

**Magnetic properties of  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$ : Mössbauer spectroscopy and first-principles calculations**I. P. Raevski,<sup>1</sup> S. P. Kubrin,<sup>1</sup> S. I. Raevskaya,<sup>1</sup> D. A. Sarychev,<sup>1</sup> S. A. Prosandeev,<sup>1,2</sup> and M. A. Malitskaya<sup>1</sup><sup>1</sup>*Research Institute of Physics and Physics Department, Southern Federal University, Rostov on Don, 344090, Russia*<sup>2</sup>*Physics Department, University of Arkansas, Fayetteville, Arkansas 72701, USA*

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Magnetic properties of magnetoelectric  $\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PFN) have been studied with the help of Mössbauer spectroscopy. In contrast to the belief that Nb and Fe are randomly distributed in the lattice, we found that the Fe ions occupy two crystallographic positions, which differ by the quadrupole splitting and magnetic field mirroring the difference in the nearest neighbor environment of the Fe ions. The ratio of the weights of these positions is 2.3, at 14 K. First-principles calculations provide a microscopic insight of this finding.

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**I. INTRODUCTION**

$\text{PbFe}_{1/2}\text{Nb}_{1/2}\text{O}_3$  (PFN) is a multiferroic promising a very good magnetoelectric performance, under a field-cooling protocol.<sup>1</sup> PFN undergoes phase transitions, on cooling, from the cubic paraelectric to tetragonal ferroelectric phase, at  $T_{C1} \approx 370\text{--}380$  K, and then to the rhombohedral<sup>1–3</sup> (or monoclinic)<sup>4,5</sup> ferroelectric phase, at  $T_{C2} \approx 350\text{--}360$  K, and, finally, to the *G*-type antiferromagnetic (AFM) phase at  $T_N \approx 150$  K.<sup>2,6–8</sup> It is believed that such a magnetic order is a result of the crystallographic disorder of the Fe and Nb positions over the same cubic sites resulting in a large number of the antisite defects.<sup>2</sup> However, limited Fe segregation<sup>6,9</sup> or some unknown special crystallographic order<sup>10,11</sup> can also be in line with this magnetic order. NMR studies of <sup>93</sup>Nb and <sup>17</sup>O revealed two types of Nb ions in PFN lattice.<sup>11</sup> However, microscopic data about Fe clustering have been absent.

Besides the AFM phase transition, PFN exhibits also a lower-temperature magnetic anomaly at  $T_1 \approx 10\text{--}20$  K.<sup>5,12–14</sup> This anomaly was, at first, attributed to the superexchange interaction taking place via  $-\text{Fe}-\text{O}-\text{Nb}-\text{O}-\text{Fe}-$  pathways caused by the local short-range chemical ordering of the  $\text{Fe}^{3+}$  and  $\text{Nb}^{5+}$  ions.<sup>12</sup> However, experiments on the temperature and magnetic field dependency of the magnetic susceptibility have shown that this anomaly marks the magnetic glass phase transition rather than the AFM or ferromagnetic (FM) phase transition.<sup>5,6,13,14</sup> This kind of spin glass phase transition implies the presence in the lattice of PFN of dynamic spin variables, in addition to the *G*-type antiferromagnetic order. The presence of such dynamic spins was supposed in Ref. 6 as a result of the existence of the disconnected subspace of isolated Fe 3*d* ions as additions to the segregated finite Fe clusters. However, still, there is a lack of a microscopic model of this phenomenon. Indeed, Fe segregation would result in a large space charge, which can misbalance the crystal lattice. To answer the aforementioned questions, we employed Mössbauer spectroscopy in combination with first-principles calculations. These data reveal unusual Fe clustering in the lattice, owing to the strong electron-electron correlations in the 3*d* shell of Fe.

**II. EXPERIMENT**

Mössbauer spectra were recorded in the transmitting mode with the help of an MS1104Em spectrometer by using <sup>57</sup>Co(Cr)

as the source for the gamma rays. The sample was cooled down in the chamber of an He refrigerating cryostat CCS-850 (Janis Research). The treatment of the spectra was done with the UNIVEMMS code.<sup>8</sup> The isomer shifts were measured with respect to alpha-Fe, at 14 and 300 K. In order to record a high-quality Mössbauer spectra, we enriched PFN with <sup>57</sup>Fe isotope at the level of 15% of the total Fe content. The <sup>57</sup>Fe-enriched sample was obtained by a solid state reaction of the starting oxides at 1000 °C. The phase purity of the sample was controlled by the x-ray diffraction and only the rhombohedral perovskite phase was detected at room temperature. As soon as, in the <sup>57</sup>Fe-enriched sample, the relative value of the Mössbauer effect at  $T < T_N$  did not exceed 2%, we appreciably increased the recording time, in order to obtain good enough statistics. As a result, the Mössbauer spectrum recorded at 14 K contained nearly 7 000 000 counts that is about 30 times larger than, to the best of our knowledge, in the Mössbauer spectra of PFN recorded in the AFM phase by other authors.<sup>15</sup> Figure 1 presents the resulting Mössbauer spectrum of PFN obtained at 14 K. The analysis of this spectrum by using only one sextet, as it was assumed in previous works,<sup>15</sup> gives a very high value of the chi-squared criterion of fitting (Pearson criterion), of about 4.13. Normally, this value should be close to 1. When we used for fitting two sextets, the chi-squared value was reduced by about 2.5 times, and proved to be much closer to 1, (chi square equals 1.66 in this fit). Each of these sextets corresponds to the well-known Mössbauer spectrum of  $\text{Fe}^{3+}$ . Indeed, the isomer shift (IS), for both sextets, is approximately of the same magnitude, and its value (about 0.54 mm/s relative to metallic iron) shows that all Fe ions are in the  $\text{Fe}^{3+}$  state. The magnitude of the magnetic hyperfine field at the Fe nuclei (*H*) in two sextets differs by about 10%. This difference can be caused by a different number of Fe ions in the nearest surrounding of the Fe ions. The ratio of the sextets' areas *S* is 2.3 at 14 K. One can assume that the origin of these two sextets is the presence, in the crystal lattice of PFN, of two different Fe positions differing by their environment. Below, we will discuss a possible scenario for this environment, based on our first-principles calculations.

At room temperature, the Mössbauer <sup>57</sup>Fe spectrum of PFN appears to be a doublet (Fig. 2), which is a consequence of the disorder in PFN, or a special order, of the ions of  $\text{Fe}^{3+}$  and  $\text{Nb}^{5+}$  having rather different charges, and producing a

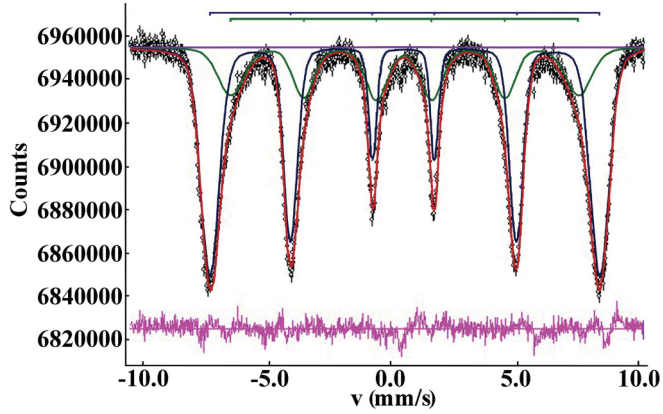


FIG. 1. (Color online) Mössbauer spectrum at 14 K of the PFN sample enriched by the  $^{57}\text{Fe}$  isotope. Points mark the experimental data; the red solid line is the result of fitting the spectrum by two sextets shown by different lines.

strongly inhomogeneous electric field (see also Refs. 15–17 and references therein). In contrast to this, the Mössbauer  $^{57}\text{Fe}$  spectrum of the highly ordered (in the rock-salt structure)  $\text{PbFe}_{1/2}\text{Sb}_{1/2}\text{O}_3$  perovskite appears to be a singlet, at room temperature.<sup>18</sup> These data imply that the Fe ions in PFN are either disordered or ordered in other than the rock-salt structure. By taking into account that, in the low-temperature AFM phase, there are two Fe positions, it is natural to use two doublets for fitting the Mössbauer spectra in the paramagnetic phase. We performed the fitting of the spectrum obtained at room temperature in two ways, assuming the presence in the spectrum of one and two doublets (see Table I). Although both resulting fits provide approximately the same Pearson  $\chi^2$  magnitudes, with both values close to 1, the line width  $\Gamma$  in these fits becomes somewhat smaller, when using two doublets. Both doublets have an IS of 0.41 mm/s inherent to  $\text{Fe}^{3+}$  (relative to the metallic iron). Notice that Refs. 15–17 also report for PFN a similar value of IS. When fitting the spectrum by two doublets, we obtained a large difference between the corresponding quadrupole splitting  $E^Q$  values (see Table I), implying that the surroundings of the corresponding  $\text{Fe}^{3+}$  ions in two different Fe positions may differ appreciably. A specific microscopic model will be discussed below.

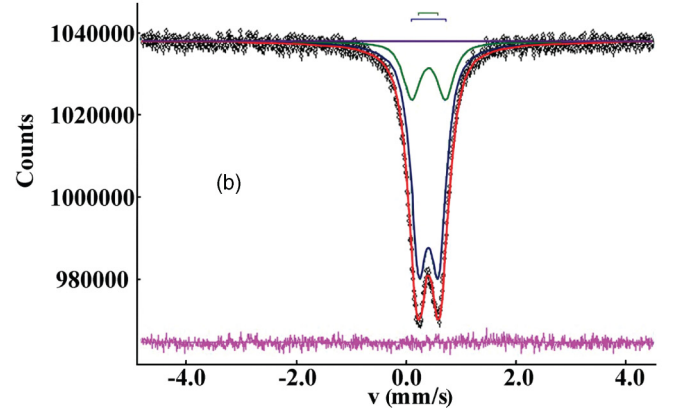
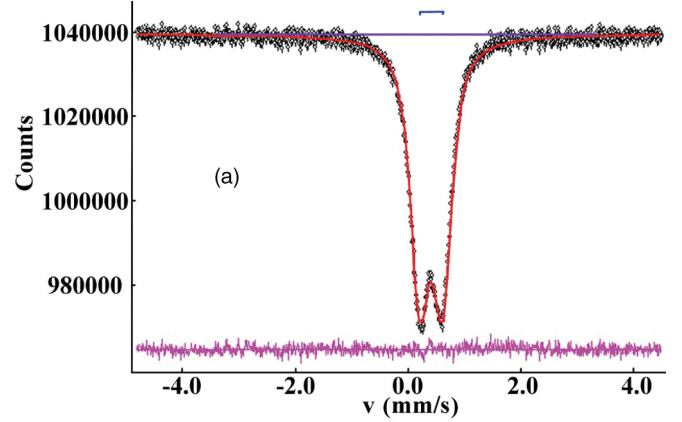


FIG. 2. (Color online) Mössbauer spectrum at 300 K of the PFN sample enriched by the  $^{57}\text{Fe}$  isotope. Points mark the experimental data; the red solid line is the result of fitting the spectrum by (a) one doublet and (b) two doublets shown by different lines.

### III. THEORY

To get microscopic insight into the crystal and magnetic structures of double perovskites, we employed the *ab initio* package VASP,<sup>19</sup> with the LDA-PAW pseudopotentials<sup>20</sup> in the LSDA +  $U$  approximation. For the sake of comparison, besides PFN, we calculated also  $\text{PbFe}_{1/2}\text{Sb}_{1/2}\text{O}_3$  (PFS) and  $\text{PbFe}_{1/2}\text{Ta}_{1/2}\text{O}_3$  (PFT). The  $U$  parameter was employed only on the Fe sites, and  $U$ , at first, was equal to 4 eV (then we

TABLE I. Parameters of Mössbauer spectra of the PFN sample enriched by the  $\text{Fe}^{57}$  isotope, measured at 300 and 14 K. IS is the isomer shift relative to  $\alpha\text{-Fe}$ ;  $\varepsilon$  is the apparent quadrupole shift;  $E^Q$  is the quadrupole splitting;  $H$  is the magnetic hyperfine field;  $S$  is the relative area of the doublet (sextet);  $\Gamma$  is the linewidth of the Mössbauer spectrum;  $\chi^2$  is the chi-squared criterion of fitting (Pearson criterion).

$T$ (K)	Components used		IS $\pm$ 0.05 (mm/s)	$\varepsilon \pm$ 0.02 (mm/s)	$E^Q \pm$ 0.05 (mm/s)	$H \pm$ 0.5 (kOe)	$S \pm$ 0.5 (%)	$\Gamma \pm$ 0.05 (mm/s)	$\chi^2$
	for spectrum deconvolution								
300 K	One doublet		0.41		0.40		100	0.40	1.01
	Two doublets	1	0.41		0.35		77.7	0.36	0.99
14 K		2	0.41		0.62		22.3	0.38	
	One sextet		0.54	0.05		483.8	100	1.03	4.13
	Two sextets	1	0.54	0.05		488.9	69.5	0.90	1.66
		2	0.55	0.02		434.9	30.5	1.23	

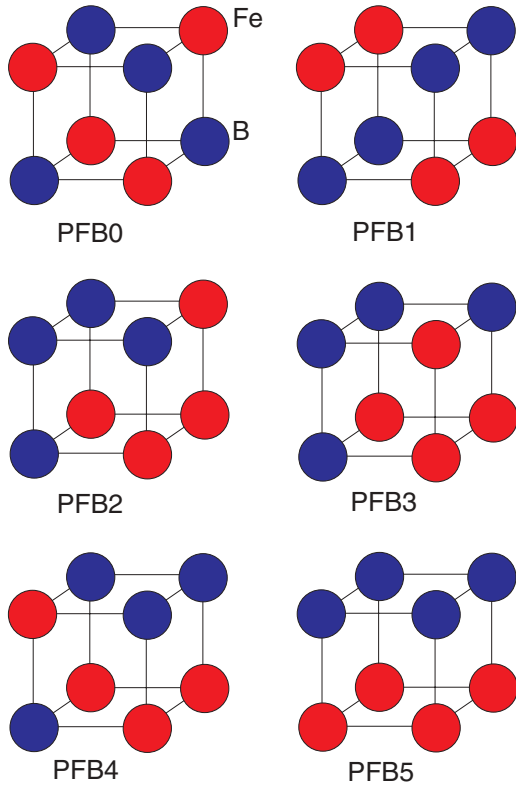


FIG. 3. (Color online) Different chemical configurations of Fe in a  $2 \times 2 \times 2$  supercell of PFB (B = Nb, Ta, and Sb).

varied it to see the difference). The  $k$  mesh and supercell were  $3 \times 3 \times 3$  and  $2 \times 2 \times 2$ , respectively, and included four Fe and four B ions (B = Nb, Ta, Sb). The translation vectors were initially selected as (200), (020), and (002), but, then, were relaxed without any restrictions. We tried several chemical configurations shown in Fig. 3 for the ions on the cube (each of these configurations was translated in all three directions, as described above). Table II provides the energies (in eV) obtained by us in this self-consistent spin-dependent calculation. For all configurations, an AFM order of the nearest spins corresponds to the ground magnetic state.

By comparing the energies in Table II, one can see that, in PFN and PFT, the ground state is the AFM configurations of PFB4 and PFB5, while, for PFS, the ground state is PFB0.

TABLE II. Energy difference (eV), with respect to PFB0, in different chemical configurations of PFB (B = Nb, Ta, and Sb), as obtained from the present first-principles calculations.

Configuration	B = Nb	B = Ta	B = Sb
PFB0	0	0	0
PFB1	0.3324	0.35876	0.78895
PFB2	0.09034	0.07298	0.60445
PFB3	-0.05398	-0.09746	0.65441
PFB4	-0.36283	-0.41624	0.30435
PFB5	-0.49511	-0.5606	0.28831

This striking difference corresponds to the above mentioned<sup>18</sup> difference in the shape of the Mössbauer spectra of PFS and PFN: The former, at room temperature, presents a singlet, while the latter is a doublet.

Our calculations show that all these configurations in PFN have a polarization along the [111] direction, with a magnitude of  $0.55\text{--}0.6 \text{ C/m}^2$ . The tilting angle is also in the [111] direction, and reaches 0.12 radians. The calculated value of polarization correlates rather well with the one experimentally determined at room temperature, from the hysteresis loop measurement in PFN ceramics, and having a value of about  $0.3 \text{ C/m}^2$ ,<sup>21</sup> taking into account that the crystallites in ceramics are oriented randomly.

In order to study the dependence of the result on the choice of  $U$ , we performed calculations for PFN in the LDA approximation, which showed that the ground state is PFB0, rather than PFB4 or PFB5. Notice that PFB0 cannot have the  $G$ -type AFM order, but has the  $I$ -type AFM order, instead. It is interesting that LSDA calculations, with  $U = 0$ , provided a very different result, with respect to  $U = 4 \text{ eV}$ . According to these calculations, the ground state is the antiferromagnetic PFB4 configuration, though PFB0, still, has a close energy. However, when using  $U = 2 \text{ eV}$  and  $U = 6 \text{ eV}$ , we got, again, as in the case of  $U = 4 \text{ eV}$ , that the ground state is the AFM PFB4 and PFB5 configurations. Thus, the stability of these configuration owes to the strong electron-electron interaction in the  $3d$  shell of Fe.

#### IV. DISCUSSION

Our theoretical analysis of the calculated crystal positions of Fe in double perovskites PFB (B = Nb, Ta, and Sb) has revealed that there are, at least, four different sorts of such positions for  $^{57}\text{Fe}$  Mössbauer probe atoms, which can be recognized by Mössbauer spectroscopy (Fig. 4): (i) Fe in Fe chains with the coordination number of each Fe by other Fe ions equal to 2,  $\nu = 2$ ; (ii) Fe in the Fe chains or Fe planes having coordination number  $\nu = 4$ ; (iii) Fe surrounded by only nonmagnetic ions,  $\nu = 0$ , and, finally, (iv) Fe is surrounded by six other Fe ions,  $\nu = 6$ . Let us consider the example of the most populated configuration. Notice that configuration

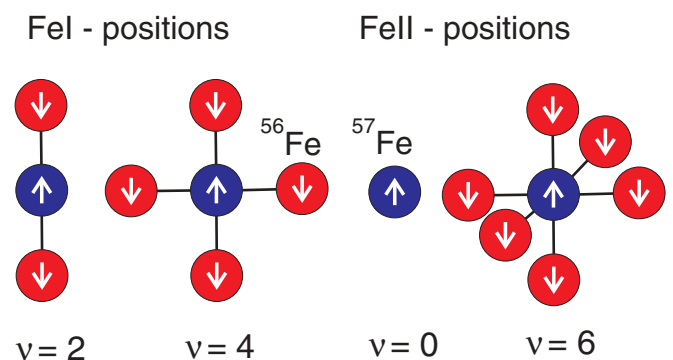


FIG. 4. (Color online) Classification of the  $^{57}\text{Fe}$  Mössbauer probe atom's positions in disordered double perovskites PFB (B = Nb, Ta) in our model. Only Fe ions are shown. See the text for the description of the notations.

PFB5, though having the lowest internal energy in PFN and PFT, has a smaller configurational weight compared to PFB4. In configurations PFB4, one Fe ion has  $\nu = 4$ , two have  $\nu = 2$ , and one has  $\nu = 0$ . If one considers a simple model, in which the quadrupole moment is composed from the charges of the Fe and nonmagnetic B ions occupying the ideal cubic positions then the cases of  $\nu = 2$  and  $\nu = 4$  can be joined in one group (to be denoted as the FeI position), because they have the same finite quadrupole moment, whereas the cases  $\nu = 0$  and  $\nu = 6$  organize another group (to be denoted as the FeII position) with zero quadrupole moment (the real quadrupole moment in these positions can be finite because of the inhomogeneous strain). In reality, the quadrupole moment may depend on some other parameters, and we simply assume that there are two groups of the Fe positions, FeI and FeII, one with a larger and the other with a smaller quadrupole moment. The same groups of Fe positions have different hyperfine magnetic splitting. Indeed, at low temperatures, the weight of the  $\nu = 0$  position in the FeII group was found in our calculations large compared to the  $\nu = 6$  position. At the same time, one can assume that the  $\nu = 0$  position, which does not have other Fe ions in the nearest environment, possesses a less hyperfine magnetic field than the field at the (more Fe-dense) FeI positions (in our first-principles calculations, we see this by the magnitude of the magnetic moment on the corresponding Fe positions). In configuration PFB4, there is a 3:1 proportion of the FeI and FeII positions. On the basis of the analysis of our experimental data one can conclude that the more populated sextet may correspond to the FeI positions having a larger quadrupole moment and hyperfine magnetic field compared to the less populated FeII positions (at low temperatures, mostly  $\nu = 0$ ). Thus, the FeII positions are responsible for sextet 2. This model, indeed, corresponds to our experimental data showing a larger apparent quadrupole shift and hyperfine magnetic field in the first sextet compared to the second one. The experimental ratio of the sextet's areas 2.3 is close to the model ratio 3. Another situation may occur at room temperature, where the weight of the  $\nu = 0$  position in the Mössbauer spectrum can be smaller than the weight of the  $\nu = 6$  configuration (because of the stronger thermally stimulated dynamics at the  $\nu = 0$  positions at high temperatures). Notice that in the simple point-charge model, the quadrupole moment of the  $\nu = 6$  configuration is much smaller than the quadrupole moment at the FeI positions (supposedly, mostly  $\nu = 4$  from the FeI group at high temperatures). This estimation corresponds to our experimental data showing that, at room temperature, the less populated doublet (hypothetically, the FeI position) has a larger quadrupole splitting than the more populated doublet (hypothetically,  $\nu = 6$  positions belonging to the FeII group).

In our opinion, percolation of the AFM interactions through the lattice is the most important clue for the formation of the mean-field Neel temperature. Without such a percolation, the Neel temperature should disappear, but a glass state can emerge instead. The coexistence of the mean-field (infinite) percolation cluster together with the finite-size percolation clusters is a well-known consequence of the theory of percolation.<sup>22</sup> Thus, the presence in the lattice of the FeI positions belonging to the infinite AFM percolation cluster, from the one hand, and of the separated Fe islands possessing

a finite total spin, from the other hand, well corresponds to the magnetic phase diagram of PFN involving two different magnetic phase transition temperatures. Kleemann *et al.*<sup>6</sup> related the coupling of the spins of the lone Fe positions surrounded by only nonmagnetic ions to the low-temperature glass phase transition. Our calculations confirm that such positions are rather probable in PFN, and, according to our classification, they belong to the FeII group. We relate the coupling of the spins in the FeII group to the spin-glass phase transition, while, we think that the FeI group is responsible for the formation of the AFM phase. It is worth noting that, in well-ordered PFS, there is only one group,  $\nu = 0$ , but this group is responsible for the weak AFM coupling of the I type, instead of the glass phase, because of the high degree of ordering. Thus, in the well-ordered double perovskites, one should expect only one low-temperature phase transition. Interestingly, such behavior was experimentally observed in highly ordered double perovskite  $\text{SrFe}_{1/2}\text{Sb}_{1/2}\text{O}_3$ , by means of neutron scattering.<sup>23</sup>

In order to compare our model with experiment quantitatively, one needs to calculate the hyperfine magnetic fields, quadrupole moments, apparent quadrupole shift, and quadrupole splitting in different chemical configurations. First-principles calculations of these quantities require further theoretical fundamental studies and implementations in the codes. We believe the way of the straight first-principles calculations, which was recently employed in Ref. 24 for the calculation of  $^{17}\text{O}$  NMR spectra, is most promising.

In conclusion, we managed to experimentally find two different crystallographic positions of Fe in PFN. On the basis of first-principles calculations, we have shown that the Fe ions in PFN and PFT experience clustering and, simultaneously, exist as lone impurities in the matrix of nonmagnetic ions. In the disordered environment, the lone Fe ions and other Fe clusters having total spin moment can organize a ferromagnetic phase, on field cooling, or the glass phase, on zero-field cooling, in line with the existing experiments.<sup>6,25</sup> The other Fe positions belonging to the infinite percolation AFM cluster are responsible for the formation of the Neel temperature. We speculate that these two groups of the  $^{57}\text{Fe}$  Mössbauer probe atom positions, one being responsible for the spin-glass phase and the other for the AFM phase, can be distinguished by Mössbauer spectroscopy because these positions possess different quadrupole moment and hyperfine magnetic field. In contrast to PFN and PFT, we found out that Fe in PFS does not have the intention to clustering, and rather organizes the rock-salt ordered structure having the AFM order of Fe of the I type. Thus, by controlling the clustering phenomena, one may control important magnetic and, very probably, magnetoelectric properties of double perovskites.

#### ACKNOWLEDGMENT

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- <sup>1</sup>A. Levstik, C. Filipic, and J. Holc, *J. Appl. Phys.* **103**, 066106 (2008).
- <sup>2</sup>V. A. Bokov, I. E. Mylnikova, and G. A. Smolenskii, *Sov. Phys. JETP* **15**, 447 (1962).
- <sup>3</sup>K. H. Ehses and H. Schmid, *Z. Kristallogr.* **162**, 64 (1983).
- <sup>4</sup>W. Bonny, M. Bonin, Ph. Sciau, K. J. Schenk, and G. Chapuis, *Solid State Commun.* **102**, 347 (1997).
- <sup>5</sup>S. P. Singh, S. M. Yusuf, S. Yoon, S. Baik, N. Shin, and D. Pandey, *Acta Mater.* **58**, 5381 (2010).
- <sup>6</sup>W. Kleemann, V. V. Shvartsman, P. Borisov, and A. Kania, *Phys. Rev. Lett.* **105**, 257202 (2010).
- <sup>7</sup>I. P. Raevski, S. P. Kubrin, S. I. Raevskaya, V. V. Titov, D. A. Sarychev, M. A. Malitskaya, I. N. Zakharchenko, and S. A. Prosandeev, *Phys. Rev. B* **80**, 024108 (2009).
- <sup>8</sup>I. P. Raevski, S. P. Kubrin, S. I. Raevskaya, V. V. Stashenko, D. A. Sarychev, M. A. Malitskaya, M. A. Seredkina, V. G. Smotrakov, I. N. Zakharchenko, and V. V. Eremkin, *Ferroelectrics* **373**, 121 (2008).
- <sup>9</sup>W. Peng, N. Lemee, M. Karkut, B. Dkhil, V. V. Shvartsman, P. Borisov, W. Kleemann, J. Holc, M. Kosec, and R. Blinc, *Appl. Phys. Lett.* **94**, 012509 (2009).
- <sup>10</sup>C. Meneghini, S. Ray, F. Liscio, F. Bardelli, S. Mobilio, and D. D. Sarma, *Phys. Rev. Lett.* **103**, 046403 (2009).
- <sup>11</sup>V. V. Laguta, J. Rosa, L. Jastrabik, R. Blinc, P. Cevc, B. Zalar, M. Remskar, S. I. Raevskaya, and I. P. Raevski, *Mater. Research Bull.* **45**, 1720 (2010).
- <sup>12</sup>H. Schmid, *Ferroelectrics* **162**, 317 (1994).
- <sup>13</sup>A. Falqui, N. Lampis, A. Geddo-Lehmann, and G. Pinna, *J. Phys. Chem. B* **109**, 22967 (2005).
- <sup>14</sup>G. M. Rotaru, B. Roessli, A. Amato, S. N. Gvasaliya, C. Mudry, S. G. Lushnikov, and T. A. Shaplygina, *Phys. Rev. B* **79**, 184430 (2009).
- <sup>15</sup>Y. Yang, J.-M. Liu, H. B. Huang, W. Q. Zou, P. Bao, and Z. G. Liu, *Phys. Rev. B* **70**, 132101 (2004).
- <sup>16</sup>C. N. W. Darlington, *J. Phys.: Condens. Matter* **3**, 4173 (1991).
- <sup>17</sup>F. N. A. Freire, H. H. B. Rocha, M. R. P. Santos, P. B. A. Fechine, F. M. M. Pereira, R. S. T. M. Sohn, I. F. Vasconcelos, and A. S. B. Sombra, *J. Mater. Sci.* **43**, 75 (2008).
- <sup>18</sup>I. P. Raevskii, D. A. Sarychev, S. A. Bryugeman, L. A. Reznichenko, L. A. Shilkina, O. N. Razumovskaya, V. S. Nikolaev, N. P. Vyshatko, and A. N. Salak, *Crystallogr. Rep.* **47**, 1012 (2002).
- <sup>19</sup>G. Kresse and J. Hafner, *Phys. Rev. B* **47**, 558 (1993); G. Kresse and J. Furthmuller, *ibid.* **54**, 11169 (1996).
- <sup>20</sup>G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999).
- <sup>21</sup>I. P. Raevskii, S. T. Kirillov, M. A. Malitskaya, V. P. Filippenko, S. M. Zaitsev, and L. G. Kolomin, *Inorg. Mater.* **24**, 217 (1988).
- <sup>22</sup>D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Taylor & Francis, London, 1994).
- <sup>23</sup>E. J. Cussen, J. F. Vente, P. D. Battle, and T. C. Gibb, *J. Mater. Chem.* **7**, 459 (1997).
- <sup>24</sup>D. L. Pechkis, E. J. Walter, and H. Krakauer, *J. Chem. Phys.* **135**, 114507 (2011).
- <sup>25</sup>R. Blinc, P. Cevc, A. Zorko, J. Holc, M. Kosec, Z. Trontelj, J. Pirnat, N. Dalal, V. Ramachandran, and J. Krzystek, *J. Appl. Phys.* **101**, 033901 (2007).