Magnetic Properties of Intercalated Gr/Ni (111) System

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Abstract

Intercalation of graphene (Gr) with transition metals is perspective for creating magnetic tunnel junctions and structures of the type graphene/ferromagnetic metal/substrate with perpendicular magnetic anisotropy (PMA). The paper presents the results of first-principle calculations of the magnetic properties for Gr/Fe (Co)/Ni (111) systems. *Ab initio* calculations of the electron spectrum $\varepsilon_{n,\sigma}(k)$ of the systems were performed in the framework of the spin density functional theory (SDFT). Kohn-Sham single-particle spectra $\varepsilon_{n,\sigma}(k)$ were used to determine total energies of the systems for different spin quantization axes, partial and total densities of the electron states, and also magnetic moments μ_i of all atoms. Then, using these magnetic moments, the energies of dipole-dipole interaction were obtained and the magnetic crystalline anisotropy (MCA) of the systems was studied. Copyright © VBRI Press.

Keywords: Graphene, spin density functional theory, crystalline magnetic anisotropy.

Introduction

Graphene (Gr) is a promising material for microelectronics and spintronics due to its unique electronic structure, high mobility of charge carriers and long spin-lattice relaxation time [**1, 2**]. The intercalation of graphene with transition metals is promising for creating magnetic tunnel junctions and for fabrication of the graphene-ferromagnetic metal structures possessing perpendicular magnetic anisotropy (PMA) [**3, 4**] that is the key factor for the memory storage. It is known that the graphene-coated metal films formed on various substrates have different anisotropy of their magnetic properties. For the development of spintronics, it is extremely interesting to find combinations of magnetic coatings and substrates that provide PMA. Therefore, the magnetic anisotropy of thin films was intensively studied in the last years. However, to the best of our knowledge, all existing first-principle calculations of the magnetic anisotropy of graphene-capped ultrathin films were performed only for magnetic layers on the nonmagnetic substrates. In the present work we report for the first time *ab initio* calculations of the magnetic anisotropy of Gr/Fe/Ni (111) and Gr/Co/Ni (111) systems. These systems are of great interest, because, firstly, they can be easily formed by intercalating graphene grown on the Ni (111) surface with Fe and Co, and, secondly, the layers of iron and cobalt are of unusual *fcc* structure [**5**].

Method of calculation

Ab initio calculations were performed using the pseudopotential approach implemented in the Quantum Espresso software package [**6**]. The completely relativistic PAW pseudopotentials and the generalized gradient approximation (GGA) for the exchange-correlation energy were used. A Monkhorst-Pack partition of the Brillouin zone into $12 \times 12 \times 2$ *k*- points was used for the Gr/Fe (Co)/Ni systems.

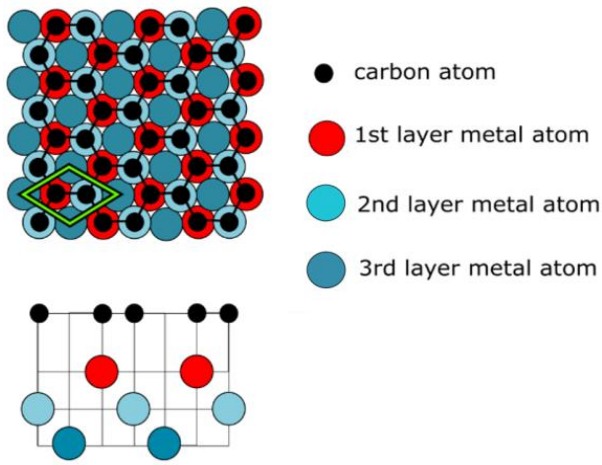

Fig. 1. Atomic structure of the Gr/Co(Fe)/Ni(111).

The initial configurations of the valence electrons had the form of $2s^2p^2$ (C), $3s^2p^63d^64s^2$ (Fe), $3s^2p^63d^74s^2$ (Co) and $3s^2p^63d^84s^2$ (Ni). The maximal energy of plane waves in the wave function decompositions was limited to 300 Ry. All of the self-consistent loops were iterated until the total energy difference of the systems between the adjacent iterating steps became less than 10^{-6} eV. The structural model of the Gr/Fe (Co)/Ni systems (**Fig. 1**) corresponded to the results of Ref. [**7**]. It was assumed that the layers of intercalated iron and cobalt possess the same structure as the Ni (111) substrate. Nickel (111) layers were simulated by two-dimensional hexagonal Bravais lattices with the lattice parameter of 2.42 Å. The supercells were made up of seven nickel atoms (one atom per layer), of one to five iron (cobalt) atoms and two carbon atoms of the graphene layer (**Fig. 1**). The distance between the top metal layer and graphene was assumed to be 2.07 Å. The value of the vacuum spacer was 15 Å. For all atomic configurations, structural optimization was carried out. The values of the atomic magnetic moments for the Gr/Fe/Ni (111) system and the contribution of the C-p_z orbitals to the formation of the Dirac cone were calculated in [**7**]. The results are in a qualitative agreement with the experimental data obtained in [**5**].

The novelty of the present work is the study of magnetic crystalline anisotropy (MCA) of the intercalated Fe and Co layers. To study MCA, it is necessary to consider the total energy of the system for different spin quantization axes. Only taking into account the spin-orbit interaction (SOI), one can obtain the angular dependence of the energy $E(\theta,\varphi)$, where θ and φ are the azimuth and polar angles defining the direction of the spontaneous magnetic moment $\boldsymbol{\mu}_i$. However, the dependence of the total energy on the azimuthal angle was not taken into account in our calculations. The total energy of the system can be represented as a sum of the single-particle band energy E^{band} and the classical energy E^{md} of magnetic dipole-dipole interaction.

$$E^{tot} = E^{band} + E^{md}, \quad (1)$$

$$E^{band} = \sum_{\sigma,\nu} \varepsilon_{\nu,\sigma} = \sum_{\sigma} \int^{\varepsilon_F} \varepsilon n_\sigma(\varepsilon) d\varepsilon\,, \quad (2)$$

$$E^{md} = \frac{1}{2} \sum_{i,k} \frac{\boldsymbol{\mu}_i \boldsymbol{\mu}_k \boldsymbol{R}_{ik}^2 - 3(\boldsymbol{\mu}_i \boldsymbol{R}_{ik})(\boldsymbol{\mu}_k \boldsymbol{R}_{ik})}{\boldsymbol{R}_{ik}^5}. \quad (3)$$

$$\Delta E^{tot} = \Delta E^{band} + \Delta E^{md}\,, \quad (4)$$

$$\Delta E^{band} = E_{\perp}^{band} - E_{||}^{band}\,,\ \Delta E^{md} = E_{\perp}^{md} - E_{||}^{md}$$

In (2) $\varepsilon_{\nu,\sigma}$ are the single-particle Kohn-Sham energies, σ is the spin index. In accordance with the "local force theorem" [**8**], we neglected the change of "double counting" energy from the angle θ. So, our research is based on calculating the spectrum $\varepsilon_{n,\sigma}(\boldsymbol{k})$, the total density of states $n_\sigma(\varepsilon)$ (DOS) and the partial density of states (PDOS), which allow finding the occupation numbers of atomic orbitals $N_{i,\alpha,\sigma}$, the atomic magnetic moments $\boldsymbol{\mu}_i$ and the total energies of the systems. A standard procedure [**9**] to evaluate MCA from first principles comprises two steps. First, scalar-relativistic self-consistent spin-polarized calculations are performed in order to determine the magnetic ground state. After that the SOI is included and the total energy of the system is determined as a function of the magnetic moment direction. The MCA is then found as a difference of the non-self-consistent total energy values for out-of-plane ($\Delta E_{\perp}^{tot}$) and in-plane ($\Delta E_{\parallel}^{tot}$) magnetization. In this paper MCA of ΔE^{tot} is determined as a difference between self-consistent values of the corresponding energies in accordance with the equation (4).

Results and discussion

At the first stage, for all of the considered systems, we have calculated the magnetic moments of the Ni, Fe, and Co atoms located in different layers of isostructural films, which are needed to determine the dependencies $E^{md}(\theta)$. It follows from the calculations that six Ni (111) layers should be used for an adequate description of the massive nickel film.

The dependencies illustrating the changes in the magnetic moments of Fe atoms with an increase in the depth of their localization are shown in **Fig. 2** for the free-standing 6-monolayer films with the clean and graphene-coated surfaces. It is clearly seen from the figure that graphene has a significant effect on the magnetic properties of atoms located in the first four monolayers.

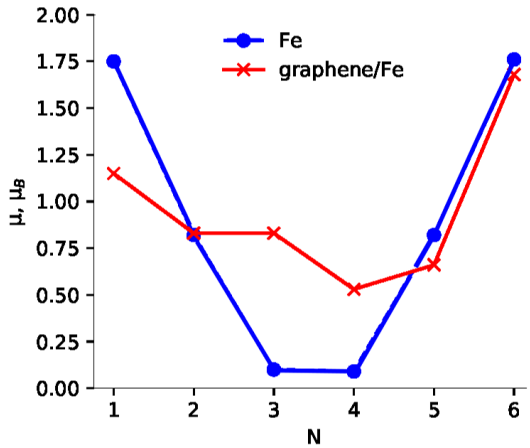

Fig. 2. Magnetic moments of Fe atoms located in different layers of free-standing Fe (111) and Gr/Fe(111) films.

Graphene-coated Fe and Ni free-standing films.

Angular dependencies $E^{band}(\theta)$ for free-standing films of Fe and Ni have been calculated within the range of 0° to 180°. The results are presented in **Fig. 3**. They show that the nickel monolayer has an in-plane magnetic anisotropy (IMA), while the iron layer is of perpendicular magnetic anisotropy (PMA). Therefore, the dipole-dipole interaction can change the direction of magnetization only in iron film. For this film the calculated angular dependence can be represented as:

$$E^{band}(\theta) = K_0{}^{Fe} + K_1{}^{Fe} \sin^2\theta \quad (K_1{}^{Fe} > 0),$$

while for the nickel layer the dependence is : $E^{band}(\theta) = K_0{}^{Ni} + K_1{}^{Ni}\cos^2\theta + K_2{}^{Ni}\cos^4\theta$. Here, the constants K_0 are the maximum values of the total energy of the systems, which are always negative. In addition, $|K_0| >> K_1, K_2$. For the Ni monolayer the dependence $E^{band}(\theta)$ (**Fig. 3a**) is well approximated by the last expression at $K_2{}^{Ni} \cong K_1{}^{Ni} = 0.38$ meV/cell. Magnetic anisotropy of the Fe monolayer is described by only one constant $K_1{}^{Fe}$ whose value is 0.92 meV/cell. It is approximately equal to ΔE^{band}. The obtained value of uniaxial anisotropy constant is close to the first anisotropy constant $K_1 = 0.7$ meV/cell of Fe on MgO [**4**].

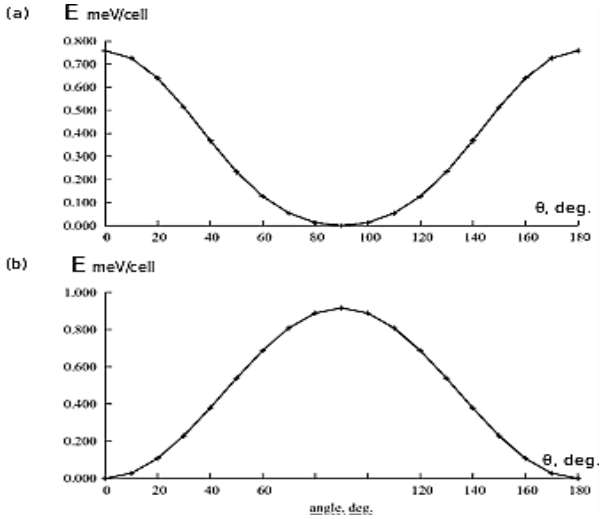

Fig. 3. Dependencies of the energy E^{band} on the polar angle θ calculated for monolayers of nickel (a) and iron (b).

The values of ΔE^{band}, ΔE^{md} and ΔE^{tot} as the functions of the number of monolayers in the free-standing Fe (111) and Gr/Fe (111) films are shown in **Fig. 4**. For ultrathin iron films with the number of monolayers $N \leq 3$, the atomic magnetic moments are ordered perpendicular to the surface. This is due to the fact that $|\Delta E^{band}| > |\Delta E^{md}|$ and $\Delta E^{band} < 0$. In the case of $N \geq 4$, the dipole-dipole interaction changes the perpendicular orientation of the magnetic moment of iron film to the longitudinal one (in the film plane).

Graphene coating of free-standing films reduces the atomic magnetic moments and leads mainly to the decrease of the dipole-dipole interaction. In this case, the values of ΔE^{band} change insignificantly. As a result, the rotation of the magnetic moments of iron atoms from the perpendicular orientation to the longitudinal one occurs when the number N of iron monolayers becomes greater than six. Thus, the presence of graphene on the surface of the iron film with the *fcc* structure significantly enhances its PMA. This effect can be due to the hybridization of C $2p_z$ and Fe *3d* electrons at the Gr/Fe (111) interface. Since graphene not only enhances the magnetic anisotropy of iron films, but also protects them from exposure to atmospheric oxygen [**10**], such films can be promising for practical applications.

In regard to free-standing nickel films, our pseudopotential calculations have shown that the values ΔE^{band} (and ΔE^{tot}) > 0 for all N even without taking into account the dipole-dipole interaction. The magnetic moments are always ordered in the (111) plane, and the nickel films demonstrate IMA. This conclusion is also valid for graphene coated nickel films.

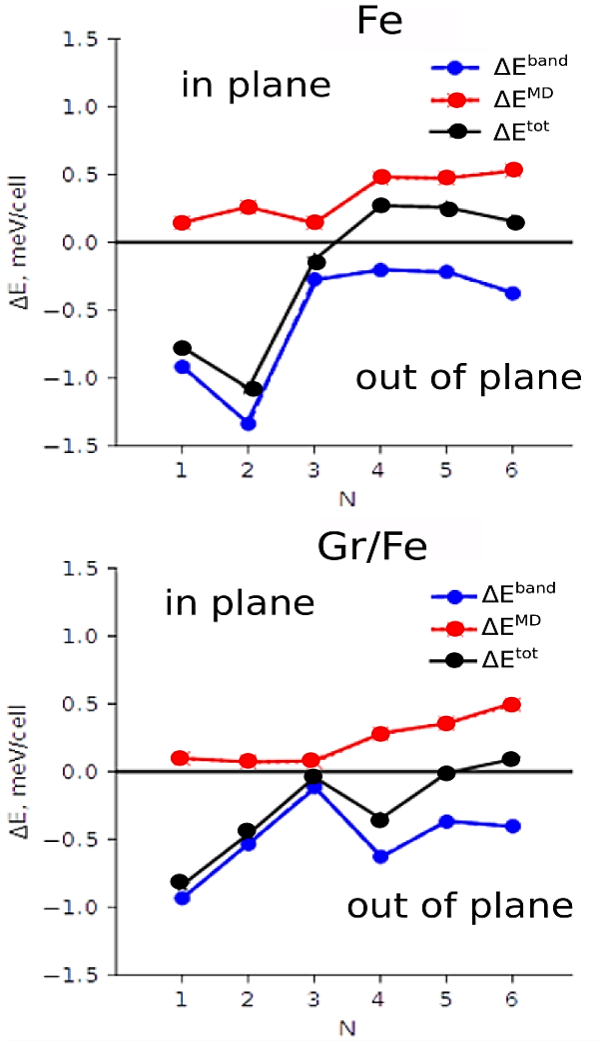

Fig. 4. Dependencies of the energy changes ΔE^{band}, ΔE^{md} and ΔE^{tot} on the number N of iron monolayers in the clean and graphene-coated free-standing films.

Gr/Fe/Ni (111) system

After considering the anisotropy of free-standing films, similar calculations have been performed for the Gr/Fe/Ni (111) system at the different numbers N of Fe monolayers. At N = 1 – 4, the dependence $E^{tot}(\theta)$ of the entire system is determined by the substrate, which was modeled by six monolayers of ferromagnetic nickel. In all the cases considered, ordering of the magnetic structure of the Fe(N)/Ni systems occurs along the plane, which is due to the contribution of anisotropy of nickel. In the Gr/Fe/Ni (111) system, PMA occurs only when the nickel substrate is set to be nonmagnetic at the initial step. The corresponding results are presented in

Table 1. The role of graphene is to decrease the magnetic moment of the surface monolayer and the energy of the dipole-dipole interaction. An interesting result for Gr/Fe(N) films on the nonmagnetic Ni (111) substrate is that a change in the type of iron anisotropy (from PMA to IMA) occurs at approximately the same number of iron monolayers as in a similar structure without graphene. Obviously, the assumption of a nonmagnetic nickel substrate can hardly be implemented in an experiment. It is desirable to have either a nonmagnetic substrate, or synthesize an ultrathin nonmagnetic layer between iron and nickel. In [**11**], such a change in the sign of the constant of anisotropy depending on the thickness of the cobalt layer located on a nonmagnetic substrate was observed for Gr/Co/Ir(111).

Table 1. The values of ΔE^{band} (meV/cell) and ΔE^{md} (meV/cell) as the functions of the number N of Fe monolayers in the Gr/Fe(N)/Ni system.

N	1	2	3	4	5	6
ΔE^{band} (Fe(N)/Ni)	-0.88	-0.55	-0.38	-0.25	-0.56	-0.12
ΔE^{md} (Fe(N)/Ni)	0.12	0.22	0.14	0.39	0.45	0.60
ΔE^{band} (Gr/Fe(N)/Ni)	-0.37	-0.07	-0.02	-0.63	-0.36	-0.19
ΔE^{md} (Gr/Fe(N)/Ni)	0.09	0.02	0.09	0.30	0.39	0.45

Gr/Co/Ni (111) system

At the final stage of our study the calculations of the magnetic anisotropy were per formed for both the free-standing cobalt films and the Gr/Co/Ni (111) system. The results obtained for the different numbers of cobalt layers have shown that in most cases the films demonstrate IMA ($\Delta E^{tot} > 0$). PMA can be only observed for one Co monolayer in the Co/Ni (111) system and the first two Co monolayers in the case of Gr/Co/Ni (111).

Conclusion

In this work the *ab initio* pseudopotential method was used for the first time to study the magnetic anisotropy of thin (up to 6 monolayers) cobalt and iron films on Ni (111) with both clean and graphene-coated surfaces. The calculations were performed for the *fcc* structure of metal films, which is typical of the substrate and the intercalated layers. The magnetic moments of all atoms of the structures are calculated and the total energies of the systems are determined for various orientations of the magnetization vector relative to the film surface. It is shown that for Fe films the value of the uniaxial anisotropy constant is close to the first anisotropy constant of iron monolayer on MgO [**4**]. The results obtained have revealed an increase in the perpendicular magnetic anisotropy of free-standing iron thin layers coated with graphene that corresponds to the experimental data of [**5**].

In the future, it is promising to consider the magnetic properties of intercalated films of iron and cobalt on the nonmagnetic hexagonal substrate of boron nitride, which has a very small lattice mismatch with graphene. Our preliminary results show that PMA is maintained in the Gr/Fe/BN (0001) system in the range up to five monolayers of iron.

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Author's contributions

Conceived the plan: S.D, I.P; Performed the computer expeirments: S.D, E.M; Data analysis: S.D, E.M, I.P; Wrote the paper-S.D, I.P. Authors have no competing financial interests.

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