Unraveling the Suppression of Oxygen Octahedra Rotations in $A_3B_2O_7$ Ruddlesden-Popper Compounds: Engineering Multiferroicity and Beyond

Yajun Zhang,[1,2] Jie Wang,[2,*] and Philippe Ghosez[1,†]

[1]*Theoretical Materials Physics, Q-MAT, CESAM, Université de Liège, B-4000 Liège, Belgium*

[2]*Department of Engineering Mechanics and Key Laboratory of Soft Machines and Smart Devices of Zhejiang Province, Zhejiang University, 38 Zheda Road, Hangzhou 310027, China*

The competition between polar distortions and BO_6 octahedra rotations is well known to be critical in explaining the ground state of various ABO_3 perovskites. Here, we show from first-principles calculations that a similar competition between interlayer rumpling and rotations is playing a key role in layered Ruddlesden-Popper (RP) perovskites. This competition explains the suppression of oxygen octahedra rotations and hybrid improper ferroelectricity in $A_3B_2O_7$ compounds with rare-earth ions in the rocksalt layer and also appears relevant to other phenomena like negative thermal expansion and the dimensionality determined band gap in RP systems. Moreover, we highlight that RP perovskites offer more flexibility than ABO_3 perovskites in controlling such a competition and four distinct strategies are proposed to tune it. These strategies are shown to be promising for designing new multiferroics. They are generic and might also be exploited for tuning negative thermal expansion and band gap.

The competition between lattice polar distortions and BO_6 octahedra rotations is a usual and central issue in the physics of ABO_3 perovskites. As highlighted in the seminal work of Zhong and Vanderbilt [1] and further discussed by Sai and Vanderbilt [2], this competition plays a key role in understanding the phase diagram of $SrTiO_3$. It was also shown to lower significantly the ferroelectric phase transition temperature of $PbTiO_3$ [3]. This competition is not universal and it was found that, in the regime of large rotation amplitudes, these distortions can eventually cooperate and favor each other [4,5]. Competition remains, however, the most generic behavior and contributes to explain the scarcity of ABO_3 ferroelectric compounds [6]. Relying on this competition, tuning the balance between polar and rotation motions by external stimuli has been shown to provide versatile opportunities for realizing new functionalities [7–12].

$A_3B_2O_7$ Ruddlesden-Popper (RP) compounds form a family of layered perovskites in which $A_2B_2O_6$ double-perovskite blocks alternate with rocksalt AO layers. They can nowadays be grown with good atomic control [13,14] and recently have attracted a growing interest for accessing functional properties inaccessible in the parent ABO_3 perovskites [15–20]. Intriguingly, experiments focusing on different compounds seem to suggest a common feature: the rotations of BO_6 octahedra appearing in ABO_3 perovskites are often partly or completely suppressed in related RP structures [19–23]. Moreover, decreasing the tolerance factor, which typically enhances the rotations in ABO_3 perovskites, seems inefficient to recover the full rotation

patterns in RP systems like $SrR_2Fe_2O_7$ (R = rare-earth ion) [20].

Further clarifying the behavior of rotations in RP systems is not only of academic interest but reveals also essential information for material design. On the one hand, suppression of the typical rotation patterns (i.e., $a^-a^-c^+$ in Glazer's notations) [24] required for producing hybrid improper ferroelectricity (HIF) [15,25] limits in practice the realization of multiferroic RP compounds [20–22]. On the other hand, the suppression of rotations in $Ba_{n+1}Zr_nS_{3n+1}$ with $n = 1$ and 2 directly decreases the band gap to about 1.3 eV [23]. Also, negative thermal expansion (NTE) in $Ca_3Mn_2O_7$ is demonstrated to happen only in the RP phase with suppressed rotations, while it does not appear in its ABO_3 phase [19].

Despite their key role, very limited information is presently available regarding the behavior of rotations in RP systems. Do they eventually compete with other distortions? Is it eventually possible to promote or suppress them as required to achieve some desired properties?

In order to address these questions, we report here a systematic first-principles study of RP perovskites. Taking recently synthesized $SrTb_2Fe_2O_7$ with the $a^-b^0c^0/b^0a^-c^0$ rotation motions as a prototypical example, we highlight a competition between rotations and rumpling at the rocksalt-perovskite interfaces, which significantly suppresses the rotations, as polarization does in $PbTiO_3$. Based on this knowledge, we propose simple and independent strategies to control such a competition in order to recover the $a^-a^-c^+$ rotation patterns for realizing HIF. These strategies
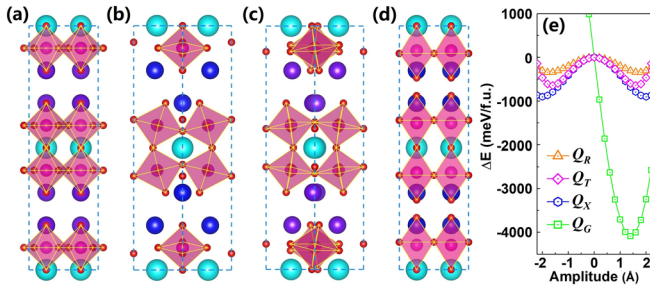
FIG. 1. Schematic view of (a) $a^0a^0c^+$ rotations, (b) $a^-b^0c^0/b^0a^-c^0$ tilts, (c) $a^-a^-c^0$ tilts, and (d) rumpling, (e) PESs with respect to the amplitude of four distortions.

not only provide platforms to realize room-temperature multiferroics but also suggest effective ways to tune the strength of NTE and the band gap in RP systems.

First-principles calculations were performed within the projector augmented-wave (PAW) method implemented in the VASP package [26,27]. Technical details are provided in the Supplemental Material [28].

First, we look for the ground state (GS) structure of $SrTb_2Fe_2O_7$ with rare-earth ions in the rocksalt layers. Starting from the distortion-free $I4/mmm$ reference phase, various possible structures are explored by condensing individually or jointly (i) $a^0a^0c^+$ rotations (X_2^+), (ii) $a^0a^0c^-$ rotations (X_1^-), (iii) $a^-b^0c^0/b^0a^-c^0$ tilts (X_3^-), (iv) $a^-a^-c^0$ tilts (X_3^-), (v) in-plane polar motions (Γ_5^-), and (vi) in-plane antipolar motions (M_5^+). The schematic view of $a^0a^0c^+$ rotations, $a^-b^0c^0/b^0a^-c^0$ tilts, and $a^-a^-c^0$ tilts are shown in Figs. 1(a)–1(c). The scheme of $a^0a^0c^-$ rotations, in-plane polar motions, and in-plane antipolar motions can be found in Ref. [18]. All the structures are fully relaxed with ferromagnetic (FM), as well as A-type, C-type, and G-type antiferromagnetic (AFM) orders. Consistent with experiments, the G-type AFM $P4_2/mnm$ phase is found to be the GS [20], being 87 meV/f.u. lower than the ferroelectric $A2_1am$ phase. In this GS, the original $a^-a^-c^+$ rotation patterns of $TbFeO_3$ are changed to $a^-b^0c^0/b^0a^-c^0$ when forming RP $SrTb_2Fe_2O_7$. Interestingly, as allowed by symmetry, atomic rumpling (Γ_1^+) naturally appears at the rocksalt-perovskite interfaces, as shown in Fig. 1(d). This atomic rumpling consists in opposite motions of cations (R and Fe) and oxygens at each interface, yielding an interface dipole. Hereafter, a positive value of rumpling will refer to the distortions with dipoles pointing from the rocksalt layer to the perovskite layer, as naturally appearing during the relaxation.

It is well known that HIF arises in RP systems from the trilinear coupling of the polarization with $a^0a^0c^+$ rotations and $a^-a^-c^0$ tilts [15–17,19]. So, the disappearance of rotations in the $P4_2/mnm$ phase prevents the emergence of ferroelectricity. To uncover why rotations are suppressed, we perform a systematic analysis of the potential energy surface (PES).
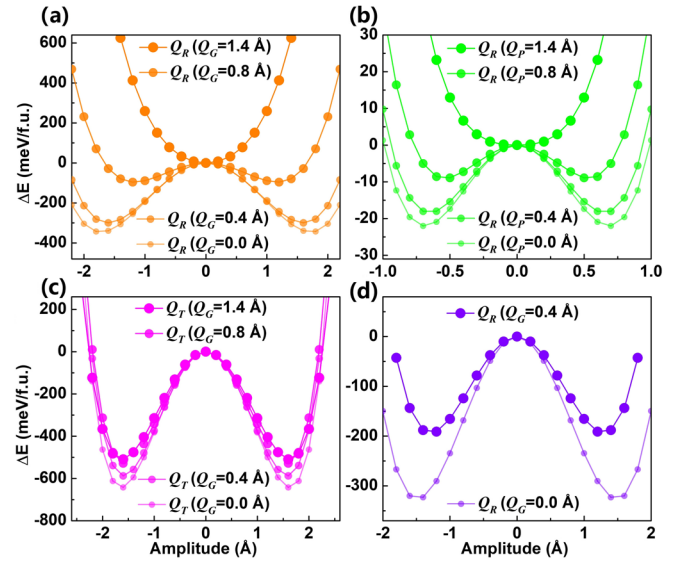

FIG. 2. PESs in terms of given mode amplitudes for distinct compounds: (a) $a^0a^0c^+$ rotations Q_R in $SrTb_2Fe_2O_7$ at fixed rumpling amplitude Q_G, (b) $a^0a^0c^-$ rotations Q_R in $PbTiO_3$ at fixed polarization amplitude Q_P, (c) $a^-a^-c^0$ tilts Q_T in $SrTb_2Fe_2O_7$ at fixed rumpling amplitude Q_G and (d) $a^0a^0c^+$ rotations Q_R in $Ca_3Mn_2O_7$ with and without fixed rumpling amplitude Q_G as in the GS.

In order to be able to treat the rumpling of Γ_1^+ symmetry as an additional explicit degree of freedom, we define a new reference $I4/mmm^\star$ phase in which rumpling in each plane has been artificially removed from the $I4/mmm$ phase by putting cations and oxygens in the same average plane. Then, the stability of rumpling, $a^-b^0c^0/b^0a^-c^0$ tilts, $a^-a^-c^0$ tilts and $a^0a^0c^+$ rotations are examined by condensing them in this $I4/mmm^\star$ reference. As expected, from Fig. 1(e), the energy evolution related to rumpling (Q_G) and $a^-b^0c^0/b^0a^-c^0$ tilts (Q_X) which appear in the GS exhibit respectively shifted single-well and double-well shapes. In particular, the rumpling causes a much stronger lowering of energy. To our surprise, the PESs associated with $a^-a^-c^0$ tilts (Q_T) and $a^0a^0c^+$ rotations (Q_R) also exhibit double-well characteristic, so questioning the microscopic mechanism of their disappearance in the GS.

The answer is provided in Fig. 2(a), reporting the PESs of $a^0a^0c^+$ rotations at fixed amplitudes of rumpling: the negative curvature at the origin is progressively renormalized and becomes positive at $Q_G = 1.4$ Å. This evolution is strikingly similar to that of ferroelectric $PbTiO_3$ shown in Fig. 2(b), with the only difference that rumpling has been replaced by polar distortions. In other words, although rotations are dynamically unstable in the $I4/mmm^\star$ phase, their unstable character is suppressed by a competition with rumpling, reminiscent of the competition with polar distortions in ABO_3 perovskites. Nevertheless, although the energy coupling of rotation motions with polar distortions is biquadratic at lowest order ($\delta_{RP}Q_R^2Q_P^2$) in ABO_3

perovskites [1], the one with rumpling (Γ_1^+) also includes a term linear in Q_G in RP compounds. So, the energy of $a^0a^0c^+$ rotations including specific interactions with rumpling can be expressed as follows:

$$E_R \propto \alpha_R Q_R^2 + \beta_R Q_R^4 + \lambda_{RG} Q_R^2 Q_G + \delta_{RG} Q_R^2 Q_G^2, \quad (1)$$

where the first two terms are associated with the intrinsic double-well of rotations ($\alpha_R < 0$ and $\beta_R > 0$) while the last two terms relate to their lowest couplings with rumpling. The sign of Q_G is fixed here to a positive value since the rumpling relaxation is intrinsic to the layer interface. Amazingly, λ_{RG} appears to be slightly negative while δ_{RG} is large and positive. This highlights that the competition between rotations and rumpling originates from the positive biquadratic coupling term and confirms the similarity with mode competition in ABO_3 perovskites. As highlighted in Fig. 2(c), this biquadratic competition is much smaller for $a^-a^-c^0$ tilts and even lower for $a^-b^0c^0/b^0a^-c^0$ tilts (see Figs. S2–S3 and Table S1 of the Supplemental Material [28]). Combined with the hierarchy of the wells in Fig. 1(e), this naturally explains the GS of $SrTb_2Fe_2O_7$ [20].

In line with the seminal idea of Pauling [45], the instability of rotation and tilt motions in perovskites with a small tolerance factor relates to their ability to decrease the energy by optimizing A cations and oxygens coordination. Here, interface rumpling (similar to polar motions in ABO_3 perovskites) also affects cation-oxygen distances. Our bond valence calculations [28] show that when rumpling naturally appears at the interface due to symmetry breaking, it already contributes to improve significantly atomic coordination and so suppresses rotations that would induce overcoordination if they were preserved (see Fig. S4 of the Supplemental Material [28]). The stronger competition of rumpling with rotations rather than with tilts relates to the way rotations and rumpling similarly tune some of the Tb-O distances (see Fig. S5 of Ref. [28]).

The competition between $a^0a^0c^+$ rotations and rumpling is quite general and can be extended to other RP systems like the widely investigated $Ca_3Mn_2O_7$. As depicted in Fig. 2(d), although the double-well PES of rotations is preserved, the energy lowering and amplitude of distortions with the lowest energy are notably reduced upon the condensation of rumpling with GS amplitude.

Comparing $SrTb_2Fe_2O_7$ and $Ca_3Mn_2O_7$, it is natural to question why rotations are completely suppressed in $SrTb_2Fe_2O_7$ while partly preserved in $Ca_3Mn_2O_7$. More strikingly, it seems that rotations and HIF disappear in most RP perovskites made of $Pnma$ $R^{3+}B^{3+}O_3$ compounds [20–22], while they survive in RP perovskites made of $Pnma$ $A^{2+}B^{4+}O_3$ compounds (A = alkaline-earth ion) [15,19,46].
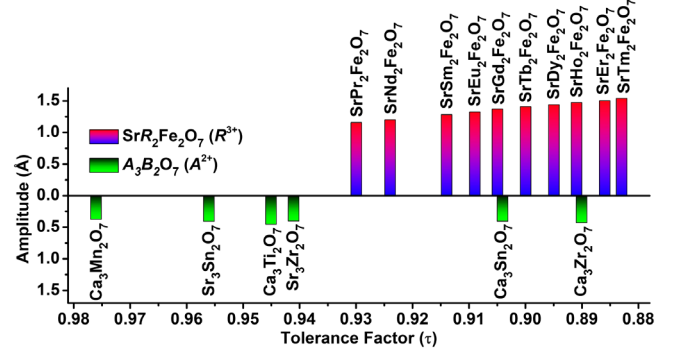

FIG. 3. Comparison of rumpling amplitudes in the GS phase of a series of RP perovskites ($P4_2/mnm$ phase and $A2_1am$ phase, respectively, for compounds with R^{3+} and A^{2+} ions in the rocksalt layer).

We unveil now that these distinct behaviors arise from different amplitudes of rumpling. Figure 3 compares the rumpling amplitude in a series of RP perovskites with R^{3+} and A^{2+} ions in the rocksalt layer. It is clear that the rumpling amplitude of $SrR_2Fe_2O_7$ compounds is much larger than that of $A_3B_2O_7$. This can be rationalized by the fact that positively charged RO^{1+} layers attract negatively charged oxygen while such an effect is ruled out in charge neutral AO^{0+} layers. For system with larger rumpling like $SrTb_2Fe_2O_7$, the energy cost of $a^0a^0c^+$ rotations due to the competition with rumpling overwhelms its energy lowering, leading to an overall suppression of rotations.

Now that the reason underlying the disappearance of $a^0a^0c^+$ rotations is well understood, another important issue is how to recover $a^-a^-c^+$ rotations and related HIF. Based on the above knowledge, the key to stabilize $a^0a^0c^+$ rotations is tuning its competition with rumpling. Obviously, from Eq. (1), the appearance of $a^0a^0c^+$ rotations requires $\alpha_R + \lambda_{RG}Q_G + \delta_{RG}Q_G^2 < 0$. Therefore, one possible strategy is increasing the amplitude of negative α_R, which can be achieved *a priori* from an appropriate tuning of the tolerance factor. An alternative strategy is to decrease the amplitude of rumpling in order to decrease positive $\delta_{RG}Q_G^2$. Combining these ideas with the recent progress in preparing high-quality RP structures, several practical strategies for engineering $a^0a^0c^+$ rotations are now proposed and their efficiencies in tuning the rotations are systematically inspected.

As a first strategy, we explore how to properly tune the tolerance factor. Pitcher *et al.* [20] tried to induce $a^-a^-c^+$ rotations in $SrR_2Fe_2O_7$ by decreasing the A-site cation radius in the *rocksalt* layer. The ineffectiveness of this method can be understood from the above results: the rumpling amplitude of $SrR_2Fe_2O_7$ in Fig. 3 notably increases as the tolerance factor decreases. So, although this method makes α_R more negative [see Fig. S3(b) of the Supplemental Material [28]] and favors $a^0a^0c^+$ rotations, the effect is overcompensated by the increase of rumpling
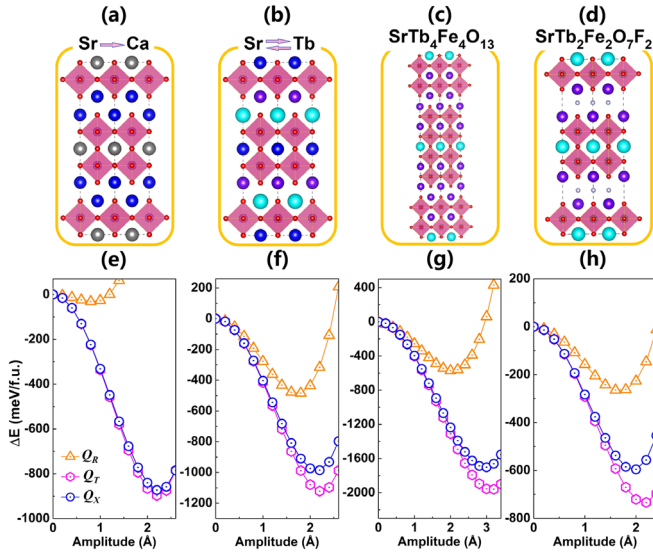
FIG. 4. (a)–(d) Several practical strategies to engineering rotations. PESs with respect to the amplitude of $a^0a^0c^+$ rotations, $a^-a^-c^0$ tilts, and $a^-b^0c^0/b^0a^-c^0$ tilts with fixed rumpling for (e) $CaTb_2Fe_2O_7$, (f) $SrTb_2Fe_2O_7$ by exchanging Tb^{3+} at the rocksalt layer with Sr^{2+} at the perovskite layer, (g) $SrTb_4Fe_4O_{13}$, and (h) $SrTb_2Fe_2O_7F_2$.

amplitude. Consequently, $\alpha_R + \lambda_{RG}Q_G + \delta_{RG}Q_G^2$ remains positive and $a^0a^0c^+$ rotations cannot be stabilized. In addition, the negative curvature of $a^-b^0c^0/b^0a^-c^0$ tilts exceeds that of $a^-a^-c^0$ for all the $SrR_2Fe_2O_7$ as shown in Fig. S3(b) of the Supplemental Material [28]. Therefore, the proper way to recover $a^-a^-c^+$ rotations is substituting either a smaller cation at the A site or a larger cation at the B site in the *perovskite* layer. In such cases, only α_R is notably modified. To check this approach, Sr is replaced by smaller Ca in $SrTb_2Fe_2O_7$ as shown in Fig. 4(a). With a fully structural relaxation starting from possible phases, the most stable phase is the ferroelectric $A2_1am$ phase. We plot in Fig. 4(e) the PESs of Q_R, Q_T, and Q_X with fixed rumpling. Comparing to the PESs of $SrTb_2Fe_2O_7$, our expectation is confirmed that the double wells of Q_R and Q_T are preserved in presence of rumpling and Q_T yields larger energy lowering than Q_X. This demonstrates that introduction of a smaller A-site cation in the perovskite layer rather than rocksalt layer is effective in stabilizing rotations and tilts. Although $CaTb_2Fe_2O_7$ itself is difficult to synthesize due to phase separation, Pitcher *et al.* show that making $(Ca_ySr_{1-y})_{1.15}Tb_{1.85}Fe_2O_7$ and $Ca_3Ti_2O_7$ solid solutions is an alternative way to recover the desired $a^-a^-c^+$ rotation patterns and room-temperature multiferroicity [20]. Doping with a larger B-site cation has similar effect: it decreases the tolerance factor and enhances the instability of rotations [47,48], and should only slightly affect the rumpling.

Based on the knowledge that charge neutral AO rocksalt layers induce smaller rumpling, it can be expected that exchanging the position of Tb^{3+} and Sr^{2+} can be a second strategy to decrease rumpling and recover rotations, in a way similar to what was done in $La_2SrCr_2O_7$ [49]. Rather than considering all possible configurations, we simply explore here the consequences of exchanging TbO layers and SrO layers as shown in Fig. 4(b). Comparing all the possible phases, we find that the ferroelectric Aa phase is the lowest energy structure and the rumpling amplitude is significantly reduced. The PESs in Fig. 4(f) further support that $a^0a^0c^+$ rotations and $a^-a^-c^0$ tilts are unstable and a larger energy lowering is obtained from $a^-a^-c^0$ tilts than $a^-b^0c^0/b^0a^-c^0$ tilts.

Since rumpling mainly originates from the rocksalt layer, a third strategy might be to increase the thickness n of the perovskite layer in order to reduce the rocksalt-perovskite layer ratio and weaken the effect of rumpling [50]. With the dramatic advances in experimental techniques, RP perovskites with n up to 4 and even 5 have been successfully synthesized [51,52]. For $n = 3$, the opposite in-plane displacements of the A-site atom cancel each other and the structure is paraelectric. Here we present the results for $n = 4$ to validate our expectations. The corresponding structure is displayed in Fig. 4(c). After structural relaxation of possible phases, the ferroelectric $A2_1am$ phase is found to be the GS. The coexistence of $a^0a^0c^+$ rotations and $a^-a^-c^0$ tilts is also verified by the PESs shown in Fig. 4(g). In addition to the interesting multiferroic nature, sizable increase of tilts is also obtained, which opens up a new perspective for enhancing magnetoelectric (ME) coefficient since the amplitude of the ME coupling increases with the amplitude of the tilts [20].

Finally, a fourth strategy to recover the rotations is topochemical fluorination. Recently, Zhang *et al.* found that topochemical fluorination is a promising paradigm for enhancing the rotations and tilts [21,53]. Despite the paraelectric $A2/a$ phase with the $a^-a^-c^-$ rotations and the $Pnam$ phase with $a^-a^-c^+$ rotations are the GSs, it provides the possibility of enhancing rotations. The fluorinated $SrTb_2Fe_2O_7$ with fluorine inserted into the rocksalt layer is schematically shown in Fig. 4(d). We found that the ferroelectric $A2_1am$ phase with E-type AFM order has the lowest energy indicating the feasibility of fluorination controlled ferroelectricity. Besides the enhanced rotations, the rumpling is significantly reduced and even becomes negative, which facilitates the appearance of $a^0a^0c^+$ rotations and $a^-a^-c^0$ tilts as shown in Fig. 4(h).

After highlighting the ferroelectric GS obtained from different strategies, we now focus on the amplitude of the in-plane ferroelectric polarization. The calculated values are 7.2, 10.3, and 26.5 $\mu C/cm^2$ for $SrTb_2Fe_2O_7$ with the SrO layer at the rocksalt layer, $SrTb_4Fe_4O_{13}$ and $SrTb_2Fe_2O_7F_2$, respectively. These values are comparable with $Ca_3Mn_2O_7$ and $Ca_3Ti_2O_7$ [15,16]. Among the three cases, Fe is Fe^{3+} in $SrTb_2Fe_2O_7$ and $SrTb_4Fe_4O_{13}$, while it is changed to Fe^{4+} in $SrTb_2Fe_2O_7F_2$. Perovskites with Fe^{3+}

usually exhibit Néel temperature (T_N) of more than 600 K [41,54]. By tuning tolerance factor through substitution of smaller Ca^{2+} and $Ca_3Ti_2O_7$, Pitcher *et al.* have realized the room-temperature multiferroicity in $SrTb_2Fe_2O_7$ [20]. To determine the T_N of cation ordered $SrTb_2Fe_2O_7$ and $SrTb_4Fe_4O_{13}$, spin dynamic calculations have been performed, which show T_N of 380 and 650 K, respectively. The results indicate that beyond tuning the tolerance factor, engineering of cation order and the rocksalt-perovskite layer ratio are promising alternative strategies for designing room-temperature multiferroics.

Perovskites with Fe^{4+} only have T_N ranging from 111–134 K (Ba, Sr, $CaFeO_3$) [55–57], suggesting that $SrTb_2Fe_2O_7F_2$ is not suitable for room-temperature multiferroic application. Nevertheless, it shows strong electron instability and orbital ordering. The related Jahn-Teller distortions may survive above room temperature, like in $RMnO_3$ [58]. Recent works have revealed the strong coupling between Jahn-Teller distortions and rotations [59–62]. Similar to the ME coupling in RP systems, notable coupling between polarization and Jahn-Teller distortions can be expected since they are controlled by the same lattice distortions, which makes $SrTb_2Fe_2O_7F_2$ an attractive candidate to realize electric field tuning of electronic property at room temperature [61].

Finally, we argue that the competition between rumpling and rotations is a rather generic feature of RP systems, which can be extended to halide and chalcogenide perovskites (see Fig. S6 of the Supplemental Material [28]), and may also be relevant to other classes of layered perovskites like Aurivillius or Dion-Jacobson. In addition, such competition may be essential for understanding recent experimental observations. First, it naturally explains the $Pnma(a^-a^-c^+) \rightarrow P4_2/mnm(a^-b^0c^0/b^0a^-c^0) \rightarrow I4/mmm(a^0a^0c^0)$ transitions of $Ba_{n+1}Zr_nS_{3n+1}$ as n decreases [23]. Additionally, the suppression of $a^0a^0c^+$ rotations increases the bandwidth of d_{xy} orbitals and is responsible for the decreased band gap with $n = 1$ and 2 [23]. The competition mechanism may also help rationalizing the uniaxial NTE observed in $Ca_{n+1}Mn_nO_{3n+1}$ and $Ca_{n+1}Ge_nO_{3n+1}$ [19,63,64]: (i) NTE happens in the RP phase with $a^0a^0c^-$ rotations, while it does not appear in $I4/mcm$ $CaMnO_3$ with the same rotation motions. This can be partly ascribed to the competition between rumpling and rotations in the RP phase, which hardens the rotation distortions and decreases the energy barrier of the trapping mechanism [19]. (ii) the NTE increases as n decreases and reaches the maximum at $n = 1$ [63], which may be rationalized from the increased competition between rumpling and rotations since the role of rumpling is enhanced as n decreases.

In conclusion, the origin of the suppression of in-phase rotations in RP $SrTb_2Fe_2O_7$ is explained from their strong competition with atomic rumpling at the rocksalt-perovskite interface. Practical strategies have been proposed to tune the mode competition and stabilize simultaneously in-phase rotations and out-of-phase tilts for realizing appealing room-temperature multiferroics. The design rules stated here are not limited to ferrites, but are also relevant to a large variety of magnetic perovskites with *Pnma* symmetry, guiding the realization of multiferroism in different RP systems. More generally, this competition mechanism may also be relevant to explain phenomena like NTE and band gap evolution, and the proposed strategies are promising for further tuning of such properties.

---

[*] jw@zju.edu.cn
[†] Philippe.Ghosez@uliege.be

[1] W. Zhong and D. Vanderbilt, Phys. Rev. Lett. **74**, 2587 (1995).
[2] N. Sai and D. Vanderbilt, Phys. Rev. B **62**, 13942 (2000).
[3] J. C. Wojdeł, P. Hermet, M. P. Ljungberg, P. Ghosez, and J. Iniguez, J. Phys. Condens. Matter **25**, 305401 (2013).
[4] U. Aschauer and N. A. Spaldin, J. Phys. Condens. Matter **26**, 122203 (2014).
[5] T. Gu, T. Scarbrough, Y. Yang, J. Íñiguez, L. Bellaiche, and H. J. Xiang, Phys. Rev. Lett. **120**, 197602 (2018).
[6] N. A. Benedek and C. J. Fennie, J. Phys. Chem. C **117**, 13339 (2013).
[7] J. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. Li, S. Choudhury, W. Tian, M. Hawley, B. Craigo *et al.*, Nature (London) **430**, 758 (2004).
[8] H. Jang, A. Kumar, S. Denev, M. D. Biegalski, P. Maksymovych, C. Bark, C. T. Nelson, C. Folkman, S. H. Baek, N. Balke *et al.*, Phys. Rev. Lett. **104**, 197601 (2010).
[9] C.-J. Eklund, C. J. Fennie, and K. M. Rabe, Phys. Rev. B **79**, 220101(R) (2009).
[10] S. Bhattacharjee, E. Bousquet, and P. Ghosez, Phys. Rev. Lett. **102**, 117602 (2009).
[11] J. Gazquez, M. Stengel, R. Mishra, M. Scigaj, M. Varela, M. A. Roldan, J. Fontcuberta, F. Sánchez, and G. Herranz, Phys. Rev. Lett. **119**, 106102 (2017).
[12] T. Kim, D. Puggioni, Y. Yuan, L. Xie, H. Zhou, N. Campbell, P. Ryan, Y. Choi, J.-W. Kim, J. Patzner *et al.*, Nature (London) **533**, 68 (2016).
[13] J. Lee, G. Luo, I.-C. Tung, S. Chang, Z. Luo, M. Malshe, M. Gadre, A. Bhattacharya, S. Nakhmanson, J. Eastman *et al.*, Nat. Mater. **13**, 879 (2014).

[14] Y. Nie, Y. Zhu, C.-H. Lee, L. F. Kourkoutis, J. A. Mundy, J. Junquera, P. Ghosez, D. Baek, S. Sung, X. Xi *et al.*, Nat. Commun. **5,** 4530 (2014).

[15] N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. **106,** 107204 (2011).

[16] Y. S. Oh, X. Luo, F.-T. Huang, Y. Wang, and S.-W. Cheong, Nat. Mater. **14,** 407 (2015).

[17] A. T. Mulder, N. A. Benedek, J. M. Rondinelli, and C. J. Fennie, Adv. Funct. Mater. **23,** 4810 (2013).

[18] X.-Z. Lu and J. M. Rondinelli, Nat. Mater. **15,** 951 (2016).

[19] M. S. Senn, A. Bombardi, C. A. Murray, C. Vecchini, A. Scherillo, X. Luo, and S.-W. Cheong, Phys. Rev. Lett. **114,** 035701 (2015).

[20] M. J. Pitcher, P. Mandal, M. S. Dyer, J. Alaria, P. Borisov, H. Niu, J. B. Claridge, and M. J. Rosseinsky, Science **347,** 420 (2015).

[21] R. Zhang, M. S. Senn, and M. A. Hayward, Chem. Mater. **28,** 8399 (2016).

[22] R. Zhang, A. S. Gibbs, W. Zhang, P. S. Halasyamani, and M. A. Hayward, Inorg. Chem. **56,** 9988 (2017).

[23] W. Li, S. Niu, B. Zhao, R. Haiges, Z. Zhang, J. Ravichandran, and A. Janotti, Phys. Rev. Mater. **3,** 101601 (2019).

[24] A. Glazer, Acta Crystallogr. Sect. B **28,** 3384 (1972).

[25] N. A. Benedek, J. M. Rondinelli, H. Djani, P. Ghosez, and P. Lightfoot, Dalton Trans. **44,** 10543 (2015).

[26] G. Kresse and J. Hafner, Phys. Rev. B **47,** 558 (1993).

[27] P. E. Blöchl, Phys. Rev. B **50,** 17953 (1994).

[28] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevLett.125.157601, which includes Refs. [29–44], for the (i) computational details, (ii) ground state properties of $R\text{FeO}_3$, (iii) strength of the competition of rumpling and rotations and tilts, (iv) cristallochemical origin of competition between rumpling and rotations and tilts, and (v) the competition between rumpling and rotations in $\text{Ba}_3\text{Zr}_2\text{S}_7$ and $\text{Cs}_3\text{Sn}_2\text{I}_7$.

[29] J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, Phys. Rev. Lett. **100,** 136406 (2008).

[30] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, and A. P. Sutton, Phys. Rev. B **57,** 1505 (1998).

[31] V. I. Anisimov, F. Aryasetiawan, and A. Lichtenstein, J. Phys. Condens. Matter **9,** 767 (1997).

[32] H. J. Monkhorst and J. D. Pack, Phys. Rev. B **13,** 5188 (1976).

[33] R. D. King-Smith and D. Vanderbilt, Phys. Rev. B **47,** 1651 (1993).

[34] H. T. Stokes, D. M. Hatch, B. J. Campbell, and D. E. Tanner, J. Appl. Crystallogr. **39,** 607 (2006).

[35] R. F. Evans, W. J. Fan, P. Chureemart, T. A. Ostler, M. O. Ellis, and R. W. Chantrell, J. Phys. Condens. Matter **26,** 103202 (2014).

[36] A. A. Mostofi, J. R. Yates, G. Pizzi, Y.-S. Lee, I. Souza, D. Vanderbilt, and N. Marzari, Comput. Phys. Commun. **185,** 2309 (2014).

[37] X. He, N. Helbig, M. J. Verstraete, and E. Bousquet, arXiv:2009.01910.

[38] M. K. Warshi, V. Mishra, A. Sagdeo, V. Mishra, R. Kumar, and P. Sagdeo, Ceram. Int. **44,** 8344 (2018).

[39] S. Geller, J. Chem. Phys. **24,** 1236 (1956).

[40] M. Marezio, J. Remeika, and P. Dernier, Acta Crystallogr. Sect. B **26,** 2008 (1970).

[41] M. Eibschütz, S. Shtrikman, and D. Treves, Phys. Rev. **156,** 562 (1967).

[42] I. D. Brown, Chem. Soc. Rev. **7,** 359 (1978).

[43] I. D. Brown and D. Altermatt, Acta Crystallogr. Sect. B **41,** 244 (1985).

[44] N. Brese and M. O'keeffe, Acta Crystallogr. Sect. B **47,** 192 (1991).

[45] L. Pauling, J. Am. Chem. Soc. **51,** 1010 (1929).

[46] S. Yoshida, K. Fujita, H. Akamatsu, O. Hernandez, A. S. Gupta, F. G. Brown, H. Padmanabhan, A. S. Gibbs, T. Kuge, R. Tsuji *et al.*, Adv. Funct. Mater. **28,** 1801856 (2018).

[47] X. Liu, B. Chen, J. Lu, Z. Hu, and X. Chen, Appl. Phys. Lett. **113,** 242904 (2018).

[48] X. Liu, J. Wu, X. Shi, H. Zhao, H. Zhou, R. Qiu, W. Zhang, and X. Chen, Appl. Phys. Lett. **106,** 202903 (2015).

[49] R. Zhang, B. M. Abbett, G. Read, F. Lang, T. Lancaster, T. T. Tran, P. S. Halasyamani, S. J. Blundell, N. A. Benedek, and M. A. Hayward, Inorg. Chem. **55,** 8951 (2016).

[50] T. Birol, N. A. Benedek, and C. J. Fennie, Phys. Rev. Lett. **107,** 257602 (2011).

[51] J. Haeni, C. Theis, D. Schlom, W. Tian, X. Pan, H. Chang, I. Takeuchi, and X.-D. Xiang, Appl. Phys. Lett. **78,** 3292 (2001).

[52] W. Tian, J. Haeni, D. G. Schlom, E. Hutchinson, B. Sheu, M. Rosario, P. Schiffer, Y. Liu, M. A. Zurbuchen, and X. Pan, Appl. Phys. Lett. **90,** 022507 (2007).

[53] R. Zhang, G. Read, F. Lang, T. Lancaster, S. J. Blundell, and M. A. Hayward, Inorg. Chem. **55,** 3169 (2016).

[54] I. Sosnowska, M. Loewenhaupt, W. David, and R. Ibberson, Physica (Amsterdam) **180B,** 117 (1992).

[55] N. Hayashi, T. Yamamoto, H. Kageyama, M. Nishi, Y. Watanabe, T. Kawakami, Y. Matsushita, A. Fujimori, and M. Takano, Angew. Chem. Int. Ed. **50,** 12547 (2011).

[56] T. Takeda, Y. Yamaguchi, and H. Watanabe, J. Phys. Soc. Jpn. **33,** 967 (1972).

[57] S. Kawasaki, M. Takano, R. Kanno, T. Takeda, and A. Fujimori, J. Phys. Soc. Jpn. **67,** 1529 (1998).

[58] J. Alonso, M. Martinez-Lope, M. Casais, and M. Fernandez-Diaz, Inorg. Chem. **39,** 917 (2000).

[59] J. H. Lee, K. T. Delaney, E. Bousquet, N. A. Spaldin, and K. M. Rabe, Phys. Rev. B **88,** 174426 (2013).

[60] Y. Zhang, M. M. Schmitt, A. Mercy, J. Wang, and P. Ghosez, Phys. Rev. B **98,** 081108(R) (2018).

[61] J. Varignon, N. C. Bristowe, and P. Ghosez, Phys. Rev. Lett. **116,** 057602 (2016).

[62] L. Chen, C. Xu, H. Tian, H. Xiang, J. Íñiguez, Y. Yang, and L. Bellaiche, Phys. Rev. Lett. **122,** 247701 (2019).

[63] C. Ablitt, A. A. Mostofi, N. C. Bristowe, and M. S. Senn, Front. Chem. **6,** 455 (2018).

[64] M. S. Senn, C. A. Murray, X. Luo, L. Wang, F.-T. Huang, S.-W. Cheong, A. Bombardi, C. Ablitt, A. A. Mostofi, and N. C. Bristowe, J. Am. Chem. Soc. **138,** 5479 (2016).