Theoretical study of graphite intercalated with water cyclic hexamers

R.M. Torres-Rojas[*], R. Baquero

Departamento de Física, Cinvestav, Instituto Politécnico Nacional 2508, San Pedro Zacatenco, 07360, Gustavo A. Madero, Ciudad de México, Mexico

A B S T R A C T

Water-treated graphite has attracted attention as a possible room-temperature superconductor. In this work, we use density functional theory to calculate the structural and electronic properties of crystal graphite intercalated with cyclic water hexamers. We treat two different stackings of this system. In the first, we consider an *AB* stacking which is typical of graphite. In the second, we consider two configurations of an *AA* stacking which is typical of the superconducting graphite intercalation compounds. All three of the configurations studied are stable and in all three cases, we found the system to be a semimetal. Certain impurities or hydrostatic pressure might change the system into a metal, which seems more suitable for studying its behaviour as a superconductor. This is the first work that considers a crystal structure in the problem of water-treated graphite.

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1. Introduction

Pablo Esquinazi's group [1] reported that by mixing 100 mg of ultra-pure graphite powder into 20 ml of distilled water and letting it dry, some hints of superconductivity appear at room temperature. Naturally, research in this direction has been increasing since this discovery. Nevertheless, to the best of our knowledge, no calculation of the structural and electronic properties of a bulk sample of graphite intercalated with water has been performed. This is the subject of the present study.

Carbon has a large number of allotropes, such as diamond [2], graphite [3,4], fullerenes [5], nanotubes [6–8], and graphene [9]. Superconductivity has been reported in all of them, for example, 4 Å nanotubes with a superconducting critical temperature, T_c, ($\leq 20\ K$), [10], fullerenes doped with potassium ($T_c = 18\ K$) [11], diamond doped with boron ($T_c = 4\ K$) [12] and, more recently, Li-decorated monolayer graphene ($T_c \simeq 5.9\ K$) [13]. Furthermore, some evidence of superconductivity has been found in pyrolytic graphite [14,15], as well as surface superconductivity in rhombohedral graphite with *ABC* stacking [16]. In graphite intercalation compounds (GICs) in which the graphite has been intercalated with alkaline and alkaline earth metals, superconductivity has also been found. Hannay et al. [17] reported the first superconducting GIC, C_8K ($T_c = 0.15\ K$); this was followed by other reports, such as [18–21]. The highest T_c (11.5 K) for a GIC has been found in C_6Ca

[22,23].

Water tends to form clusters of a certain number of molecules $(H_2O)_n$ ($n = 2,3,...$) that interact through hydrogen bonds (HB). In general, for $n = 3-5$, the oxygen ions form a planar ring and the free hydrogen ions point alternately up and down with respect to the plane of the ring [24–26]. In the case of an odd number of free hydrogen bonds, the appearance of two parallel bonds is unavoidable. When $n = 6$, the most stable configurations of the hexamers are as follows: a prism (9), a cage (8), a book (7) and a cyclic isomer (6) [24,25,27–29], although their energy does not differ greatly; the numbers in parenthesis represent the number of hydrogen bonds that are active in forming each configuration. The hexamers are the most studied configuration since they form a cluster in three dimensions [30].

As early as the 1950s, Pierce and Smith [31,32] reported absorption and desorption of water on graphite surfaces. More recently, the characteristics of water on graphite and graphene surfaces have been studied [33–44]. Water intercalated in graphite was also reported [45–50]. A detailed study of the crystallographic and electronic structure of bulk graphite intercalated with water has not been undertaken and it could shed some light on the properties of this interesting system that has been reported as a possible room-temperature superconductor. Theoretical studies on water intercalated in graphitic structures using molecular dynamics have been reported [36,40,47–49]. Water is treated in such a way that the geometric structure is not well established. Studies of water into other carbon allotropes have been reported [44,48,51–54].

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* Corresponding author.
  E-mail address: rtorres@fis.cinvestav.mx (R.M. Torres-Rojas).

2. Our considered structure

In 1924, Bernal [3] reported graphite as an ensemble of parallel hexagonal sheets of carbon atoms arranged in an *AB* stacking. Later on, W. G. Wyckoff [58] reviewed graphite with the lattice parameters given by Baskin and Mayer, $a = 2.46$ Å and $c = 6.67$ Å [59]. In this paper, we will study both *AB* (spatial group $P6_3/mmc$) and *AA* stacking (spatial group $P6/mmm$) [60].

We propose a new configuration (we call it *GrapH$_2$O*) for graphite intercalated with water molecules which, to the best of our knowledge, is new. We considered a model of intercalated cyclic hexamers of water molecules between the carbon sheets of graphite oriented parallel to the graphite planes. The water molecules constituting the hexamer interact with each other through the hydrogen bonds. The second OH bond points towards the carbon planes [36,40]. The water-graphite interaction takes place through van der Waals forces. (see Fig. 1).

We selected a cyclic hexamer (see Fig. 2) because it is the smallest cluster of water molecules in 3D and they are seen as the building blocks of ice; in addition, the honeycomb-like lattice of the sheets of carbon in graphite is similar to the hexamer arrangement of the water molecules. Furthermore, the in-plane C_1-C_1 distance in graphite (2.456 Å) [58] is similar to the one in the water hexamer (2.708 Å) [28] (d_{OO}), differing by less than 10%. Cyclic hexamers have been considered on different carbon surfaces, such as graphite and graphene [39,43,44] and only cyclic water hexamers have been

Fig. 2. The intercalated cyclic water hexamer (see Table 3) (a) top view, (b) side view. (A colour version of this figure can be viewed online.)

detected so far on metal surfaces [61–66]. Studies of water between sheets of graphite have been carried out, but none in crystalline form.

In this work, we have considered three configurations. First, the typical *AB* stacking of graphite (*GrapH$_2$O$_a$*) where the *O*-ions of the hexamer are positioned between two carbon ions belonging to adjacent sheets. The two *AA* stackings, *GrapH$_2$O$_b$* and *GrapH$_2$O$_c$* are typical of the superconducting GICs [17–23]. In the first case, the *O*-ions of the hexamer are located halfway between two carbon ions belonging to adjacent sheets. In the second, the *O*-ions of the hexamer are located halfway between the centers of two carbon rings belonging to adjacent sheets (see Fig. 3).

3. Computational details

We used the density functional theory [67,68] with linearized augmented plane waves plus local orbitals (LAPW + lo) [69] as in the Wien2K code [70]. We used both the local density approximation (LDA) [71] and the generalized gradient approximation (GGA) [72]. We performed an optimization procedure for all the structures proposed, first optimizing the volume and then the c/a ratio. The procedure was repeated iteratively so as to obtain the lattice parameters of the proposed structure, and stopped when the obtained lattice parameters were changing by less than 0.001 Bohrs. Finally, we performed a further optimization procedure of the internal parameters in order to obtain the atomic positions. The results appear in Tables 1–3.

For the convergence criteria we used $10^{-5}Ry$ for the energy, $10^{-3}mRy/au$ for the force and a cut off $R_{mt}K_{max} = 7.0$ for graphite and 2.8 for *GrapH$_2$O*. We also used $31 \times 31 \times 10$ *k*-points for graphite *AB*, $25 \times 25 \times 15$ *k*-points for graphite *AA*, and $15 \times 15 \times 9$ *k*-points for *GrapH$_2$O*. The Muffin-tin radii, in Bohr units, were selected as 1.27 for carbon, 1.14 for oxygen and 0.61 for hydrogen.

4. Results and discussion

We first calculated the structural and electronic properties of *AA* and *AB* graphite (see Table 1) so as to have a clear reference to compare with *GrapH$_2$O*. It can be seen that taking the average between the calculation of the *a*-lattice parameter using the LDA and the GGA approximations we get values that are very close to the experimental ones. Nevertheless, the *c*-lattice parameter is substantially overestimated when the GGA is used. This anomaly is known and has been obtained by various different codes, as the Wien2K code [73], the STATE code [74], the Quantum Espresso [75] and VASP [76,77]. There is no explanation of this unfortunate result in the literature. As we shall see, in our *GrapH$_2$O* models the same problem occurs in the *AB* stacking, while in the *AA* stackings it does not occur.

Fig. 1. a) View of the cyclic water hexamers intercalated into graphite. The free OH bond of each water molecule points to the carbon planes. Van der Waals forces contribute to maintaining the structure. b) Definition of the in-plane distances C_1-C_1 and C_1-C_2 in a graphite layer. (A colour version of this figure can be viewed online.)