

Electronic structure and magnetic properties of graphite intercalated with 3d-metals

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Received December 23, 2013

Electronic structure and magnetic properties of graphite-based systems with intercalated 3d-transition metal atoms (V, Cr, Mn, Fe, Co, Ni) were calculated *ab initio* using the density functional theory. The presence of different magnetic states depending on the type of inserted M atoms is revealed for hexagonal $P6/mmm$ and $P6_3/mmc$ crystall structures. The values of magnetic moments appeared to be governed by the $p-d$ hybridization, and by variations of exchange interactions with intercalation. The results of calculations clearly indicate itinerancy of the 3d-electrons of inserted M atoms.

PACS: 71.20.Tx Fullerenes and related materials; intercalation compounds;
75.10.Lp Band and itinerant models;
75.30.Cr Saturation moments and magnetic suscepti;
81.05.U- Carbon/carbon-based materials.

Keywords: intercalated graphite, electronic structure, magnetic moments, MC_6 .

1. Introduction

Graphite is well known and investigated for decades material due to its quasi-two-dimensional structure, which gives rise to highly anisotropic electronic properties and provides an exciting avenue for testing physical concepts in lower dimensions [1–3]. Graphene, a single layer of graphite with two-dimensional structure and unique physical properties, recently emerged as one of the most promising low-dimensional nanomaterials [4,5]. Basically, both these materials are nonmagnetic ones, however a moderate magnetism can be induced by ion implantation and point defects [5,6]. On the other hand, due to the layered hexagonal crystal structure of graphite, there is also a possibility to induce ferromagnetism by intercalation of magnetic 3d-metal ions into the van der Waals gap between carbon layers [7,8].

The carbon atoms within the basal plane are bound together by strong covalent σ -bonds, while atoms in adjacent

layers are weakly bound by van der Waals bonds [8,9]. As a result it is easy to intercalate graphite with alkali metals, and this intercalation changes both the crystal and electronic structures [1,2]. The intercalation of atoms M into graphite can transform the stacking sequence of hexagonal planes from ABAB... to aligned graphene planes with M atoms inserted into a α superlattice — $A\alpha A\alpha A\alpha$. Whereas the intercalation increases noticeably the interlayer separation (by 10% in LiC_6), the intralayer lattice constant a is only slightly dilated [2].

Researches of magnetic and transport properties of carbon compounds with magnetic 3d-metals have high potential in a context of spintronics and its practical applications. The different valences of the 3d-atoms result in a range of induced magnetic moments and peculiar spatial spin density distribution, what is needed for spintronic applications. It is anticipated, that selective induction of spin-polarization can be utilized in spintronic and nanoelectronic devices.

The basic aim of the present work is to study how the intercalation of different 3d-metal ions ($M = \text{Cr, Mn, Fe, Co}$) affects the electronic structure and magnetic properties of graphite. Obviously, the hybridization between the p -states of carbon and $3d$ -states of a guest metal is expected, and the methods of the density functional theory (DFT) can be applied. The specific tasks of this study are to investigate theoretically magnetic characteristics of the intercalated graphite-based systems and to reveal electronic structure features which can promote magnetic ordering in these systems, and also transition to the half-metal state.

2. Electronic structure and magnetism

In order to analyze the magnetic properties of graphite intercalated with 3d-metals, the *ab initio* calculations of the electronic structure and magnetic moments of MC_6 compounds were carried out within DFT. We have taken into consideration hexagonal crystal structures, corresponding to the space groups $P6/mmm$ and $P6_3/mmc$ [10]. The structural parameters of MC_6 were chosen according to data of Refs. 8,10.

Ab initio calculations of the electronic structure of MC_6 were performed by employing a full-potential all-electron linear muffin-tin orbital method (FP-LMTO, code RSPt [11,12]). This full-potential method was successfully applied for complex systems with open [13] and layered [9] structures having substantially inhomogeneous charge densities. The exchange-correlation potential was treated within both the local spin density approximation (LSDA, [14]) and the generalized gradient approximation (GGA, [15]) of the DFT. In our calculations the spin-orbit coupling was taken into account, though its effect appeared to be very small comparatively with scalar relativistic effects.

In this work the valence electronic charge densities of MC_6 were calculated, and the corresponding results for FeC_6 are shown in Fig. 1. The evaluated electronic charge densities of other MC_6 compounds appeared to be similar.

The distribution of charge density in the carbon basal plane clearly indicates the covalent character of corresponding σ -bonds. On the other hand, the charge density of Fe atom is more localized, and the chemical bond of Fe with atoms of carbon has presumably ionic character, due to the notable charge transfer.

In addition, to investigate the chemical bonding in MC_6 , the balanced crystal orbital overlap populations BCOOP [16] was calculated within the FP-LMTO technique. The BCOOP is defined as the orbital population weighted density of states with a “balancing” denominator [17], and this method is similar to the well known COOP, which is the solid-state generalization of the quantum chemical quantity called crystal orbital overlap population. A knowledge of the M–C bonding is important to understand the role of implanted 3d-magnetic atoms for different types of magnetic ordering [7]. In our case it was found that hybridization of p -states of carbon and d -states of transition metal M is small, and this provides partially ionic–partially metallic character of M–C bonds (see Fig. 2).

The calculated within LSDA magnetic moments of MC_6 are in both $P6/mmm$ and $P6_3/mmc$ structures the induced spin polarization appears for V, Cr, Mn, Fe, and Co intercalation, providing magnetic moments listed in Table 1 (per corresponding MC_6 formula unit). The intercalation of graphite with Ni does not result in a magnetic state for both structures. For all intercalated atoms M the induced magnetic moment differs in $P6/mmm$ and $P6_3/mmc$ structures, due to different average M–C bonding. The smaller corresponding bonding lengths, the larger is the magnetization.

When the total magnetic moment decreases along the series Mn–Fe–Co, the corresponding localized moments in MT-sphere are obviously reduced in magnitude. At the same time, a weak spin density develops in the interstitial region between the atomic sites. In the case of NiC_6 the filling of all $3d$ -orbitals and hybridization of the $3d$ -orbitals with p -orbitals of carbon, results in zero magnetic moment.

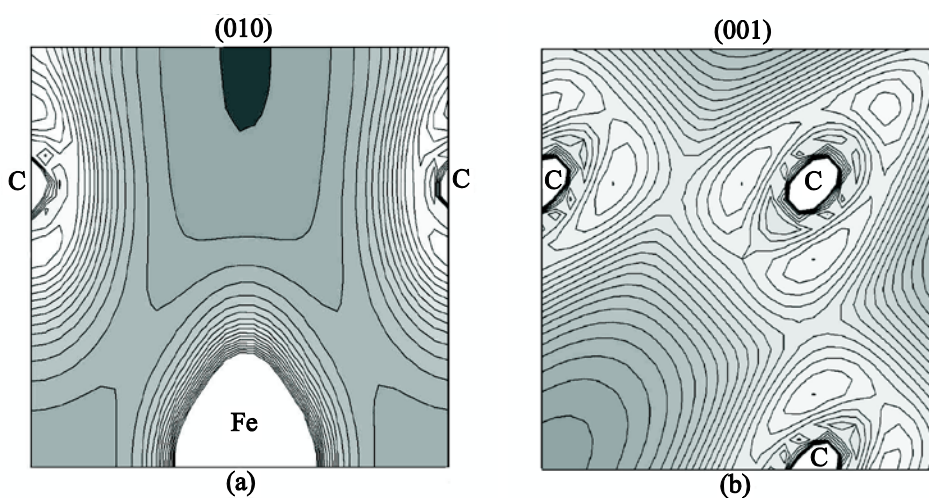


Fig. 1. Contour plots of total valence-electron charge density of FeC_6 in $P6_3/mmc$ structure: in the vertical (010) plane (a), and in the basal (001) plane (b).

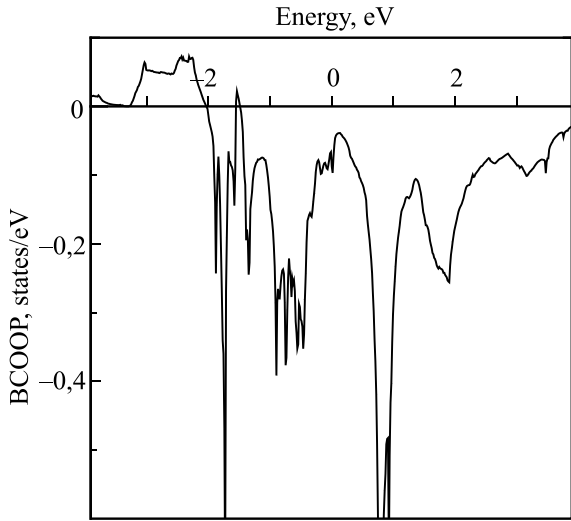


Fig. 2. Calculated BCOOP of FeC_6 in $P6_3/mmc$ structure.

Table 1. Magnetic moments of MC_6 (per formula unit)

Structure	M	Magnetic moment (μ_B)
$P6/mmm$	V	0.88
	Cr	1.59
	Mn	2.89
	Fe	1.99
	Co	0.99
$P6_3/mmc$	V	1.42
	Cr	2.53
	Mn	2.66
	Fe	1.78
	Co	0.24

As can be seen from the calculated densities of electronic states (DOS) $N(E)$ in Figs. 3, 4, 5, 6, and 7, M intercalated graphite basically develops a metallic state. The spin-polarized $N(E)$ revealed that the presence of $3d$ -atoms substantially enhances DOS at the Fermi level E_F , comparatively with the semimetallic pure graphite [9].

Analysis of the calculated $N(E)$ indicates that for Mn, Fe, and Co intercalation the spin-majority d -states are situated predominantly below the Fermi level, whereas the main contribution to $N(E_F)$ comes from the spin-minority d -states of the $3d$ -metal atom (see Figs. 5, 6, and 7). It should be noted that in MnC_6 , FeC_6 , and CoC_6 there is very small contribution of the spin-majority states to $N(E_F)$. The corresponding “pseudo-gap” in $N(E)$ for the spin-majority states provides a possibility of formation of spin half-metal state.

On the other hand, in VC_6 and CrC_6 there are substantial and competing contributions to $N(E_F)$ from both spin-majority and spin-minority d -states (see Figs. 3 and 4), which make impossible realization of half-metal state. The

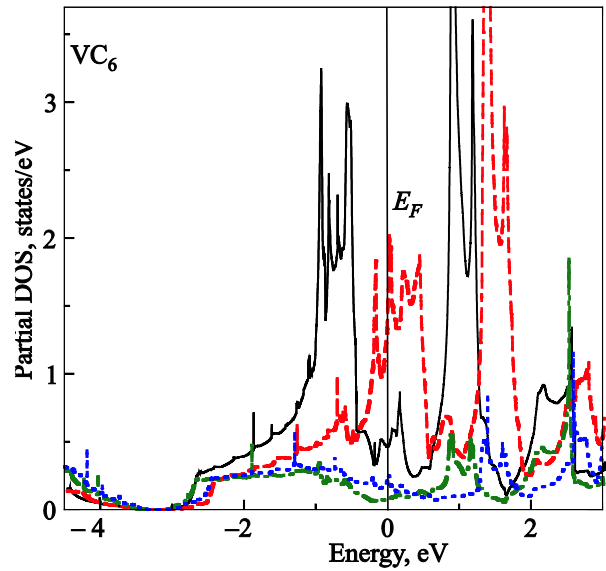


Fig. 3. Calculated spin-majority (V is solid line, C is dashed-dotted line) and spin-minority (V is dashed line, C is dotted line) partial DOS for the configuration $P6/mmm$ of VC_6 . The position of Fermi level at 0 eV is marked by a vertical line.

dominating p -orbitals of carbon are strongly hybridized with d -states in all studied MC_6 compounds, however the differences between spin-majority and spin-minority DOS of carbon are small, as well the corresponding contributions to magnetic moments of MC_6 . In case of Ni intercalation, the almost filled $3d$ -orbitals virtually do not provide spin-polarized DOS at the Fermi level, and this explains the nonmagnetic behavior of NiC_6 .

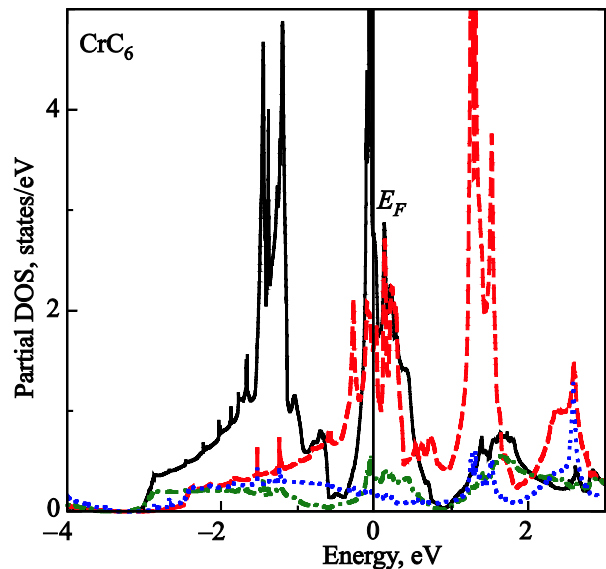


Fig. 4. Calculated spin-majority (Cr is solid line, C is dashed-dotted line) and spin-minority (Cr is dashed line, C is dotted line) partial DOS for the configuration $P6/mmm$ of CrC_6 . The position of Fermi level at 0 eV is marked by a vertical line.

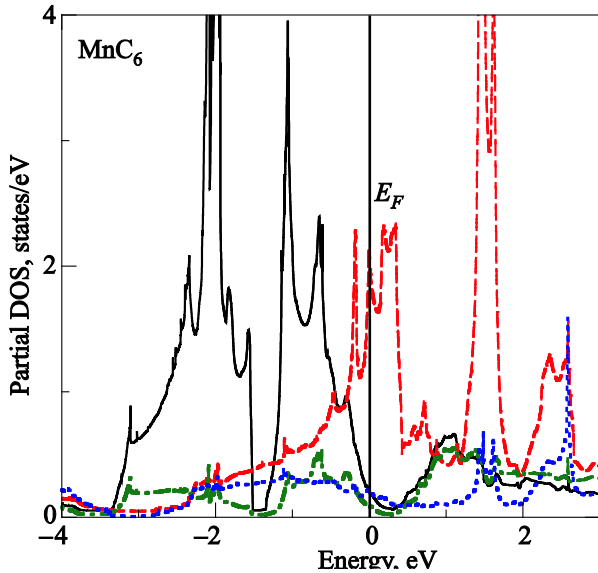


Fig. 5. Calculated spin-majority (Mn is solid line, C is dashed-dotted line) and spin-minority (Mn is dashed line, C is dotted line) partial DOS for the configuration $P6/mmm$ of MnC_6 . The position of Fermi level at 0 eV is marked by a vertical line.

3. Conclusion

In order to investigate a possibility to obtain the half-metal state in carbon-based materials, we have studied the spin-polarized electronic structure of graphitic network intercalated with 3d-transition metal atoms V, Cr, Mn, Fe, Co, and Ni. The electronic structure of these graphitic systems is modified after intercalation due to hybridization

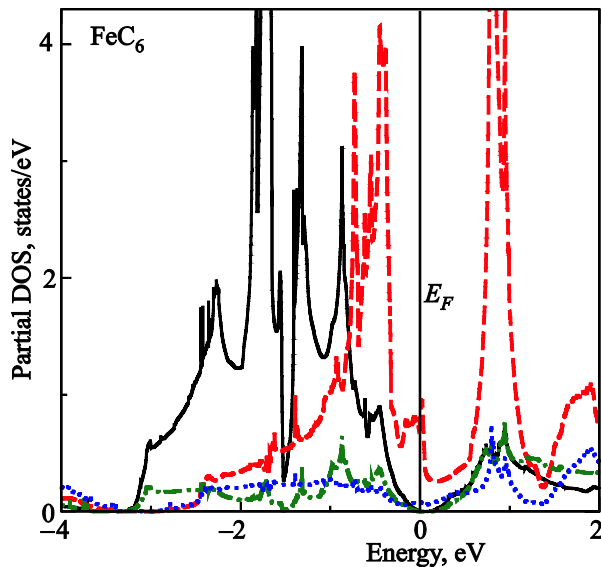


Fig. 6. Calculated spin-majority (Fe is solid line, C is dashed-dotted line) and spin-minority (Fe is dashed line, C is dotted line) partial DOS for the configuration $P6/mmm$ of FeC_6 . The position of Fermi level at 0 eV is marked by a vertical line.

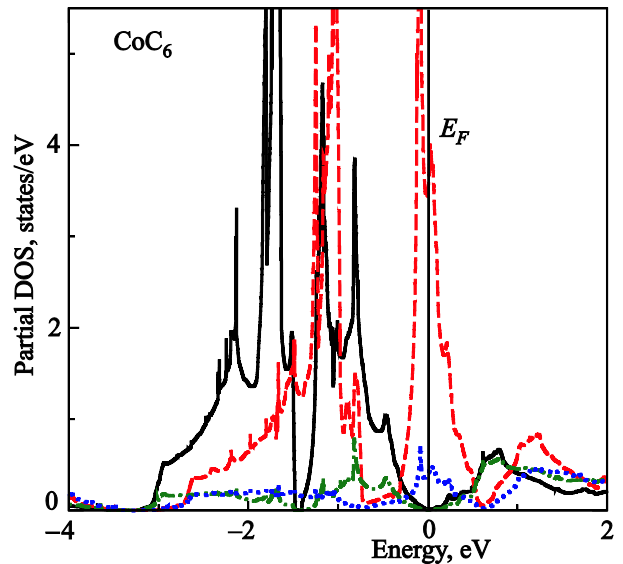


Fig. 7. Calculated spin-majority (Co is solid line, C is dashed-dotted line) and spin-minority (Co is dashed line, C is dotted line) partial DOS for the configuration $P6/mmm$ of CoC_6 . The position of Fermi level at 0 eV is marked by a vertical line.

of the carbon p -orbitals with the d -orbitals of a transition metal. It appears that V, Cr, Mn, Fe, and Co induce spin-polarization in hexagonal configurations, whereas Ni provides a metallic system with zero magnetic moment. As a result, the hybridization and spin polarization due to intercalated magnetic 3d-transition metal atoms appears to be favorable for realization of graphite-based ferromagnetic half-metal state in MnC_6 , FeC_6 and CoC_6 systems.

This work was performed using computational facilities of grid-cluster ILTPE — B. Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine.

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