The collinear $\uparrow\uparrow\downarrow\downarrow$ magnetism driven ferroelectricity in double-perovskite multiferroics

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Abstract. The multiferroics of collinear $\uparrow\uparrow\downarrow\downarrow$ magnetism driven ferroelectricity is one type of the magnetically driven ferroelectrics, which attracts much attentions due to their strong magnetolectric coupling. Here, we summarize the recent progress in this multiferroics with double-perovskite crystal structure, besides $\text{Y}_2\text{CoMnO}_6$, $\text{Lu}_2\text{CoMnO}_6$, $\text{Y}_2\text{NiMnO}_6$ and $\text{In}_2\text{NiMnO}_6$ etc.. It is revealed that there are also many uncertainties in present research, making this field fulling of challenges and opportunities.

1. Introduction

Multiferroics, in which ferromagnetic and ferroelectric orders coexist and couple with each other, have attracted much attention due to their interacting fundamental physics and potential applications to memory and magnetic storage devices[1, 2]. Multiferroic materials are divided into two types by Khomskii in 2009[3]. Type-I multiferroics exhibit good ferromagnetism and ferroelectricity but weak magnetoelectric (ME) coupling, because the ferromagnetism and ferroelectricity have different sources and appear largely independently of one another. For the Type-II multiferroics, the polarization is usually much smaller and the transition temperature is relatively lower than type-I, but it exibits strong ME coupling since the ferroelectricity is induced by magnetic order, which is important for the electric control of magnetism or vice versa[4]. There are two magnetic configurations as the source of ferroelectricity. One is a noncollinear or a spiral magnetic order, which is usually found in frustrated systems. The other is a collinear magnetic structure, typically an up-up-down-down ($\uparrow\uparrow\downarrow\downarrow$) magnetic structure, which causes an exchange striction and thus breaks inversion symmetry to get a polarization.

The $\uparrow\uparrow\downarrow\downarrow$ magnetic structure can be divided into two classes according to the orientation of $\uparrow\uparrow\downarrow\downarrow$ spin order. One is called E-type antiferromagnetic (AFM) state that the $\uparrow\uparrow\downarrow\downarrow$ spin alignment along the in-plane [110] direction, as shown in Fig.1(a). This E-type AFM state has taken place in the orthorhombic RMnO$_3$ perovskites where R is a small rare earth, such as $\text{HoMnO}_3$ and $\text{YMnO}_3$[5]. The exchange striction effect here leads to the alternation of the long and short Mn-Mn bonds in the $ab$ plane and meanwhile causes the oxygen ions to shift perpendicular to the Mn-Mn bonds, thus producing a polarization along the shift direction[6]. The other $\uparrow\uparrow\downarrow\downarrow$ magnetic structure has been firstly found in Ca$_3$CoMnO$_6$[7, 8], where the $\uparrow\uparrow\downarrow\downarrow$ spin order is along the Co-Mn chains ($c$-axis), calling as E*-type AFM
Figure 1. Schematic representation of spin configuration (a) E-type antiferromagnetic state of $R_2NiMnO_6$, squares and circles denote the $Ni^{2+}$ and $Mn^{4+}$ ions, respectively; (b) $E^*$-type antiferromagnetic state of $R_2CoMnO_6$, squares and circles denote the $Co^{2+}$ and $Mn^{4+}$ ions, respectively. The up and down spins are represented by the white and black filling. (c) The monoclinic structure of $R_2CoMnO_6$ or $R_2NiMnO_6$. 

state (Fig. 1(b)). The exchange striction in $Ca_3CoMnO_6$ arises from the stronger exchange interaction between adjacent metal ions with identical spin (next-nearest-neighbor (NNN) Co-Co and Mn-Mn) than that between adjacent metal ions with opposite spins (nearest-neighbor (NN) Co-Mn)[9]. Recently, this $\uparrow\downarrow\downarrow\downarrow$-type multiferroics have been extended to double perovskites $R_2CoMnO_6[10, 11, 12, 13, 14]$ and $R_2NiMnO_6[15, 28]$, where the $R_2CoMnO_6$ belongs to $E^*$-type ($\uparrow\downarrow\downarrow\downarrow$ along Co-Mn chains) while $R_2NiMnO_6$ belongs to E-type ($\uparrow\uparrow\downarrow\downarrow$ in Ni-Mn plans).

For these double perovskite multiferroics, the ferroelectricity is also mainly from the magnetically induced exchange striction effect. However, the origin of magnetic order and the polarize direction are still under debate. Then, we will summarize recent progress in this multiferroics.

2. $R_2CoMnO_6$

The structure of $R_2CoMnO_6$ is monoclinic lattice (P2$_1$/n). As shown in Fig. 1(c), the MnO$_6$ and CoO$_6$ octahedral are corner-sharing and alternate along all a, b, and c directions in double-perovskite. This structural characteristic is obviously different from that of $Ca_3CoMnO_6$, in which the MnO$_6$ and CoO$_6$ octahedral are face-sharing along c direction and CoMnO$_6$ chains are isolated by Ca ions. Thus, the NNN Co-Co or Mn-Mn distances in $R_2CoMnO_6$ are much larger (e.g. 7.41Å in $Lu_2CoMnO_6$ and 7.46Å in $Y_2CoMnO_6$) than those of $Ca_3CoMnO_6$ (5.29 Å). Hence, the exchange interactions of NNN Co-Co/Mn-Mn are greatly weakened and not comparable to those of the NN Co-Mn. Although the $R_2CoMnO_6$ belongs to $E^*$-type multiferroics, the origin of ME properties should be different from that of $Ca_3CoMnO_6$.

Not mentioned the ME origin, the existence of $E^*$-type AFM order and ferroelectricity in reported $R_2CoMnO_6$ is still controversial. As we know, R is a small rare earth in RMnO$_3$ with $\uparrow\downarrow\downarrow\downarrow$-type magnetic structure. The reported $\uparrow\uparrow\downarrow\downarrow$-type multiferroics of $R_2CoMnO_6$ also have a small rare earth R, such as $Lu_2CoMnO_6[10, 11]$, $Yb_2CoMnO_6[12]$, $Y_2CoMnO_6[13]$ and $Sm_2CoMnO_6[14]$. The $E^*$-type magnetic order and multiferroic behavior of $Y_2CoMnO_6$ and $Sm_2CoMnO_6$ are still controversial. Only the $Lu_2CoMnO_6$ and $Yb_2CoMnO_6$ are clarified to be a $\uparrow\uparrow\downarrow\downarrow$ magnetically induced ferroelectricity by neutron diffraction[11, 12]. We will take the most reported $Y_2CoMnO_6$ and $Lu_2CoMnO_6$ as examples to demonstrate the progress in this series.

For $Y_2CoMnO_6$, the $E^*$-type magnetism driven ferroelectricity has been firstly reported by
Sharma et al.[13]. And they claim that $Y_2CoMnO_6$ undergoes the ME transition at relatively higher temperature 80 K. However, such ground state contradicts the reports before, in which the magnetic ground state of $Y_2CoMnO_6$ is ferromagnetic (FM) ordering[17, 18, 19]. This controversy attracts much attention from theory and experiment. The recent experimental study of $Y_2CoMnO_6$ nearly confirms the FM ground state[20, 21], although E*-type magnetism is obtained from the first-principles calculations[22, 23]. The results from the first-principles calculations observe that besides the E*-type AFM ground state, the metastable FM state is only a little higher in energy. Moreover, the ground state depends on the Hubbard $U$ values, for which the FM state could be the ground state at $U > 1.8$ eV while E*-type magnetism is the ground state at $U < 1.8$ eV[22]. In addition to the uncertainty on the ground state, the direction of electric polarization based on the presumed ME state is also controversial. Some suggest that the polarization is along $c$-axis (Fig. 2(a)), where the ferroelectricity is from the exchange-striction induced non-centrosymmetric structural distortions of inequivalent Co-Mn bonds along $c$-axis[13, 23]. Others think that the electric polarization aligns along the $b$-axis (Fig. 2(b)), where the ferroelectricity is generated by the net displacements of O ions along the $b$-axis[22]. Consequently, there are many uncertainties in the research of $Y_2CoMnO_6$, especially the existence of ME preterites should be clarified first.

![Figure 2](image1.png)

**Figure 2.** [22]The exchange striction induced displacements of (a) Co and Mn ions along $c$-axis and (b) O ions along $b$-axis, where open circles represent the corresponding ionic positions after the displacement.

![Figure 3](image2.png)

**Figure 3.** (a) The definition of exchange parameters in the ↑↓↑↓ magnetic order. (b)[23] Schematic crystal field level diagrams of the high-spin Co$^{2+}$ and Mn$^{4+}$. The $e_g$ electrons hopping leads to a FM coupling while the $t_{2g}$ electrons hopping to a AFM coupling.

Unlike $Y_2CoMnO_6$, the ME behavior of $Lu_2CoMnO_6$ has reached consensus. The ME coupling in $Lu_2CoMnO_6$ has been reported by Yáñez-Vilar et al.[10] firstly, they report that $Lu_2CoMnO_6$ shows an E*-type magnetic order below 43 K, and ferroelectricity below 35 K that is strongly coupled to a net magnetism. However, their experiments are based on polycrystals, resulting in a question about whether ME behavior is intrinsic or is an extrinsic feature of polycrystal. Until recently, Chikara et al. have reported their results of electric polarization and magnetization measurements in $Lu_2CoMnO_6$ single crystals, which establish that the ME behavior of $Lu_2CoMnO_6$ is an intrinsic effect but not due to grain boundaries or other extrinsic effects of polycrystals[11]. Although the ME behavior of $Lu_2CoMnO_6$ is thus clarified, the direction of electric polarization is still controversial, as mentioned in $Y_2CoMnO_6$. The early experimental[10] results show that the polarization is along $c$-axis (Fig. 2(a)), parallel to the Co-Mn chains, while the newly experiment[11] reports that the electric polarization aligns along the $b$-axis (Fig. 2(b)), perpendicular to the magnetic field. Whether the electric polarization
Table 1. The reported exchange parameters $J$ (meV) of $\text{Y}_2\text{CoMnO}_6$ and $\text{Lu}_2\text{CoMnO}_6$.

|       | $J_1$  | $J_2$ | $J_3$ | $J_4$ | $J_5$ | $J_6$ |
|-------|--------|-------|-------|-------|-------|-------|
| $\text{Y}_2\text{CoMnO}_6$ | 0.99   | -4.5  | 0.14  | 0.22  |       |       |
| $\text{Y}_2\text{CoMnO}_6$ | 0.678  | -5.113| 0.398 | -0.878| -0.629| 0.576 |
| $\text{Lu}_2\text{CoMnO}_6$ | -2.8   | -7.8  | 0.1   |       |       | 0.1   |

along $c$ or $b$ axis will determine the ferroelectricity origin. The electric polarization along $c$ is from the consideration of domain boundaries between $\uparrow\uparrow\downarrow\downarrow$ FM domains, producing an electric polarization within each domain boundary by exchange-striction induced inversion symmetry breaking (Fig. 2(a)). And the electric polarization along $b$ is due to the $\text{O}$ ions on the two neighboring chains shifting coherently along the $b$-axis (Fig. 2(b)) under the exchange striction. Based on the reported results from experiment and theory, it is more reasonable that the electric polarization of $\text{R}_2\text{CoMnO}_6$ should be along the $b$-axis.

As we mentioned above, both ferroelectricities are related to an exchange striction, which is certainly from the special $\uparrow\uparrow\downarrow\downarrow$ order. Therefore, the origin of such $\uparrow\uparrow\downarrow\downarrow$ order is the deep source of the ME property of $\text{R}_2\text{CoMnO}_6$. According to the $\uparrow\uparrow\downarrow\downarrow$ origin of $\text{Ca}_3\text{CoMnO}_6$ that the NNN $\text{Co-Co/Mn-Mn}$ exchange interactions larger than the NN $\text{Co-Mn}$ plays an important role, the exchange interactions of $\text{R}_2\text{CoMnO}_6$ are widely investigated by theory. As shown in Table. I, the exchange interactions of NN $\text{Co-Mn}$ intra-chain $J_1$, NN $\text{Co-Mn}$ inter-chain $J_2$, NN $\text{Co-Co/Mn-Mn}$ inter-chain $J_3/J_4$ and NNN $\text{Co-Co/Mn-Mn}$ intra-chain $J_5/J_6$ (Fig. 3(a)) are calculated from the first-principles[23, 22, 24]. These values reflect that the NN $\text{Co-Mn}$ inter-chain is a relatively strong FM interaction ($J_2 < 0$), which is significantly stronger than other interactions. Especially, the NN $\text{Co-Mn}$ intra-chain interaction $J_1$ is a weak AFM exchange for $\text{Y}_2\text{CoMnO}_6$ and a weak FM exchange for $\text{Lu}_2\text{CoMnO}_6$, corresponding to the closest total-energy of FM and $\uparrow\uparrow\downarrow\downarrow$ order. Such weak interactions could be disturbed by some other factors, thus resulting in the special $\uparrow\uparrow\downarrow\downarrow$ order.

Then, the large magnetic exchange anisotropy and possible origin of $\uparrow\uparrow\downarrow\downarrow$ order are discussed by analyzing the orbital occupations. From all the reported electronic structure of $\text{R}_2\text{CoMnO}_6$[23, 22, 24], the valences for $\text{Co}$ and $\text{Mn}$ ions are $4+$ and $2+$, respectively, and both are in high-spin state. The schematic energy level and possible interactions are illustrated in Fig. 3(b). The NN $\text{Co-Mn}$ interactions are dominated by the FM superexchange (SE) via a hopping of $\text{Co}^{2+}$ $e_g$ electrons to the empty $\text{Mn}^{4+}$ $e_g$ states or half-occupied $t_{2g}$ states. However, a AFM direct-exchange (DE) between the partially occupied $\text{Co}^{2+}$ $t_{2g}$ states and the half occupied $\text{Mn}^{4+}$ $t_{2g}$ states would weaken the FM exchange interaction. As we know, the SE is more influenced by the $\text{Co-O-Mn}$ angle, while the DE is by the $\text{Co-Mn}$ distance. Here, the $\text{Co-O-Mn}$ angles along $J_1$ and $J_2$ are similar, but the $\text{Co-Mn}$ distance along $J_1$ is more or less smaller than that along $J_2$. Therefore, the AFM DE is weaker than FM SE of the NN $\text{Co-Mn}$ interchain ($J_2$), where a robust FM interaction is formed. When the larger AFM DE is comparable with FM SE of the NN $\text{Co-Mn}$ intrachain ($J_1$), the competition between the FM SE and AFM DE results in a weak AFM or FM interactions along $\text{Co-Mn}$ chains. Based on the discussions above, our group have proposed that the $\uparrow\uparrow\downarrow\downarrow$ ground state originates from the strong competition between the FM SE and AFM DE along $J_1$, like a frustration. As the temperature gets lower, the system chooses a crystal distortion or a $\text{Co-Mn}$ dimerization to release the competition (frustration), because a definite AFM DE is dominant between the shortened $\text{Co-Mn}$ sites while a FM interaction should be the case between the elongated $\text{Co-Mn}$ sites[23]. Besides, Zhang et. al. have suggested that the $\text{Co-Mn}$ antisite defects observed from experiment could introduce an extra $\text{Co-Co/Mn-Mn}$ interactions.
AFM exchange, which may disturb the competition and result in the $\uparrow\downarrow\downarrow\downarrow$ ground state[24].

3. $R_2NiMnO_6$

The structure of $R_2NiMnO_6$ is also monoclinic lattice, which is nearly the same with $R_2CoMnO_6$ (Fig. 1(c)). However, the magnetic ground state of $R_2NiMnO_6$ is an E-type configuration, which has been firstly predicted in $Y_2NiMnO_6$ from the first-principles design by Kumar et al.[15]. The E-type magnetic structure consists of $\uparrow\downarrow\downarrow\downarrow$ spin chains in $ab$ plane (Fig. 1(a)), with an out-of-plane FM coupling. Such E-type magnetism breaks inversion symmetry and generates a ferroelectric polarization. Meanwhile, the origin of the special E-type magnetic state is proposed by the competition between the AFM NNN Ni-Ni and FM NN Ni-Mn interactions. The frustration is released by increasing (decreasing) the distance between $\uparrow\downarrow\downarrow\downarrow$ spin chains and the E-type magnetic state is thus formed. This ME origin seems more reliable than that mentioned in $R_2CoMnO_6$, since the intraplane NNN Ni-Ni distance is much smaller than the interplane NNN Co-Co/Mn-Mn distance in $R_2CoMnO_6$. Thus, the NNN Ni-Ni interaction here could be comparable with the NN Ni-Mn interaction, which results in frustration and further E-type magnetism.

Nevertheless, such prediction has not been confirmed on consensus by experiment. The nanocrystal $Y_2NiMnO_6$ synthesized by sol-gel method exhibits a ferroelectric transition at 573 K, far above the Curie temperature of 92 K[25]. These results are not consistent with the theoretical prediction: for one hand, the $\uparrow\downarrow\downarrow\downarrow$ magnetic order is not certain from experiment; for the other hand, the ferroelectricity is not driven by magnetostriction, where the ferroelectric transition temperature is far above the magnetic ordering temperature. Another experimental group has reported an appearance of ferroelectric polarization coinciding with the magnetic phase transition at about 67 K and has further proposed that the ferroelectricity originates from the Ni$^{2+}$/Mn$^{4+}$ charge ordering and the $\uparrow\downarrow\downarrow\downarrow$ spin ordering[26]. Such results indicate that the ferroelectricity is driven by E-type magnetism and is thus consistent with the theoretical prediction. However, a recent experiment has showed that $Y_2NiMnO_6$ displays a canted FM order at 81 K, not an E-type magnetism, and hence the ferroelectricity is absent[27]. Therefore, the magnetic ground state and related ME phenomenon of $Y_2NiMnO_6$ need more investigations to clarify.

Based on the consensus that the magnetic ground state should change from FM for $La_2NiMnO_6$ to AFM for $Y_2NiMnO_6$ due to a decrease of the R ionic size, most efforts are made to explore the double perovskites with small R ions. In$_2NiMnO_6$ with small In$^{3+}$ ions (0.92Å) is thus prepared as a candidate for ME multiferroics[28, 29]. Yi et al. have reported that In$_2NiMnO_6$ is an AFM with a Neel temperature of 26 K from experiment, and have further indicated that the AFM order is E-type magnetic order by the first-principles calculations[28]. However, a noncollinear magnetic order has been obtained by Terada et al., which results in a ferroelectric polarization of $30\mu C/m^2[29]$. Accordingly, the magnetic ground state of In$_2NiMnO_6$ is also controversial.

4. Conclusions

All in all, the $\uparrow\downarrow\downarrow\downarrow$ magnetism driven ferroelectricity is at the beginning. The exploration of new material is just on the way. More and more experiments are working to improve the quality of sample and the accuracy of numerical measure. Different theoretical methods are about to clarify the phenomenon and seek the deep origin. Although there are still many questions and controversy, we could predict that in the near future, this field will be very active both in basic physics and applications.
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