature and structure of the observed samples.

We have calculated the Γ-point phonon density of tcl-16 by a TBMD calculation of the velocity correlations. The Raman spectra have been directly derived from MD simulations,[21] within the bond polarizability model due to Bermejo *et al.*[22] This model, thanks to the fine transferability of the bond polarizability parameters, is known to give good results for diamond and graphitelike materials, fullerenes included.[23] In Fig. 6 we show the theoretical Raman spectra of tcl-16 for the different components of the Raman tensor. The spectra are characterized by the presence of a strong anisotropy between the zz component and the xx and yy components, as given by the reversal in the intensity of the

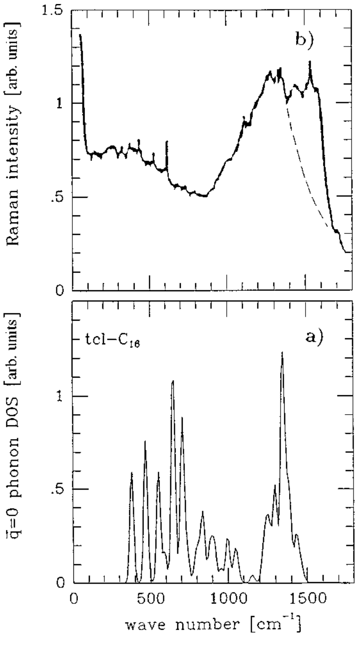

FIG. 7. Comparison between experimental Raman data (Ref. 24) (b) and vibrational spectrum obtained by a TBMD simulation (a).

two major peaks located at 1190 cm^{-1} and 1020 cm^{-1}, respectively. For comparison, diamond displays only one peak at 1330 cm^{-1}, the higher value of the frequency reflecting the higher value of the bulk modulus. Such a change in the Raman tensor components from the c axis to the xy plane is structurally consistent with the fact that bonds along the z axes are longer (and weaker) than those of the xy plane.

In Fig. 7(a) we report the total zone-center phonon density as obtained from MD simulations. This includes, besides Raman-active modes, also infrared-active and silent modes belonging to various irreducible representation of the crystal point group. In the next section we discuss these results in the light of recent Raman scattering data collected for crystalline carbon materials and intermediate phases which occur during the growth process of diamondlike films.

V. CONCLUSION

The relatively high stability of tcl-16, which is comparable to $R8$, bc-8, and st-12 phases, suggests it as a possible intermediate phase in the transformation from sp^2 to sp^3 carbon networks and that it can be competitive with other well-known sp^3 crystalline forms. We have given some qualitative and quantitative arguments along this line, in particular for the transformation from bct-4 to tcl-16. This conversion to tcl-16 seems to be easier than to diamond itself, due to the structural affinity between bct-4 and tcl-16. Moreover, in the polymerization of C_{60} fullerites under pressure,[20] the presence of five-membered rings is believed to be important for the transformation into diamondlike forms, by incorporating pentagonal rings in a tridimensional structure. Thus, tcl-16 could be favored with respect to diamond, londsdaleite, or bc-8 sp^3 networks, which are constituted only of hexagons. These phases should have a higher-energy barrier for their transformation, needing complicated bond-breaking and rebonding mechanisms, which is certainly difficult at the comparatively low temperatures (700–900 K) used, e.g., in the experiments of Kozlov *et al.*[20]

As a matter of fact, in another work, Kozlov *et al.*[24] have found the presence of a *noncubic (*or *hexagonal)* phase of diamond in diamond films produced by laser ablation of fullerite compressed at 2.6 GPa at the temperature of 700 K.

Unfortunately the samples are not yet good enough to allow for a realistic comparison between these different sets of experimental data and our spectra. In Fig. 7(b) we show the measured Raman spectrum for the above phase. The high-frequency part of the Raman spectra (around 1500 cm^{-1}) is probably due to graphitic regions included in the diamondlike samples, and it is obviously absent in the theoretical spectra. Moreover, the low-frequency structure below 400 cm^{-1}, not predicted in the theory as well, has also an extrinsic origin and can be attributed to impurities. Still, there is no acceptable correspondence of the experimental Raman spectrum with the calculated ones, whereas some general feature of the total phonon spectrum show some similarity with the experiment [Figs. 7(a) and 7(b)]. Thus we can argue that at present no evidence for tcl-16 has been found despite its intriguing position in the phase diagram of carbon. If any such form occurs as microcrystals in the samples of Kozlov *et al.*, they should be heavily perturbed by defects and impurities.

In conclusion, we predict a triclinic form of diamond which displays interesting properties, such as a high stiffness comparable with that of diamond and a high stability even at low pressure. This may indicate the possibility of a new (intermediate or final) phase in the growth of diamond films or in the transformation of fullerite. Our calculations show that it could be a stable phase of carbon at medium-range pressure; in particular, it displays interesting properties for the uniaxial load case. In this perspective this phase is even more interesting than the extensively studied bc-8 phase.

ACKNOWLEDGMENT

This work was partially supported by INFM in the framework of the Advanced Research Project PRA97 ‘‘CLASS.’’

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*Permanent address: International School for Advanced Studies, via Beirut 4 I-34014 Trieste, Italy, and Istituto Nazionale per la Fisica della Materia (INFM)

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