Prediction for new magnetoelectric fluorides

Prediction for new magnetoelectric fluorides

G Nénert[1] and T T M Palstra

Solid State Chemistry Laboratory, Zernike Institute for Advanced Materials, University of Groningen, Nijenborg 4, 9747 AG Groningen, The Netherlands

E-mail: gwilherm.nenert@cea.fr

Abstract
We use symmetry considerations in order to predict new magnetoelectric fluorides. In addition to these magnetoelectric properties, we discuss which among these fluorides are the ones susceptible to present multiferroic properties. We emphasize that several materials exhibit ferromagnetic properties. This ferromagnetism should enhance the interplay between the magnetic and dielectric properties in these materials.

1. Introduction

In recent years, there has been a renewed interest in the coexistence and interplay of magnetism and electrical polarization [1–3]. This interest has been concentrated on multiferroics and magnetoelectric materials. In multiferroics, a spontaneous polarization coexists with a long-range magnetic order. In magnetoelectrics (we consider here only the linear effect), the polarization is induced by a magnetic field in a magnetically ordered phase [4]. In the Landau theory framework, multiferroics which are not magnetoelectric possess at least a coupling of the type $P^2 M^2$ (P: polarization, M: total magnetization) while linear magnetoelectrics are characterized by terms like $P M^2$ or $L M P$ (L: antiferromagnetic order parameter) [5]. Terms like $P^2 M^2$ are of higher degree than $P M^2$ or $L M P$ terms. Consequently, we expect a stronger interplay between the dielectric and magnetic properties in linear magnetoelectrics than in simple multiferroics (e.g. $YMnO_3$ [6]). More complicated coupling terms can also characterize the magnetoelectric effect (e.g. magnetic gradient) [7]. These kinds of terms are outside the purpose of the present contribution. In the search for materials exhibiting a strong coupling of magnetism and polarization, the most promising ones are multiferroics exhibiting linear magnetoelectric properties. These materials are scarce. Thus, it is of interest to look for new magnetoelectric materials independently.

Recent efforts have concentrated on two main ideas: magnetic frustration and breaking of the inversion center due to an antiferromagnetic ordering. These approaches have been

---

[1] Author to whom any correspondence should be addressed. Present address: CEA-Grenoble DRFMC/SPSMS/MDN, 17 rue des martyrs 38054, Grenoble Cedex, France.

the ideas of, on the one hand, Katsura [8] and Sergienko [9] and on the other hand those of Mostovoy [10]. These various authors described in the case of non-collinear magnets a possible mechanism for magnetoelectricity and polarization induced by antiferromagnetic ordering, respectively. The new mechanism proposed by Katsura *et al* does not involve the Dzyaloshinskii–Moriya (DM) interaction, contrary to what has been reported for typical magnetoelectric compounds such as Cr_2O_3 [11]. Most of the recent research on multiferroics concerns centrosymmetric oxides [12]. These materials exhibit a breaking of the symmetry giving rise to a spontaneous polarization which may or may not be reversible by application of a magnetic field. The idea of using symmetry analysis to predict magnetoelectric compounds is not new. The first reported magnetoelectric compound, Cr_2O_3, was predicted to be magnetoelectric prior to any experimental evidence [14]. It is the same philosophy that we aim to take here.

In this paper, we present a symmetry analysis of selected materials. All these materials should exhibit magnetoelectricity based on symmetry arguments. We made a literature survey considering various magnetically ordered compounds for which neutron data were available. We made a systematic symmetry analysis of all the studied compounds (about 50 materials). We present here only our investigation of selected fluorides. This choice is motivated by two reasons. The first one is that there is a need to look for materials other than oxides if we are searching for new materials since magnetoelectric/multiferroic materials are scarce. The second reason is that polarization cannot exist in conducting materials. Thus, the high charge transfer in the fluorides make them good candidates for experimental investigations.

Several fluorides have been reported to crystallize in a polar structure. Consequently, in addition to magnetoelectric properties, several fluorides are potentially ferroelectric. When this is the case, we discuss this possibility in the light of known ferroelectrics related to the material under investigation. All the compounds discussed in this article have been the subject of detailed crystallographic and magnetic studies by means of neutron diffraction. We present below the results of our search for new magnetoelectric fluorides.

2. Study of α-KCrF₄

α-KCrF$_4$ is the first in the selected fluorides we present with possible magnetoelectric properties. The crystal structure of α-KCrF$_4$ is orthorhombic (space group *Pnma* (no. 62), $a = 15.76$ Å, $b = 7.43$ Å, $c = 18.38$ Å). It consists of infinite columns of CrF$_6$ octahedra sharing edges along the b axis (see figure 1) [15].

This compound possesses a high magnetic frustration among the fluorides that we present here. It orders antiferromagnetically only under $T_N = 4$ K with a quasi-1D behavior. We present in figure 2 a representation of its magnetic structure as determined from neutron scattering [16].

There are three inequivalent Cr^{3+} ions per unit cell, and they occupy the Wyckoff position 8d. Consequently, we have eight different magnetic sites all carrying one spin S_j. We can define the following eight magnetic vectors (one ferromagnetic and seven antiferromagnetic ones):

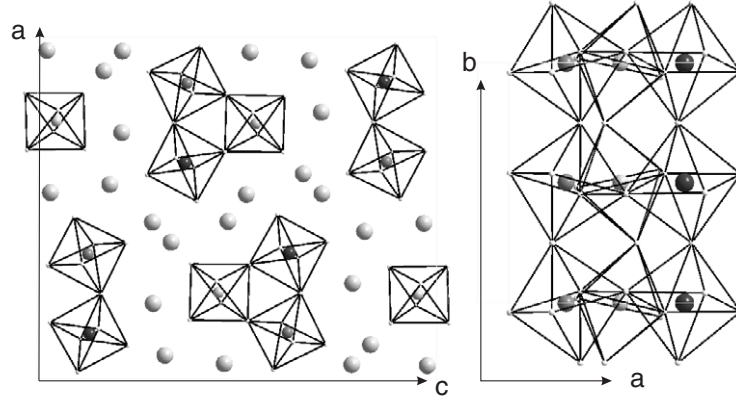$$\vec{M} = \vec{S_1} + \vec{S_2} + \vec{S_3} + \vec{S_4} + \vec{S_5} + \vec{S_6} + \vec{S_7} + \vec{S_8}, \tag{1}$$

$$\vec{L_1} = \vec{S_1} - \vec{S_2} + \vec{S_3} - \vec{S_4} + \vec{S_5} - \vec{S_6} + \vec{S_7} - \vec{S_8}, \tag{2}$$

$$\vec{L_2} = \vec{S_1} + \vec{S_2} - \vec{S_3} - \vec{S_4} + \vec{S_5} + \vec{S_6} - \vec{S_7} - \vec{S_8}, \tag{3}$$
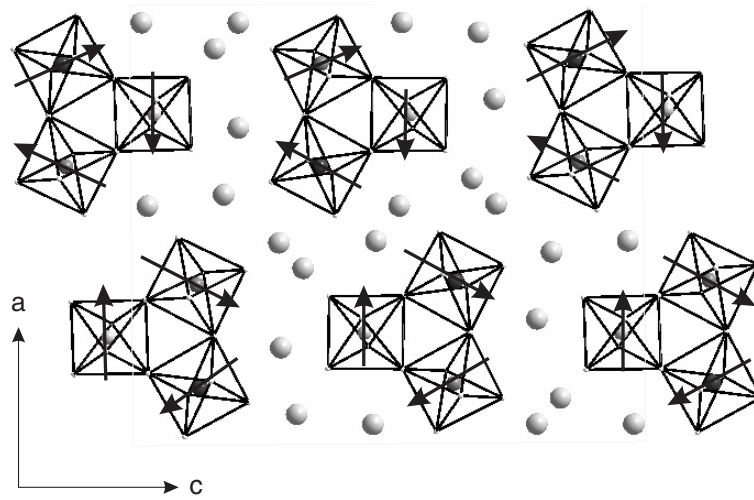
$$\vec{L_3} = \vec{S_1} - \vec{S_2} - \vec{S_3} + \vec{S_4} + \vec{S_5} - \vec{S_6} - \vec{S_7} + \vec{S_8}, \tag{4}$$

$$\vec{L_4} = \vec{S_1} + \vec{S_2} + \vec{S_3} + \vec{S_4} - \vec{S_5} - \vec{S_6} - \vec{S_7} - \vec{S_8}, \tag{5}$$

$$\vec{L_5} = \vec{S_1} - \vec{S_2} + \vec{S_3} - \vec{S_4} - \vec{S_5} + \vec{S_6} - \vec{S_7} + \vec{S_8}, \tag{6}$$

Figure 1. Crystal structure of $KCrF_4$ projected along the b axis (left) and the c axis (right). We show the Cr^{3+} sites in their octahedral environment. The white atoms are the K^+ atoms. The different gray scales represent the three inequivalent Cr^{3+} sites.

Figure 2. Magnetic structure of $KCrF_4$ in the (a, c) plane. Arrows indicate the magnetic moments on the chromium atoms with a quasi-$120°$ configuration.

$$\vec{L_6} = \vec{S_1} + \vec{S_2} - \vec{S_3} - \vec{S_4} - \vec{S_5} - \vec{S_6} + \vec{S_7} + \vec{S_8}, \tag{7}$$

$$\vec{L_7} = \vec{S_1} - \vec{S_2} - \vec{S_3} + \vec{S_4} - \vec{S_5} + \vec{S_6} + \vec{S_7} - \vec{S_8}. \tag{8}$$

Lacorre and collaborators have also investigated the transformation properties of the different components of the magnetic vectors. We reproduce in table 1 the results of their derivations [16].

As stated above, we need to look for the possible LMP terms allowed by symmetry. These terms are the signature of the linear magnetoelectric effect. For this, we need to know what the transformation properties of the polarization components are. It is sufficient to look at the transformation properties of the different polarization components under the effect of the generators of the space group. In table 2, we present the transformation properties of the polarization components in the space group $Pnma$.

Table 1. Magnetic components classified by irreducible representation.

IR	Magnetic components
Γ_1	L_{1x}, L_{2y}, L_{3z}
Γ_2	M_x, L_{3y}, L_{2z}
Γ_3	L_{2x}, L_{1y}, M_z
Γ_4	L_{3x}, M_y, L_{1z}
Γ_5	L_{5x}, L_{6y}, L_{7z}
Γ_6	L_{4x}, L_{7y}, L_{6z}
Γ_7	L_{6x}, L_{5y}, L_{4z}
Γ_8	L_{7x}, L_{4y}, L_{5z}

Table 2. Transformation properties of the polarization components for the space group $Pnma1'$ associated to $\mathbf{k} = 0$.

|	2_{1x}	2_{1z}	$\bar{1}$
P_x	1	−1	−1
P_y	−1	−1	−1
P_z	−1	1	−1

According to tables 1 and 2, we can determine the allowed LMP terms which may be present and giving rise to an induced polarization under magnetic field. We know that, below T_N, the magnetic structure is described by the irreducible representation Γ_6. It is experimentally observed that $L_{4x} > L_{6z}$ and $L_{7z} \simeq 0$ [16]. Taking into account these experimental results, we find that the most relevant magnetoelectric terms are $L_{4x}P_yM_z$ and $L_{4x}P_zM_y$. Consequently, an induced polarization may appear along P_y (P_z) if one applies a magnetic field along z(y). Since this compound is centrosymmetric, it cannot exhibit a multiferroic character.

3. Study of KMnFeF$_6$

The fluoride KMnFeF$_6$ exhibits a partial ordering of the Mn and Fe atoms giving rise to an enlargement of the unit cell compared to the usual tetragonal tungsten bronze type [17]. The family of tetragonal tungsten bronze and related bronzes have been extensively investigated due to their ferroelectric properties [18]. This compound crystallizes in the space group $Pba2$ (no. 32); the Mn and Fe ions order on the 8c Wyckoff position of the structure and occupy statistically the 4b Wyckoff position. This compound is magnetically frustrated due to the presence of triangular cycles of antiferromagnetic interactions. All the Mn and Fe cations have an octahedral environment of fluorine atoms. In the (a, b) plane, Mn and Fe ions alternate along the c axis. The magnetic structure is presented in figure 3 [17]. Although the ferroelectric properties have not been investigated to our knowledge, this compound is likely to present a multiferroic character below T_C. Indeed since many materials of this family are ferroelectric, it is likely that this compound possesses such property.

Although exhibiting magnetic frustration, the compound KMnFeF$_6$ orders ferrimagneti-cally below $T_C = 148$ K with a ratio $\frac{\Theta}{T_C} = 3$. The magnetic structure is identical to the chemical unit cell and thus $\vec{k} = \vec{0}$. The symmetry analysis by Bertaut's method gives rise to the results presented in table 3 [17, 19].

The neutron data show that the best model for the magnetic structure is given by the Γ_4 mode. The corresponding magnetic space group is thus $Pb'a2'$, which has the magnetic point group $m'm2'$. According to [4], we have a linear magnetoelectric effect which is allowed having
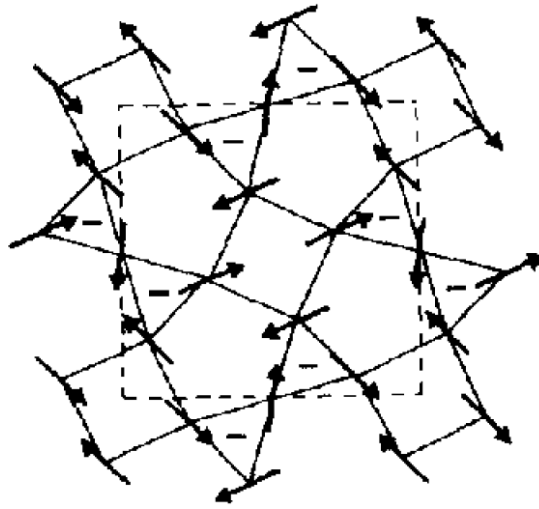
Figure 3. Magnetic structure of KMnFeF$_6$ in the (a, b) plane. Arrows indicate the magnetic moments on the iron atoms (mostly along the a axis) from [17].

Table 3. Irreducible representations for the space group $Pba21'$ associated to $\mathbf{k} = 0$.

Modes	x	y	z	Magnetic space groups
Γ_1	G_x	A_y	C_z	$Pba2$
Γ_2	C_x	F_y	G_z	$Pba'2'$
Γ_3	A_x	G_y	F_y	$Pb'a'2$
Γ_4	F_x	C_y	A_y	$Pb'a2'$

the following terms (after transformation of the coordinate system):

$$[\alpha_{ij}] = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{23} \\ 0 & \alpha_{32} & 0 \end{pmatrix}.$$

We recall that KMnFeF$_6$ possesses a polar structure and is likely to be ferroelectric. Consequently, KMnFeF$_6$ is a multiferroic material which exhibits a strong interplay between magnetism and polarization below $T_C = 148$ K. Moreover, we notice here that it would be one of the scarce ferrimagnetic compounds possessing such properties. The application of a magnetic field below T_C along the c axis (direction of spontaneous polarization) should create a polarization along the b axis (term α_{23}) and vice versa (term α_{32}). Thus it will be possible to switch the polarization direction under the application of a magnetic field. This is of high interest for technological applications. Another remarkable feature is that this compound orders at 148 K, which is much higher than recently reported multiferroic compounds [12].

4. Study of two members of the Ba$_6$M$_n$F$_{12+2n}$ family

In the previous fluorides, the magnetic frustration appeared in corner-sharing octahedra, which leads to a single type of interaction. Lacorre and co-workers have been also investigating compounds like Ba$_2$Ni$_3$F$_{10}$ ($n = 9$) and Ba$_2$Ni$_7$F$_{18}$ ($n = 21$), which are members of the Ba$_6$M$_n$F$_{12+2n}$ family [20, 21]. In this family, where M = Ni, there are not only corner-sharing octahedra but also edge-sharing octahedra. Both types of interaction exist in the Ba$_2$Ni$_3$F$_{10}$ and

Table 4. Irreducible representation for the space group $P11'$ associated to $\mathbf{k} = (0, 0, 0)$.

	h_1
Γ_1	1

$Ba_2Ni_7F_{18}$ compounds. These compounds have been investigated by means of powder neutron diffraction at room and low temperatures.

We start by looking at the $Ba_2Ni_3F_{10}$ material. This compound crystallizes in the space group $C2/m$ (no. 12) containing three different Ni^{2+} per unit cell. Two Ni ions occupy the Wyckoff position 4i and the other one occupies the Wyckoff position 4h. Below $T_N = 50$ K, an antiferromagnetic ordering starts to develop, characterized by a magnetic wavevector $\overrightarrow{k} = (0, 0, 1/2)$. None of the (hkl) magnetic reflections satisfy the C-centering of the chemical cell but rather a primitive lattice. Lacorre and collaborators have shown that the magnetic space group is $P2/m'$, in which the magnetic moments lie in the ac plane. Consequently, the magnetic point group of this compound below its T_N is $2/m'$. According to [4], a linear magnetoelectric effect is allowed, having the following expression:

$$[\boldsymbol{\alpha_{ij}}] = \begin{pmatrix} \alpha_{11} & 0 & \alpha_{13} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{pmatrix}.$$

Consequently, induced polarization can be observed along the three crystallographic directions under the application of an applied magnetic field. This material is not multiferroic since its structure is centrosymmetric. Moreover the structure remains centrosymmetric in the magnetic ordered phase. Consequently no spontaneous polarization can develop below and above T_N.

The other member of the family of interest is for $n = 21$. $Ba_2Ni_7F_{18}$ crystallizes in the polar space group $P1$ (no. 1) containing four inequivalent sets of Ni^{2+} ions. Each Ni^{2+} ion occupies the Wyckoff position 1a in the general position. From all the fluorides that we treat here, it is the second fluoride that we discussed which orders ferrimagnetically under $T_C = 36$ K. Due to the low symmetry of the crystal, we have to deal here with magnetic components along the three crystallographic directions. While all the already studied fluorides exhibit magnetic frustrations, it is not the case in this compound. We mean there is no competition between next-nearest neighbors. Below T_C, all the new magnetic reflections can be indexed in the same cell as the chemical one. Consequently, the star of the magnetic wavevector has only one arm. The irreducible representations associated to the space group $P1$ with $\overrightarrow{k} = \overrightarrow{0}$ are given in table 4.

According to table 4, there is only one possibility for the magnetic space group, which is $P1$. Referring to [4], a linear magnetoelectric effect is allowed with non-zero components:

$$[\boldsymbol{\alpha_{ij}}] = \begin{pmatrix} \alpha_{11} & \alpha_{12} & \alpha_{13} \\ \alpha_{21} & \alpha_{22} & \alpha_{23} \\ \alpha_{31} & \alpha_{32} & \alpha_{33} \end{pmatrix}.$$

Consequently, $Ba_2Ni_7F_{18}$ is a potential multiferroic material (polar structure and ferrimagnetic below $T_C = 36$ K). Moreover, irrespective of the direction of an applied magnetic field, the polarization parallel to the magnetic field will increase due to the magnetoelectric effect below T_C.
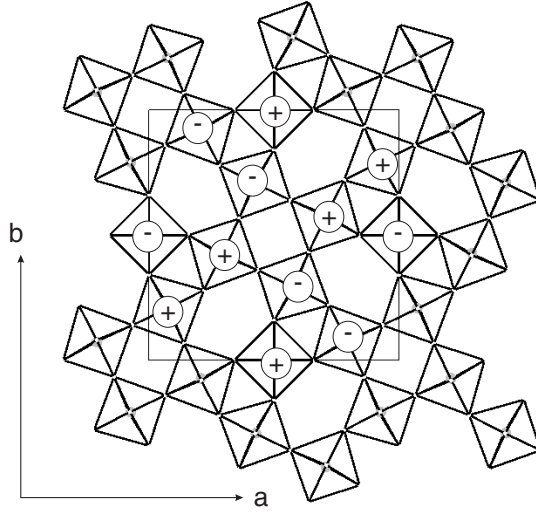
Figure 4. Magnetic structure of CsCoF$_4$ in the (a, b) plane. Plus and minus signs indicate the magnetic moments along the c axis (up or down).

5. Study of CsCoF$_4$

CsCoF$_4$ is the last compound among the fluorides that we investigate in the light of a possible magnetoelectric effect. This compound crystallizes in the non-polar space group $I\bar{4}c2$ (no. 120) with two different Co^{3+} Wyckoff positions in the unit cell: 4d and 16i. The antiferromagnetic order occurring below $T_N = 54$ K is characterized by a magnetic wavevector $\vec{k} = \vec{0}$ [22]. This structure is also magnetically frustrated due the presence of ferromagnetic interactions within an antiferromagnetic plane, as described in figure 4.

Based on geometrical considerations and comparison with magnetic structure of compounds of the same family (namely LiCoF$_4$), the authors proposed some constraints on the orientation of the magnetic moments. From these considerations, they found that the magnetic space group of CsCoF$_4$ is $I\bar{4}'$. The corresponding magnetic point group is $\bar{4}'$. If one compares this magnetic point group with the ones listed in [4], we observe that a linear magnetoelectric effect is possible along several directions:

$$[\boldsymbol{\alpha_{ij}}] = \begin{pmatrix} \alpha_{11} & \alpha_{12} & 0 \\ -\alpha_{12} & \alpha_{11} & 0 \\ 0 & 0 & \alpha_{33} \end{pmatrix}.$$

6. Discussion

In the previous sections we have investigated the magnetic symmetry of various fluorides. We shall discuss here the common mechanism which may give rise to the magnetoelectric effect in the studied fluorides and compare it to other known magnetoelectric fluorides such as BaMnF$_4$ [23]. But prior to this, we should stress that there is an upper bound for the magnetoelectric effect [24], which is defined as

$$\alpha_{ij} \leqslant \varepsilon_0 \mu_0 \varepsilon_{ii} \mu_{jj}. \tag{9}$$

ε_{ii} and ε_0 are respectively the permittivity of free space and the relative permittivity of the considered material, while μ_{jj} and μ_0 are the relative permeability and the permeability of

free space, respectively. As a consequence of equation (9), the magnetoelectric effect will remain small compared to unity except possibly in ferroelectric and ferromagnetic materials. Thus multiferroic magnetoelectric materials with ferromagnetic order are the most interesting. Among the various compounds that we have investigated, $KMnFeF_6$ and $Ba_2Ni_7F_{18}$ are likely to be good representatives of such materials.

Various mechanisms may contribute to the magnetoelectric effect. In the old literature, we can count about four different mechanisms which may participate in the magnetoelectric effect [25]. We can consider the molecular field theory expression of a magnetic field for the magnetoelectric susceptibility.

$$H = H_0 + V \tag{10}$$

where the Hamiltonian H_0 describes the spin system in the presence of a magnetic field and the perturbation V is linear in the electric field.

$$H_0 = \tfrac{1}{2} \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - D \sum_j \left(S_i^z \right)^2 - \mu \mathbf{H} \cdot \sum_i \mathbf{S}_i. \tag{11}$$

V represent the changes of the various tensors due to the presence of an electric field: single-ion anisotropy, g-factor, symmetric exchange and Dzyaloshinskii–Moriya interactions. For the detailed expression of V, we refer the reader to the literature (see [25]). It has been shown that in the presence of an electric field the changes of the g factor are predominant at low temperature in $GdAlO_3$ compared to the changes for the other tensors, but not any more above 1.2 K ($T_N = 3.78$ K) [25]. It is thus difficult to determine which parameter has the most important contribution since this depends not only on the compound but also on the temperature. The change of the anisotropy energy, exchange and g value due to the electric field have been proposed for the origin of the magnetoelectric effect in Cr_2O_3 [11]. These various mechanisms are susceptible to playing a role in the magnetoelectric effect in the fluorides that we have presented in the previous sections.

The main difference between the various fluorides that we present is the presence of inversion symmetry. The Dzyaloshinskii–Moriya (DM) interaction (antisymmetric exchange) is allowed only when the inversion symmetry is broken at the ligand ion mediating the exchange [26]. Therefore, when the crystal structure has inversion symmetry, the external electric field $\mathbf{E}$ induces the DM interaction. Thus the DM vector can be defined as $\mathbf{D}_{ij} \propto \mathbf{E} \times \mathbf{e}_{ij}$, with $\mathbf{e}_{ij}$ being the unit vector connecting the two sites i and j. This is the mechanism which has been proposed to explain the magnetoelectric effect in $ZnCr_2Se_4$ [27]. One may expect that the contribution of the DM mechanism to the magnetoelectric effect is higher for compounds which allow a spontaneous DM interaction (i.e. not induced by the electric field $\mathbf{E}$). In this perspective, we expect that the almost collinear magnetic structure of $CsCoF_4$ will give rise to a negligible DM contribution to the predicted magnetoelectric effect. We note that DM interactions do not result systematically in a magnetoelectric contribution as in the case of α-Fe_2O_3 [26] or CoF_2 [28], which are piezomagnetic materials.

The fluorides that we present in this contribution possess various symmetry properties. We can classify them into two types of crystal structure: polar and non-polar. In the first category, we count $KMnFeF_6$ and $Ba_2Ni_7F_{18}$. In the other category, we have $KCrF_4$, $Ba_2Ni_3F_{10}$ and $CsCoF_4$. As a consequence of their polar structure, $KMnFeF_6$ and $Ba_2Ni_7F_{18}$ are potentially multiferroic and thus ferroelectric at room temperature. If their ferroelectric properties can be confirmed experimentally, the mechanism for this ferroelectricity remains to be investigated. Several multiferroic fluorides have been investigated theoretically and experimentally [23, 29]. It has been shown that the typical charge transfer towards empty d orbitals responsible for ferroelectricity such as in $BaTiO_3$ is not active in $BaMF_4$ (M = Mn, Fe, Co, and Ni). The ferroelectric instability in the multiferroic barium fluorides arises solely due to size

8

effects [29]. In the light of the occupied d orbitals in $KMnFeF_6$ and $Ba_2Ni_7F_{18}$, it could be that the cooperative displacements of K^+ and Ba^{2+} respectively would be responsible for the ferroelectric instability. Obviously, this hypothesis remains to be confirmed experimentally.

7. Conclusion

In conclusion, we have shown from symmetry analysis that several fluorides are likely to be magnetoelectric. Several of them may exhibit a multiferroic character coupled to an induced polarization under the application of a magnetic field. Most of them exhibit magnetic frustration. We present here possible magnetoelectrics which are among the scarce ferrimagnetic systems. This ferromagnetism may enhance the interplay between polarization and magnetism for the case of multiferroic materials. The mechanisms for potential ferroelectricity and the magnetoelectric effect remain to be investigated. We expect that this work will stimulate experimental investigations of the dielectric properties of the above-reported fluorides.

Acknowledgments

References

[1] Fiebig M 2005 *J. Phys. D: Appl. Phys.* **38** R123
[2] Eerenstein W, Mathur N D and Scott J F 2006 *Nature* **442** 759
[3] Cheong S-W and Mostovoy M 2007 *Nat. Mater.* **6** 13
[4] Authier A (ed) 2003 *International Tables for Crystallography* vol D *Physical Properties of Crystals* (Dordrecht: Kluwer–Academic)
[5] Tolédano J-C and Tolédano P 1987 *The Landau Theory of Phase Transitions* (Singapore: World Scientific)
[6] Nugroho A A, Bellido N, Adem U, Nénert G, Simon Ch, Tjia M O, Mostovoy M and Palstra T T M 2007 *Phys. Rev.* **75** 174435
[7] Harris A B, 2006 *Preprint* cond-mat/0610241
[8] Katsura H, Nagaosa N and Balatsky A V 2005 *Phys. Rev. Lett.* **95** 057205
[9] Sergienko I A and Dagotto E 2006 *Phys. Rev.* B **73** 094434
[10] Mostovoy M 2006 *Phys. Rev. Lett.* **96** 067601
[11] Rado G T 1962 *Phys. Rev.* **128** 2546
      Rado G T 1961 *Phys. Rev. Lett.* **6** 6009
      Date M, Kanamori J and Tachiki M 1961 *J. Phys. Soc. Japan* **16** 2589
[12] Blake G R *et al* 2005 *Phys. Rev.* B **71** 214402
      Chapon L C *et al Phys. Rev. Lett.* **93** 177402
      Aliouane N *et al* 2006 *Phys. Rev.* B **73** 20102
      Goto T *et al* 2005 *Phys. Rev.* B **72** 220403
      Kimura T, Goto T, Shintani H, Ishizaka K, Arima T and Tokura Y 2003 *Nature* **426** 55
      Hur N, Park S, Sharma P A, Ahn J S, Guha S and Cheong S-W 2004 *Nature* **429** 392
      Sergienko I A, Sen C and Dagotto E 2006 *Phys. Rev. Lett.* **97** 227204
[13] Goshen S, Mukamel D, Shaked H and Shtrikman S 1969 *J. Appl. Phys.* **40** 1590
      Goshen S, Mukamel D, Shaked H and Shtrikman S 1970 *Phys. Rev.* B **12** 4679
[14] Dzialoshinskii I E 1960 *Sov. Phys.—JETP* **10** 628
[15] Kissel D and Hoppe R 1987 *Z. Naturf.* B **42** 135
[16] Lacorre P, Leblanc M, Pannetier J and Ferey G 1991 *J. Magn. Magn. Mater.* **94** 337
      Lacorre P, Leblanc M, Pannetier J and Ferey G 1987 *J. Magn. Magn. Mater.* **66** 219–24
[17] Lacorre P, Pannetier J and Ferey G 1991 *J. Magn. Magn. Mater.* **94** 331
[18] Foster M C, Brown G R, Nielson R M and Abrahams S C 1997 *J. Appl. Crystallogr.* **30** 495

     Miles G C, Stennett M C, Pickthall D, Kirk C A, Reaney I M and West A R 2005 *Powder Diffr.* **20** 43

     Cross L E and Neurgaonkar R R 1992 *J. Mater. Sci.* **27** 2589

[19] Bertaut E F 1968 *Acta Crystallogr.* A **24** 217

[20] Lacorre P, Pannetier J and Ferey G 1987 *J. Magn. Magn. Mater.* **66** 213

[21] Renaudin J, Ferey G, Kozak A, Samouel M and Lacorre P 1988 *Solid State Commun.* **65** 185

[22] Lacorre P, Pannetier J, Fleischer T, Hoppe R and Ferey G 1991 *J. Solid State Chem.* **93** 37

[23] Fox D L, Tilley D R, Scott J F and Guggenheim H J 1980 *Phys. Rev.* B **21** 2926

[24] Brown W F, Hornreich R M and Shtrikman S 1968 *Phys. Rev.* **168** 574

[25] de Alcantara Bonfim O F and Gehring G A 1980 *Adv. Phys.* **29** 731

[26] Moriya T 1960 *Phys. Rev.* **120** 91

     Dzyaloshinskii I 1958 *J. Phys. Chem. Solids* **4** 241

[27] Shiratori K and Kita E 1980 *J. Phys. Soc. Japan* **48** 1443

[28] Borovik-Romanov A S 1959 *Sov. Phys.—JETP* **9** 1390

     Borovik-Romanov A S 1960 *Sov. Phys.—JETP* **11** 786

[29] Ederer C and Spaldin N A 2006 *Phys. Rev.* B **74** 020401(R)

     Yoshimura M and Hidaka M 2005 *J. Phys. Soc. Japan* **74** 1181

     Ederer C and Spaldin N A 2006 *Phys. Rev.* B **74** 024102