1. Introduction

Multiferroic materials simultaneously possess magnetic and electrical order parameters. Often multiferroics show coupling between magnetic and electric degrees of freedom [1–5]. The coupling promises numerous applications, but at the moment it is far from being fully understood. Materials with strong magneto-electric (ME) coupling are still a great challenge. Currently there is an active search for multiferroic materials with strong ME correlations [6, 7].

ME coupling can appear due to spin–orbit interaction in certain crystals. This coupling is relatively weak. Another way to get strongly coupled magnetic and electrical moments is to develop hybrid ferroelectric-ferromagnetic (FE-FM) layered materials where mechanical stress between the layers produces strong correlations between magnetization and polarization [8–11]. Recently another promising possibility of ME coupling was suggested in granular materials where small metallic ferromagnetic grains are embedded into the FE matrix or these grains are located in close proximity to the FE substrate [12]. The presence of small metallic grains increases the strength of Coulomb interaction which provides the necessary coupling between the FE and FM degrees of freedom.

In granular multiferroics the intergrain exchange coupling \( J \) crucially depends on the properties of the FE substrate, in particular, on its dielectric permittivity \( \varepsilon \) [12, 13]. Due to temperature dependence of dielectric permittivity, \( \varepsilon(T) \), the exchange interaction depends non-monotonically on...
temperature leading to the onset of ferromagnetic ordering in granular multiferroics in the finite temperature range around the ferroelectric–paraelectric phase transition point.

On the mean-field level the properties of these materials have been well understood [12]. However, in real granular systems the long-range magneto-dipole interaction and magnetic anisotropy play a crucial role in their magnetic behavior. Magneto-dipole interaction cannot be treated within the mean field approach. In this paper we address the question of robustness of ME coupling against the influence of magneto-dipole interaction using numerical modeling. We investigate the equilibrium and non-equilibrium meta-stable states in granular multiferroics and study the magnetic phase diagram appearing in the system with temperature dependent exchange interaction. In addition, we show that an unusual blocking phenomenon can appear in composite multiferroics.

To be more specific, we study the magnetic behavior of composite multiferroics in which magnetic grains are embedded inside the FE matrix. We consider the case when \( T_{C}^{\text{FM}} < T_{C}^{\text{FE}} \), where \( T_{C}^{\text{FM}} \) is the Curie temperature of the FE matrix and \( T_{C}^{\text{FE}} \) is the Curie temperature of the material of which FM grains are made. Typical materials for magnetic grains are Ni, Co and Fe with Curie temperatures 600 K, 1400 K, and 1000 K, respectively. The FE materials have much lower Curie temperature. We focus on the temperature range \( T \ll T_{C}^{\text{FM}} \) and \( T \sim T_{C}^{\text{FE}} \), when all the grains are in the FM state. We study the magnetic phase diagram of granular multiferroics beyond the mean-field approximation using Monte-Carlo simulations. In particular, we study the combined effect of magnetic anisotropy, the long-range magneto-dipole (MD) interaction and the exchange coupling. We show that there is strong ME coupling in the system. The coupling is robust with respect to moderate MD interaction. However it disappears for strong MD interaction, essentially stronger than the exchange coupling.

Three-dimensional (3D) nanostructures composed of single-domain ferromagnetic particles has been intensively studied both experimentally and theoretically [14–22]. The interplay of magnetic anisotropy, long-range magneto-dipole interaction and short range exchange interaction defines the magnetic state of these system. Depending on the ratio of these interactions different magnetic states are possible in granular ferromagnets [23, 24]. Among them are superparamagnetic (SPM), super spin-glass (SSG) and superferromagnetic (SFM) states.

The most studied situation is related to the case of large intergrain distances (\( \gtrsim 2 \text{nm} \)) and small exchange interaction where magnetic state is defined by the competition of MD interaction and anisotropy [21, 25, 26]. The magnetic anisotropy is responsible for ‘blocking’ phenomena and defines the blocking temperature \( T_{b} \) [18, 27]. The weak MD interaction modifies the blocking temperature, while the strong MD interaction leads to the SSG state [28–32].

For systems with small distances between grain surfaces (\( \sim 1 \text{nm} \)) the exchange interaction is crucial. It leads to the formation of the SFM state [23, 33–36]. In such systems the SPM-SFM transition occurs. Even a weak exchange interaction can influence the magnetic state of the system [34]. In particular, the FM ordering with long range ferromagnetic correlations appears.

Different theoretical methods have been used to study granular magnets. The mean-field approach allows to study granular systems with finite short range exchange interaction and zero (or weak) MD interaction neglecting fluctuation effects [37, 38]. The modeling based on the Landau–Lifshitz equation allows considering the MD, magnetic anisotropy and exchange interactions [39]. However, this approach needs to be generalized in the presence of thermal fluctuations by introducing the Langevin forces [40]. These fluctuations are important for granular magnetic systems since the granular magnetic moment is relatively small and fluctuation effects are pronounced especially near the phase transitions. However, the inclusion of Langevin forces in the nonlinear spin dynamics is not numerically efficient. Therefore we use Monte-Carlo (MC) simulations which allow to study phase transitions in composite multiferroics with strong long-range MD interaction and arbitrary thermal fluctuations [14, 15, 21, 24, 26, 41–45].

MC modeling strongly depends on the degree of anisotropy. At strong anisotropy the problem reduces to the Ising model with magnetic moment of each particle having only two directions defined by the anisotropy axis. In this case the MC modeling is very efficient and is based on the trial spin flips. Another type of MC modeling is used for the Heisenberg model with arbitrary magnetization direction. This model is more general but it requires more computational time due to spin rotations over the the whole sphere. For strong anisotropy the MC algorithms (especially for Heisenberg model) usually become inefficient. Thus, it is a challenge to create an efficient universal MC algorithm [43, 44, 46, 47]. We have written the MC code combining random spin-flips and random spin-rotations. Such a combination allows to simulate system with arbitrary anisotropy.

The paper is organized as follows. In section 2 we formulate our main results. In section 3 we discuss the model of composite multiferroics and introduce important physical quantities which we calculate. We discuss our results in section 4. The details of our numerical calculations are presented in appendix A.

2. Main results

The non-monotonic temperature dependence of exchange interaction in composite multiferroics leads to the unusual evolution of the magnetic state with temperature. The intergrain exchange interaction has either a peak or dip in the vicinity of the FE phase transition due to coupling of electric and magnetic degrees of freedom. In the mean field approximation the peak in the exchange interaction leads to the onset of the FM state in the vicinity of FE phase transition. The dip in the exchange interaction suppresses the FM state in the vicinity of the FE Curie point. We use Monte-Carlo simulations to show that MD interaction and anisotropy do not suppress the magnetoelectric coupling in these materials, however their interplay produces a new type of hysteresis. Our results are the following:
1) The Monte-Carlo simulations reproduce the mean field results in the absence of MD interaction and magnetic anisotropy. Similar to the mean field approach, the FM state exists in the vicinity of the FE Curie point and the disordered state appears away from this region.

2) The finite MD interaction does not suppress the FM ordering in the vicinity of the FE phase transition even if the MD interaction is twice stronger than the exchange interaction. The presence of MD interaction leads to domain formation and the splitting of the uniform FM state. This result is similar to [34], where a weak FM interaction leads to the formation of FM domains.

3) The magnetic state depends on the strength of MD interaction outside the FM region: the system is in the SPM state for weak MD interaction and in the antiferromagnetic stripe phase for strong MD interaction.

4) The magnetic anisotropy does not influence the FM state. However, it prevents the formation of vortices in the transition region and leads to a widening of FM domains.

5) The ‘blocking phenomenon’ does not appear at finite magnetic anisotropy and zero MD interaction at considered temperatures meaning that the system has enough time to reach the ground state such that the non-equilibrium state does not appear.

6) The ‘blocking phenomenon’ appears at finite magnetic anisotropy and finite MD interaction. The temperature hysteresis loop occurs due to non-monotonic behavior of exchange interaction versus temperature. The origin of this hysteresis is related to the presence of stable magnetic domains which are robust against thermal fluctuations.

7) The AFM stripes appear in the case of dip in the exchange interaction.

Below we discuss these results in details.

3. The model

3.1. Magnetic subsystem

We model a composite multiferroic as an ensemble of FM grains embedded into the FE matrix. All grains are homogeneously magnetized (single domain) FM particles of the same volume $V$ and saturation magnetization $M_s$. For temperatures $T \ll T_C$, the saturation magnetization $M_s$ is a constant. Each grain with volume $V$ has a magnetic moment $\mu = M_s V$ and is treated as a point dipole located at the center of the grain. The grains are pinned to the sites of the regular cubic lattice with lattice spacing $a$ and can freely rotate adjusting their magnetic moments. We discuss the choice of the lattice type in section 4.3.

The whole system is modeled as a 3D lattice of classical spins, with magnetic moment of the $i$th grain being $\mu_i = \mu S_i$ where the unit vector $S_i = (S_i^x, S_i^y, S_i^z)$ is the spin of $i$th particle representing the direction of the magnetic moment.

We assume that each grain has a uniaxial anisotropy. Spatial distributions of anisotropy axes varies in different experiments and depends on the preparation condition. The anisotropy axes can be homogeneously distributed over the solid angle, or uniformly distributed in a certain plane. In our simulations we assume that the easy axes of all grains are oriented in the z-direction. This situation is realized in samples prepared in an external uniform magnetic field [36].

The Hamiltonian of the system has the form

$$H = H_{\text{exc}} + H_{\text{dip}} + H_{\text{an}}.$$  \hspace{1cm} (1)

The first term, $H_{\text{exc}}$, describes the exchange coupling between grains

$$H_{\text{exc}} = -J \sum_{\langle i,j \rangle} S_i \cdot S_j,$$  \hspace{1cm} (2)

where the sum $\langle i,j \rangle$ is over the nearest neighbour pairs of grains.

The second term, $H_{\text{dip}}$, in (1) describes the long-range MD interaction between magnetic moments $\mu_i$ and $\mu_j$ of individual grains

$$H_{\text{dip}} = g \sum_{i<j} \frac{S_i \cdot S_j \cdot r_{ij}^2 - 3(S_i \cdot r_{ij})(S_j \cdot r_{ij})}{r_{ij}^5},$$  \hspace{1cm} (3)

where the distance $r_{ij}$ between sites $i$ and $j$ is measured in units of lattice spacing $a$, $g = g_{dip} a^2/(4\pi a^3)$ is the MD interaction constant and summation is over all different pairs of spins.

The third term, $H_{\text{an}}$, in (1) describes uniaxial anisotropy energy

$$H_{\text{an}} = -K \sum_i (e_z \cdot S_i)^2,$$  \hspace{1cm} (4)

where $K$ is the temperature independent magnetic anisotropy energy of a single grain. The unit vector $e_z$ defines the direction of the anisotropy easy axis.

We consider the energy parameters $(J, g, K, T)$ in arbitrary units. Parameters $g$ and $K$ depend on a grain volume and can be controlled by varying the grain size. The dipole coupling $g$ additionally depends on the lattice spacing $a$. This allows one to vary parameters $g$ and $K$ in a wide range. The exchange interaction is proportional to the grain surface and correspondingly scales with the volume as $V^{2/3}$. Moreover, the ratio of MD and exchange interactions can be controlled by varying the interparticle distance $a$. The MD interaction decays as $1/a^5$ with distance, while the exchange interaction decays exponentially $e^{-\kappa a}$, where $\kappa$ is the inverse length characterizing the localization length of electron wave functions. It depends on the band structure of the surrounding FE matrix and the Fermi energy of electrons inside grains.

3.2. Ferroelectric subsystem

The dielectric permittivity $\epsilon(T)$ of the FE matrix has a peculiarity in the vicinity of the phase transition point, $T_{\text{FE}}^{\text{crit}}$ [48]. This peculiar behavior of $\epsilon(T)$ combined with the Coulomb blockade effects leads to unusual temperature behavior of the exchange interaction $J(T)$ [12, 13]. Depending on the system parameters the exchange interaction $J(T)$ has either peak or dip in the vicinity of the FE phase transition. Below we assume that FE matrix is isotropic. Also we neglect all striction effects. This is a reasonably good approximation for
polymer or organic FEs with numerous metallic inclusions. We discuss these assumptions in more details in section 4.3.

The dependence of the intergrain exchange interaction $J$ on the FE permittivity $\varepsilon$ is the signature of magneto-electric coupling emerging in composite multiferroics. As was recently predicted such a dependence has the form [12]

$$J(T) = J_0 e^{-\alpha d_{gr}/\varepsilon},$$

(5)

where parameter $J_0 > 0$ is the $\varepsilon$-independent part of the exchange interaction, it decays exponentially with intergrain distance $a$, $d_{gr}$ is a diameter (the size) of the grain, $\alpha$ is a numerical coefficient of order one.

The dielectric permittivity $\varepsilon$ has a peak at $T_{FE}$. As a result, depending on the value of the numerical coefficient $\alpha$, the exchange interaction has either a peak at large intergrain distances, $a > d_{gr}/\alpha$), or a dip at small intergrain distances, $a < d_{gr}/\alpha$). When the permittivity $\varepsilon(T)$ reaches its maximum value at $T_{FE}$ the Coulomb blockade is suppressed, the electron wave functions become weakly localized and strongly overlapped and, as a result, it leads to enhanced exchange interaction (at $a > d_{gr}/\alpha$) [12].

In the case of the peak in $J(T)$ the FM state appears in the vicinity of the FE Curie temperature, while away from $T_{FE}$ the system is in the SPM state [12]. It leads to the unusual magnetic phase diagram, namely, (i) the FM phase comes up in a finite region around FE Curie point, (ii) there are two phase transitions into an SPM phase at temperatures $T_{C}$ and $T_{C}^*$, $T_{C} < T_{FE}^* < T_{C}^*$. In case of the dip in $J(T)$ the opposite situation occurs: the FM state is suppressed in the vicinity of $T_{FE}$ and comes up below $T_{C}$, or above $T_{C}^*$. Such a succession of phase transitions were predicted in [12] in the mean field approximation. In this paper we are specifically interested in the role of the long range dipolar interaction and anisotropy in phase transitions from the ordered to disordered states.

To reduce calculation difficulties, below we adopt the following model functions for the $J(T)$-dependance: for large $\gamma$ we model the peak in $J(T)$ as

$$J(T) = J_0 e^{-(T-T_{FE}^*)/T_{FE}^*},$$

(6)

and for small $\gamma$ we model the dip in $J(T)$ as

$$J(T) = J_0(1 - e^{-(T-T_{FE}^*)/T_{FE}^*}).$$

(7)

Here, $w$ is the width of the exchange peak (dip) and $J_0$ is the amplitude of intergrain exchange interaction. These are simple ways to account for the peak (dip) in $J(T)$ at temperature $T = T_{FE}^*$.

3.3. Calculated thermodynamic functions

In our simulation in order to identify the magnetic phases of the model we calculated three thermodynamic functions: the magnitude of the magnetization, the cell-averaged magnetization and the nearest neighbor spin–spin correlation function. The details of the MC simulation procedure are described in appendix A.

The average of the magnitude of the magnetization $[49–52]$ is defined in a usual way

$$M(T) = \left\langle \frac{1}{N} \sum_{i=1}^{N} S_i \right\rangle,$$

(8)

where $N$ is the number of lattice sites and $\langle \rangle$ denotes the MC thermal average.

In the presence of MD interaction the lattice spins form complex magnetic patterns, including domains and vortices. Such patterns produce vanishing mean magnetization, $\langle\sum_{i}^{N} S_i\rangle = 0$, even if locally the system is in the FM state. To account for local FM correlations we introduce the cell-averaged magnetization $m(T)$ when we first perform averaging over a cell with linear size $L_c$

$$m(T) = \left\langle \frac{1}{N_c} \sum_{\alpha \in \Omega_c} \frac{1}{N} \sum_{i \in \Omega_c} S_i \right\rangle.$$  

(9)

The first summation is over $N_c = L_c^3$ grains in a given cell $\Omega_c$, the second summation is over all possible $\Omega_c$-cells. We find that the optimal size for a cell averaging is $L_c = 5$.

Next, we introduce the spin–spin correlation function $G(T)$ as an averaged correlation function for nearest-neighbour pairs of spins

$$G(T) = \left\langle \frac{1}{3N} \sum_{\langle ij \rangle} S_i \cdot S_j \right\rangle,$$

(10)

The correlation function $G$ is connected with the magneto-transport phenomena in granular magnets. The magnetoresistance (MR) of granular magnetic film is proportional to $G$. The MR measurements can be considered as one of the probes of the magnetic state in granular multiferroics.

4. Discussion

4.1. Influence of magneto-dipole interaction

In this section, we describe the magnetic phase diagram for multiferroics with large intergrain distances, $a > d_{gr}/\gamma$, when the dependence $J(T)$ has a peak around $T_{FE}^*$. We consider zero anisotropy, $K = 0$, and MD interaction, ranging from $g = 0$ to $g = 5$. For model function $J(T)$, equation (6), we use $J_0 = 2.5, w = 0.1, T_{FE}^* = 0.5$. It corresponds to Fe-grains with size $d_{gr} \approx 5–10 \text{nm}$ and the intergrain distance $a \geq 5 \text{nm}$ embedded into organic TTF-CA FE matrix. The corresponding intergrain exchange interaction is $J/k_B \approx 300 \text{ K}$. This value of intergrain exchange interaction was observed in [34]. The Curie temperature of bulk ferroelectric TTF-CA is $T_{FE}^* = 80 \text{ K}$. However, for a granular array it can be even smaller: the Curie temperature of TTF-CA in composite granular metal/FE system is $50 \text{ K}$ [53].

We start our discussion with the most simple case of zero MD interaction, $g = 0$. In figure 1 we show the temperature dependence of three thermodynamic functions $M, m, G$ and the dependence of $J(T)$ in the vicinity of $T_{FE}^*$. The corresponding snap-shots of spin arrangements are given in figure 2. The magnetic phase diagram for zero MD interaction can be obtained by inspecting the dependence of the magnetization,
M(T) (other two functions, m and G, show the similar behavior). It shows a finite FM region around $T_{C}^{EE}$ and the SPM state outside this region, see the corresponding snapshots in figure 2, panels (b) and (a), respectively. Appearance of ordered ferromagnetic phase in the vicinity of FE phase transition temperature should be considered as a consequence of strong coupling between electrical and magnetic degrees of freedom in granular multiferroics.

Also we show two mean-field transition temperatures, $T_{C}^{M}$, that occur approximately at $J(T) = T/2$. Their positions lie close to the ones obtained from MC simulation. Since the exchange interaction is finite at zero temperature we expect that one more SPM-FM transition occurs below $T = 0.3$. Magnetic phase transition at $T_{C}$ is the so-called inverse phase transition, when the ordered phase appears at a higher temperature than the disordered one. In systems with temperature independent exchange interaction there would be only one magnetic phase transition (from FM to SPM phase).

The phase diagram for weak MD interaction, $g = 0.5$ is shown in figure 3. This value of $g$ is typical of Fe-grains with size $d_g = 4$ nm, $g/k_B = (\mu_0/4\pi k_B)(2.2\mu_0 V/\lambda_{Fe}^3a^3) \approx 50$ K, $\lambda_{Fe} = 0.28$ nm is the Fe-lattice parameter [54]. The corresponding snapshots of spin configurations are shown in figures 4(a) and (c). There is the homogeneous FM state around the peak value of $J(T)$, while outside $T_{C}^{EE}$ the finite MD interaction competes with intergrain exchange interaction and causes the formation of domains of opposite magnetization, the total magnetization, $M$, averages out to zero. Domains with larger width (figure 4(a)) lead to the formation of the shoulder in the behavior of $m$ and $G$, while domains with lower width (figure 4(c)) cause the gradual decrease of

Figure 1. Magnetic phase diagram of a composite multiferroic versus temperature $T$ ($g = 0, K = 0$). Solid (red) line shows the temperature dependence of the intergrain exchange interaction, $J(T)$ (for comparison, the dependence $J(T) = T$ is also shown, straight dash–dotted (orange) line). Gray dash–dot–dotted and green dotted lines show average magnetization $M(T)$ and cell averaged magnetization $m(T)$, respectively. Blue dashed line shows the nearest neighbour correlation function $G$. Temperatures $T_{C}^{M}$ mark the positions of solutions of the mean-field equation, $J(T) = T/2$. Black arrows show the positions of corresponding snap-shots presented in figure 2.

Figure 2. Snapshots of a single magnetic layer of a composite multiferroic in the disordered SPM magnetic state, panel (a), and ordered FM state, panel (b).
m and G. At $T < 0.3$ and $T > 0.7$ thermal fluctuations exceed the exchange and MD interactions resulting in the SPM state.

At intermediate MD interaction, $g = 2.0$, (Fe-grains of size $d_{gr} = 6$ nm and interparticle distance $a = 7$ nm, $g/k_B \approx 230$ K) magnetic vortices appear around the peak value of $J(T)$ (note that $g = 2.0$ approximately corresponds to the peak value of exchange interaction, $J_0 = 2.5$). An example of such state is shown in figure 4(b). The presence of the vortices is signalled by the zero value of magnetization $M$, see figure 5. However, there are strong local ferromagnetic correlations in the system close to $T_{C_{FE}}$, as can be seen from the dependence of functions $m$ and $G$. They lead to formation of domain structures outside the $T_{C_{FE}}$-region. This correlations (and domain structure) survive in the whole studied temperature range ($0.28 < T < 0.72$).

At strong MD interaction, $g = 5.0$, (Fe-grains of size $d_{gr} = 10$ nm and interparticle distance $a = 15$ nm, $g/k_B = 470$ K) magnetic vortices coexist with small patches of domains in the vicinity of the FE Curie point, see figure 6. Away from $T_{C_{FE}}$-region spins form FM chains arranged antiferromagnetically. This is a columnar antiferromagnetic state (CAF), the ground state typical of dipolar system on a simple cubic lattice [55].

Next, we present the simulation results when the multiferroic system has a dip in the vicinity of the FE Curie point. Such a situation can occur for small intergrain distances [12], $d_{gr} < a < d_{gr}/\gamma$ (this case requires that the numerical parameter $\gamma < 1$). We use $J_0 = 0.75$, $\Delta T^\text{FE} = 0.07$, and $T_{C_{FE}} = 0.5$ to model the dependence $J(T)$, see (7). Figure 7 shows the evolution of the phase diagram with increasing dipolar coupling. The exchange interaction, $J(T)$ exceeds $T$ in the whole temperature range, except the close vicinity of FE transition. It leads to formation of a homogeneous FM state at $g = 0.0$, and vortex states at $g = 0.5$ and $g = 2.5$ outside of $T_{C_{FE}}$-region. Close to $T_{C_{FE}}$ the system is in the SPM state at $g = 0.0$ and $g = 0.5$. The SPM state gradually transforms into a CAF state with increasing dipolar interaction, see figure 7(c). It is signalled by the finite negative value of function $G$ close to $T_{C_{FE}}$.

### 4.2. Influence of magnetic anisotropy

Magnetic anisotropy is crucial for the formation of the magnetic state in granular magnets. In granular materials it is much stronger than in bulk magnets due to surface and shape effects [16, 18]. The magnetic relaxation time in a system of non-interacting magnetic particles exponentially depends on the ratio of their anisotropy energy and temperature, $\tau_r \sim \exp(K/(k_B T))$. At low temperatures, when the relaxation time becomes larger than the characteristic measurement
Figure 5. Magnetic phase diagram of a composite multiferroic versus temperature $T$ for intermediate magneto-dipole interaction ($g = 2.0$, $K = 0$). All notations are defined in figure 1.

Figure 6. Upper panel: the magnetic phase diagram of a composite multiferroic versus temperature $T$ for strong magneto-dipole interaction ($g = 5.0$, $K = 0$). All notations are defined in figure 1. Bottom panels: antiferromagnetic pattern of FM chains at low temperatures (left); magnetic vortex coexisting with domain patches in the vicinity of $T_{c}^{m}$ (right).
time, the measured magnetic properties characterize a non-equilibrium, or ‘blocked’, state. The blocking effect unambiguously manifests itself in the zero field cooling/field cooling MC simulation [56].

MC simulation starts with a certain non-equilibrium state and the system ‘relaxes’ to the equilibrium state via discrete steps during the simulations. If a number of MC steps $N_{MC}$ (which can be associated with measurement time if the attempt frequency of the system is known) exceeds a certain value $N_r$ (which can be associated with the relaxation time $\tau$) then the system relaxes to the equilibrium state during simulations. Otherwise, the system is locked into some non-equilibrium magnetic state.

Blocking effects cause the dependence of the measured state (final state of simulations) on the system initial state. As we demonstrate below this is not the case if the simulation performed with zero MD interaction, $g = 0$, MC results do not depend on the initial state of the system. Thus, we conclude that for this case $N_{MC} \gg N_r$. To simulate systems with large $K$ (as for example $K = 6.0$ presented below) we use special algorithm for MC moves with spin flips, details are presented in the appendix A.

Figure 8 shows the magnetic phase diagram of a granular multiferroic with strong anisotropy, $K = 6.0$, and without MD coupling, $g = 0$. Such a big value of $K$ (it is twice as large as the peak value of the exchange interaction) takes place for a system of $d_{gr} = 6$ nm Fe-grains, with anisotropy constant $K = 0.8 \cdot 10^{-6}$ erg cm$^{-3}$ [16]. Temperature dependence of thermodynamic functions $M$, $m$ and $G$ is consistent with the prediction of the mean-field theory, namely, the FM state appears in the vicinity of FE phase transition and on both sides of $T_{C_{FE}}$ there are disordered states. The temperature range for FM phase is much wider as compared to the case of $K = 0$. At the SPM-FM transition points, $T_{c1} \approx 0.32$ and $T_{c2} \approx 0.64$, the exchange interaction is approximately four times smaller than the temperature. Directions of magnetic moments in the disordered state are mostly concentrated along the anisotropy axis (Ising-type behavior) (see the inset in figure 8). The magnetic anisotropy alone does not qualitatively change the magnetic phase diagram of composite multiferroics.

The interplay of dipolar interaction and anisotropy energy in systems of dipoles on a simple cubic lattice with fixed anisotropy axes can lead to the appearance of frozen metastable domain states [57]. This domains depend explicitly
on the history and relax towards the ordered state only at extremely large time scales [57]. In a multiferroic system this can be further complicated by the presence of the temperature dependent exchange interaction.

To illustrate the formation of frozen history-dependent states due to combined influence of MD interaction and anisotropy energy in figure 9 we present the behavior of thermodynamic functions $M$, $m$ and $G$ when (i) the simulation starts at a lower temperature, $T = 0.28$, and then the temperature increases (left panel), and (ii) the simulation starts at a higher temperature, $T = 0.72$, and then the temperature decreases (right panel). In both cases the starting spin configuration for initial temperature point is the FM state along $z$ direction. After a certain number of MC steps the resulting spin configuration is used for the next temperature point and so on. When the simulation starts at $T = 0.28$ the system have sufficient time to relax towards the disordered SPM state. On the other hand, when the simulation starts at higher temperatures the system is driven through the region of enhanced exchange interaction.
interaction (peak in \( J(T) \)). It creates domain states (similar to those presented at figures 4(a) and (c)) that turns out extremely robust with lowering of the temperature. As a result the system is locked into one of these metastable domain states and the final state of the system at the lower temperature is not an SPM state. This results in different values of functions \( m \) and \( G \) at \( T = 0.28 \). Such a difference does not appear at \( T = 0.78 \), this temperature is high enough to let the system free from the metastable domain states.

Another interesting question is the effect of variation \( J \) at fixed temperature on the magnetic behavior. Figure 10 shows the behavior of \( M \), \( m \) and \( G \) as a function of exchange coupling parameter \( J \) at fixed temperature \( T = 0.3 \) \((K = 3.0, \ g = 0.5)\). The exchange coupling parameter is allowed to change from \( J_1 = 0 \) up to some finite value \( J_2 \) and then return back to \( J_1 \) (left panel). In other simulation we change \( J \) in a reverse order starting from \( J_2 \) down to \( J_1 \) and then back to \( J_2 \) (right panel). In both cases the initial state is the FM ordering along z axis. Obviously, such a non-monotonic behavior of \( J \) can reflect, in part, the variation of \( J \) in composite multiferroics. Hysteresis behavior in all three functions clearly indicates the presence of long-living metastable states. The temperature hysteresis of magnetic properties can be considered as the signature of ‘blocking’ phenomenon.

4.3. Applicability of results

In this paper we focused on the case of a regular array of magnetic grains. In real materials the grains are randomly distributed over FE matrix, resulting in random MD and exchange interactions that can lead to formation of a glassy state rather than the SFM or SPM state. Dipolar interaction has a large effect on the magnetization relaxation in a random ensemble of magnetic particles [58]. On the other hand, as far as macroscopic observables are concerned, it was shown that, despite quantitative differences, systems of ordered dipoles (located on a simple cubic, a body-centered cubic and face-centered cubic lattices) demonstrate qualitatively very similar behavior to the systems with positional and orientational disorder [59]. We expect, that in granular multiferroics, as far as the robustness of order-disorder transition to the presence of dipole–dipole interaction is concerned, such a transition survives at other types of dipoles distribution and does not change qualitatively the discussed phase diagram.

In our model we considered a 3D multiferroic material produced via bottom-up method. A different, top-down fabrication based on layer by layer growth, is used to produce a single layer of magnetic grains. From experimental point of view a layer system, consisting of FE substrate and thin granular ferromagnet film, is even more interesting. For several layers of grains the influence of FE substrate on the exchange interaction decays with increasing of the distance between the FE surface and the grain layer. In such 2D systems the influence of MD interaction on the magnetic phase diagram is different from the 3D case. The behavior of 2D multiferroical materials requires separate investigation.

Another important aspect of our model is that granular medium is supposed to be insulating. It occurs when the grain concentration is below the percolation limit. In such a granular medium the FE matrix crucially influences the intergrain exchange interaction. If the magnetic grains were in contact with each other the system would be conductive with delocalized electron wave functions. It would lead to total suppression of Coulomb blockade effects which are the basis of ME coupling in composite multiferroics.

Recently several experiments were reported on granular multiferroics in which magnetic insulating grains were embedded into FE matrix [60–62]. Due to insulating nature of magnetic grains in these materials the ME coupling considered in the present paper is prohibited. However, ME coupling appears in these materials due to strain mediated mechanism. BaTiO\(_3\) and PZT ferroelectrics were used in these experiments. These FEs have large electrostriction coefficient and are rather rigid [63]. This leads to a relatively strong ME coupling. To avoid the influence of the strain mediated coupling polymer or organic FEs are ordinarily used [64]. For example, P(VDF-TrFE) has 2 order of magnitude smaller electrostriction and is very soft [63]. Estimates given in [12, 13] show that polymer or organic FEs are the most prominent candidates for observation of ME coupling considered in the present paper. Therefore we exclude the strain mediated ME coupling from our consideration bearing in mind polymer FEs.

To our knowledge, the granular multiferroics (with necessary parameters, such as small intergrain spacing, metal FM grains and suitable FE material) were not fabricated. Therefore we were unable to compare our results with experimental data and provide here any experimental \( J(T) \) dependencies. However, granular magnets with insulting matrix were extensively studied in the past. In some papers the room temperature intergrain exchange interaction was reported [34]. We used this data to estimate the possible peak value of the intergrain exchange interaction.

Also, we assume that dielectric permittivity of FE matrix is isotropic. This is indeed the case for a number of relaxor FE polymers (for example, P(VDF-TrFE), [65]). Even if FE crystal is anisotropic it is unlikely that such an anisotropy persists in granular materials. Randomly distributed metallic grains provide appearing of numerous crystallites with randomly oriented anisotropy axes. Thus, granular FE should be isotropic even at the mesoscale level.

5. Conclusion

We studied the competition of magneto-dipole, anisotropy and exchange interactions in composite three-dimensional multiferroics—materials with magnetic grains embedded into the FE matrix. The peculiarity of composite (or granular) multiferroics is related to the fact that interparticle interaction is affected by the FE matrix. Granular multiferroics show the magneto-electric coupling effect. Using Monte Carlo simulations we showed that magneto-dipole interaction does not suppress the ferromagnetic correlations in granular multiferroics caused by the interaction of the ferroelectric matrix and...
magnetic subsystem. Thus, MD interaction does not suppress the ME effect in granular multiferroics. However, the presence of magneto-dipole interaction influences the order–disorder transition: depending on the strength of magneto-dipole interaction the transition from the FM to the SPM state is accompanied either by creation of vortices or domains of opposite magnetization.

We showed that a ‘blocking phenomenon’ appears at finite magnetic anisotropy and finite MD interaction. The temperature hysteresis loop occurs due to non-monotonic behavior of exchange interaction versus temperature. The origin of this hysteresis is related to the presence of stable magnetic domains which are robust against thermal fluctuations.

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Appendix A. Calculation procedure

We use classical Monte Carlo (MC) simulations and the standard Metropolis algorithm to model magnetic properties of the system [24, 66–70]. We consider an L × L × L (L = 20) cubic lattice with periodic boundary conditions. To efficiently evaluate the long-range MD interaction in systems with relatively small number of particles (as, for example, L = 5, 6, 7 considered in [21, 67]) one has to implement Ewald summation technique [71, 72]. We account the MD interaction by direct summation in the real space applying the minimum image convention [71]. In terms of the range of the interaction that have been taken into account, this scheme is equivalent to the fast Fourier transform method used for micromagnetic simulations [73, 74].

We use the FM state ordered along the z-direction, $S_i = e_z$, as an initial spin configuration for simulating at the first temperature point. The resulting spin state is used as an initial state for the next temperature point and so on. To study hysteresis effects we make two passages: first, we start with low temperature and increase the temperature during our study hysteresis effects we make two passages: first, we start with

One MC step consists of $L \times L \times L$ consecutive changes in the lattice spin orientations. We calculated the change in the energy of the system $\Delta H$: if change is negative, $\Delta H < 0$, a new state is accepted; if change is positive, $\Delta H > 0$, the new state is accepted with probability $e^{-\Delta H / T}$. In our simulations we use $N_{MC} \approx 12000$ MC steps per spin and study 60 samples in every 200 MC steps to calculate thermal properties.

To check the stability of the final configuration on the number of MC steps we increased the number of MC steps five times (up to $N_{MC} = 6 \cdot 10^5$) and found no difference in the resulting state.

We generate the update in spin directions in two ways. First, the spin orientations were distributed uniformly over the unit sphere’s surface [72]

$$\cos \theta_i = \xi_i, \quad \varphi_i = \pi \xi_i,$$

where $\xi, \xi_i$ are some random numbers from the interval $(-1, 1)$. This algorithm becomes inefficient at low temperatures or strong anisotropy. In this case the majority of randomly chosen spin directions has to be rejected due to large energy change $\Delta H$. We use such an update to check the results of the second algorithm with tuned step of change in the spin direction.

Our main algorithm for spin change was an algorithm where a new spin direction is chosen within a small angle near a given spin $S_i$ [41]. First, a random unit vector $\mathbf{w}$ perpendicular to the chosen spin $S_i$ is generated. Then new trial configuration is chosen as

$$S_i' = \cos \theta_i S_i + \sin \theta_i \mathbf{w},$$

where $\theta_i$, the rotation angle from $S_i$ to $S_i'$, is chosen according to

$$\cos \theta_i = 1 + \xi (\cos \theta_{\text{max}} - 1),$$

$\xi$ is a random number varying in the interval $(0, 1)$, the angle $\theta_{\text{max}}$ is a maximum allowed amplitude for the change of the polar angle $\theta_i$ of the initial spin $S_i$, $0 < \theta_{\text{max}} \leq \pi$. The new spin direction $S_i'$ lies within a cone around the initial direction with aperture angle $2\theta_{\text{max}}$ and all the directions inside this cone can be reached with the same probability [41]. The value of $\theta_{\text{max}}$ is adjusted after one full MC sweep over the lattice to keep, when possible, the number of accepted spin changes around $\sim 50\%$. Also we kept the lower bound for $\theta_{\text{max}} \gtrsim \pi/6$ to prevent too small MC moves which are inefficient to thermalize the system.

This algorithm is not valid at low temperatures [24] or strong anisotropy, $K \gg 1$, when the system tends to the Ising limit which does not allow the spin flips. We improve the situation allowing spins to flip with a certain small probability $\langle 0.1–0.2 \rangle$. With this modification we reproduce the correct values of the critical temperature $T_c$ for the Heisenberg, $T_c \approx 1.44$, [49–52, 68–70, 75] and the Ising, $T_c \approx 4.51$, for models [76].

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