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Spin and orbital magnetic moments and spin anisotropy energies of light rare earth atoms embedded in graphene: A first-principles study

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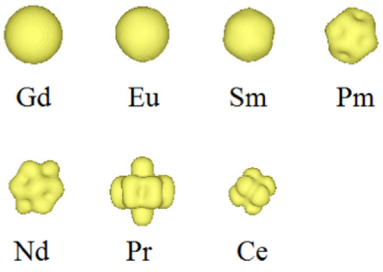
HIGHLIGHTS

- We calculate the properties of light rare earth atoms embedded in graphene.
- There are obvious orbital magnetic moments.
- The shapes of the 4*f* electron clouds are presented.
- The spin anisotropy energies can be as large as tens of meV.

GRAPHICAL ABSTRACT

Spin and orbital magnetic moments and spin anisotropies of light rare earth atoms embedded in graphene were systemically studied. The shapes of the 4*f* electron clouds were given.



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ABSTRACT

The geometries, electronic structures, spin magnetic moments (SMMs), orbital magnetic moments (OMMs) and spin anisotropy energies (SAEs) of light rare earth atoms (La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd) embedded in graphene were studied by using first-principles calculations based on Density Functional Theory (DFT). The spin-orbital coupling effect was taken into account and GGA+*U* method was adopted to describe the strongly localized and correlated 4*f* electrons. There is a significant deformation of the graphene plane after doping and optimization. The deformation of Gd doped graphene is the largest, while Eu the smallest. The results show that the valence is +3 for La, Ce, Pr, Nd, Pm, Sm and Gd, and +2 for Eu. Except Eu and Gd, there are obvious OMMs. When the spin is in the Z direction, the OMMs are −0.941 μ_B, −1.663 μ_B, −3.239 μ_B, −3.276 μ_B and −3.337 μ_B for Ce, Pr, Nd, Pm and Sm, respectively, and point the opposite direction of SMMs. All the doped systems except Gd show considerable SAEs. For Ce, Pr, Nd, Pm, Sm, and Eu, the SAEs are −0.928 meV, 20.941 meV, −8.848 meV, 7.855 meV, 75.070 meV and 0.810 meV, respectively. When the spin orientation is different, different orbital angular moments lead to apparent charge density difference of the 4*f* atoms, which can also explain the origin of SAEs.

1. Introduction

As a new material, Graphene [1–3] has a two-dimensional structure and many unique properties. Related researches have received widespread attention [4]. For example, it can be used in

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flexible displays [5], spintronics [6,7] and spin qubits [8–10]. Graphene is a very versatile material. In order to have a better application, its electronic structure should be manipulated [11], so there are many studies focusing on adsorption [12] or embedding with other atoms. For example, Nitrogen doping is an effective way to tailor the properties of graphene [13]. Furthermore, Ni embedded in graphene [14,15], Au embedded in graphene [16] and transition metal atoms embedded in graphene [17] have been systematically studied. As a specific example, Gao [18] reported the first-principles calculation results of the geometric structure and electronic structure of the IVA group atoms adsorbing on graphene. Adsorbing or embedding other atoms in graphene can be realized experimentally. Adsorbing is relatively easy. For embedding, high-energetic electrons can be used to knock C atoms from graphene and create vacancies which can then be occupied by other atoms [19,20]. Furthermore, TEM can achieve nearly single atom accuracy, being a method for manipulation and characterization.

Although there are lots of researches on adsorption and doping with other atoms, it rarely refer to the magnetic anisotropy (or spin anisotropy) and orbital angular moment. In the practical application, spin anisotropy energy (SAE) [21,22] is an important parameter. It can prevent the spin flip caused by the quantum tunneling and thermal noise, thus stabilizing the direction of the spin, implementing the information storage. Meanwhile, orbital moment and related phenomena such as orbital ordering [23] are of great significance and have been extensively studied [24,25]. For example, Pavarini and Koch [26] have given the origin of orbital order in $LaMnO_3$.

It is well known that the magnetic property of the rare earth (RE) atom is determined by its 4*f* shell. The highly degenerate *f*-shells ensure the orbital degrees of freedom are not quenched. This effect is different from the case of *d* electrons, where the quenching of the orbital momentum usually happens. So the RE atom is likely to have apparent orbital angular momentum and strong spin anisotropy. But so far we don't find related studies about the spin anisotropy of RE atoms adsorbing or doping in graphene. The only related research of Liu [27] reported RE atoms (Nd, Gd, Eu and Yb) adsorbing on graphene and its growth morphology. But in their calculations, the 4*f* electrons were frozen, so they can't give the orbital moment and spin anisotropy.

We have carried on a systematic study about the light RE atoms (RE = La, Ce, Pr, Nd, Pm, Sm, Eu and Gd) doped graphene using the first-principles calculations based on Density Functional Theory (DFT). This paper reports our methods and results of spin magnetic moments (SMMs) and orbital magnetic moments (OMMs) and spin anisotropy energies.

2. Models and methods

The primitive cell of graphene includes two Carbon atoms. The calculated lattice constant is 2.456 Å, which is consistent with the results of Liu [27]. To embed RE atoms and reduce the influence of the periodic images, a 7×7 super cell including 98 carbon atoms was used. When doping, a carbon atom is replaced with a light RE atom and the vacuum layer is 18 Å in the direction perpendicular to the graphene plane. Fig. 1 shows the schematic view of the structure of the optimized Gd doped graphene. From the lateral view, it can be clearly seen that RE atom embedding causes deformations.

For the pristine graphene and the doped systems including La, Ce, Pr, Nd, Pm, Sm, Eu and Gd, *Vienna Ab-inito* Simulation Package (VASP) [28–31] was used to calculate related properties. Projection augmented wave (PAW) [31,32] method was used to describe the interaction of the valence electrons and the ions. Plane wave was used to expend the wave functions of the valence electrons. Through convergence test and considering the computational cost, the plane-wave cutoff energy was set to be 350 eV. The generalized gradient approximation (GGA) of Perdew, Burke and Ernzerhof (PBE) [33] was used to describe the exchange correlation energy.

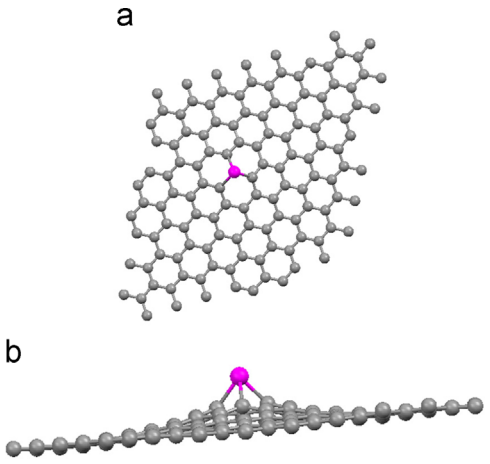

Fig. 1. Schematic view of the structure of the Gd doped graphene, (a) top view; (b) lateral view.

The 4*f* electrons of RE atoms were considered as valence electrons. In view of the strong correlation of 4*f* electrons, the $+U$ [34] method was used. The *U*-values are 6.48 eV, 6.34 eV, 6.62 eV, 6.89 eV, 7.15 eV, 7.40 eV and 8.00 eV for Ce, Pr, Nd, Pm, Sm, Eu and Gd, respectively [35,36]. Considering the spin-orbit coupling effect in the calculation, and *k*-space grid points are set as $3 \times 3 \times 1$ generating by Monkhorst–Pack method. When performing the geometry optimization, the forces on all atoms are less than 0.02 eV/Å after the relaxation. In the static calculation, different spin orientations were set to obtain the SAEs. The self-consistent method was used to calculate the total energy and the energy difference between two consecutive iterations is less than 1×10^{-7} eV.

3. Results and discussions

3.1. Geometric structures

Table 1 shows the related lattice parameters of the eight doped systems and the bonding energies. *d* is the distance from the RE atom to the nearest C atom. Δh is the distance between the C atom nearest to the dopant and the graphene plane, which reflects the deformation of the graphene plane. The bonding energy E_b is calculated by $E_b = E_G + E_{RE} - E_{total}$, and E_G represents the total energy of the graphene with a carbon atom vacancy; E_{RE} represents the energy of a free RE atom; E_{total} represents the total energy of the optimized doped system. It can be seen that the deformation

Table 1
The optimized lattice parameters and the bonding energies.

Dopant	*d* (Å)	Δh (Å)	E_b (eV)
La	2.342	0.885	7.127
Ce	2.319	0.850	7.480
Pr	2.300	0.884	6.281
Nd	2.292	0.913	5.546
Pm	2.276	0.895	4.942
Sm	2.260	0.900	4.178
Eu	2.447	0.739	3.367
Gd	2.233	0.933	6.661