Geometrical origin of ferrimagnetism and superparamagnetism in Fe-based double perovskite multiferroics

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We show that a superstructure of antiferromagnetically interacting Fe$^{3+}$ ($S = 5/2$) ions in double perovskites AFe$_{1/2}$M$_{1/2}$O$_3$ exhibits a ferrimagnetic ordering below $T_{Ic} \approx 5.6 J_1 / k_B \approx 50$ K, which is close to room temperature. Small clusters of the same structure exhibit a superparamagnetic behavior at $T \lesssim T_{Ic}$. The possibility of formation of such clusters explains the room-temperature (superpara) magnetism in 3d-metal based oxides.

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I. INTRODUCTION

An experimental quest to find a room-temperature multiferroic with high magnetoelectric coupling is stimulated by wide prospects they open for applications in the field of information and energy-saving technologies. They may form the basis for a fabrication of novel functional devices: highly sensitive magnetic sensors, capacitance electromagnets, elements of magnetic memory and others. Spintronics, an emerging branch of microelectronics which manipulates the electron spin rather than its charge, has need for a room-temperature ferromagnetic semiconductor.

The rich family of Fe-based double perovskites AFe$_{1/2}$M$_{1/2}$O$_3=\text{A}_2\text{FeMO}_6$ (with non-magnetic ions A=\text{Pb, Ca, Sr, Ba} and M=\text{Nb, Ta, Sb}) is in the focus of the studies as it includes PbFe$_{1/2}$Nb$_{1/2}$O$_3$(PFN) and PbFe$_{1/2}$Ta$_{1/2}$O$_3$(PFT) systems, where the multiferroicity was reported more then fifty years ago.

In AFe$_{1/2}$M$_{1/2}$O$_3$ compositions, Fe$^{3+}$ and M$^{5+}$ cation positions may be ordered or disordered within simple cubic B-sublattice of perovskite structure ABO$_3$. The degree of chemical ordering depends on the strength of electrostatic and elastic energies and, in particular, on the ionic radii of these cations. It is commonly accepted that PFN and PFT are chemically disordered compounds due to almost equal ionic radii of Fe$^{3+}$ and Nb$^{5+}$ or Ta$^{5+}$ 8 while Sb-contained compounds can be chemically ordered up to 90% because Sb$^{5+}$ is much larger than Fe$^{3+}$. 9 Magnetism of the compositions is due to Fe$^{3+}$, $S=5/2$ ions that occupy half of octahedral sites of the perovskite lattice. The magnetic moments of the Fe$^{3+}$ ions interact via various superexchange paths,

\[ \hat{H} = \frac{1}{2} \sum_{\mathbf{R,r}} J_{\mathbf{R,r}} \hat{S}_{\mathbf{R}} \hat{S}_{\mathbf{R+r}}. \]  

The disorder prevents an experimental access to the values of the interactions. In a recent publication, some of us have argued that the largest superexchange values are the nearest-neighbor (NN) Fe-Fe interaction (Fe ions are separated by the edge of perovskite unit cell and interact via the shortest Fe-O-Fe path) $J_1 \sim 50 - 70$ K and the next-nearest-neighbor interaction (Fe ions are separated by the face diagonal of the cell) $J_2 \approx 0.04 J_1$. 10 The interaction values $J_1, J_2$ are similar to the values in orthoferrite $\text{RFeO}_3$ ($\text{R=}$Y or a rare earth) and bismuth ferrite $\text{BiFeO}_3$ compounds. Note that both exchange couplings have antiferromagnetic sign. We thus have two substantially different magnetic energy scales: $S(S+1)J_1 = 8.75 J_1$, which corresponds to temperatures of several hundred Kelvins, and $S(S+1)J_2/k_B \sim 20$ K. Note that many of Fe-based double perovskites have an antiferromagnetic phase transition in the latter temperature range. 12,21 It means that the probability to find a pair of Fe ions separated by the face diagonal of the perovskite cell is much higher than to find a nearest-neighbor Fe pair that is caused by partial chemical ordering of cations. Two multiferroic compounds, PFN and PFT, exhibit a magnetic transition at $T_N \sim 150$ K. This means that the probability to find a pair of NN Fe ions is enhanced in these compounds. But it leads to the increase of the temperature, at which the antiferromagnetic order is established. 22,23 For instance, in the more concentrated compound PbFe$_{2/3}$W$_{1/3}$O$_3$ it increases up to 380 K. 23

Recent reports on room-temperature multiferroicity of PFT/lead zirconate titanate (PZT) 24,25 and PFN/PZT 26 and $[\text{Pb(Fe}_{2/3}\text{W}_{1/3})\text{O}_3]$/PZT 27 solid solution systems are a real challenge for the solid state theory. One of the questions is the nature of large room-temperature magnetic response of the systems (non-linear magnetization curves and hysteresis loops) that imply the existence of Fe spins alignment in a part of the sample with uncompensated magnetic moment. On the qualitative level, it was suggested that the clustering of Fe ions is responsible for the appearance of the uncompensated magnetic moment. 28,29 We should mention that the clustering of...
Fe ions form locally fragments of AFeO$_3$ structure, where Fe spins form the simple cubic lattice. Thus, it can lead only to G-type antiferromagnetic ordering within the fragments, and produces a small or vanishing uncompensated magnetic moment. It can not convincingly explain the observation of room-temperature hysteresis loops.

A small canting of predominantly antiferromagnetic Fe spins due to the antisymmetric Dzyaloshinskii-Moriya interaction $H_{DM} = \mathbf{D} \cdot \mathbf{S}_1 \times \mathbf{S}_2$ causes weak ferromagnetism in orthoferrites RFeO$_3$, R$^{3+}$ being Y or a rare earth ion. It was suggested that the canting may cause also the uncompensated magnetic moment in AFeO$_3$ structure that is formed by the Fe ions clustering in the double perovskites. But the moment seems to be too small to explain the effect. In the ordered state of RFeO$_3$, the canting angle $\phi \sim 10$ mrad results in the moment $\sigma \sim 0.05\mu_B$ per Fe ion. But such a moment was never observed in the antiferromagnetically ordered state of PFN neither in magnetic nor in neutron studies. A possible reason is that the Dzyaloshinskii-Moriya vector for a Fe-O-Fe bond may be written as $\mathbf{D} = d[r_1 \times r_2]$, where $d$ is a scalar value, and $r_i$ is a unit vector in the direction from oxygen to spin $\mathbf{S}_i$. Thus, its value depends on the Fe-O-Fe bond angle $D \propto \sin \theta$, which is substantially larger in AFe$_{1/2}$M$_{1/2}$O$_3$ ($170^\circ < \theta < 180^\circ$) than in the orthoferrites ($140^\circ < \theta < 157^\circ$).

In this paper, we quantitatively consider another scenario for the room-temperature magnetism of bulk PFT/PZT and PFN/PZT systems and superparamagnetism often observed in PFN nanoparticles or even ceramics and thin films. We explain it by the existence of regions with a special chemical order (a sub-nano-size superstructure) that results in a ferrimagnetic ordering of antiferromagnetically interacting Fe$^{3+}$ $S = 5/2$ spins. This explanation was implicitly assumed in Ref. where the observed slightly asymmetric EPR line shapes above room temperature were simulated by a model involving the presence of thermally fluctuating superparamagneticlike nanoclusters. Note that our explanation does not demand the clusterization, as the stoichiometry AFe$_{1/2}$M$_{1/2}$O$_3$ is retained within the $2 \times 2 \times 2$ supercell of the superstructure. Using the high-temperature expansion (HTE) we show that a macroscopic number of spins orders at about the room temperature, whereas small clusters (studied by exact diagonalization method) exhibit a crossover between paramagnetic and superparamagnetic behavior.

![Diagram](image)
of the exchange interaction. We use an originally developed C++ program, for the generation of the definition files for spin structures studied in this work.

In order to simulate the behavior of the exchange interaction, we have performed full exact diagonalization studies (ED) of thermodynamic properties of clusters shown in Fig. 1b, and in Fig. 2 using J. Schulenburg’s spinpack. The susceptibility $\chi(T)$ is calculated as the ratio of the induced magnetization $M$ to the field $H$. We use the “vanishing” magnetic field $H = 10^{-5}J_1/g\mu_B$ unless otherwise noted.

III. RESULT AND DISCUSSION

A. Ferrimagnetic superstructure

The simplest way to model the (partial) disorder in the distribution of Fe and M ions between the sites of the B-sublattice of the perovskite structure is to consider a periodic lattice with a supercell containing several perovskite cells and study such periodic systems with different versions of chemical order (ion distributions). Such an approach was suggested in Ref. 31 for a $2 \times 2 \times 2$ supercell, where 6 configurations PFBO...PFB5 (see Fig. 3 of Ref. 8 and Fig. 3 of Ref. 31) of chemical ordering are possible in the double perovskites. It was shown that the total energy is substantially different for different configurations. Moreover, the hierarchy of the energies depends on the type of M-ion. In Ref. 8, it was found that the PFB2 configuration shown in the inset of Fig. 1 has an energy close to the most stable configurations (PFB5 for M=Nb,Ta and PFBO for M=Sb), and has a ferrimagnetic ground state (see Table II of Ref. 8). Below, we consider the ferrimagnetism of PFB2 superstructure in more detail.

The PFB2 chemical order has two inequivalent Fe sites. Within the B-sublattice of the perovskite structure, Fe1 has six Fe2 NN ions, whereas three Fe2 sites in the supercell has only two Fe1 NN ions (insets in Fig. 1a,b). In other words, Fe2 sites form a superstructure of corner-shared octahedra, Fe1 sites being in the center of each octahedron. The interaction value between the two sublattices is $J_1$, and within Fe2 sublattice is $J_2 \ll J_1$. Thus, the spin system satisfies the requirements of the Lieb-Mattis theorem with $g_{LM}^2 = J_2/4$ (see Eq.(2) of the Ref. 42). Moreover, it is close to the special case $g_{LM}^2 = 0$. According to the theorem (see also the consideration of frustration $J_2 \neq 0$ in the Ref. 43, the PFB2 ground state corresponds to a ferrimagnetic ordering of Fe spins with a magnetic moment of $\mu_B S \approx 10 \mu_B$ per supercell, or $2.5 \mu_B$ per Fe ion. This moment value is much larger than the value provided by Dzyaloshinskii-Moriya interaction for realistic values of local lattice distortions.

We use the [4,4] Padé approximant of the HTE series to analyse the susceptibility data. For a magnetic
superstructure with the PFB2 spin arrangement the temperature dependence of the inverse susceptibility $\chi^{-1}(T)$ for $S = 5/2$ is shown in the Fig. 1a. Only NN interaction $J_1 \neq 0$ was taken into account. A reasonable estimate of the temperature for the transition into the ferrimagnetically ordered phase $T_{fe}$ is given by that point where $\chi^{-1}(T_{fe}) = 0$. The precision of the determination of critical temperatures by the zero of $\chi^{-1}$ was estimated to be about 10%. The values of $T_{fe}$ for different spin values are given in the Table I.

| Spin, $S$ | $k_B T_{fe}/J_1 S(S + 1)$ | $k_B T_{fe}/J_1$ |
|-----------|----------------------------|-----------------|
| 1/2       | 0.61                       | 0.46            |
| 1         | 0.69                       | 1.4             |
| 3/2       | 0.64                       | 2.4             |
| 2         | 0.64                       | 3.8             |
| 5/2       | 0.64                       | 5.6             |

For Fe-based double perovskites $T_{fe}$ is of the order of the room temperature, as $J_1/k_B \sim 50$ K. From the graph shown in Fig. 1, we see that in the range $T_{fe} < T < T^* \approx 0.92 J_1 S(S + 1)/k_B$, the magnetic susceptibility of the PFB2 phase exceeds the value for independent spins, $\chi(T) > \chi_p(T) = S(S + 1)/(3k_B T)$, despite the antiferromagnetic character of the exchange interaction, which suppress the magnetic response at high temperatures $T \gg J_1$. For comparison, the black thin solid line shows the susceptibility $\chi_{fccc}(T)$ of 1:1 ordered PFB0 configuration, where Fe spins form a face centered cubic lattice, and interact with $J_2 = 0.05 J_1$. We see that $\chi_{fccc}(T) < \chi_p(T)$ at all temperatures (see Appendix A).

**B. Superparamagnetism**

A sample of a disordered double perovskite compound may contain some regions with PFB2 chemical order. In the ground state, such a region possesses the total spin $S_g = (N_2 - N_1)S$, where $N_1, N_2$ are the numbers of Fe1, and Fe2 sites in that region. In order to simulate the behavior of fragments of PFB2 configuration in a Fe-based double perovskite material, we show in Figs. 1b, 2 full...
exact-diagonalization data of thermodynamic properties of clusters shown in Figs. 1 and 2a-c. Since we have found that the dependence of the inverse susceptibility as a function of normalized temperature \( k_B T / J_1 S(S+1) \) on the spin value \( S \) is weak (see Appendix A), the ED data for the simplest \( S = 1/2 \) case can be considered as representative for higher values of \( S \). The 7-site cluster shown in the Fig. 2a contains one Fe1 site interacting with six Fe2 sites via \( J_1 \) exchange. This is a particular case of the Heisenberg star model. For \( T \gg J_1 \), the susceptibility per spin tends to the Curie-Weiss asymptotic \( \chi_{\text{CW}} = \chi_0 / [1 + 4 S(S+1) J_1 / k_B T] \). In the opposite limit, the system shows a super-paramagnetic behavior, i.e. it behaves as a single super-spin \( S_g = 5S \), and the susceptibility is \( \chi_{\text{SPM}} = S_g (S_g + 1) \chi_0 / [(N_2 + N_1) S(S+1)] \) (see Fig. 1b). At temperatures \( T \sim T_J \), the system exhibits a crossover between the two regimes. The susceptibility exceeds the independent-spin value for \( T < T_J^* \approx 0.74 J_1 S(S+1)/k_B \). Similar results for a 13-site cluster (Fig. 2b) are shown in Fig. 2c (see also Fig. 8 in the Appendix).

In a real sample, an interaction between the regions of PFB2 configurations always exists. When the temperature becomes sufficiently low, the thermal and interaction energies become comparable, and a collective state of super-spins is formed. The behavior of two interacting PFB2 clusters (Fig. 2d) is shown in Fig. 2e (lines \( c_1 \) and \( c_2 \)). For temperatures \( T \gg J_1 \), the susceptibility behaves similar to the non-interacting case. In particular, it exceeds the susceptibility of independent spins \( \chi(T) > \chi_0(T) \) at \( T \lesssim T_J \) and tends to the superparamagnetic behavior down to low temperature, where it exhibits a maximum (minimum at \( \chi^{-1}(T) \) curve). Below the maximum, a singlet ground state of two interacting super-spins is formed. In reality, for large number of interacting clusters the disorder in the system favors a super-spin glass formation at temperatures governed by the low energy scale \( T < S(S+1) J_2 / k_B \).

A characteristic feature of large spin formation in a system is a non-linearity of its magnetization curve \( M(H) \), which results in the dependence of the susceptibility \( \chi = M/H \) on the field value. The Fig. 3 shows the \( \chi^{-1}(T) \) for the 7-site cluster and a finite value of the magnetic field. The susceptibility substantially deviates from the "theoretical" value \( \chi_{\text{th}} = \partial M / \partial H (H = 0) \) at low temperatures, and it does not diverge at \( T \rightarrow 0 \). Note that we have considered here only isotropic Heisenberg interactions. The magnetic anisotropy, which is always present in real compounds, would transform the non-linear magnetization curves into narrow hysteresis loops.

The model of ferrimagnetism considered here can also be applied to PFN and PFT diluted by non-magnetic Ti and Zr ions. As it was mentioned above, these
systems show a sizable magnetic moment at room temperature in spite that the concentration of Fe ions was decreased up to 10%. From a general point of view, the magnetic dilution will lead to the breaking of the infinite magnetic percolation clusters responsible for the long-range antiferromagnetic order as it was pointed out in Ref. [29]. In a small magnetic cluster the probability of creation of a ferrimagnetic configuration of spins should be enhanced due to the limited number of interacting spins. Moreover, the ferrimagnetic ordering can be realized on the edge of the (semi-)infinite antiferromagnetic cluster which size is of order of a few nanometers only because it is controlled by local fluctuations of the 1:1 composition between magnetic Fe and non-magnetic ions. Obviously, the “edge” effect becomes substantial with Ti and Zr doping.

A large room-temperature magnetic response is reported in many wide-gap diluted magnetic semiconductors, such as GaN, ZnO, and TiO$_2$ isovalently doped by transition metals in which no ferromagnetism was expected at any temperature. We think that a solution of this puzzle may be a formation of ferrimagnetic superstructure clusters similar to that we have considered here. Fig. 4 shows two examples of a planar ferrimagnetic arrangement that may be formed by magnetic impurities substituting for cations in zinc blend and wurtzite semiconductors. We see that these arrangements may form infinite two-dimensional sublattices, they also may be transformed into tree-dimensional superstructures if they will be connected by bridging spins having antiferromagnetic interactions with both planes, the planes then will be ordered parallel.

**IV. CONCLUSIONS.**

In summary, we have studied an example of a system of antiferromagnetically interacting equal spins relevant for Fe-based double perovskite compounds, and having a ferrimagnetic ground state. We have estimated the transition temperature $T_{\text{fe}}$ for a macroscopic system, and have argued that it can be close to room temperature. Such kind of ferrimagnetism may be the origin of the room-temperature magnetism of PFT/PZT and PFN/PZT systems. For small clusters of the same structure we have shown that their magnetic susceptibility exceeds the susceptibility of independent spins at temperatures $T \lesssim T_{\text{fe}}$. This gives a possible microscopic explanation for the still puzzling monotonous increase of the magnetic susceptibility with decreasing temperature below Néel temperature, which is observed practically in all Fe-based double perovskites. The ferrimagnetism of this kind may be responsible also for numerous observations of an unexpected large room-temperature magnetic response in 3$d$-metal based oxides.

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**Appendix A: Details of numerical calculations**

In the ideal 1:1 chemical order, Fe$^{3+}$ and the non-magnetic Mn$^{3+}$ ions alternate in the B position of the perovskite lattice ABO$_3$. In this configuration (called PFB0 in Ref. [31]), magnetic Fe$^{3+}$ ions form regular face centered cubic sublattice with antiferromagnetic interaction $J_2$ between nearest spins in the sublattice. The HTE results for the PFB0 lattice are shown in the Fig. 5. For such a lattice, a transition into so called I-type antiferromagnetic order (see insert of Fig. 5) occurs at $T_1 \approx -\Theta_{\text{CW},0}/5.76 \approx 0.69S(S+1)J_2/k_B$. $\Theta_{\text{CW},0} = -4S(S+1)J_2/k_B$ being the paramagnetic Curie-Weiss temperature. Note that the whole curve $\chi^{-1}(T)$ lies above the Curie-Weiss asymptotic (CW). This is a "normal" behavior when the antiferromagnetic interactions suppress the magnetic response of a spin system.

For the PFB2 spin arrangement, the temperature dependence of the susceptibility for different spin values is shown in Fig. 6. For $S = 1/2$-plot the tenth-order HTE was used. A reasonable estimate of the temperature for the transition into the ferrimagnetically ordered phase $T_{\text{fe}}$ is given by that point where $\chi^{-1}(T_{\text{fe}}) = 0$. The values of $T_{\text{fe}}$ for different spins are given in the Table I of the main text.
The behavior of a larger cluster of the PFB2 configuration shown in Fig. 2b is qualitatively similar to the previous cluster (see Fig. 8). But now at low temperatures it behaves like a larger single spin $S_g = 9S$.
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