Crystal Structure of Cold Compressed Graphite

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Through a systematic structural search we found an allotrope of carbon with *Cmmm* symmetry which we predict to be more stable than graphite for pressures above 10 GPa. This material, which we refer to as *Z*-carbon, is formed by pure sp^3 bonds and it provides an explanation to several features in experimental x-ray diffraction and Raman spectra of graphite under pressure. The transition from graphite to *Z*-carbon can occur through simple sliding and buckling of graphene sheets. Our calculations predict that *Z*-carbon is a transparent wide band-gap semiconductor with a hardness comparable to diamond.

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Thanks to the flexibility to form sp, sp^2, and sp^3 bonds, carbon is one of the most versatile chemical elements. At ambient pressure, it is usually found as graphite (the most stable structure) or as diamond, but the richness of its phase diagram does not end there. In fact, many other structures have been proposed during the past years, especially since experimental data suggested the existence of a super hard phase of carbon. Evidences for a structural phase transition in compressed graphite to this unknown phase of carbon have been reported in numerous experiments [1–7]. In fact, in the range of 10 to 25 GPa one observes an increase of the resistivity [1] and of the optical transmittance [2,3], a marked decrease of the optical reflectivity [4], changes in near *k*-edge spectra [7] and in x-ray diffraction (XRD) patterns [5–7]. Several hypothetical structures have been proposed to explain these features, such as hybrid sp^2-sp^3 diamond-graphite structures [8], *M*-carbon [9], bct-C_4-carbon [10], and *W*-carbon [11]. However, none of these structures is able to match all experimental data in an unambiguous and fully satisfactory manner.

A common way to search for new crystal structures is to perform a systematic survey of the enthalpy surface using some sophisticated structure prediction method (for discussion on such methods see Ref. [12]). Here we use the minima hopping method [13] (MHM) for crystal structure prediction [14], which was designed to explore low-enthalpy phases of materials. This method was coupled to the all-electron projector-augmented wave method as implemented in the ABINIT code [15,16]. Within the MHM, the system is moved from one configuration to the next by performing consecutive molecular dynamics escape steps and geometry relaxations. The initial velocities for the dynamics are aligned preferably along soft-mode directions in order to favor the escape to low-enthalpy structures. Revisiting already known structures is avoided by a feedback mechanism. Relaxations are performed by the fast inertia relaxation engine [17]. The local density approximation was employed based on its good description of graphite. However, the enthalpy ordering was reconfirmed within the generalized gradient approximation using two different functionals (PBE [18] and PBEsol [19]). The most promising candidate structures were then rerelaxed using norm conserving Hartwigsen-Goedecker-Hutter pseudopotentials [20]. Carefully converged Mankhorst-Pack *k*-point meshes were used together with a plane wave cutoff energy of 2100 eV. All calculations were performed at zero Kelvin, and we neglected the contribution of the zero-point motion of the nuclei to the enthalpy.

The MHM was employed using simulation cells with 4 and 8 carbon atoms at a constant pressure of 15 GPa. We found, in addition to previously proposed structures of cold-compressed graphite, a carbon phase that we call *Z*-carbon. This structure has *Cmmm* symmetry [see Fig. 1(a)] and, like diamond, is composed of sp^3 bonds. The conventional unit cell has 16 atoms with cell parameters at 0 GPa of $a = 8.668$ Å, $b = 4.207$ Å, and $c = 2.486$ Å, yielding a cell volume of $V_0 = 90.7$ Å^3. The two inequivalent carbon atoms occupy the 8*p* and 8*q* crystallographic sites with coordinates (1/3, *y*, 0) and (0.089, *y*, 1/2), where $y = 0.315$. The structure contains four-, six- and eight-membered rings, where planar four-membered rings and nonplanar eight-membered rings join together buckled graphene sheets. This structure can be interpreted as a combination of hexagonal diamond and bct-C_4-carbon [21].

In contrast to other structure prediction methods like evolutionary algorithms or random search, the efficient escape moves in the MHM are based on fundamental physical processes. Therefore, minima found consecutively during a MHM simulation are usually connected

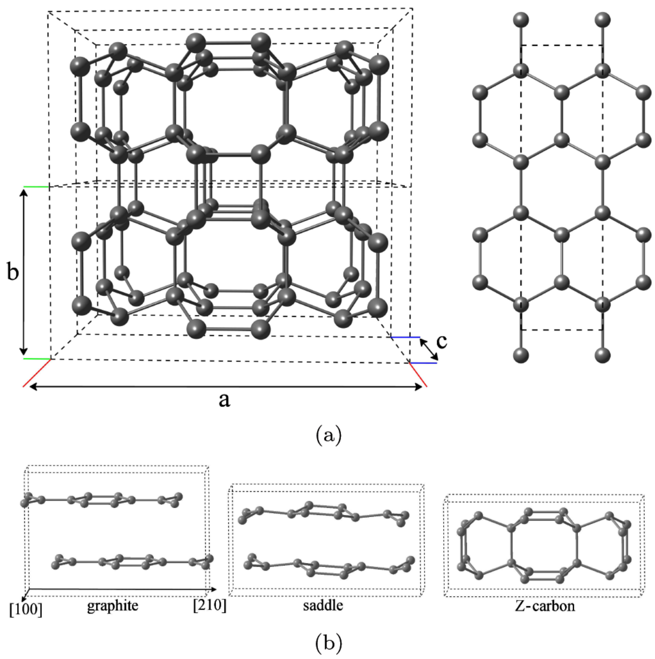

FIG. 1 (color online). (a) Structure of *Z*-carbon viewed from two different angles revealing planar four-membered and non-planar eight-membered rings forming chains along the *b* direction and channels in the *c* direction. The graphene sheets are in the *a*-*c* plane. (b) Proposed transition pathway from graphite to *Z*-carbon.

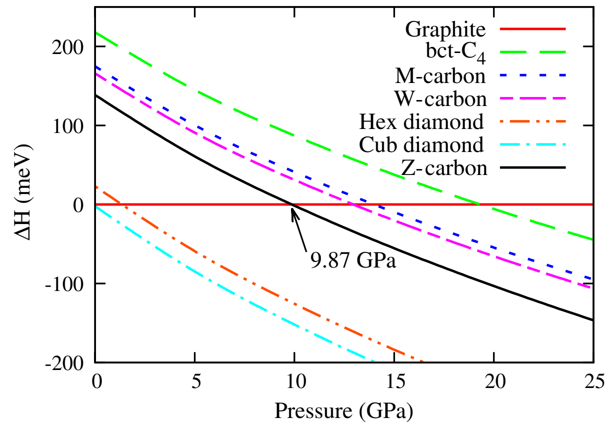

FIG. 2 (color online). Calculated enthalpy difference per atom with respect to graphite of several carbon allotropes as a function of pressure. Graphite is the horizontal line at zero. *Z*-carbon becomes more stable than graphite at around 10 GPa.

through low-enthalpy barriers. Since we have observed escape moves to and from *Z*-carbon to occur exclusively from and to graphite, we expect this transition to be the most probable. In Fig. 1(b) we show a possible transition pathway from graphite to *Z*-carbon. This process is a combination of sliding and buckling of the graphene sheets. The naturally staggered, i.e. *AB* stacked, graphene sheets slide along the [210] direction to an aligned *AA* stacking while the interlayer distance decreases, and the aligned graphene sheets deform to create an alternating armchair-zigzag buckling.

In order to investigate the relative stability of *Z*-carbon, the calculated enthalpy difference with respect to graphite of several allotropes are compared in Fig. 2 as a function of pressure. *Z*-carbon has the lowest enthalpy among all proposed cold-compressed graphite phases, becoming more stable than graphite at 9.9 GPa (around 2.5 GPa below *W*-carbon).

We further investigated the dynamical lattice stability of this phase by computing the phonon dispersion in the whole Brillouin zone. We used linear-response theory in the framework of density functional perturbation theory [22] with the ABINIT code. A proper convergence was ensured with a $12 \times 12 \times 12$ k-point sampling, a $4 \times 4 \times 4$ q-point mesh, and a cutoff energy of 800 eV. All phonon modes were real confirming the structural stability of *Z*-carbon. Furthermore, from a fit of the Murnaghan equation we obtained a bulk modulus of $B_0 = 441.5$ GPa, and using the method proposed by Gao *et al.* [23] we calculated a Vicker's hardness of $H_v = 95.4$ GPa. Both bulk modulus and hardness are extremely high and very close to the values for diamond ($B_0^{\mathrm{diamond}} = 463.0$ GPa and $H_v^{\mathrm{diamond}} = 97.8$ GPa), which is compatible with the observed ring cracks in diamond anvil cells [7].

To investigate the energy gap of this material we used the perturbative many-body *GW* technique starting from the local density approximation [24]. These calculations reveal that *Z*-carbon is an indirect band-gap material with a gap of around 4.7 eV. Therefore, this material is expected to be optically transparent in agreement with experiments [2,3].

We have gathered several experimental observations supporting our interpretation that *Z*-carbon is present in cold-compressed graphite samples. The first comes from the XRD experiment of Ref. [7]. In Fig. 3 we can see that the broadening of the XRD spectra at high pressure can be explained by the coexistence of graphite and *Z*-carbon. However, the experimental curve can also be explained to some extent by the other proposed carbon allotropes [9–11] so that this experiment alone is not conclusive.

Other signatures for *Z*-carbon can be gathered from our measurements of Raman spectroscopy under pressure. These experiments were carried out at 300 K using the 514.5 nm line excitation of an Ar^+ laser, and a Jobin-Yvon HR-800 Labram spectrometer with double-notch filtering with resolution better than 2 cm^{-1}. In the high pressure Raman measurements, we used a diamond anvil cell to apply pressure on two different samples (single crystals of graphite and highly oriented pyrolitic graphite), inside a 120 μm hole drilled in an iconel gasket. Argon and paraffin was used as the pressure medium. The pressure was determined by the ruby luminescence of a small chip (< 30 μm). The laser was focused down to 3 μm with a power of about 20 mW on the sample.

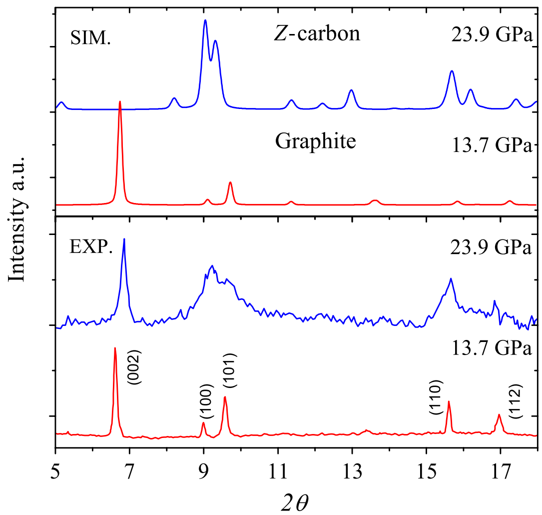

FIG. 3 (color online). Experimental XRD for cold-compressed graphite at two different pressures from Ref. [7] and simulated XRD pattern for Z-carbon (at 23.9 GPa) and graphite (at 13.7 GPa). The main characteristics of the proposed carbon are perfectly in agreement with the experimentally observed changes.

The principal Raman active mode of graphite is the G band at 1579 cm^{-1} (at 0 GPa) which originates from the sp^2 carbon atoms vibrating in-plane with E_{2g} symmetry. The effect of hydrostatic pressure on the linewidth of the G band is shown in Fig. 4. The linewidth remains nearly constant until around 9–10 GPa. Above this value, the linewidth begins to broaden rapidly, in agreement with previous results of Hanfland *et al.* [3]. (A similar broadening has also been reported for turbostratic graphitelike BC_4 under pressure [25].) This behavior is a sign of a structural transformation at this pressure, and can be explained by important changes in the Raman cross section caused by interlayer coupling and the formation of sp^3 bonds. As seen in Fig. 2, Z-carbon becomes enthalpically favored with respect to graphite at around 10 GPa, whereas all other proposed structures cross the graphite line at significantly higher pressures.

There is a further indication of the existence of Z-carbon that can be found in the Raman spectrum of graphite under hydrostatic pressure, shown in Fig. 5 for the energy range below the 1st order Raman peak of diamond (1332 cm^1 at 0 GPa) [26]. Neither graphite nor cubic diamond have Raman active peaks in the selected energy region, however we can observe that a clear peak appears at 1082 cm^{-1} for pressures higher than 9.8 GPa. This peak cannot be explained by either bct-C4-carbon, M-carbon, or by the pressure medium (argon). Experiments at ambient pressure have shown that a raman peak at 1090 cm^{-1} can be observed in samples of nanocrystalline diamond [27]. Furthermore, the presence of nanodiamond in our sample might be enthalpically possible. However, since nanodiamond has been shown to be stable in high pressure

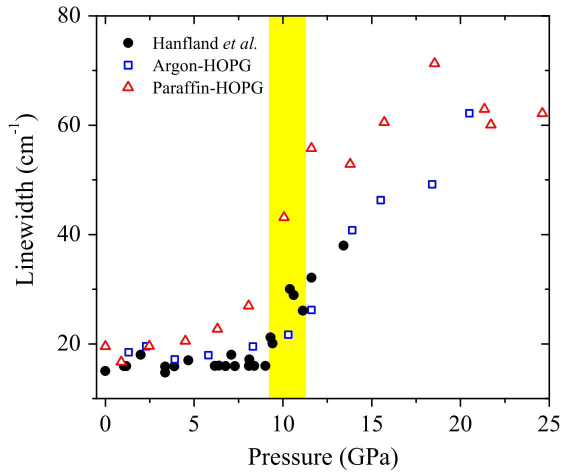

FIG. 4 (color online). Experimental linewidth of the G band of graphite under pressure. The linewidth stays nearly constant until pressures of the order of 9–10 GPa, above which the linewidth begins to broaden rapidly. This is a strong evidence for a structural transition in graphite. Experiments were conducted using highly oriented pyrophillitic graphite (HOPG) and argon (squares) or paraffin oil (triangles) as pressure transmitting media. Note that the G band broadening is fully reversible under pressure unload. The unload points are however not included for clarity. The black dots are taken from Ref. [3].

synthesis [28] and the observed G band broadening is fully reversible under pressure unload this possibility can be ruled out. Therefore, the only structures that have Raman active modes compatible with this experimental results are Z-carbon and W-carbon. For Z-carbon the frequencies are 1096.5 cm^{-1} at 10 GPa and 1110 cm^{-1} at 15 GPa. Incidentally, Z-carbon also has a Raman active A_g mode at 1348.5 cm^{-1} at 0 GPa (theoretical value). This appears as a signature of planar four-membered rings that overlaps

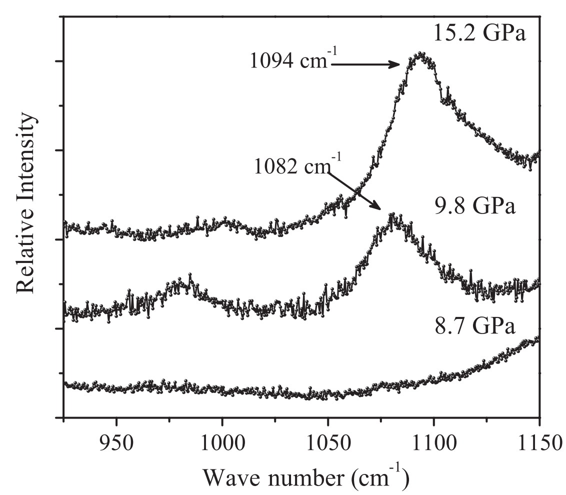

FIG. 5. Experimental Raman spectra of graphite under pressure. The peak around 1082 cm^{-1} appearing at around 10 GPa and its evolution can be explained by either Z-carbon, W-carbon, or nanocrystalline diamond.

with the so-called defect D band of graphite at around 1345.5 cm^{-1} at 0 GPa (experimental value).

In conclusion, we identified an allotropic structure of carbon, Z-carbon, that becomes more stable than graphite above 10 GPa. From all known carbon allotropes, only cubic and hexagonal diamond have lower enthalpy at high pressures. The Z-carbon structure is as hard as diamond, and is transparent in the optical region. Moreover, several experimental data are consistent with the presence of Z-carbon in samples of cold-compressed graphite: first, the features of the x-ray diffraction spectra of graphite under pressure exhibit a broadening that matches the main peaks of Z-carbon. Second, the principal Raman signal of graphite, the G band mode, suffers an abrupt increase of the linewidth above 9–10 GPa—the pressure range where Z-carbon becomes more stable than graphite. Third, a new peak at 1082 cm^{-1} appears in the Raman spectrum of graphite at around 10 GPa, at the frequency of a Raman active mode of Z-carbon. However, further comparative studies on the formation barriers of all proposed candidate structures might be needed for a conclusive determination of the structure of cold-compressed graphite.

Our work also highlights the promising prospects of the minima hopping method for crystal structure prediction [14]. The exploration of the structural variety of even simple elements such as carbon was up to now typically the subject of many different studies which were presented in numerous papers over many years. In this first application of the MHM we were able to find not only Z-carbon, but also all other known carbon phases at the given pressure condition fully automatically. We can therefore expect that this method can also find with high reliability the low energy structures of many other materials for which our knowledge is at present still rudimentary, leading to important advances in the field of solid state physics.

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