Coupling of (ferro)electricity and magnetism through Coulomb blockade in Composite Multiferroics

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Introduction. Currently composite materials with combined magnetic and electric degrees of freedom attract much of attention for their promise to produce new effects and functionalities [1–3]. The idea of using ferromagnetic and ferroelectric properties in a single phase multiferroics was developing since seventeenth [4]. However, in bulk homogeneous materials this coupling is weak due to relativistic parameter v/c, with v and c being the electron velocity and the speed of light, respectively. Only recently the new classes of two-phase multiferroic materials such as single domain multiferroic nanoparticles [5], laminates [6, 7], epitaxial multilayers [8, 9], and granular materials [10–12] were discovered giving a new lease of life to this field. So far, the interface strain generated by the ferroelectric layer was considered as the promising mechanism for strong enough magnetoelectric coupling in two-phase multiferroics materials [11–13]. This strain modifies the magnetization in the magnetic layer and the magnetic anisotropy energy.

We propose a different mechanism for magnetoelectric coupling emerging at the edge of strong long-range electron interaction, ferroelectricity, and magnetism. In composite multiferroics — materials consisting of metallic ferromagnetic grains embedded into ferroelectric (FE) matrix, Fig. 1, the origin of this coupling is twofold: i) Strong influence of FE matrix on the Coulomb gap defining the electron localization length and the overlap of electron wave functions, and therefore controlling the exchange forces. ii) Dependence of the long-range part of Coulomb interaction, and thus the exchange interaction, on the dielectric permittivity of the FE matrix.

We show that these two mechanisms compete with each other leading to the strong temperature dependence of the effective ferromagnetic exchange constant J between the ferromagnetic grains near the ferroelectric Curie temperature \( T_{C}^{FE} \). The transition temperature between ordered and disordered magnetic states can be found approximately using the equation \( J(T) = T \). Ferromagnetic (FM) state corresponds to \( J(T) > T \). If mechanism (i) is the strongest, the FM state appears at higher temperatures than the disordered (SPM) state. This rule breaks apart in composite multiferroics: the ordered (FM) state may appear at higher temperature than the disordered (SPM) state. In non-magnetic materials such a behavior is known as inverse phase transition.

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![FIG. 1. (Color online) a) Sketch of a granular multiferroic consisting of ferromagnetic grains with magnetic moments embedded in a ferroelectric matrix. Cooling typical magnetic materials the ordered phase appears at lower temperature than the disordered phase. This rule breaks apart in composite multiferroics: the ordered (FM) state may appear at higher temperature than the disordered (SPM) state. In non-magnetic materials such a behavior is known as inverse phase transition, phase diagrams b) and c). Graph d) shows the intergrain exchange constant J vs. temperature T and the packing ratio, d/a, with d and a being the average intergrain distance and the grain size, respectively.](cond-mat.mes-hall)
temperature dependence of the exchange coupling \( J \) and magnetic state with zero magnetic moments. The temperature \( T < J \) is called the blocking temperature.

In this paper we consider a different case of large exchange energy, \( J > \max(E_a, E_d) \), with negligible magnetic anisotropy, \( E_a \) and magneto-dipole interaction, \( E_d \). This situation is typical for grains of small sizes [26] [28]. In this case for temperatures \( T < J \) the system is in the FM state. The temperature \( T_m = J \) is called the ordering temperature. Below we study the influence of FE matrix on intergrain exchange interaction and on the ordering temperature \( T_m \) of granular multiferroics.

Consider the exchange interaction of two metallic ferromagnetic grains of equal sizes, \( a \). Each grain is characterized by the Coulomb energy \( E_c = e^2/(\alpha c) \) with \( e \) and \( \alpha \) being the electron charge and the average dielectric permittivity of the granular system, respectively. We assume that the Coulomb energy is large, \( E_c \gg T \) and the system is in the insulating state with negligible electron hopping between the grains. In this case the exchange interaction has a finite value due to the overlap of electron wave functions located in different grains.

We describe the coupling of each pair of electrons as \(-J_{ij}(\hat{s}_i \cdot \hat{s}_j)\) with \( h\hat{s} \) being the spin operator with indexes \( i \) and \( j \) numbering electrons in the first and the second grain, respectively, and the parameter \( J_{ij} \) being the exchange interaction of two electrons. The total exchange interaction of two grains can be written as a sum over all electrons, \( J_{tot} = -\sum_{i \neq j} J_{ij}(\hat{s}_i \cdot \hat{s}_j) \). Below for simplicity we assume that \( J_{ij} = J \) does not depend on indexes \( i \) and \( j \). Thus, the Hamiltonian has the form \( J_{tot} = -J(\hat{S}_1 \cdot \hat{S}_2) \), where \( h\hat{S}_{1,2} \) is the total spin of the first (second) grain. For temperatures \( T < J_{tot} < T_{c,FM} \) each grain is in the FM state with different grains magnetic moments being correlated such that the whole system may experience the FM phase transition.

The exchange coupling constant \( J \) has the form [29] [30]

\[
J \propto \int \int \Psi_1^*(\vec{r}_2)\Psi_2^*(\vec{r}_1)\frac{e^2}{\epsilon|\vec{r}_1 - \vec{r}_2|}\Psi_1(\vec{r}_1)\Psi_2(\vec{r}_2)d^3r_1d^3r_2.
\]

(1)

Here \( \Psi_{1,2} \) is the spatial part of the electron wave function located in the first (second) grain; \( \epsilon \) is the average dielectric permittivity. The influence of FE matrix on the exchange integral in Eq. (1) is twofold:

i) The \( \epsilon \)-dependent Coulomb interaction potential. This interaction, and thus the exchange coupling \( J \), decreases with increasing \( \epsilon \) in the vicinity of the paraelectric-ferroelectric transition temperature \( T_{c,FE} \).

ii) The \( \epsilon \)-dependent electron localization length \( \xi \),
and composite multiferroics can be formulated as follows.

\[ \xi = a / \ln(E_c^2/T^2 g_t), \]

where \( g_t \) is the average tunneling conductance. It increases with increasing \( \epsilon \) leading to larger overlap of the electron wave functions, and thus to the increase of the exchange coupling \( J \).

To summarize, there are two competing mechanisms in Eq. (1): with increasing the dielectric permittivity \( \epsilon \) the intergrain Coulomb interaction decreases, while the electron wave function overlap increases.

We now estimate the exchange coupling \( J \) in Eq. (1) using the following form of the electron wave function.

\[ \Psi_{1,2}(\vec{r}) = C \begin{cases} e^{-\frac{\xi}{2}}, & |\vec{r} + \vec{d}/2| < a, \\ e^{-|\vec{r}|d/2}, & |\vec{r} - \vec{d}/2| > a. \end{cases} \]

Here \( C = (\int |\Psi_{1,2}|^2 dV)^{-1/2} \) is the normalization constant and \( d \) is the distance between two grain centres. Equation (3) describes electrons uniformly smeared inside a grain and decaying exponentially outside the grain. Substituting Eq. (3) into Eq. (1) we find the intergrain exchange coupling constant

\[ J \sim \frac{1}{\epsilon} \left[ e^{-4\xi/d}, \quad d \gg a \\
- e^{-4(d-2a)/\xi}, \quad d - 2a \ll a. \right. \]

In general, the exchange coupling can be estimated as \( J \sim (1/\epsilon)e^{-\gamma d/\xi} \), with numerical constant \( \gamma \leq 4 \). Using Eq. (2) we find

\[ J = J_0 e^{-\gamma d/\xi}, \]

where \( J_0 > 0 \) is the exchange coupling for permittivity \( \epsilon = 1 \). The exponent in Eq. (5) has a clear physical meaning: the first term, \( \gamma d/a \), is due to \( \epsilon \)-dependent localization length \( \xi \), the second term \(-1\) is due to \( \epsilon \)-dependent Coulomb interaction. These mechanisms compete with each other.

The exchange coupling \( J \) in Eq. (5) depends on the ratio of grain sizes \( a \) and the intergrain distances \( d \). For large intergrain distances, \( \gamma d > a \), the exponent of dielectric permittivity \( \epsilon \) in Eq. (5) is positive leading to the increase of exchange coupling \( J \) due to the delocalization of electron wave functions. In the opposite case, of small intergrain distances, \( \gamma d < a \), the exchange coupling \( J \) decreases with increasing of \( \epsilon \).

The criterion of SPM - FM phase transition in composite multiferroics can be formulated as follows

\[ J(\epsilon(T_m)) = T_m. \]

Here \( J \) is the exchange coupling averaged over all pair of grains (it includes effective nearest neighbor number) and \( T_m \) is the transition (or ordering) temperature.

The temperature dependence of the dielectric permittivity \( \epsilon(T) \) of composite ferroelectrics — materials consisting of metallic grains embedded into FE matrix was discussed recently [32]. We assume that the metal dielectric constant is very large (infinite) at zero frequency. Therefore we can write for sample permittivity \( \epsilon = \epsilon_s(\Omega/\Omega_{fe}) \), where \( \epsilon_s = 1 + 4\pi \chi \) and \( \Omega, \Omega_{fe} \) being the sample and FE matrix volume, respectively and \( \chi \) is the average susceptibility of FE matrix.

To estimate the dielectric permittivity of FE matrix we consider the region between two particular neighbouring grains as thin FE film with local polarization perpendicular to the film (grain) boundaries. The direction of local polarization varies from one pair to another pair of grains, and its sign is defined by the external and internal electric fields. The origin of internal field is the electrostatic disorder inevitably present in granular materials. The behavior of local polarization is described by the Landau-Ginzburg-Devonshire (LGD) theory [34, 35].

Discussion. Figure 3 shows the average exchange coupling constant \( J \) vs. temperature. For large intergrain distances, \( \gamma d > a \), the exchange coupling \( J \) has a maximum in the vicinity of the ferroelectric Curie temperature \( T_{C FE} \), Fig. 3 (a). For small intergrain distances, \( \gamma d < a \), the exchange constant \( J \) has a minimum, Fig. 3 (b). In Fig. 3 we assume that the grain ferromagnetic Curie tem-
temperature is large, $T_{PM}^F > T_{FE}^F$. The dotted line in Fig. 3 stands for temperature and the intersections of this line with exchange coupling curve $J$ correspond to the solution of Eq. (6). The temperatures $T_{1,2,3}$ in Fig. 3 stand for different ordering temperatures of SPM - FM phase transitions and correspond to the solution of Eq. (6).

The most interesting region in Fig. 3 is the intersection of temperature $T$ dotted line with exchange coupling curve, $J$. For large intergrain distances, $\gamma d > a$ the exchange coupling $J$ exceeds the thermal fluctuations for temperatures $T_1 < T < T_2$ near the ferroelectric Curie temperature $T_{FE}^F$ leading to the appearance of the global FM state, Fig. 3(a). For temperatures $T < T_1$ or $T > T_2$ the system is in the SPM state. Interestingly, the FM state appears with increasing the temperature, in contrast to the usual case where ordering appears with decreasing the temperature. This is related to the fact that while the magnetic system becomes ordered the FE matrix becomes disordered with increasing the temperature.

For small intergrain distances, $\gamma d < a$, the exchange coupling $J$ has the opposite behavior, Fig. 3(b). The system is in the FM state for temperatures $T < T_1$ and becomes SPM for temperatures $T_1 < T < T_2$. Increasing the temperature the system first experience the transition to the FM state for temperatures $T_2 < T < T_3$ and then goes to the SPM state for temperatures above $T_3$.

Equation (6) may not have a solution at any temperatures for small enough coupling constants $J_0$ in Eq. (5). In this case the system will stay in the SPM state.

Figure 4 shows the behavior of intergrain exchange constant $J$ as a function of temperature $T$ and the packing ratio, $d/a$. The flat surface represents the temperature $T$. The regions with $J > T$ correspond to the FM state, while the regions with $J < T$ to the SPM state. Figure 4 was used to obtain the phase diagrams in Fig. 1.

To summarize, we obtain the magnetic phase diagram of granular multiferroics with several phases appearing due to the interplay of ferroelectricity, magnetism, and strong electron correlations, Fig. 3.

Validity of our results First, we assumed an insulating state of composite multiferroic due to strong Coulomb blockade, $E_c \gg \max(T, J)$. The last inequality is not valid in the close vicinity of the ferroelectric Curie temperature $T_{FE}^C$ since the charging energy $E_c$ is $\epsilon$-dependent and is strongly suppressed in the vicinity of $T_{FE}^C$. This suppression may lead to the appearance of the metallic state with different criterion of SPM - FM transition where magnetic coupling between grains occurring due to electron hopping between the grains [50, 57]. This effect was not considered here.

Above restriction is rather strong and reduces the number of possible FE materials. The Coulomb gap for 5 nm grains is $E_c = 2000/\epsilon$ K and thus $E_c < 200$ K for dielectric permittivity $\epsilon > 10$. In conventional bulk ferroelectrics, such as BTO and PZT, the dielectric permittivity is large, $\epsilon > 100$. However, in granular materials the thin FE layers are confined by grains leading to a much smaller dielectric constant [58]. Another way to reduce the dielectric constant is to use the relaxor FE matrix, such as P(VDF-TrFE) [29, 41].

Second, we assumed that all grains have equal sizes and all intergrain distances are the same. For broad distribution of grain sizes and intergrain distances the influence of FE matrix on the exchange coupling constant is smeared. This effect was not taken into account here.

Comparison with experiment. We now compare our results with available experimental data on Ni-SiO$_2$ granular system [29], where 5 nm Ni grains were embedded into SiO$_2$ matrix. This system shows an insulating behavior with activation conductivity and the SPM - FM phase transition at temperature $T_{pm} \approx 300 K \gg T_m$ with $T_m$ being the blocking temperature. The transition in this system is due to the exchange interaction between grains and can be directly compared with our results if one uses the FE matrix instead of insulting matrix SiO$_2$.

The results of Ref. [29] were repeated for Co-SiO$_2$ [28] and Fe-SiO$_2$ [32] systems with ordering temperature $T_m$ of order 300K. Currently the electron transport properties of many magnetic granular materials were studied in the vicinity of ordering temperature $T_m$ [13, 14].

Recently, several groups studied magnetic properties of CFO-PZT granular multiferroics [42, 43] and PZT-NFO, BTO-LSMO, and BNT-CFO granular multiferroics [45, 46]. These materials are good ferromagnets at room temperatures with insulating ferromagnetic grains. Our theory is not directly applicable to these studies since the electron localization length $\xi$ in these materials is defined by some intra-atomic forces instead of Coulomb blockade. However, similar to our results, the $\epsilon$-dependent intergrain Coulomb interaction should influence the temperature dependence of intergrain exchange coupling constant, $J$. 

FIG. 4. (Color online) Graphs a) and b) show the intersections of exchange coupling $J$ and the temperature $T$ in the coordinates packing ratio, $d/a$, with $d$ and $a$ being the average intergrain distance and the grain size, and temperature $T$. The regions with temperature $T > J$ correspond to the SPM state, while the region with $T < J$ corresponds to the FM state. Following a) and b) we obtain the phase diagrams b) and c) in Fig. 1.
**Conclusion.** We studied the phase diagram of composite multiferroics, materials consisting of magnetic grains embedded into FE matrix, in the regime of Coulomb blockade. We found that the coupling of ferroelectric and ferromagnetic degrees of freedom is due to the influence of FE matrix on the exchange coupling constant via screening of the intragrain and intergrain Coulomb interaction. We showed that in these materials the ordered magnetic phase may appear at higher temperatures than the magnetically disordered phase.

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