

**Influence of magnetic ordering on structural instabilities in insulating perovskites**

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We propose a general model, based on Anderson superexchange and the pseudo Jahn-Teller effect, to explain why ferroelectric and octahedral tilting distortions are favored by ferromagnetic ordering when compared to antiferromagnetic tilting distortions in  $ABX_3$  ( $A$  = alkali, alkaline-earth ion,  $f$ -filling rare earth;  $B$  = magnetic transition-metal ion;  $X = O^{2-}, F^-$ ) perovskite crystals. *Ab initio* calculations are used to check the model under a wide range of pressures for oxides and fluorides, with the latter displaying an enhancement of the ferroelectric distortion when pressure is increased.

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**I. INTRODUCTION**

Multiferroic materials and, in particular, ferroelectric ferromagnets (FFs) have attracted much attention in recent years due to their interesting fundamental properties and prospective applications in the fields of sensors and memory devices.<sup>1–5</sup> However, it has been very difficult to find examples of these kinds of materials because magnetism and ferroelectricity have almost interexcluding requirements.<sup>6</sup> In archetypical perovskites of  $ABX_3$  ( $X = O^{2-}, F^-$ ) type this search has been hampered as magnetism requires partially filled  $d$  shells on the  $B$  cation and ferroelectricity is favored when this ion has a  $d^0$  electronic configuration.<sup>6</sup> A solution suggested for this problem was to obtain magnetism through the  $d$  shell in the  $B$  anion while ferroelectricity was provided by the cation in the  $A$  position. The most studied multiferroic in recent years, BiFeO<sub>3</sub>, belongs to this family. However, one of the recurrent problems in the design of FFs has been the weak coupling between magnetism and polarization.<sup>5</sup> Using the so-called spin-lattice coupling, an alternative method for obtaining FFs that show stronger magnetoelectric coupling has been proposed recently<sup>7–9</sup> and experimentally realized for an epitaxially strained EuTiO<sub>3</sub> thin film.<sup>10</sup> The latter effect corresponds to a strong dependence of the vibrational frequencies of a material with its different magnetic states. Recently, an *ab initio* study exclusively focused on SrMnO<sub>3</sub> has obtained evidence that ferroelectric (FE) and octahedral tilting (OT) distortions are favored in the ferromagnetic (FM) states when compared to the antiferromagnetic (AF) state.<sup>7</sup> The stronger instability in the FM state leads to a crossover with the AF state when the distortions are favored by strong epitaxial strains inducing a polarized FM state. However, very little is known about the nature of the coupling, its limits and what the main parameters controlling it are. This work is aimed at clearing out these relevant issues as they are critical in order to propose more efficient materials. Along this line we present in Sec. II of this paper a model that shows that the spin-lattice coupling is a *general effect* that favors distortions in perpendicular to FM-coupled  $B$ - $X$  chains (Fig. 1) in magnetic insulators. This allows us to predict the most favorable distortions given the magnetic state of a system. An important note is that our model is not restricted to oxides but also works in other perovskites families, such as fluorides. As previously stressed by Eerenstein *et al.*,<sup>2</sup> while this family

of compounds is not so well studied as oxides, it may represent an alternative venue to search for FF. In Sec. III we provide the computational details relevant to the density functional theory (DFT) calculations carried out for a number of oxoperovskites and fluoroperovskites that support the validity of the model and whose results are described in Sec. IV. Finally, Sec. V contains a summary and some concluding remarks.

**II. THEORY**

In the model below we study the effect of small covalent bonding contributions to the force constant along FE and OT distortions that appear when symmetry is broken and which are very sensitive to the magnetic coupling along a  $B$ - $X$  chain. While factors such as cooperativity along FE chains, etc., are critical to understand the absolute value of the force constant, they are not responsive for the change with the magnetic state. As a first step we assume that  $A$  is a chemically inert ion as alkalis, alkali earth, or  $f$ -shell filling rare earths, so that active electrons (and holes) are localized in the  $X$  anions and  $B$  cations. This localization is a well-known characteristic of ionic insulators where the Wannier functions are centered on the ions<sup>11</sup> and allow using ideas traditionally employed in molecular bonding. This assumption is common in solid-state physics and is present in Anderson's superexchange model<sup>12</sup> and the Goodenough-Kanamori rules,<sup>13</sup> showing that the *main physics* of magnetic coupling in the insulating perovskites can be captured by considering a simple  $B$ - $X$ - $B$  molecular chain (Fig. 1). After carrying out *ab initio* calculations (see Sec. IV) we will find that the previous conditions are necessary for the FE to be stronger in the FM state than in the AF state.

In order to represent the electronic structure of a cubic perovskite we will use the three molecular orbitals depicted in Fig. 2. The first orbital is a bonding  $p_\sigma$  function localized around the ligand  $X$ ,  $\phi_{Xb}$ , that represents the fully occupied  $O(2p)$  band in oxides. The other two are the nonbonding  $\phi_{Bn}$  and the antibonding  $\phi_{Ba}$  orbitals, arising mainly from two  $t_{2g}$   $d$ -shell functions of the metal  $B$  and that correspond, respectively, with the lower and upper limits of the partially occupied valence band in the magnetic solid. We choose the  $d$  orbitals on the metal to be of  $t_{2g}$  type as they are the first to fill, and have been shown to participate in the OT instability<sup>14</sup> and

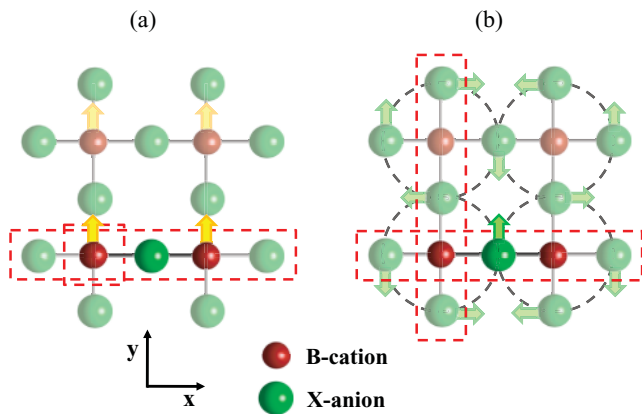


FIG. 1. (Color online) Illustration of the FE distortion along the  $y$  axis, denoted as  $FE_y$  (a) and the in-plane ( $xy$ ) OT distortion, denoted as  $OT_{xy}$  (b). The rectangles with slashed borders contain the  $B$ - $X$  chains that participate in the spin-lattice coupling in each distortion around the low-leftmost  $B$  cation. Note that in (a) one of the chains is perpendicular to the picture's plane. In both cases the  $B$ - $X$ - $B$  molecule described in the model is highlighted with respect to the  $BX_2$  plane where it is embedded.

the hybridization leading to FE distortions both in crystals<sup>15</sup> and FE-type off-center movements in isolated impurities.<sup>16-18</sup> If the ligand's orbital is full and we consider that the  $d$  orbitals of the metals are half-filled, we have a total of four electrons. Note that in order to simplify the discussion we do not take into account Jahn-Teller distortions and orbital ordering which are necessary to discuss non-half-filled electron configurations such as  $d^2$  or  $d^4$ . The Anderson superexchange model<sup>12</sup> uses these orbitals to predict that the ground state in cubic magnetic insulating perovskites is AF. Here, we will use the formulation of this model by Hay *et al.*<sup>19</sup> in terms of configuration interaction to describe the ground state of a three-ion  $B$ - $X$ - $B$  linear molecule. In this localized model FM states correspond with spin triplets ( $T$ ) while AF states are represented by spin singlets ( $S$ ). Given symmetry and spin constraints, the lowest AF and FM states can be written as

$$|\psi_S\rangle = \lambda_1 |\phi_{Xb}\uparrow, \phi_{Xb}\downarrow, \phi_{Bn}\uparrow, \phi_{Bn}\downarrow| + \lambda_2 |\phi_{Xb}\uparrow, \phi_{Xb}\downarrow, \phi_{Ba}\uparrow, \phi_{Ba}\downarrow|, \quad (1)$$

$$|\psi_T\rangle = |\phi_{Xb}\uparrow, \phi_{Xb}\downarrow, \phi_{Bn}\uparrow, \phi_{Ba}\uparrow|, \quad (2)$$

where two vertical lines denote a Slater determinant. It is important to note that in  $\Psi_S$ ,  $\lambda_1 > \lambda_2$  as the first term in Eq. (1) has a lower energy than the second one, and so  $\lambda_2 < 1/\sqrt{2}$ , due to normalization. In cubic geometry the strong  $\sigma$ -antibonding character of  $\phi_{Ba}$  increases the energy of the FM state and leads to an AF ground state.<sup>13,19</sup>

Let us now consider the representation of FE and OT distortions within the model. FE distortions can be described by the cooperative motion of all  $B$  cations in the same direction with respect to the  $A$  and  $X$  ions of the lattice, while the OT distortions correspond with the cooperative rigid rotation of the  $X$  anions inside a plane perpendicular to a Cartesian axis. Global and local (within the three-atom chain) illustrations of these distortions are shown in Fig. 1. It is important to note that from a local point of view both distortions just induce the

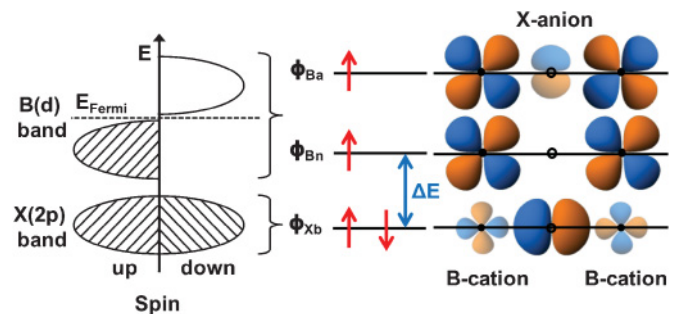


FIG. 2. (Color online) Typical band scheme for a FM  $ABX_3$  perovskite (left-hand side) and its correspondence with the orbital scheme used in the model (middle). These orbitals are illustrated on the right-hand side and are a  $\sigma$ -bonding orbital centered on the  $X$  anion ( $\phi_{Xb}$ ) and a nonbonding and an antibonding orbital centered on the  $B$  cation ( $\phi_{Bn}$  and  $\phi_{Ba}$ , respectively).  $\Delta E$  is an important excitation within the model.

relative displacement of some ion(s) in *perpendicular* to some  $X$ - $B$  chain and, as a consequence, have the same symmetry.

We will now use the pseudo Jahn-Teller (PJT) coupling theory<sup>15</sup> to determine the relative stability of the FM and AF phases. This theory for electron-vibration coupling quantitatively describes the change of covalent bonding (sometimes called hybridization in the solid-state community) under the action of a symmetry-breaking distortion and is equivalent to other approaches<sup>20,21</sup> as the calculation of the derivative of the covalent interaction integral. It has been used to explain both FE (Ref. 15) (in particular, the  $d^0$  rule) and OT (Ref. 14) distortions. As a salient feature, the PJT theory gives the *changes* on the force constant  $K$ , associated with a normal mode of a distortion ( $Q$ ) due to the electron-phonon coupling. Working in second-order perturbation,  $K$  is written as<sup>15</sup>

$$K = K_0 - \sum_i \frac{|F_{0i}|^2}{E_i - E_0}. \quad (3)$$

Here  $F_{0i} = \langle \psi_0 | dV/dQ | \psi_i \rangle$  is the electron-phonon coupling constant, whereas  $V$  denotes the electron-nuclear interaction operator, and  $\Psi_0$ ,  $\Psi_i$ ,  $E_0$ , and  $E_i$  are, respectively, the wave functions and energies of ground and excited states. The first term in Eq. (3),  $K_0 = \langle \psi_0 | d^2V/dQ^2 | \psi_0 \rangle$ , is positive and corresponds with the resistance that the system presents against being distorted due to keeping the bonding pattern typical of the cubic situation.<sup>15</sup> Since the total electron density is very similar for FM and AF states, we do not expect any significant difference on the  $K_0$  contribution for these states. The second term in (3) favors distortion and describes the adaptation of the electron density to the new geometry, including all new covalencies allowed due to symmetry breaking.

We will now show the main result of the paper, that, given the above conditions, covalent contributions in FM states induce stronger stabilization than in AF states, leading to softer frequencies. Upon following either the FE or OT distortions, perturbation theory allows the FM state [Eq. (2)] to mix with the following excited state:

$$|\psi_T^e\rangle = |\phi_{Xb}\uparrow, \phi_{Bn}\uparrow, \phi_{Bn}\downarrow, \phi_{Ba}\uparrow|. \quad (4)$$

When we include these covalent contributions, the triplet wave function can be approximately written as

$$|\psi_T(Q)\rangle \approx \frac{1}{\sqrt{N}} \left( \left| \psi_T + \frac{F}{\Delta} Q |\psi_T^e\rangle \right\rangle \right). \quad (5)$$

On the other hand, the first contribution to the AF state (involving  $\lambda_1$ ) *cannot* mix with any excited state after distortion due to symmetry restrictions, while the second term (involving  $\lambda_2$ ) can mix with the following one:

$$|\psi_S^e\rangle = 1/\sqrt{2}(|\phi_{Xb}\uparrow, \phi_{Bn}\downarrow, \phi_{Ba}\uparrow, \phi_{Ba}\downarrow| + |\phi_{Xb}\downarrow, \phi_{Bn}\uparrow, \phi_{Ba}\uparrow, \phi_{Ba}\downarrow|). \quad (6)$$

It is important to note that the new mixings both in the AF and FM states involve the *same* virtual excitation of an electron from the  $\phi_{Xb}$  orbital to the  $\phi_{Bn}$  orbital, and are associated to the *same* electron-phonon matrix element [see Eq. (3)] that we denote as  $f$ :

$$F_T = \langle \psi_T | \frac{dV}{dQ} | \psi_S^e \rangle = \langle \phi_{Xb} | \frac{dV}{dQ} | \phi_{Bn} \rangle = f, \quad (7)$$

$$F_S = \langle \psi_S | \frac{dV}{dQ} | \psi_S^e \rangle = \lambda_2 \sqrt{2} \langle \phi_{Xb} | \frac{dV}{dQ} | \phi_{Bn} \rangle = \lambda_2 \sqrt{2} f. \quad (8)$$

Moreover, the transition energy  $\Delta E = E_i - E_0$  between the ground state and the virtual excited state is exactly the same in both cases (Fig. 2). Using all these considerations we can obtain the force constants of the AF and FM states,

$$K_{\text{FM}} = K_0 - \frac{|f|^2}{\Delta E}, \quad (9)$$

$$K_{\text{AF}} = K_0 - 2|\lambda_2|^2 \frac{|f|^2}{\Delta E}. \quad (10)$$

As shown above,  $\lambda_2 < 1/\sqrt{2}$ , thus the force constant of the FM state for FE and OT distortions should always be *smaller* than the one corresponding to the AF state if the electrons are localized in the  $B$ - $X$  chains.

TABLE I. Calculated values of FE and OT frequencies (in  $\text{cm}^{-1}$ ) for different magnetic states (FM, AF-A, AF-C, AF-G) of  $\text{CaMnO}_3$ ,  $\text{SrMnO}_3$ ,  $\text{KVF}_3$ , and  $\text{KMnF}_3$  studied in the paper.  $R$  and  $M$  labels in OT distortions make reference to the point in the Brillouin zone where these modes are calculated. Values in parentheses were taken from (Ref. 7).

	CaMnO <sub>3</sub>				SrMnO <sub>3</sub>			
	FM	AF-A	AF-C	AF-G	FM	AF-A	AF-C	AF-G
FE <sub>z</sub>	63 <i>i</i>	66 <i>i</i>	260	261	163 <i>i</i> (109 <i>i</i> )	151 <i>i</i>	183	216(121)
FE <sub>x,y</sub>	63 <i>i</i>	56 <i>i</i>	77	264	163 <i>i</i> (109 <i>i</i> )	66 <i>i</i>	63	216(121)
OT <sub>xz,yz</sub> ( <i>R</i> )	260 <i>i</i>	241 <i>i</i>	240 <i>i</i>	204 <i>i</i>	187 <i>i</i> (199 <i>i</i> )	147 <i>i</i>	166 <i>i</i>	63 <i>i</i> (85 <i>i</i> )
OT <sub>xy</sub> ( <i>R</i> )	260 <i>i</i>	257 <i>i</i>	196 <i>i</i>	204 <i>i</i>	187 <i>i</i> (199 <i>i</i> )	192 <i>i</i>	48 <i>i</i>	63 <i>i</i> (85 <i>i</i> )
OT <sub>xy</sub> ( <i>M</i> )	270 <i>i</i>	255 <i>i</i>	192 <i>i</i>	200 <i>i</i>	182 <i>i</i> (90 <i>i</i> )	178 <i>i</i>	53	42(40 <i>i</i> )
	KVF <sub>3</sub>				KMnF <sub>3</sub>			
	FM	AF-A	AF-C	AF-G	FM	AF-A	AF-C	AF-G
FE <sub>z</sub>	212	209	230	230	206	204	211	215
FE <sub>x,y</sub>	212	221	220	230	206	209	209	215
OT <sub>xz,yz</sub> ( <i>R</i> )	70 <i>i</i>	53 <i>i</i>	36 <i>i</i>	37 <i>i</i>	65 <i>i</i>	66 <i>i</i>	56 <i>i</i>	57 <i>i</i>
OT <sub>xy</sub> ( <i>R</i> )	70 <i>i</i>	68 <i>i</i>	54 <i>i</i>	37 <i>i</i>	65 <i>i</i>	63 <i>i</i>	57 <i>i</i>	57 <i>i</i>
OT <sub>xy</sub> ( <i>M</i> )	64 <i>i</i>	62 <i>i</i>	22 <i>i</i>	23 <i>i</i>	38 <i>i</i>	63 <i>i</i>	52 <i>i</i>	54 <i>i</i>

### III. COMPUTATIONAL DETAILS

We have carried out *ab initio* calculations based on DFT to show the validity of the model and its implications. In order to perform these calculations we have used the CRYSTAL09 package that employs localized Gaussian basis sets to represent the Bloch orbitals.<sup>22</sup> All ions except for  $\text{Sr}^{2+}$  have been described by all-electron basis sets. Due to the problems arising on describing magnetic systems with local density approximation (LDA) or semilocal generalized gradient approximation (GGA) approaches, we have treated the exchange and correlation of the the electrons through a 1-parameter hybrid DFT functional that mixes exact exchange with WC exchange and PBE correlation (B1WC)<sup>23</sup> and allows to obtain the geometry, band gaps, and magnetic states in the perovskites with great accuracy and reliability, not requiring the input of any semiempirical parameter by the user.

### IV. RESULTS

To test the model we have performed frozen-phonon calculations for the cubic phase of a number of oxides and fluorides whose ions at the  $B$  position display different electron fillings of their  $d$  shell. In particular, we used  $\text{CaMnO}_3$ ,  $\text{SrMnO}_3$ , and  $\text{KVF}_3$  crystals where  $B$  ions have a  $d^3$  configuration, while in  $\text{KMnF}_3$  it has a  $d^5$  configuration. These calculations were carried out using a doubled ten-ion cell and a  $8 \times 8 \times 8$  sampling of reciprocal space at the FM equilibrium lattice parameter. In all the studied cases we have found that the frequency for FE and OT distortions is *lower* for the FM state than for the AF-G one (see Table I and Fig. 3 for an illustration of the modes). For example, in  $\text{SrMnO}_3$  and in agreement with Eqs. (6) and (7), we find that the FM state is more unstable with respect to FE and OT modes than the AF-G one as their frequencies are, respectively, 163*i* and 187*i*  $\text{cm}^{-1}$  for FM and 216 and 63*i*  $\text{cm}^{-1}$  for AF-G. These values are compatible with those obtained by Lee *et al.*<sup>7</sup> (Table I), taking into account that their use of GGA +  $U$  leads to some errors such as the overestimation of the lattice parameter ( $a_0 = 3.865 \text{ \AA}$ ) with respect to the

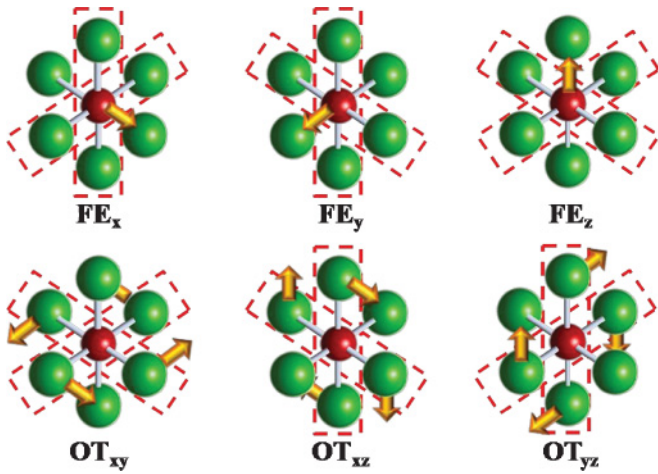


FIG. 3. (Color online) Graphical representation of the different FE and OT distortions considered in the paper for the  $BX_6$  octahedron contained in the cubic unit cell. The red dashed rectangles indicate the two  $B-X$  chains that may favor or hinder each distortion depending on the magnetic coupling existing along them.

experiment ( $a_0 = 3.80 \text{ \AA}$ ) while B1WC performs much better ( $a_0 = 3.799 \text{ \AA}$ ). Both DFT results show a large change in frequencies that can qualitatively change the behavior of the system with respect to certain distortion. It is important to note here that Ray and Waghmare<sup>9</sup> have found in  $YFeO_3$  lower frequencies for FE modes in the AFM states than for FM states. However, this system is outside the scope of the present model since the FE modes are mainly localized around the  $A$  cation ( $Y$ ), which has a chemically active  $d^0$  electronic configuration. Moreover, our calculations show that OT modes, which only involve  $O^{2-}$  ions, have frequencies which are more unstable in the FM state ( $349i$  and  $91i \text{ cm}^{-1}$ ) than in the AFM state ( $331i$  and  $87 \text{ cm}^{-1}$ ), in agreement with the model and the fact that tilting is associated with the  $t_{2g}$  shell of the  $B$  ion.<sup>14</sup>

The model also works in fluorides such as  $KVF_3$ , but the difference between FM and AFM frequencies is smaller than in the oxides (Fig. 4). This fact can be related to the larger lattice parameter and smaller covalency exhibited by fluorides as both factors reduce the value of the vibronic constant  $f$ . Moreover, we calculated the value of these frequencies when the pressure over the system is varied between  $-10$  and  $30 \text{ GPa}$ , finding that the conclusions of the model remain valid over a large range of lattice parameters for all systems (see Fig. 4). While in oxides higher pressures increase the FE frequency, leading, eventually, to the destruction of the instability, in fluorides the opposite behavior is observed and the FE distortion may be triggered by pressure (Fig. 4). This difference in behavior may be exploited to obtain fluoride FFs under pressure.

A most important part of the model is that the distortions are favored or hindered in perpendicular to the  $B-X-B$  direction, depending on the magnetic coupling existing along the ion chain. It is well known that in bulk perovskites there are many kinds of globally AFM crystals that present internally some FM interactions. For example, the AF-C and AF-A patterns are FM (AF) along the  $z$  axis ( $xy$  plane) and the  $xy$  plane ( $z$  axis), respectively. These electronic states break the symmetry and allow in-plane and out-of-plane distortions to have different frequencies, as predicted by the model. This, in turn, may lead to the design of patterned distortions in the crystal by controlling the electronic state. To illustrate the concept, let us consider the AF-A case, where the FM coupling is localized in  $xy$  planes (see Fig. 3). According to the model, the distortions are favored in directions which are perpendicular to each FM chain. As the main contribution to a FE distortion comes from the off centering of the  $B$  ions that sit in the crossing of two  $B-X$  chains [Fig. 1(a)], the most favored FE distortion in the AF-A state is along the  $z$  axis perpendicular to the FM planes ( $FE_z$  according to Fig. 3). On the other hand, in-plane FE distortions ( $FE_x, FE_y$ ) are favored only by a single FM chain (Fig. 3), so the frequency for this mode is expected to be smaller than the axial one. To check these predictions we

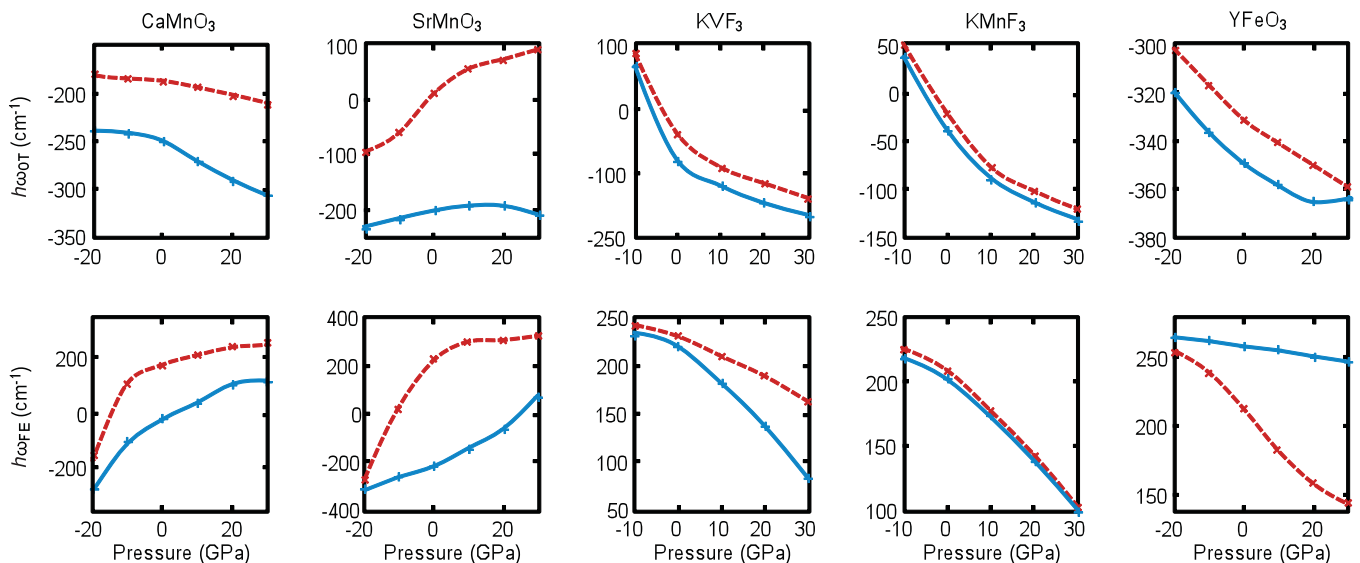


FIG. 4. (Color online) Variation of the OT (top) and FE (bottom) frequencies for the FM (solid blue lines) and AFM (dashed red lines) states in  $CaMnO_3$ ,  $SrMnO_3$ ,  $KVF_3$ ,  $KMnF_3$ , and  $YFeO_3$ . A negative value of the frequency indicates instability ( $K < 0$ ).

have performed *ab initio* calculations on a 20-ion  $\sqrt{2} \times \sqrt{2} \times 2$  supercell with a  $8 \times 8 \times 6$   $k$ -point mesh. As shown in Table I, the prediction above is fully supported by *ab initio* calculations. Turning to OT distortions, we find that they only involve the  $X$  anions which are placed inside a single  $B$ - $X$  chain. Since an OT involves the cooperative rotation of anions located on different chains [Fig. 1(b)], we find that the most favored OT in the AF-A state is the rotation of the anions contained inside the plane. As can be seen in Table I, the frequency of  $R$ - and  $M$ -type in-plane rotations ( $OT_{xy}$ ) are clearly lower than those involving ligands along the  $z$  axis ( $OT_{xz}$ ,  $OT_{yz}$ ). We can reason similarly for the AF-C phase, where we find that the in-plane  $FE_x$ ,  $FE_y$  modes and the  $OT_{xz}$ ,  $OT_{yz}$  modes that involve anions sitting in the  $z$  axis are favored with respect to the axial  $FE_z$  mode and in-plane  $OT_{xy}$  rotations. Thus, full numerical results show the correctness of the model for a large variety of systems and conditions.

## V. CONCLUSIONS

In summary, in this work we have (a) shown that, depending on how FM- and AF-coupled  $B$ - $X$  chains are distributed inside a perovskite, we should expect different distortions, and (b) give the rules that allow predicting the particular distortions to be expected. These rules, combined with electron doping, strain and/or hydrostatic pressures can be used to induce particular patterns in the distortions of a crystal. Another interesting consequence of the model is that magnetic domain walls may not just separate two different magnetic phases, but will have a particular nuclear distortion pattern associated with the geometry of the wall and the nature of the separated phases. This distortion pattern will contribute to fix the domain wall and reduce its mobility. We would finally like to point out how these rules stress the importance of dimensionality to design multiferroic materials. In a cubic perovskite, the superexchange interaction favors AF states with respect to the

FM states for each possible  $B$ - $X$  chain that can be placed along any of the three directions of space. Thus, in the cubic crystal, the magnetic phases can be ordered in terms of increasing energy as  $AF-G < AF-C < AF-A < FM$ . On the other hand, FE distortions are favored along the direction perpendicular to a FM chain, and the maximum instability is obtained perpendicular to a FM plane. Thus, the optimal way to obtain a distortion that will bring a FM-FE state below the AF-paraelectric state is to have a bidimensional structure such as layered compounds and oxide heterostructures but that can never be realized in a typical  $ABX_3$  cubic perovskite either in bulk or thin film. An example of this kind of system is a  $SrMnO_3/SrTiO_3$  heterostructure where the magnetic layers of material are isolated from each other by one or more layers of  $SrTiO_3$ , which is diamagnetic. Thus, as magnetism occurs in a plane, the difference in energy between the FM and AF phase for the paraelectric phase in the heterostructure has to be reduced to that of the bulk crystal. On the other hand, as distortions are favored in the direction perpendicular to the plane, the stabilization due to the distortion should be similar to that found in the bulk. Preliminary DFT calculations in the  $SrMnO_3/SrTiO_3$  interface clearly show that in the FM phase the  $SrMnO_3$  layer is polarized in perpendicular to the magnetic plane while the AF phase is not. Moreover, our DFT calculations show that the differences between oxides and fluorides can make the latter family an interesting prospect to find viable FFs at high pressures as, unlike with most oxides, in fluorides an increase in pressure favors FE distortions.

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