

Mechanical properties of graphite oxides: *Ab initio* simulations and continuum theoryAndrei Incze,¹ Alain Pasturel,¹ and Philippe Peyla^{1,2}¹*Laboratoire de Physique et de Modélisation des Milieux Condensés, UJF, CNRS, Maison des Magistères, Boîte Postale 166, 38042 Grenoble Cedex 9, France*²*Laboratoire de Spectrométrie Physique, UJF, CNRS, Saint-Martin d'Hères 38402 Cedex, France*

(Received 10 May 2004; published 30 December 2004)

The mechanical properties of oxidized graphitic layers are calculated by atomic *ab initio* simulations and continuum theory of elasticity. The adsorption of atomic oxygen atoms induces a nanocorrugation as well as a local bonding reinforcement that modify the bending coefficient of a graphite layer. As a matter of fact, a surface oxygen composition of 12.5% leads to an increase of the rigidity coefficient by more than a factor of 40. We thus demonstrate that oxidation also has a considerable impact on the mechanical properties of graphite structures.

DOI: 10.1103/PhysRevB.70.212103

PACS number(s): 73.22.-f, 46.70.-p, 68.60.-p

INTRODUCTION

In recent years, the physical and chemical properties of graphite oxide (GO) have been studied in great detail, both theoretically and experimentally. One of the most important characteristics of GO is its high faradaic capacity in lithium cell systems^{1,2} in which it has been demonstrated that this material has remarkable swelling properties as a layered host for Li intercalation. GO is also used in multilayer electronically conducting films,³ in encapsulation of metallic and ferromagnetic nanoparticles,^{4,5} and in tethered membranes.⁶ Graphite oxide fibers have been obtained⁷ and used in reinforcement of plastics. GO, also known as graphitic acid, has been used for over a century in very different fields. However, relatively little has been reported regarding the mechanical properties of GO structures despite their increasing use in composite materials.

There are different ways of GO preparation, all involving treating graphite with strong oxidizing agents.⁶ Thus a wide variety of composition can be obtained making the structure analysis very difficult. However, Phaner-Goutorbe *et al.*⁸ have shown with x-ray photoelectron spectroscopy and scanning tunneling microscope experiments that a soft oxidation of a highly oriented pyrolytic graphite sample can give rise to a very reproducible nano-organization of adsorbed oxygen atoms with the occurrence of epoxy bonds. The presence of epoxy groups was also proposed by Lerf *et al.*⁹ and by Heyong *et al.*¹⁰ In the following, we use this picture to modelize a generic GO and to study its mechanical properties.

In this Brief Report, we show that the presence of atomic oxygen atoms chemisorbed on a graphite basal plane surface can change the mechanical properties of the carbon atomic planes drastically. The elastic bending coefficient D is enhanced by more than a factor of 40 for only an oxygen concentration of 12.5%. In the following, we show that this rigidification is due to a nanostructuring of the basal plane surface induced by oxygen atoms. Results are obtained by coupling *ab initio* calculations with the continuum elasticity theory.

AB INITIO CALCULATIONS

Calculations were performed using the *ab-initio* total energy and molecular dynamics program VASP (Vienna *Ab initio* Simulation Package).^{11,12} Ultrasoft Vanderbilt pseudopotentials^{11,13} were used to approximate the electron-ion interactions. A cutoff energy of 270 eV was used for carbon and oxygen. The generalized gradient approximation was used to allow for exchange and correlation in the Perdew-Wang form.¹⁴ We model a graphite surface by introducing a supercell of (8×9) graphitic sheet with periodic boundary conditions applied along the planar directions to simulate an infinite graphitic layer. The surface is simulated by periodically repeated slabs of a graphitic monolayer parallel to it with a vacuum region of 9 Å. The equilibrium C-C distance has been found to be equal to 1.42 Å. This slab contains 288 carbon atoms with oxygen atoms located on one side of the surface or on both sides. The number of oxygen atoms varies from 12 (4.16%) to 36 (12.5%). Each oxygen is located in the bridge position (epoxy bonds) which is known to be the most stable site.¹⁵ For each composition, the oxygen sites were constrained to be as far as possible from each other to avoid any chemical interactions between O adatoms. No symmetry was imposed to build the oxygen network. For each concentration, total energy calculations were performed by using one k point at the Γ point.

Relaxation of the whole structure leads to a corrugation of the hexagonal basal plane (Fig. 1). However, the hexagonal symmetry is preserved and no topological defects are revealed. Let us mention that a folding of the graphite planes by oxygen atoms was suggested by Riley in 1945 and Clauss *et al.*¹⁶ in 1957 from geometrical considerations about chemical bonds involved in GO. However, this folding has never been measured nor calculated. This configuration represents our reference state. This GO structure is deformed in order to obtain its mechanical properties. A displacement along the z axis [perpendicular to the basal (x, y) plane] is imposed on each atom

$$\zeta = \zeta_0 \cos(2\pi x/L_x), \quad (1)$$

where L_x and L_y are the lateral dimensions of the periodic structure. This deformation bends the structure by creating

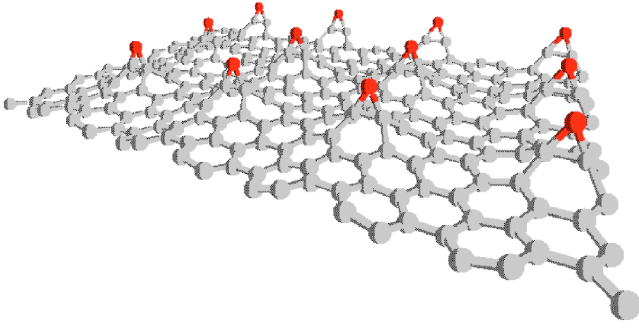


FIG. 1. Graphite basal plane in presence of adsorbed oxygen atoms (epoxy groups). A nanocorrugation of the atomic plane is created (gray represents carbon, dark gray represents oxygen). The out-of-plane atomic displacements have been magnified by a factor of 7 in order to visualize the corrugation.

curvature. It also extends the structure by increasing the interatomic distances. Calculations are carried out with different values of the amplitude ζ_0 of the displacement ranging from 0 to 1.8 Å. The biggest value of ζ_0 has been carefully chosen in order to preserve the harmonicity of each interatomic potential, i.e. only elastic effects are considered here. Let us mention that in the deformed states, the C-O bond lengths have been kept equal to those found in the reference state. For the oxygen composition of 4.16% and for $\zeta_0=1.8$ Å, a local relaxation related to o atom displacements has been performed. We have checked that such displacements are indeed negligible, which confirms the above assumption. The variation of the total energy ΔE_{ab} (*ab* means *ab initio*) for each value of ζ_0 has been plotted in Fig. 2 for both a pure graphite sheet and a GO plane with a 4.15% oxygen concentration; $\zeta_0=0$ is the reference state.

We have calculated ΔE_{ab} for different oxygen concentrations. Our results, displayed in Fig. 3 for $\zeta_0=1.8$ Å, show that the energetic cost of the deformation Eq. (1) increases drastically with oxygen concentration.

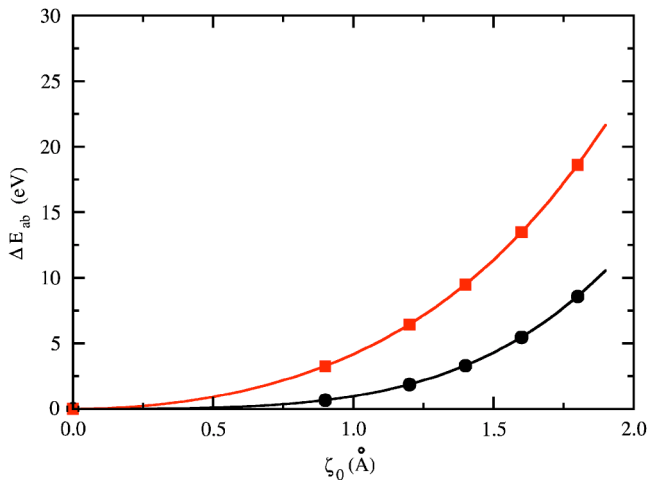


FIG. 2. Variation of ΔE_{ab} with respect to the deformation amplitude ζ_0 given by Eq. (1) for a pure graphite plane (circles) and for the GO structure (squares) represented in Fig. 1 (4.15% of oxygen concentration). A perfect agreement is found by fitting the *ab initio* results with Expression (3) of our continuum model (see below).

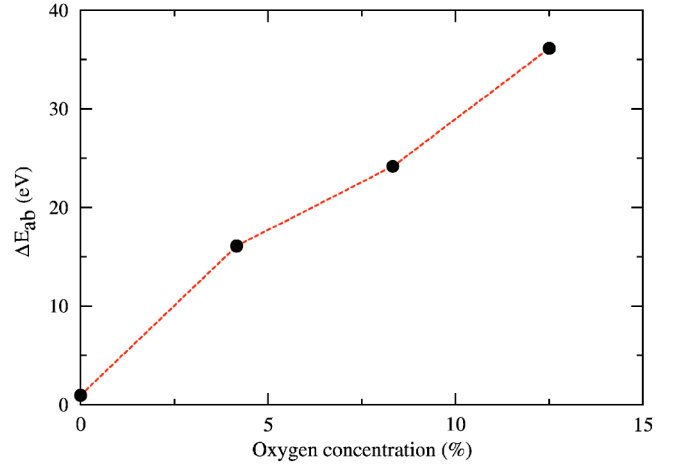


FIG. 3. Variation of the elastic energy ΔE_{ab} created by displacing each atom according to Eq. (1) with $\zeta_0=1.8$ Å for different oxygen concentrations.

In order to get further insights into the strong modification of mechanical properties of this GO structure we will consider a continuum elastic model of a thin elastic plate that is strained with a displacement given by Eq. (1).

CONTINUUM MODEL

Let us consider a thin elastic flat plate parallel to a (x, y) plane with lateral dimensions L_x and L_y . If this plate is deformed according to the displacement given by Eq. (1), we call κ its curvature and ϵ_{xx} the in-plane deformation. For small values of the deformation amplitude ζ_0 , $\kappa \approx d^2\zeta/dx^2$, and $\epsilon_{xx} \approx (d\zeta/dx)^2$. The elastic energy density (energy per unit surface) is¹⁷

$$\mathcal{E} = \frac{1}{2}D\kappa^2 + \frac{1}{2}\Lambda\epsilon_{xx}^2, \quad (2)$$

where D is the elastic bending coefficient and Λ is the elastic extension coefficient of the plate. The first and the second term are usually denominated as the bending and the membrane term, respectively. Using Eq. (1) and integrating expression (2) on the whole surface, we get the total variation of elastic energy of the deformed plate (the reference state is the one for which $\zeta=0$)

$$\Delta E_c = 4\pi^4 \frac{L_y}{L_x^3} D \zeta_0^2 + 6\pi^4 \frac{L_y}{L_x^3} \Lambda \zeta_0^4. \quad (3)$$

Within this expression of ΔE_c (c meaning “continuum”), the cost in bending energy (curvature) is proportional to ζ_0^2 while the extensional energy is proportional to ζ_0^4 .

For each concentration of oxygen, we fit the *ab initio* energy ΔE_{ab} as a function of the amplitude ζ_0 with expression (3) of ΔE_c . In Fig. 2, we show the variation of ΔE_{ab} for the 4.16% oxygen GO as well as for the pure graphite layer. An excellent fit is obtained from which precise values of D and Λ coefficients are obtained for the different oxygen concentrations. In Fig. 4, we see that the elastic extension coefficient Λ is not affected by the presence of oxygen atoms while the elastic flexion coefficient D is drastically modified.

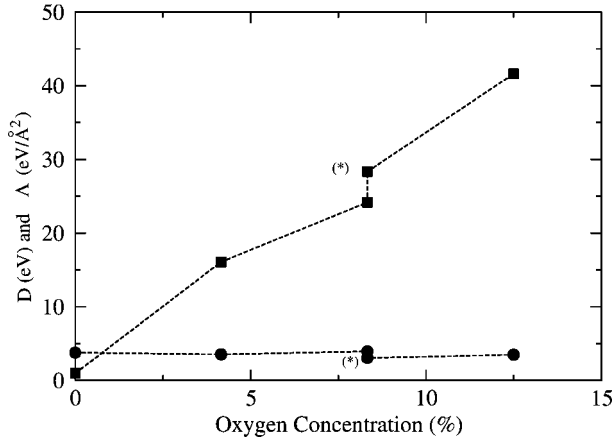


FIG. 4. Variation of the bending coefficient D (squares) and the extension coefficient Λ (circles) with respect to the oxygen concentration. Lines are just guides to the eye. The two points at the same 8.33% concentration represent two configurations of adsorbed oxygens, namely on one side or on the two sides (marked by a star) of the graphite plane.

We note that an oxygen concentration of 12.5% leads to an increase of the flexion coefficient by more than a factor of 40. We also report D and Λ values for two different oxygen configurations at 8.33%. Our results emphasize that D is mainly affected by the oxygen concentration. A value of $D=0.9$ eV is obtained for pure graphene, in very good agreement with a previous estimation.¹⁸

ORIGIN OF THE RIGIDIFICATION

We now study the effects of the rigidification in more detail. As shown below, the surface oxidation gives rise to two different effects that contribute to the enhancement of rigidity. First, each oxygen atom waves the whole carbon plane (it is a long range elastic effect.¹⁹) Thus, the carbon plane is nanostructured (corrugated) at atomic scale by oxidation (Fig. 1). This “corrugated cart board effect” increases the bending coefficient. Second; each epoxy bond rigidifies the C-C bond locally. Thus, the latter effect tends to also increase the bending coefficient. The first mentioned contribution to the bending rigidification is a global effect while the second one is a local effect. We call D_G (global) and D_L (local) the two contributions to the bending coefficient: $D=D_G+D_L$. In order to evaluate the global contribution, the oxygen atoms are eliminated, but the corrugation created by them is kept. Thus, for each oxygen concentration, we get a corresponding free-oxygen corrugated graphite plane (FOCG). Each FOCG is characterized by its corrugation $Z(x,y)$. By using the same procedure as before, each FOCG is deformed by imposing the displacement given by Eq. (1) and we calculate the corresponding elastic bending coefficient, i.e., D_G . As the corrugation is a global effect, we develop D_G as a function of the first moments of the height distribution

$$D_G = a\langle Z \rangle + b\langle Z^2 \rangle + c\langle Z^3 \rangle, \quad (4)$$

with

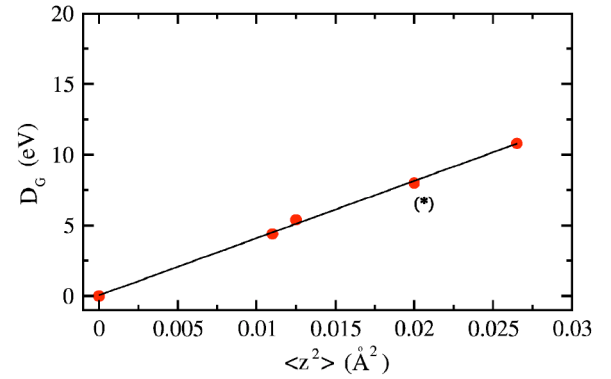


FIG. 5. The corrugation of the graphite plane by oxygen atoms contributes to the bending coefficient enhancement. Each second moment corresponds to a corrugation created by a given oxygen concentration. The line is a guide to the eye. The star indicates the configuration where oxygen atoms are adsorbed on both faces of the graphite plane.

$$\langle Z^n \rangle = \frac{1}{L_x L_y} \int_{L_x} \int_{L_y} Z^n dx dy. \quad (5)$$

As the symmetry $Z \rightarrow -Z$ does not affect the elastic properties of the structure, odd moments do not affect D_G . Thus, we can conclude that at the lowest order, D_G is a linear function of $\langle Z^2 \rangle$. The plot of D_G in Fig. 5 confirms such a behavior.

Now it is easy to obtain the local contribution to the bending coefficient, i.e., D_L which is given by $D_L = D - D_G$. As this effect is local (each oxygen contributes to locally rigidify the GO structure) D_L should vary linearly with the oxygen concentration. Indeed, Fig. 6 reveals such a linear dependence of D_L .

We note that the oxygen configuration (either oxygen atoms on one side or on both sides) at 8.33% does not affect D_L . As a matter of fact, C-C bonds are rigidified in flexion independently of the side of the oxygen adsorption (except if

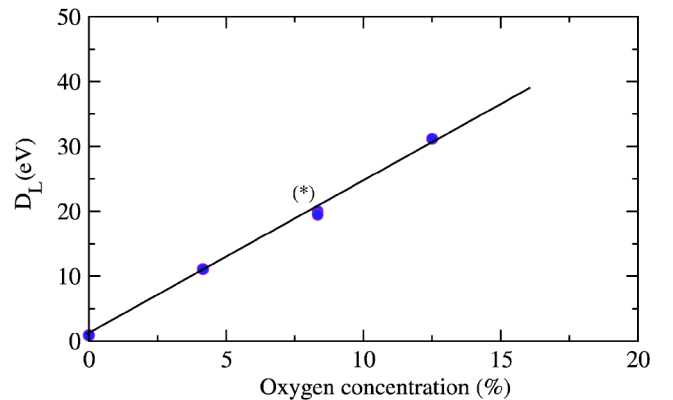


FIG. 6. Bending coefficient D_L due to the local rigidification of C-C bonds by an oxygen atom in each epoxy group. Due to that local aspect the associated bending coefficient varies linearly with respect to the oxygen concentration. The line is a guide to the eye. The star indicates the configuration where oxygen atoms are adsorbed on both faces of the graphite plane.

two oxygens were placed in front of each other on each side of the plane, which is not the case here).

CONCLUSION

In this paper we have shown that the presence of oxygen adatoms can significantly modify the mechanical behavior of graphitic systems. Atomic oxygens induce both a nanocorrugation and a local bonding reinforcement that increases drastically the bending coefficient of the graphite plane. Moreover, our study which combines *ab initio* calculations and the continuum theory of elasticity allows us to extract relevant macroscopic mechanical coefficients (bending and extension coefficients) that could be used in experiments on such materials. We speculate that such a rigidification could help in composite reinforcement.

gation and a local bonding reinforcement that increases drastically the bending coefficient of the graphite plane. Moreover, our study which combines *ab initio* calculations and the continuum theory of elasticity allows us to extract relevant macroscopic mechanical coefficients (bending and extension coefficients) that could be used in experiments on such materials. We speculate that such a rigidification could help in composite reinforcement.

-
- ¹P. Touzain and R. Yazami, *J. Power Sources* **14**, 99 (1985).
²R. Zhang, J. Y. Lee, and Z. L. Liu, *J. Power Sources* **112**, 596 (2002).
³N. I. Kovtyukova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva, and A. D. Gorchinsky, *Chem. Mater.* **11**, 771 (1999).
⁴T. Cassagneau, J. Fendler, S. A. Johnson, and T. E. Mallouk, *Adv. Mater. (Weinheim, Ger.)* **12**, 1363 (2000).
⁵T. Cassagneau and J. Fendler, *J. Phys. Chem. B* **103**, 1789 (1999).
⁶T. Hwa, E. Kokufuta, and T. Tanaka, *Phys. Rev. A* **44**, R2235 (1991).
⁷K. Leong, W. C. Forsman, and F. L. Vogel, *Mater. Sci. Eng.* **64**, 149 (1984).
⁸M. Phaner-Goutorbe, A. Sartre, and L. Porte, *Microsc. Microanal. Microstruct.* **5**, 283 (1994).
⁹A. Lerf, H. He, M. Forster, and J. Klinowski, *J. Phys. Chem. B* **102**, 4477 (1998).
¹⁰H. Heyong, J. Klinowski, M. Forster, and A. Lerf, *Chem. Phys. Lett.* **287**, 53 (1998).
¹¹G. Kresse and J. Furthmüller, *Comput. Mater. Sci.* **6**, 5 (1996).
¹²G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11 169 (1996).
¹³D. Vanderbilt, *Phys. Rev. B* **41**, 7892 (1990).
¹⁴P. Perdew and Y. Wang, *Phys. Rev. B* **33**, 8800 (1986).
¹⁵A. Incze, A. Pasturel, and C. Chatillon, *Appl. Surf. Sci.* **177**, 226 (2001).
¹⁶G. L. Riley, *Fuel* **24**, 43 (1945); A. Clauss, R. Plass, H. P. Boehm, and U. Hofmann, *Z. Anorg. Allg. Chem.* **291**, 205 (1957).
¹⁷L. D. Landau and E. Lifchitz, *Theory of Elasticity* (Mir, Moscow, (1991).
¹⁸B. I. Yakobson, C. J. Brabec, and J. Bernholc, *Phys. Rev. Lett.* **76**, 2511 (1996).
¹⁹A. Incze, A. Pasturel, and P. Peyla, *Phys. Rev. B* **66**, 172101 (2002).