

RESEARCH ARTICLE

A theoretical simulation of the magnetic properties of nanocomposites based on graphene nanoflakes

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Abstract

Using exact diagonalization, the density matrix renormalization group approach and the quantum Monte-Carlo method, we studied the peculiarities of the magnetization profiles and the possibility of spin switching for the Heisenberg spin models of low-dimensional composite magnets formed by graphene nanoclusters and complex transition-metal compounds. For these models, we found the presence of intermediate plateaus in the low-temperature magnetization profiles, which is in agreement with known experimental and theoretical studies of the magnetization profiles of nanostructured magnets with the ferrimagnetic spin ordering in the ground state. For spin-chain model of composite magnets proposed, we also found a possibility of single and double spin switching with the macroscopic jump of the ground state spin results from frustrated spin interactions.

KEYWORDS

graphene-based nanomagnets, spin switching

1 | INTRODUCTION

Graphitic clusters like graphene nanoribbons and nanoflakes with defects and/or embedded complexes of transition-metal ions have attracted much attention for applications in multifunctional spintronic devices due to their ability to switch between different spin states given external stimuli such as electric field or strain [1–4]. On the other hand, the paramagnetic complexes of transition metals are extremely sensitive to subtle structural changes in metal coordination environments [5, 6]. As a result, small changes in the geometry of the bridging ligand may be sufficient to affect the magnetic properties of the aforementioned composite nanomagnets. This opens a promising way to the targeted design of new nanostructured magnets for spin-based electronics (spintronics). In addition, at least hypothetically, the sensitivity of these nanomagnets to a change of the chemical surrounding can be used for creating new types of magnetic chemo-sensors which potentially change their magnetic states upon adsorption of small molecules in these nanomaterials.

An adequate simulation of the magnetic characteristics of such nanomaterials requires a thorough accounting of electron correlations, which cannot be done within a one-particle approximation like Hartree–Fock or whatever the Density Functional Theory (DFT) method. In this case, many-electron approaches like the Hubbard model give more relevant results but they require very large computational efforts such that the corresponding numerical study can be done only for rather small electron systems. At half filling and weak hopping, the application of degenerate perturbation theory to the Hubbard model gives the lowest-order nonzero term which is usually expressed as a nearest-neighbor Heisenberg spin Hamiltonian, the known spin formalism of valence bond theory of quantum chemistry. Definitely for physically reasonable values of hopping parameters of the Hubbard model for conjugated hydrocarbons this approach is not an accurate approximation. Nevertheless, in lieu of the perturbation theory derivation, the Heisenberg spin model can be obtained through a cluster expansion [7–9] in which the effective Heisenberg Hamiltonian is chosen to reproduce the exact Hubbard energy levels of the atomic clusters with homogeneous or almost homogeneous distribution of the electron densities on atoms (quasihomeopolar energy levels). At present, there are many successful applications of the Heisenberg spin Hamiltonian to the quantitative description of the lowest

energy levels of the interacting electrons of conjugated hydrocarbons, including graphene fragments [10–13]. It is important for our study that the above approach permits to treat not only the pure π -electron system of graphitic clusters, but also to take into account the interaction with magnetic components like complex transition-metal ions of arbitrary spin incorporated into the system.

A simplified approach to the study of the aforementioned 1D nanomagnets using the Ising-Heisenberg model has been proposed in reference [14]. This model permits usage a classic transfer matrix technique for numerical simulations of the corresponding low-temperature thermodynamics. Unfortunately, its application to our composite nanomagnets is questionable because the Ising terms of the effective model Hamiltonian may produce an unphysical energy gap, which is absent in the exact energy spectrum of the corresponding Hubbard model.

We also note that there are a number of effective hybrid approaches composed of localized spins and mobile electrons [15, 16], which may be useful in case of graphene systems with defects or dopants. Unfortunately, the corresponding many-electron generalization of these approaches like the Kondo lattice model is more complicated for the study as compared to the Heisenberg spin model. In addition, the mean field approximation for above hybrid approaches may not work properly for the description of the magnetic properties due to the overestimation of spin polarization effects.

In our present study, we consider composite periodic spin systems formed by equivalent fragments of graphene (graphene nanoflakes) linked by complex transition-metal ions (atoms) (CTM) with nonvanishing ground-state spin s . These structures can be treated as an extension of one of the first known 1D ferrimagnets, *m*-polydiphenylcarbene [17], and the carbon-chain-linked trigonal graphene considered in references [2, 3].

First, we modeled the magnetic sublattices of bipartite topology and studied numerically the lowest energy states and magnetization profiles of the corresponding Heisenberg spin models in the nearest-neighbor approximation. For this purpose, we used exact diagonalization method (ED) for small lattice clusters, the density matrix renormalization group approach (DMRG) and quantum Monte Carlo (QMC) methods.

Technically, we used standard diagonalization programs for small symmetric matrices of the lattice Hamiltonians with the matrix elements generated by the branching diagram technique for each subspace with a given value of total spin [18]. For DMRG and QMC calculations, we used our own realization of White [19] and Sandvik [20] algorithms, respectively. Our study demonstrates the existence of an intermediate magnetization plateau at low temperatures, which corresponds to the ferrimagnetic ground state and the gapped character of the excitations with the total spin larger than the one of the ground state. This peculiarity of the magnetization profile is well known for 1D magnetic materials like $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ [21, 22]. Note also that the ferrimagnetic ground state of above bipartite lattices is in agreement with the extended Lieb-Mattis theorem [8, 23, 24].

The interaction between CTM and nearest graphene nanoflake may also involve next nearest neighbor spins of the nanoflake. This leads to the frustrated character of the corresponding spin lattice and may affect the system's ground-state spin [25]. To study this, we apply the ED method to obtain the energy spectra of the spin Hamiltonians of small lattice clusters. As such, we show the possibility of single and double spin switching with macroscopic changes of the value of the system's ground-state spin, and we estimate the critical values of the model parameters which control these transitions. We also compare these results with the corresponding estimates derived from the DMRG calculations. Finally, we perform QMC simulations of the magnetization profiles of two 2D spin-lattice models for composite nanomagnets based on graphene nanoflakes and CTMs which are similar to the 2D set of triangular graphene nanoflakes linked by carbon chains or by 1,4,5 benzenetriyl units [26].

2 | COMPOSITE SPIN CHAIN SYSTEMS WITH MACROSCOPIC-SPIN GROUND STATE

To begin with, we consider the magnetic sublattices of three model 1D composite nanomagnets derived from graphene nanoflakes connected by CTMs and displayed in Figure 1. All these structures may be considered as generalizations of the 1D magnetic sublattice of one of the first pure organic ferrimagnets, *m*-polydiphenylcarbene, in which the role of a CTM is performed by a carbenic atom.

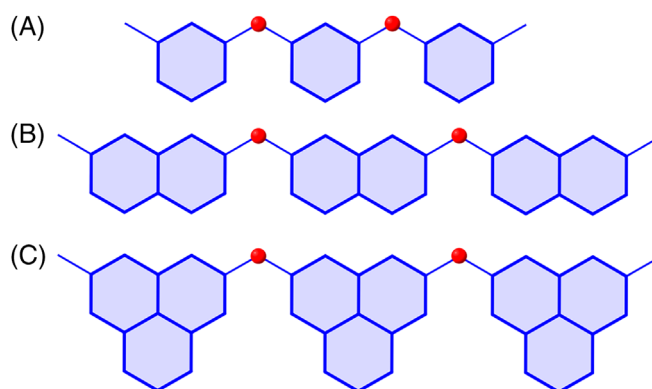


FIGURE 1 The fragments of magnetic sublattices of 1D composite nanomagnets in which red balls correspond to the CTM bridges between neighbor nanoflakes. The structures (A), (B) and (C) are formed by the nanoflakes with 1, 2 and 3 benzene rings, respectively

In this section, we use somewhat simplified Heisenberg spin Hamiltonians in the nearest neighbor approximation with idealized geometry and antiferromagnetic coupling between neighboring spins. These Hamiltonians have the following form:

$$\begin{aligned} H = & \sum_{i=1}^L (J_0 H_{\text{nf}}(i) + J \mathbf{V}(i, i)) + J \sum_{i=1}^{L-1} \mathbf{V}(i, i+1) \\ & - h \sum_{i=1}^L \left(\mathbf{S}_{\text{CTM}}^z(i) + \sum_{j=1}^n \mathbf{S}_{\text{nf}}^z(i, j) \right) \\ H_{\text{nf}}(i) = & J_0 \sum_{l < m} \mathbf{S}_{\text{nf}}(i, m) \mathbf{S}_{\text{nf}}(i, l) \\ \mathbf{V}(i, i) = & \mathbf{S}_{\text{CTM}}(i) \mathbf{S}_{\text{nf}}(i, k) \\ \mathbf{V}(i, i+1) = & \mathbf{S}_{\text{CTM}}(i) \mathbf{S}_{\text{nf}}(i+1, 1) \end{aligned} \quad (1)$$

where $H_{\text{nf}}(i)$ is the spin Hamiltonian of the i th nanoflake structural unit formed by n carbon spins ($n = 6, 10, 13$, respectively) with equal coupling constants J_0 between neighboring spins; $\mathbf{S}_{\text{CTM}}(i)$ is the spin s operator of the transition-metal complex, which belongs to the i th unit cell of the system; $\mathbf{S}_{\text{nf}}(i, m)$ is the operator of the spin- $1/2$ operator located on the m th site of the i th nanoflake unit. The interactions between i th CTM and two neighbor nanoflakes is described by operators $\mathbf{V}(i, i)$ and $\mathbf{V}(i, i+1)$. Here, $k = 3$ for the system 1(a) and $k = 5$ for systems 1(b) and 1(c).

In the Zeeman term of Equation (1), we used, for simplicity, the same g -factors for carbon and CTM carriers of spin. This permits us to use the ED simulation for finite lattice clusters in each subspace with a given value of total spin for additional checks of the results of our numerical simulation.

According to the extended Lieb–Matis theorem, at zero magnetic field the first two chain spin systems have the ground state spin $S_0 = Ls$. For the system 1(c) one arrives at $S_0 = L(s + 1/2)$, where L is the total number of the unit cells. The above 1D bipartite spin systems should have the ground state of a spin-wave structure with the macroscopic values of total spin (“ferromagnetic” ground state). In addition, for the case $s = 1/2$, all our systems should have gapless excitation energy spectra [27, 28] at any values of the coupling constant J . On the other side, according to simple perturbative analysis of the exact energy spectra of our systems at $J \ll J_0$, there is a branch of gapped excitations which approximately corresponds to excitations within the isolated nanoflake unit. As a result, similar to reference [29], this structure of the excitation spectra of our systems may lead to an intermediate plateau in the field-dependent magnetization at low temperatures, at least for the case of weak interaction between the structural units. In order to study this possibility, we performed QMC and DMRG calculations for the field dependence of the total magnetization per spin m (magnetization profile) of our systems at $s = 1/2$ and $s = 1$. The results of this numerical study are presented in Figure 2. Note that here and further the energy E , coupling constants J , magnetization m , and magnetic field h are presented in dimensionless units.

Hereinafter, for all systems, we put for simplicity $J_0 = 1$. In our calculations for infinite and finite DMRG scheme, we used up to 50 optimized states and three sweeps for finite scheme of DMRG. In the result, we found a good coincidence between ED study for finite lattice fragments, both DMRG approaches and our QMC results extrapolated to zero temperature. QMC simulations were carried out for systems consisting up to 2000 spins. Typical number of sweeps for thermalization is 5000 and 10 000 sweeps were used for averaging.

Our study demonstrate clearly the presence of the first intermediate plateaus at the magnetization per spin $m = 1/14$ and $m = 1/7$ for the system 1(a) with $s = 1/2$ and $s = 1$, respectively (A). For system 1(b), we have the first intermediate plateaus (B) at $m = 1/22$ ($s = 1/2$) and $m = 1/11$ ($s = 1$). Finally, for system 1(c), we obtain plateaus at $m = 1/14$ and $m = 3/28$ for $s = 1/2$ and $s = 1$, respectively (C).

These results correspond to the ferrimagnetic ground state of our model spin systems and the gapped character of the lowest excitations with $S > S_0$. Some other plateaus can be the result of finite size effects, especially for ED study.

3 | FRUSTRATED COMPOSITE SPIN CHAIN SYSTEMS AND SPIN SWITCHING MEDIATED BY FRUSTRATIONS

In real composite materials formed of nanoflakes and CTMs, one should take into account the possibility of effective interaction of CTM spin s with the next-nearest neighboring spins located in the nanoflake, as shown in Figure 3.

These interactions may be of the same order as the interaction with the corresponding nearest neighboring spin. In the result we obtain a frustrated spin system similar to the chain model shown in Figure 3 which has been studied in reference [25] by means of first-order perturbation theory with respect to the interactions between structural units.

According to that study, for a small coupling denoted $J \ll 1$ ($J_0 = 1$) there is a critical value of the coupling constant J' describing the next-nearest neighboring interactions at which a transition with the macroscopic jump of the ground state spin (spin switching) occurs. Moreover, this transition appears at the coupling ratio $\alpha = J'/J \sim 0.33$ regardless of the value of CTM spin s . We cannot perform a similar analysis for the model

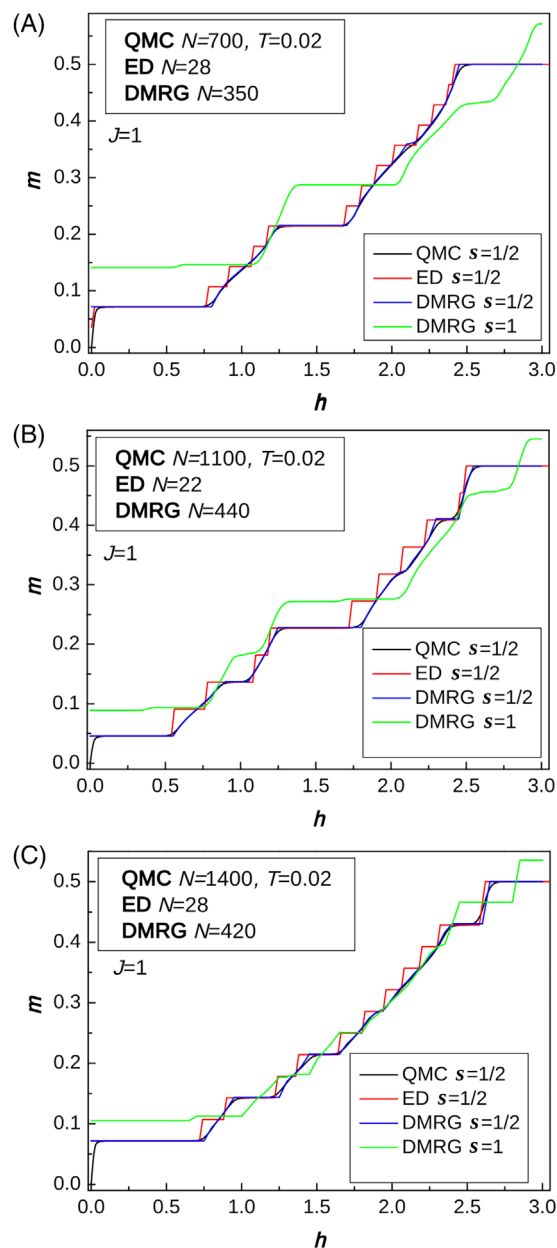


FIGURE 2 Plot of the magnetization profiles for models 1(a), 1(b), and 1(c), respectively

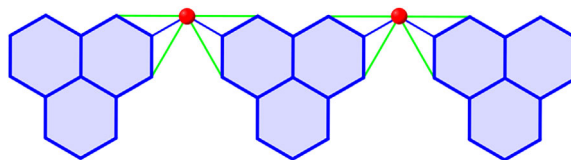


FIGURE 3 Spin model 1(c) with additional next nearest interactions between CTM spins and neighbor triangular graphene fragments described by coupling constant J' (green lines)

systems of Figure 1A,B since the corresponding first-order PT corrections to the ground state energy equals to zero. It is also of interest to study the case of intermediate values of coupling J for which the PT consideration of references [25, 30] cannot be applied.

One of the simplest ways to investigate the lowest part of the energy spectra of the composed systems formed by graphene fragments with a singlet ground state, systems 1(a) and 1(b), is to use a uniform spin s chain Heisenberg Hamiltonian with an effective

coupling between CTM spins [31]. The value of this coupling can be obtained from the intersection of two lowest exact energy levels of the system fragment formed by two CTM and one nanoflake. For this purpose and the case of CTM spin $s = 1/2$, we performed an ED study of the fragment Hamiltonians in subspaces with total spin $S = 0$ and $S = 1$ at different values of the coupling ratio α as a frustration parameter and coupling constant J . The results of this numerical study at $J = 0.1$ and $J = 1$ are presented in Figures 4 and 5.

In both cases, we found two intersection points regardless of the value of the coupling J . This means that the singlet ground state of the systems 1(a) and 1(b) with additional next-nearest neighbor interactions is stable only in some restricted ranges of α . In other words, the increased frustration leads to double spin switching and for large enough values of J' the systems returns to the “ferrimagnetic” ground state.

In order to check this conclusion, we performed the corresponding DMRG simulation for the lowest energy levels of the fragments of the above two systems formed up to 400 spins. In all DMRG calculations, we used 50 optimized states. The results of this simulation are rather close to our ED estimations. For example, for the system 1(a) with $J = 1$, we have two ED intersection points at $\alpha \sim 0.39$ and $\alpha \sim 0.96$. The corresponding DMRG estimates are $\alpha \sim 0.39$ and $\alpha \sim 0.89$.

We also performed the DMRG study of the systems 1(a) and 1(b) for CTM spin $s = 1$. Interestingly, in this case only one intersection of the lowest energy levels occurs. This corresponds to the destruction of the ground state with the macroscopic total spin (“ferrimagnetic” ground state) upon increasing frustration.

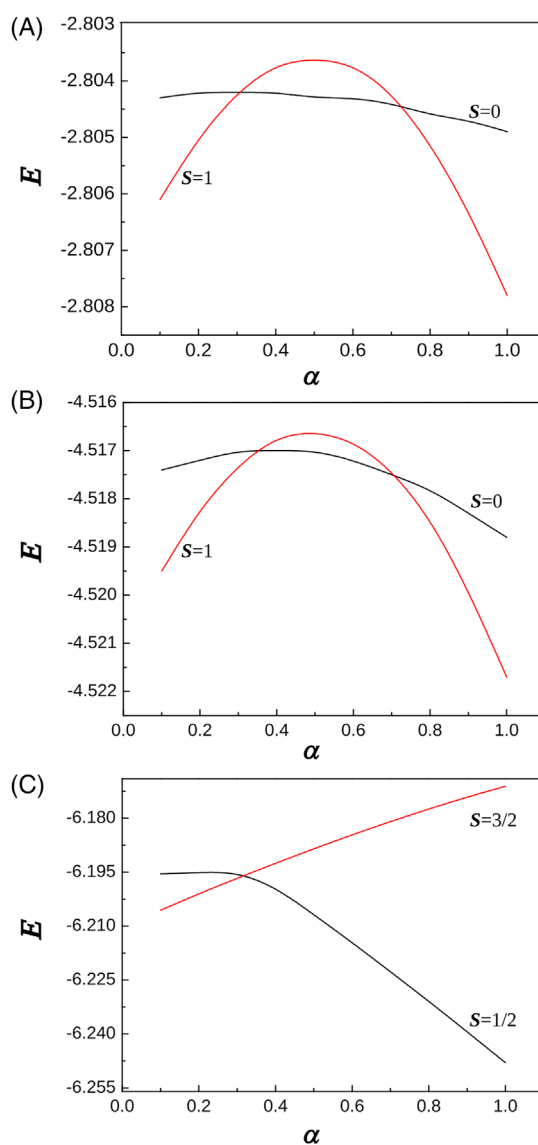


FIGURE 4 The lowest energy levels of the fragments of systems presented in Figure 1 at different values of frustration parameter α , CTM spin $s = 1/2$. (A) 8-spin fragment of the system 1(a), (B) 12-spin fragment of the system 1(b), (C) 15-spin fragment of the system 1(c). Coupling constant $J = 0.1$

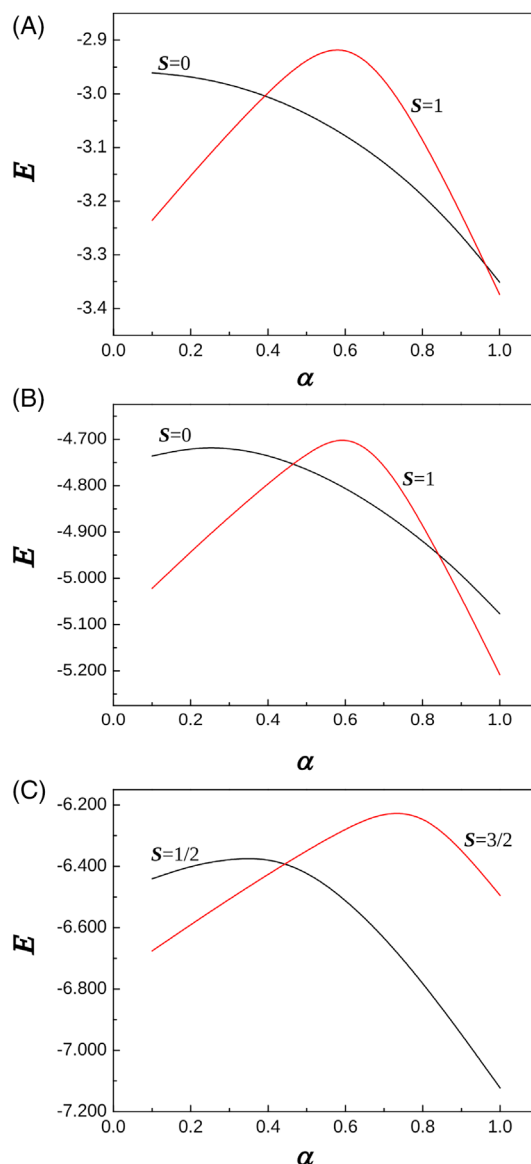


FIGURE 5 The same dependencies as in Figure 4, but for the coupling constant $J = 1$

As for the system 1(c) with additional interactions (Figure 3), the ED study gives only one intersection between the two lowest energy states (single spin switching). The results of this study are presented in Figures 4c and 5c for $J = 0.1$ and $J = 1$, respectively.

It is of interest that for $J = 0.1$, the intersection point derived from ED gives the critical frustration parameter of $\alpha \sim 0.34$, in good agreement with the PT estimate $\alpha \sim 0.33$ from [25]. The corresponding DMRG calculations with 50 optimized states for the system formed by 210 spins yields estimates of $\alpha \sim 0.33$ for $s = 1/2$ and $\alpha \sim 0.31$ for $s = 1$.

4 | TWO-DIMENSIONAL COMPOSITE SPIN SYSTEMS WITH THE MACROSCOPIC GROUND STATE SPIN

Let us now consider 2D composite magnetic systems formed by small graphene nanoflakes connected by CTMs. For two types of graphene nanoflakes formed by one and three hexagons the corresponding bipartite structures have the following form (see Figure 6):

According to the extended Lieb–Mattis theorem, these spin structures should have macroscopic ground state spin. Similar to the 1D spin system studied before, at a small interaction between structural units one may expect an appearance of intermediate plateau in the field dependence of magnetization at low temperatures and spin switching mediated by additional next-nearest neighbor interactions.

In both cases, we found intermediate magnetization plateaus, which increase in size with growing interactions between structural units of our spin lattices.

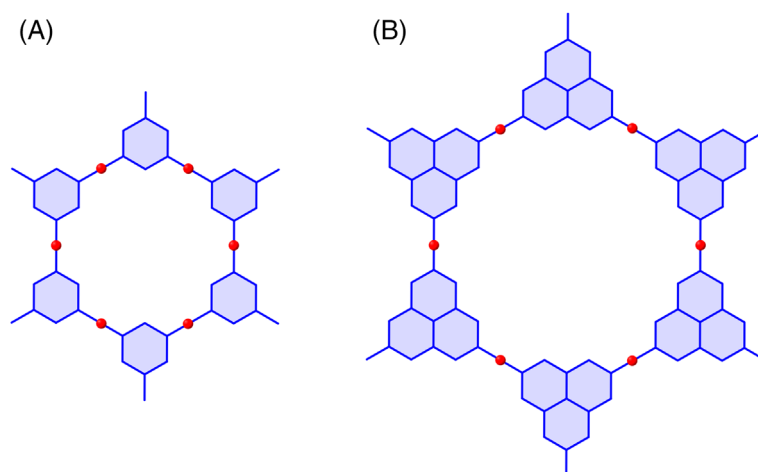


FIGURE 6 Two types of magnetic sublattices with hexagonal arrangement of the graphene fragments of the 2D model composite “ferrimagnets”

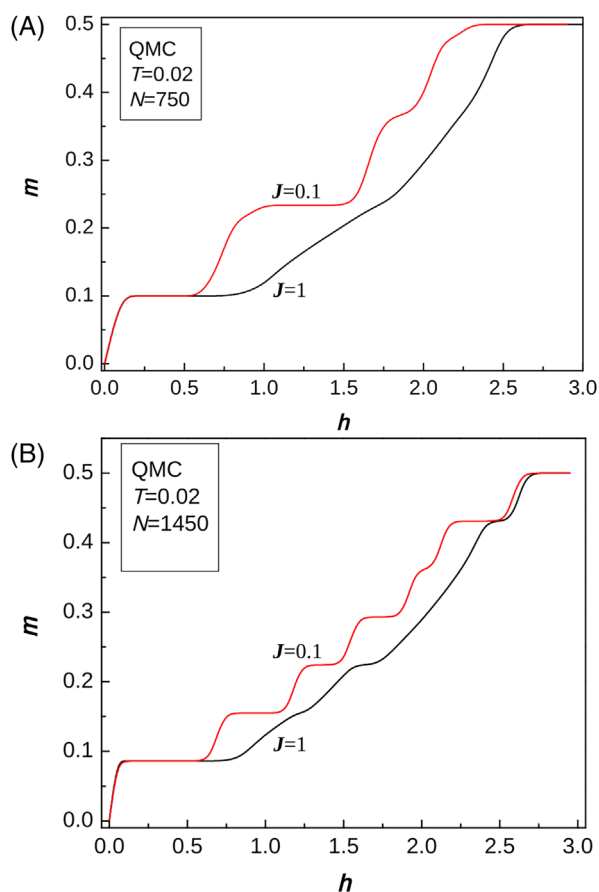


FIGURE 7 Magnetization profiles for fragments of 2D model “ferrimagnetic” sublattices presented in Figure 6a,b, respectively

For intermediate values of the interactions between structural units, we may perform only a QMC study of the magnetization profile of the finite fragments of the above 2D spin structures at CTM spin $s = 1/2$. The results of these QMC simulations are presented in Figure 7.

5 | CONCLUSIONS

We performed a numerical study of the lowest energy spectra of Heisenberg spin models for a number of composite nanomagnets based on graphene nanoflakes and complex transition-metals compounds. We also showed appearance of intermediate plateaus in low-temperature magnetization

profiles of those magnets corresponding to a macroscopic manifestation of the quantum ferrimagnetic phases. This effect is in agreement with the experimental magnetization profiles of some 1D ferrimagnets at low temperatures. We also found a possibility of single and double spin switching with the macroscopic jump of the ground state spin mediated by the frustrated interactions between nanoflakes and CTMs.

AUTHOR CONTRIBUTIONS

Vladyslav O. Cheranovskii: Conceptualization; data curation; formal analysis; investigation; methodology; project administration; resources; software; supervision; validation; writing – original draft; writing – review and editing. **Victor V. Slavin:** Conceptualization; data curation; formal analysis; investigation; methodology; resources; software; validation; writing – original draft; writing – review and editing. **Andrei L. Tchougréeff:** Conceptualization; data curation; formal analysis; investigation; methodology; resources; software; validation; writing – original draft; writing – review and editing. **Richard V. Dronskowski:** Conceptualization; data curation; formal analysis; investigation; methodology; software; validation; writing – original draft; writing – review and editing.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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