Magnetic interactions in disordered perovskite PbFe$_{1/2}$Nb$_{1/2}$O$_3$ and related compounds. Dominance of nearest-neighbor interaction.

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We show that the magnetism of double perovskite AFe$_{1/2}$M$_{1/2}$O$_3$ systems may be described by the Heisenberg model on the simple cubic lattice, where only half of sites are occupied by localized magnetic moments. The nearest-neighbor interaction $J_1$ is more than 20 times the next-nearest neighbor interaction $J_2$, the third-nearest interaction along the space diagonal of the cube being negligible. We argue that the variety of magnetic properties observed in different systems is connected with the variety of chemical ordering in them. We analyze six possible types of the chemical ordering in $2 \times 2 \times 2$ supercell, and argue that the probability to find them in a real compound does not correspond to a random occupation of lattice sites by magnetic ions. The exchange $J_2$ rather than $J_1$ define the magnetic energy scale of most double perovskite compounds that means the enhanced probability of 1:1 short range ordering. Two multiferroic compounds PbFe$_{1/2}$M$_{1/2}$O$_3$ (M=Nb, Ta) are exceptions. We show that the relatively high temperature of antiferromagnetic transition is compatible with a layered short-range chemical order, which was recently shown to be most stable for these two compounds. We show also that one of the types of ordering has ferrimagnetic ground state. The clusters with short-range order of this type may be responsible for a room-temperature superparamagnetism, and may form the cluster glass at low temperatures.

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I. INTRODUCTION.

The compound PbFe$_{1/2}$Nb$_{1/2}$O$_3$ (PFN) is one of the first multiferroics reported. It remains to be in focus of the attention of multiferroic community despite the long story of studies, the magnetic properties of PFN are not fully understood. It belongs to the family of double perovskites AFe$_{1/2}$M$_{1/2}$O$_3$=A$_2$FeMO$_6$ with a nonmagnetic cation in A site ($A$=Pb,Ca,Sr,Ba) of the perovskite structure ABO$_3$ and a distribution of the magnetic Fe$^{3+}$ and a nonmagnetic M$^{3+}$ cations (M=Nb,Ta,Sb) in six-coordinated B-site of the structure (see Fig. 1).

The magnetic properties of these compounds are defined by Fe$^{3+}$, $S=5/2$ ions that occupy half of sites of simple cubic lattice (sublattice B of perovskite structure), and interact via various superexchange paths.

It is natural to compare the magnetism of AFe$_{1/2}$M$_{1/2}$O$_3$ compounds with ortoferrites RFeO$_3$ (R=Y or a rare earth) and bismuth ferrite BiFeO$_3$, with a similar perovskite structure where Fe occupy every B site. All these compounds exhibit essentially antiferromagnetic ordering (with a small cantiug of predominantly antiferromagnetic spins) below the transition temperature, which varies in the range $620 < T_N(1) < 740$ K [10,12]. The nearest-neighbor Fe-Fe interaction (via Fe-O-Fe path) was estimated as $J_1 \sim 50$ K [11,13,18] the next-nearest-neighbor being much smaller $\alpha = J_2/J_1 \sim 0.05$ [13,18].

If one assume (i) a random occupation of the site B by Fe and M ions (the X-ray diffraction and Mössbauer spectra support this assumption for most of M ions), and (ii) a similar value of Fe-O-Fe superexchange, we may expect the Néel temperature $T_N(0.5) \sim 0.5T_N(1) > 300$ K. This estimate comes from an analogy with $T_N(x)$ behaviour in the disordered perovskite system KMn$_x$Mg$_{1-x}$F$_3$ [19,20] which agree with theoretical considerations of dilute...
Heisenberg magnets. Contrary to these expectations, most of the AFe$_{1/2}$M$_{1/2}$O$_3$ compounds exhibit a magnetic anomaly at $T \sim 25$ K. One observes $T_{N} \sim 150$ K only for PbFe$_{1/2}$M$_{1/2}$O$_3$ (M=Nb,Ta). It seems that at least one of the above assumptions (i), (ii) is false.

Evidences for partial chemical ordering in B sublattice come from experiments and theory. The disorder in the distribution of Fe and M ions was modeled in the Ref. 7 and 27 by a set of 6 periodic lattices PFB0...PFB5 with the supercell containing $8 = 2 \times 2 \times 2$ perovskite cells with different versions of chemical order (ion distributions) within the cells (see Fig. 2). It was shown that the total energy is different for different configurations and the hierarchy of the energies depends on the type of M-ion.

Recent reports on room-temperature multiferroicity of PFN/PbZr$_x$Ti$_{1-x}$O$_3$ and of related solid solution systems PbFe$_{1/2}$Ta$_{1/2}$O$_3$/PbZr$_x$Ti$_{1-x}$O$_3$ and Pb(Fe$_{2/3}$W$_{1/3}$)O$_3$/PbZr$_x$Ti$_{1-x}$O$_3$ evidences in favor of presence in these systems of magnetic interactions $J$ with the energy scale $S(S+1)J/k_B = 8.75J/k_B \sim 300$ K. In the Ref. 32 the nearest-, second-, and fourth-nearest-neighbor exchange interactions between Fe$^{3+}$ ions were found from LSDA+$U$ calculations for PbFe$_{1/2}$Ta$_{1/2}$O$_3$. The nearest-neighbor exchange occurs (in our notations, see Eq. [1]) to be $J_1/k_B \approx 42$ K, it gives $S(S+1)J/k_B = 366$ K.

In this work, using first-principle calculations, we find the values of exchange interaction between nearest-, second-, and third-nearest-neighbor Fe$^{3+}$ ions in PFN, and confirm the validity of the assumption (ii), i.e. we show that the the nearest-neighbor interaction dominates, and its value is close to that found for RFeO$_3$ and PbFe$_{1/2}$Ta$_{1/2}$O$_3$ compounds. So, the peculiarities of magnetic properties of AFe$_{1/2}$M$_{1/2}$O$_3$ compounds are related with chemical ordering in B-sublattice.

![FIG. 2. (Color online) Magnetic ground states for different chemical configurations of Fe$^{3+}$ (open circles) in a 2x2x2 supercell of AFe$_{1/2}$Nb$_{1/2}$O$_3$ (A=Pb,Ba, only B-sublattice sites are shown). Green filled circles denote non-magnetic Nb$^{5+}$ ions. PFB0a is the I-type order of the fcc lattice.](image1)

![FIG. 3. (Color online) Upper panel: The excited magnetic states of PFB4 chemical order that were used for the calculations of the interactions. Lower panel: Additional magnetic structures, which were used for the check of the mapping of LSDA+$U$ on the Heisenberg model.](image2)

### II. METHOD

The density functional theory calculations were performed using the full-potential local-orbital (FPLO) code. We have used the default FPLO basis, which is claimed to be technically complete, i.e. the FPLO code developers have checked the convergence of the electronic density with respect to the number of basis functions for a huge number of compounds, including 3d-metal oxides. The FPLO basis consists from localized atomic-like functions defined by angular $nl$-quantum numbers and the number of numerical radial functions per orbital. Each valence states can come as single, double or triple state, which means that there are 1, 2 or 3 radial basis functions for this $nl$-quantum number. The default basis for Fe is: single 3s3p4p, and double 4s5p6d, for O: single 1s3d, double 2s2p, for Pb: single 5s5p6d, double 6s6p, for Nb: single 4s4p5p, and double 5s4d. The exchange and correlation potential of Perdew and Wang was employed as well as the FPLO implementation of the LSDA+$U$ method in the atomic limit scheme, and parameters $U \equiv F^0 = 4$ and 6. The intra-atomic exchange parameters were fixed at the values $F^2 = 49B + 7C = 10.3$ eV, and $F^4 = 63C/5 = 7.5$ eV, which corresponds to Racah parameters $B = 1015$ cm$^{-1}$, $C = 4800$ cm$^{-1}$ for free Fe$^{3+}$ ion.

The calculations were made for $2 \times 2 \times 2$ 40 atom supercell PbFe$_{3}$Nb$_{1}$O$_{24}$ (symmetry group P1, #1) shown schematically in the Fig. 1. The $4 \times 4 \times 4$ k-mesh was used for the Brillouin zone integration. First, we have defined the magnetic interaction for cubic perovskite structure that corresponds to the paraelectric phase of PFN with the experimental lattice parameter $a = 4.01$ Å, and PFB4 chemical order (Fig. 3). Then we have checked that the interaction values are essentially the same for all kinds of chemical orders and for actual distorted perovskite struc-
The ion coordinates for all possible types of the chemical ordering shown in the Fig. 2 were taken from the results of full relaxation\cite{7} that has been performed in the Ref.\cite{7}

The total energies for different structural and magnetic configurations were obtained, and the results were mapped onto an effective Hamiltonian

$$\hat{H} = E_n + \frac{1}{2} \sum_{\mathbf{R}, \mathbf{g}} J_\mathbf{g} \mathbf{S}_\mathbf{R} \mathbf{S}_{\mathbf{R} + \mathbf{g}},$$

where $E_n$ is a non-magnetic, spin-independent part of the energy, which depends on chemical configuration\cite{7}

The spin-dependent part of the interaction has the form of a Heisenberg term. The sum goes over the lattice sites $\mathbf{R}$ occupied by magnetic Fe$^{3+}$ ions, vectors $\mathbf{g}$ join interacting spins. The $2 \times 2 \times 2$ supercell allows to determine the values of nearest-, second-nearest-, and third-nearest-neighbor interactions $J_1, J_2, J_3$, which correspond to sites separated by the edge, face diagonal, and space diagonal of perovskite unit cell. For a given spin configuration, the total energy per supercell is

$$E_c = \langle \hat{H} \rangle = E_n + \frac{1}{2} \sum_{\mathbf{s}, \mathbf{g}} J_{\mathbf{g}} \langle \hat{\mathbf{S}}_{\mathbf{s}} \hat{\mathbf{S}}_{\mathbf{s} + \mathbf{g}} \rangle,$$

where $\mathbf{s}$ is the magnetic ion position within the cell, $\langle \hat{\mathbf{S}}_{\mathbf{s}} \hat{\mathbf{S}}_{\mathbf{s} + \mathbf{g}} \rangle = cS^2$, $c = +1(-1)$ for parallel (anti-parallel) spin arrangement.

III. RESULTS

The details concerning the calculated electronic structure of PFN are given in the Appendix [A]. Here we concentrate on the magnetic interactions. The results for the total energy calculations for different spin arrangement in PFB4 chemical order (Figs.\cite{13}) of ideal cubic perovskite structure are given in the Table I. The expressions for the magnetic energy for the considered supercells are given in the second column of the Table II. The third column of the table gives the energies that we obtained in LSDA+U calculations for fully relaxed supercells\cite{13,55}.

Using the formulas from the Table II we find the expressions for the magnetic interactions in the PFB4 chemical configuration

$$J_5 = (E_{4,c} - E_{4,b}) / 16S^2,$$

$$J_1 = (E_{4,b} - E_{4,a}) / 4S^2 + 4J_3,$$

$$J_2 = (E_{4,\text{fm}} - E_{4,\text{a}}) / 16S^2 - J_1 / 2.$$

Substituting the values of energy differences from the Tables\cite{14,11} into these equations, we obtain the values of the interactions given in the Table III. The last row of the table shows the results for fully relaxed lattice\cite{12}. Our calculations of the total energies confirm the results of Ref.\cite{7,22} but we find that the lowest energy for 2nd configuration corresponds to ferrimagnetic type of ordering PFB2\cite{23,30}.

The Table IV shows the results of the check of the quality of our mapping of LSDA+U on the Heisenberg model\cite{1}.
TABLE IV. Check of the mapping. DFT energy differences ($U = 4$ eV) are compared with the results for the model, Eq. (1), which assumes $J_i$ to be independent on the chemical configuration.

| $\Delta E/S^2$, meV | DFT | Model | Value |
|---------------------|------|-------|-------|
| $(E_{5,\text{fm}} - E_{5,\alpha})/S^2$ | 146.6 | 16$J_1$ | 156.5 |
| $(E_{3,\text{fm}} - E_{3,\alpha})/S^2$ | 113.4 | 12$J_1$ | 117.3 |
| $(E_{2,\text{fm}} - E_{2,\alpha})/S^2$ | 108.3 | 12$J_1$ | 117.3 |
| $(E_{2,\alpha} - E_{2,\text{fm}})/S^2$ | 76.7 | 8$J_1 + 16J_2$ | 81.6 |
| $(E_{1,\text{fm}} - E_{1,\alpha})/S^2$ | 5.3 | $16J_2 + 32J_3$ | 3.3 |
| $(E_{1,\alpha} - E_{1,\text{fm}})/S^2$ | 79.9 | 8$J_1 + 16J_2$ | 81.6 |
| $(E_{0,\text{fm}} - E_{0,\alpha})/S^2$ | 11.1 | $32J_2$ | 6.7 |

IV. DISCUSSION

A. Superexchange interaction

Our calculations strongly suggest that the magnetism of $\text{AF}_{1/2}\text{M}_{1/2}\text{O}_3$ systems may be described by the Heisenberg model on the lattice, which is obtained from the simple cubic lattice by removing half of its sites, the nearest-neighbor interaction $J_1$ being dominant.

![FIG. 4. (Color online) The geometry of Fe₁-O-Fe₂ superexchange path.](image)

The dominance of $J_1$ is an expected result. The magnetic interactions between $\text{Fe}^{3+}$ ions are due to the superexchange mechanism, which has a local nature for 3$d$-metal compounds. The ion $\text{Fe}^{3+}$ has $d^5$ electronic configuration. For this configuration, the fourth-order many-body perturbation theory expression for the superexchange via a single intervening oxygen ion (Fig. 4) may be written in a simple form (see Appendix B for the derivation)

$$J_\alpha \approx KV_{pd\sigma,1}V_{pd\sigma,2} \left(0.475 + 0.617 \cos^2 \alpha\right),$$

$$= J_{180} \left(0.475 + 0.617 \cos^2 \alpha\right)/1.092$$

$$= J_{180} \cos^2 \alpha + J_{90} \sin^2 \alpha$$

where $\alpha$ is the Fe-O-Fe bond angle; $K$ is given by $K = (5/8) U$, does not depend on the bond geometry, $V_{pd\sigma,i}$ are the Slater-Koster parameters for the electron hopping integrals between Fe and O ions, which depend only on the Fe-O bond-lengths.

The dependence of the Fe-O-Fe superexchange on the square of the bond angle cosine $\cos^2 \alpha$ was established for the orthoferrites $\text{RFeO}_3$ in the Ref. [40] in the form given by Eq. (8). For the $\text{RFeO}_3$ family, the bond angle varies between 157° in LaFeO$_3$ to 142° in LuFeO$_3$, the Fe-O bond-length being approximately constant $\approx 2.01$ Å. Substituting the LuFeO$_3$ parameters $\cos^2 \alpha \approx 0.618$ and $J/k_B \approx 48.4 \pm 2$ K into Eq. (7), we find for $J_{180}/k_B \approx 62$ K, which is comparable with our $J_1$ value calculated for $U = 6$. As a result, the assumption (i) from the Introduction is thus confirmed.

Our formula (6) shows also that the Fe-O-Fe superexchange depends on the Fe-O bond lengths $R_i$. The hopping integrals $V_{pd\sigma,i}(R_i)$ decrease with the increase of the bond length [42]. This means that the superexchange should decrease with the increase of lattice parameter if the bond angle remains constant. The results shown in the Table III follows this tendency.

We may compare our results also with the Ref. [32] where the values for $J_1$, $J_2$, and forth-neighboring $J_4$ were obtained for PFB0 = $\frac{1}{2}$ (111) and PFB5 = $\frac{1}{4}$ (100) configurations (Fig. 2). If we express the results from the Table III of Ref. [32] in our notations, we obtain $-2J_1/k_B = J_2/k_B \approx 0.9$ K, and $-2J_2/k_B = J_4/k_B \approx 2.8$ K for PFB0, and $-2J_1/k_B = J_2/k_B \approx 42$ K, $-2J_2/k_B = J_4/k_B \approx 0.5$ K, $-2J_2/k_B = J_3/k_B \approx 2.8$ K for PFB5. The results of Ref. [32] confirm the dominance of $J_1$ nearest-neighbor Fe-O-Fe interaction. The absolute value of the interaction is smaller, but we should take into account that the authors of the Ref. [32] have used $U = 9$ eV value in those calculations. Note that they obtained $J_1/k_B \approx 50$ K for LaFeO$_3$, which is slightly smaller than experimental value $59$ K derived from $T_N = 740$ K using high-temperature expansion.

B. Collective magnetic properties

The way how the half of sites of simple cubic lattice are occupied by the interacting Fe spins determine the magnetic properties of the system. In this work, we model the disordered system by $2 \times 2 \times 2$ supercell periodic lattice. If we take into account only nearest-neighbor interaction $J_1$, then magnetic ions form three dimensional lattice in PFB2 and PFB3 configurations (Fig. 2). Thus, only these configurations may possess a magnetic long-range order at non-zero temperature. Other configurations have lower dimensionalities and thus have no ordering at finite temperatures. Actually, small next-nearest neighbor interactions (like $J_2$, $J_3$) will ensure the ordering, but the temperature will be substantially lower (see below the consideration of PFB5 structure in the subsection IV C).

The simplest molecular field approach gives for the ferrimagnetic ordering temperature (see Appendix C for the
will be dominated by PFB3 configuration. So, within our
magnetic properties of an AFe
1
metals the transition temperature by the factor \( \sim \)
have in mind that the molecular field theory overesti-
933(758) K, \( T \)
S
have equal spins
net Y
antiferromagnetically coupled magnetic sublattices. An-
due to different spin values of ions occupying different
meet PFB2 configuration is
So, in the case of random distribution, the probability to
and PFB4 configurations \( 2 + 2 \times 6 \), and 24 times PFB3
Fig. 2 We will meet 2 times the configuration PFB0, 6 times PFB1 and
PFB5 configurations, 8 times PFB2, and 24 times PFB3 and PFB4 configurations \( 2 + 2 \times 6 + 8 + 2 \times 24 = 70 \). So,
in the case of random distribution, the probability to
meet PFB2 configuration is \( P_2 = 8/70 \approx 0.11 \), and to
meet PFB3 configuration is \( P_3 = 24/70 \approx 0.34 \). Thus
the magnetic properties of an AFe
1/2M
1/2O
3
compound will be dominated by PFB3 configuration. So, within our
simple model of disorder the transition temperature would
be several hundreds K. As we have mentioned in the
introduction, more sophisticated treatment of the disorder
results in \( T_N \sim 300 \) K.\cite{22} Evidently, the assumption (i) is in contradiction with the observed values of transition and Curie-Weiss temperatures.

The distribution of Fe and M ions over B sites de-
dpends on the ratio of ionic radii of Fe and M metal ions,
the growth condition of the sample etc. When the ra-
dius of M\(^{5+}\) ion is larger than that of Fe\(^{3+}\), the or-
dered PFB0 configuration becomes most probable.\cite{22}
This is often the case for M=Sb.\cite{22} For such an 1:1 or-
dered systems, magnetic Fe\(^{3+}\) ions form regular face cen-
tered cubic sublattice with interaction \( J_2 \) between nearest spins in the sublattice. The Curie-Weiss temperature is
\( \Theta_{CW,0} = 4S(S + 1)J_2/k_B \). The magnetic ground state of such Heisenberg lattice is so called I-type order, which
is denoted as PFB0a on the Fig. 2. The transition tem-
perature was studied in Ref.\cite{34} using high temperature series expansion. It occurs to be spin independent and
equals \( T_I \approx - \Theta_{CW,0}/5.76 \). The Table V compares the
calculated values of \( T_I \) with the temperature \( T_{max} \) of the magnetic susceptibility anomaly observed in 1:1 ordered
AFe
1/2M
1/2O
3
compounds.

| \( U \), eV | \( \Theta_{CW,0} \), K | \( T_I \), K | \( T_{max} \), K |
|----------------|----------------|----------------|----------------|
| 4              | -151           | 26             |                |
| 6              | -70            | 12             |                |
| \( \text{Sr(Fe}_{1/2}\text{Sb}_{1/2})\text{O}_3 \) \(^a\) | -221           | 38             | 36             |
| \( \text{Ca(Fe}_{1/2}\text{Sb}_{1/2})\text{O}_3 \) \(^b\) | -89            | 15             | 17             |

\(^a\) Reference 24
\(^b\) Reference 23

C. Magnetism of the PbFe
1/2M
1/2O
3
compounds

The total energies of various chemical configurations (see Fig. 2) of Fe in a \( 2 \times 2 \times 2 \) supercell of PbFe
1/2M
1/2O
3
(M=Nb, Ta, Sb) were calculated in Ref.\cite{7} using the LSDA+U functional. For the PFN and PbFe
1/2Ta
1/2O
3
(M=Nb, Ta) compounds, the layered PFB5a configuration has the lowest energy, in contrast to PbFe
1/2Sb
1/2O
3
, where the PFB0 1:1 chemically ordered configuration is most favorable\cite{27} (see also Table I). The PFN and PbFe
1/2Ta
1/2O
3
compounds are especially interesting because they are multiferroics and exhibit fer-
roelectric transition (\( T_C \approx 380, 270 \) K for M=Nb, Ta) in addition to antiferromagnetic transition. As we have mentioned in the Introduction, the peculiarity of mag-
etic properties of these two compounds is that those Néel temperature \( T_N \sim 150 \) K is much higher than the
transition temperature for other double perovskites. A layered Heisenberg model with the nearest neighbor interaction \( J_1 \) within the layer and an interlayer interaction \( J_2 \) was thoroughly studied in the past (see Ref. \[1] and references therein). It was established that the transition temperature has logarithmic dependence on \( J_1/J_1 \) ratio

\[
\frac{T_N}{T_{N,sc}} \approx \frac{1}{1 - k \ln(J_1/J_1)},
\]

where \( T_{N,sc} \) is the transition temperature for the G-type antiferromagnetic ordering of simple cubic lattice (\( J_1 = J_1 \)), and \( k \approx 1/3 \). The equation (11) was found to work in the wide range of values 0.001 \( \leq J_1/J_1 \leq 0.5 \) it gives \( T_N/T_{N,sc} \approx 0.30, 0.39, 0.57 \) for \( J_1/J_2 = 0.001, 0.01, 0.1 \) respectively. Taking \( T_N \approx 600 \text{ K} \), we obtain reasonable values for \( T_N \approx 180, 234, 342 \), respectively, if we assume that PFN and PbFe\(_1/2\)Ta\(_{1/2}\)O\(_3\) have the totally ordered layered structure.

In reality, both compounds are disordered and the results of the supercell calculations indicate only what kind of short-range chemical order is more favorable. Below \( T_N \), the neutron diffraction studies \[21,22] reveal a G-type antiferromagnetic order with magnetic moments \( \mu \approx 2.8 \mu_B \) sitting at every site of the simple cubic lattice. It is clear that this is an averaged picture with a "half of Fe\(^{3+}\) ion" in every site of B-sublattice of the structure. The value of \( \mu \) is about half of the value expected for Fe\(^{3+}\) ion \( \mu_{Fe} = 5 \mu_B \).

In contrast to neutron diffraction, local probe methods such as Nuclear Magnetic Resonance (NMR) and Mossbauer spectroscopy provide local structure information. In this respect, we can mention \(^{17}\)O NMR data \[23\] which may confirm our theoretical prediction that PFB5 configuration gives major contribution to the antiferromagnetic ground state of PFN or PbFe\(_1/2\)Ta\(_{1/2}\)O\(_3\). Indeed, \(^{17}\)O NMR spectrum consists of two distinct components: narrow and very broad lines. One can see from Fig. 2 that each O ion connects only two cations forming three different pathways along (100) cubic directions: Fe-O-Fe, Fe-O-Nb, and Nb-O-Nb. The first two configurations are responsible for the broad component in \(^{17}\)O NMR spectrum as O nucleus is closely adjacent to the magnetic Fe\(^{3+}\) ion. The last configuration does not contain magnetic ions therefore is responsible for the narrow component in NMR spectrum. Among all chemical configurations shown in Fig. 2, the PFB5 configuration has a largest number of nonmagnetic Nb-O-Nb chains. Assuming, for example, random distribution of Fe and Nb ions we have relative weight of the Nb-O-Nb pathways only 0.19, while the NMR data predicts 2-2.5 times larger value. This suggests that the layered PFB5 chemical configuration can dominate among other chemical ordering. The nonrandom distribution of magnetic and nonmagnetic cations in PFN is also supported by \(^{93}\)Nb NMR measurements. The NMR data have been interpreted in a model which assumes existence of Fe rich, Nb poor and Fe poor, Nb rich regions in PFN.

The Table 1 shows that the PFB2fe configuration has the total energy, which is close to the lowest PFB5 configuration. This is the case also for PbFe\(_1/2\)Ta\(_{1/2}\)O\(_3\) and PbFe\(_1/2\)Sn\(_{1/2}\)O\(_3\). A sample of a disordered double perovskite compound may contain some regions with PFB2 chemical order. In the ground state, such a region possess the moment \( \mu_g = N_c \mu_c \), where \( N_c \) is the number of supercells in the region, \( \mu_c = 10 \mu_B \) is the moment of the supercell. Large moment of the region will persist for \( T < T_{2f_e} \). Therefore, it can not be excluded that such regions exist in the systems PbFe\(_1/2\)Ta\(_{1/2}\)O\(_3\)/PbZr\(_x\)Ti\(_{1-x}\)O\(_3\) and PbFe\(_1/2\)W\(_{1/3}\)O\(_3\)/PbZr\(_x\)Ti\(_{1-x}\)O\(_3\) and are responsible for for large room-temperature magnetic response and magnetoelectric coupling in spite that the long-range magnetic order establishes far below the room temperature.

V. CONCLUSION

Based on LSDA+U calculations, we have found that AF\(_1/2\)M\(_1/2\)O\(_3\) double perovskite compounds may be described by antiferromagnetic \( J_1 - J_2 \) Heisenberg model on the lattice, which is obtained from the simple cubic lattice by removing half of its sites. The dominant magnetic interaction is Fe-O-Fe superexchange \( J_1 \) between Fe\(^{3+}\) (S=5/2) ions occupying nearest-neighbor positions within the B-sublattice of ABO\(_3\) perovskite structure. The next-nearest-neighbor interaction \( J_2 \) which corresponds to sites separated by the face diagonal of perovskite unit cell is much smaller. The estimated values of the exchange paramaters are close to the values reported for Fe-based perovskites RFeO\(_3\), where all octahedral sites are occupied by Fe ions. The distribution of Fe\(^{3+}\) and M\(^{2+}\) ions over B sites of perovskite lattice determine the magnetic properties of the double perovskites. Our results suggest that the distribution is not random. The typical value of the magnetic transition temperature \( T_N \sim 25 \text{ K} \) in most of the paraelectric double perovskite compounds allows to conclude that the probability to find there a nearest-neighbor pair of Fe (interacting with \( J_1 \) exchange value) is suppressed compared the probability to find the next-nearest pair, and the magnetic energy scale is determined by \( J_2 \). In accord with Ref. \[7\] we argue that two multiferroic compounds PbFe\(_1/2\)Nb\(_{1/2}\)O\(_3\) and PbFe\(_1/2\)Ta\(_{1/2}\)O\(_3\) (\( T_N \sim 150 \text{ K} \)) have predominantly layered PFB5 (see Fig. 2) short-range ordering where the B-sublattice is formed by alternating Fe and M(=Nb or Ta) planes.

We have also found that Fe ion in double perovskites may form a sub-nano-sized superstructure (PFB2 chemical order in the Fig. 2) having the room temperature ferrimagnetic order. Such ferrimagnetism of geometrical origin \[24\] may represent an interesting alternative to the room-temperature ferromagnetism in wide-gap semiconductors, which is in the focus of recent studies. Formation of the PFB2 superstructure in ferroelectric double
perovskites will lead to the room-temperature multiferroism where ferroelectric and ferrimagnetic type order can coexist, at least at a nanoscale level. Recent observations of the room-temperature multiferroism in complex systems on the base of the double perovskites 28–31 are possibly provided by nano-regions of the ferrimagnetic PFB2 superstructure rather than by simple local clustering of Fe ions as this will lead only to increase of Neel temperature.

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Appendix A: Detail of the LSDA+U calculations

Total and projected densities of states are shown in the Fig. 5. As expected, the largest spin splitting occurs for Fe 3d-states. The Table VI shows the values of magnetic moments localized on the Fe ions. They are close to the isolated Fe$^{3+}$ ion value 5$\mu_B$. In the groundstate PFB4a configuration, the polarization do not exceed 0.03$\mu_B$ for oxygen ions, and 0.04$\mu_B$ for Nb ions. In the ferromagnetic state, the polarization of some oxygens and Nb ions reaches 0.14$\mu_B$ and 0.12$\mu_B$ respectively. We see that the localized moment description of the magnetism in PFN by the model Hamiltonian 1 is adequate.

Appendix B: Three center cation-anion-cation model

Here we will calculate the superexchange for the case when it is mediated by one anion where the CF splitting will be neglected. Then we choose the coordinate system having the anion in the origin, and the vector radii of the cations are

$$R_1 = (0, 0, -1) R_1,$$

$$R_2 = (\sin \alpha, 0, -\cos \alpha) R_2,$$

where $\alpha$ is the angle between bonds (Fig. 4). A general fourth-order many-body perturbation theory expression for the superexchange between two ions in $d^5$ configuration reads (cf. Eqs. (9),(10) of the Ref. 44)

$$J = -\frac{1}{285^2 \Delta_{eff}^2} \left( \frac{r^2}{U_{eff}} + \frac{2}{2 \Delta_{eff} + U_p} \right) E_{\beta\beta} \quad (B1)$$

TABLE VI. The magnetic moments (in the units of Bohr magneton $\mu_B$) localized on different Fe ions of PFB4 chemical configuration in various magnetic states depicted in Figs. 2.

| $U$, eV | $a$, Å  | Fe1 | Fe2 | Fe3 | Fe4 |
|---------|---------|-----|-----|-----|-----|
| a       | 4       | 4.01| 4.45| 4.45| -4.39| -4.52|
|         | 6       | 4.01| 4.77| 4.77| -4.71| -4.85|
|         | 4       | 3.95| 4.49| 4.49| -4.42| -4.56|
|         | $\sim$ 3.94 | 4.43| 4.43| -4.35| -4.45|
| b       | 4       | 4.01| 4.49| -4.45| 4.43| -4.51|
|         | 6       | 4.01| 4.79| -4.77| 4.73| -4.85|
|         | 4       | 3.95| 4.52| -4.49| 4.45| -4.55|
|         | $\sim$ 3.95 | 4.49| -4.43| 4.41| -4.45|
| FM      | 4       | 4.01| 4.50| 4.50| 4.48| 4.50|
|         | 6       | 4.01| 4.80| 4.80| 4.75| 4.85|
|         | 4       | 3.95| 4.53| 4.53| 4.49| 4.54|
|         | $\sim$ 3.95 | 4.50| 4.49| 4.47| 4.45|

$^a$ Fully relaxed lattice from the calculations in the Ref. 8.
where
\[
E_{\beta\gamma} = \sum_{m,m',n,n'} t_{1,m,\beta,n} t_{2,m',\beta,n} t_{1,m,\beta,n} t_{2,m',\beta,n} \tag{B2}
\]
\[
U_{\text{eff}} = U_d + 4J_H, \tag{B3}
\]
\[
\Delta_{\text{eff}} = \Delta + 28J_H/9. \tag{B4}
\]
The d-ions are assumed to be in the high-spin state \((S = 5/2)\), \(U_d (U_p)\) is the the Coulomb repulsion between two meron ions on the same \((d\text{-}p})\)orbital, \(J_H \equiv \frac{2}{3}B + C\) is the Hund exchange in the \(d\)-shell expressed in terms of Racah parameters, and \(\Delta\) is the charge transfer energy (see Ref. [13] for the discussion of the approximations behind the Eq. [B1], and the description of the realistic many-body \(p - d\) Hamiltonian). According to Harrison model[18] the hopping \(t_{\alpha,m,\beta,n}\) between \(m\)-th \(d\)-function of metal ion \(\alpha = 1, 2\) and \(n\)-th \(p\)-function of ligand \(\beta\) is expressed via direction cosines \(l, m, n\) of the vector \(\mathbf{R}_\beta - \mathbf{R}_\alpha\), and two Slater-Koster[19] parameters \(V_{\text{pd}}(R), V_{\text{d}}(R)\), which depend on sorts of metal ion and on the distance \(R = |\mathbf{R}_\beta - \mathbf{R}_\alpha|\); \(r \approx 0.8\) is a reduction factor that is caused by dependence of the hoppings on the number of 3d electrons.

In the case of single ligand, the index \(\beta\) may be dropped, and it is convenient to write
\[
E \equiv \sum_{n,n',m,m'} t_{1,m,n} t_{2,m',n'} t_{1,m,n} t_{2,m',n'} = \sum_{n,n',m} t_{1,m,n} t_{2,m',n} \sum_{m'} t_{2,m',n} t_{2,m',n'} .
\]

The Slater-Koster tables[15] gives for the first transition metal-anion pair
\[
t_{1z2z} = \frac{1}{2} t_{1z2z} = -V_{\text{pd}}(1) ,
\]
other hoppings are zero. So
\[
\sum_m t_{1,m,n} t_{2,m',n'} = \delta_{nn'} \sum_m t_{1,m,n}^2 = \delta_{nn'} T_{1n}
\]
\[
T_{1x} = T_{1y} = -V_{\text{pd}}(1) , \quad T_{1z} = V_{\text{pd}}(1)
\]
then
\[
E \equiv \sum_{n,n'} \delta_{nn'} T_{1n} \sum_{m'} t_{2,m',n} T_{2n} \sum_{n} T_{1n} T_{2n} = \sum_{n,n'} \delta_{nn'} T_{1n} T_{2n} = \sum_{n} T_{1n} T_{2n}
\]
\[
T_{2n} = \sum_{m'} t_{2,m',n}^2 .
\]

For the second anion-TMI pair the hoppings are given in tables VIII. This gives us
\[
T_{2x} = \sin^2 \alpha V_{\text{pd}}(2) + \cos^2 \alpha V_{\text{pd}}(2) ,
\]
\[
T_{2y} = V_{\text{pd}}(2) ,
\]
\[
T_{2z} = \cos^2 \alpha V_{\text{pd}}(2) + \sin^2 \alpha V_{\text{pd}}(2)
\]

And we obtain
\[
E = V^2_{\text{pd}}(3) (T_{2x} + T_{2y} + V^2_{\text{pd}}(1) T_{2z} \tag{B5}
\]
\[
= V^2_{\text{pd}}(1) (\sin^2 \alpha V^2_{\text{pd}}(2) + \cos^2 \alpha V^2_{\text{pd}}(2) + \sin^2 \alpha V^2_{\text{pd}}(2) + \sin^2 \alpha V^2_{\text{pd}}(2) + \sin^2 \alpha V^2_{\text{pd}}(2) \tag{B6}
\]
\[
= V^2_{\text{pd}}(1) (\sin^2 \alpha V^2_{\text{pd}}(2) + \cos^2 \alpha V^2_{\text{pd}}(2) + \sin^2 \alpha V^2_{\text{pd}}(2) + \sin^2 \alpha V^2_{\text{pd}}(2) + \sin^2 \alpha V^2_{\text{pd}}(2) \tag{B6}
\]

In the last equality we have introduced the ratio \(r = V_{\text{pd}}(1) / V_{\text{pd}}(2) \approx -2.16\) [17].

Finally, we obtain the Eq. (4) of the main text with
\[
K = \frac{r^2}{U_{\text{eff}}} + \frac{2}{2\Delta_{\text{eff}} + U_p} \tag{B7}
\]

**Appendix C: Transition temperature**

Here we give the derivation of Eqs. (9), (10) for transition temperatures within the molecular field approximation (see e.g. Ref. [19]).

In the PFB2Fe configuration we have two sublattices: Fe1 with spin up and Fe2 with the spin down. In a supercell, one of the ions belongs to sublattice Fe1 and three to the sublattice Fe2. The molecular fields acting on the magnetic moments are

\[
H_2 = -\lambda M_1, \tag{C1}
\]
\[
H_1 = -\lambda M_2, \tag{C2}
\]
\[
\lambda = \frac{2J_1}{N\mu^2} \tag{C3}
\]

where \(N\) is the number of supercells, \(\mu = g\mu_B\), \(g\) is the \(g\)-factor of the Fe\(^{3+}\) ion, \(\mu_B\) is the Bohr magneton, \(M_1\) \((M_2)\) is the magnetization of Fe1(Fe2) sublattice. The magnetization, in its turn, is defined by the molecular field

\[
M_s = N n_s \mu B S_\text{B}(\frac{\mu S}{k_B T} H_s) \tag{C4}
\]

\[
\approx \frac{C_s}{T} H_s \tag{C5}
\]

where \(s = 1, 2\), \(n_s\) is the number of ions in the supercell that belongs to the sublattice \(s\), \(n_2 = 3n_1 = 3\),

\[
C_s = \frac{N n_s \mu^2 S(S + 1)}{3k_B} \tag{C6}
\]

is the corresponding Curie constant, \(B_L(x) \equiv [(2L + 1)/2L] \text{coth} [(2L + 1)/2L] x/2L - (1/2L) \text{coth} x/2L \) is the Brillouin function. The equality (C5) follows from the expansion \(B_L(x) \approx (L + 1)x/3L\), which is valid for small \(x\). Substituting the value of molecular field from Eqs. (C1) into Eqs. (C5), we obtain the system of equations for the sublattice magnetizations in the absence of the external field

\[
\begin{cases}
T M_1 + C_1 \lambda M_2 = 0, \\
C_2 \lambda M_1 + T M_2 = 0,
\end{cases}
\]
TABLE VII. Hoppings $t_{2m'n'}$ between $t_{2g}$ orbitals and ligand p-functions

| n\m | xy   | yz   | za   |
|------|------|------|------|
| x    | 0    | 0    | $-\cos \alpha \left[ \sqrt{3} \sin^2 \alpha V_{pdx} + (1 - 2 \sin^2 \alpha) V_{pdx} \right]$ |
| y    | $\sin \alpha V_{pdx}$ | $-\cos \alpha V_{pdx}$ | 0 |
| z    | 0    | 0    | $-\sin \alpha \left[ \sqrt{3} \cos^2 \alpha V_{pdx} + (1 - 2 \cos^2 \alpha) V_{pdx} \right]$ |

TABLE VIII. Hoppings $t_{2m'n'}$ between $e_g$ orbitals and ligand p-functions

| n\m | $x^2 - y^2$ |
|------|-------------|
| x    | $\sqrt{2} \sin^3 \alpha V_{pdx} + \sin \alpha \left( 1 - \sin^2 \alpha \right) V_{pdx}$ |
| y    | $\sin \alpha \left( \cos^2 \alpha - \frac{\sin^2 \alpha}{2} \right) V_{pdx} - \sqrt{3} \cos^2 \alpha V_{pdx}$ |
| z    | $-\cos \alpha \left[ \sqrt{2} \sin^2 \alpha V_{pdx} - \sin^2 \alpha V_{pdx} \right]$ |

which has trivial solution $M_1 = M_2 = 0$ above the transition temperature $T > T_{fe}$. Nonzero values of the magnetizations becomes possible if the determinant of the coefficients of $M_1$ and $M_2$ is zero. This condition yields

$$(T_{fe})^2 = C_1 C_2 \left( \frac{2J_1}{N\mu^2} \right)^2,$$  

(C7)

and we obtain Eq. (9). At lower temperatures $T < T_{fe}$, the system becomes non-linear as the argument of the Brillouin function grows.

The calculation for PFB3a magnetic ordering is more involved. We have four sublattices shown on the Fig. 2. Curie constants are equal $C = N\mu^2 S(S + 1)/3k_B$, and we have four equations

$$
\begin{align*}
TM_{B,1} &= CH_{B,1} = -C\lambda (M_{A,1} + M_{A,2}), \\
TM_{B,2} &= CH_{B,2} = -C\lambda M_{A,1}, \\
TM_{A,1} &= CH_{A,1} = -C\lambda (M_{B,1} + M_{B,2}), \\
TM_{A,2} &= CH_{A,2} = -C\lambda M_{B,1}.
\end{align*}
$$  

(C8)

Again, at the transition temperature, the determinant of the coefficients should vanish. This gives a biquadratic equation

$$T^4 - 3(C\lambda)^2 T^2 + (C\lambda)^4 = 0.$$  

(C9)

The transition temperature is given by largest positive root of the Eq. (C9), as it corresponds to the temperature where the non-trivial solution appears when we approach the transition from the paramagnetic side. We thus obtain the Eq. (10).
The $J_1, J_2$ values for the orthoferrites YFeO$_3$ and LuFeO$_3$ were obtained in Ref.13 from the high temperature analysis of the paramagnetic susceptibility. In our notations, they are $J_1/k_B = 54.4 \pm 2$ K, $J_2/k_B = 2.4 \pm 0.4$ K, for YFeO$_3$, and $J_1/k_B = 48.4 \pm 2$ K, $J_2/k_B = 0.2 \pm 0.2$ K for LuFeO$_3$. Note that the author of the Ref.13 use another definition of the exchange, and we have multiplied his values by the factor (-2) for the comparison with our values. The inelastic neutron scattering studies (4-6) shows that $J_1, J_2$ have almost the same values for all RFeO$_3$ family, the small variations being due to the Fe-O-Fe angle variations (6).