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Abstract
Recently, on the basis of symmetry considerations, we predicted that KMnFeF$_6$ and Ba$_2$Ni$_7$F$_{18}$ are likely magnetoelectric multiferroic materials. In this contribution, we investigate using Landau theory and crystal structure considerations the polarization and the linear magnetoelectric effect in these materials. Based on these two examples, we show that any magnetoferroelectric will display additional electrical polarization below its magnetic ordering temperature. This additional electrical polarization is not related to the linear magnetoelectric effect. Its magnitude depends on the dielectric susceptibility.

1. Introduction

In recent years, the coupling between magnetic and dielectric properties in transition metal oxides has given rise to a significant research effort [1–3]. This effort is governed by the emergence of new fundamental physics and potential technological applications [2, 3]. This recent research is mostly concentrated on oxides [4]. We think it is very important to search for new materials, especially for materials other than oxides [5, 6]. Since multiferroic and magnetoelectric properties rely on symmetry considerations, the use of group theory is of prime importance in looking for new materials. The use of symmetry arguments in order to predict new multiferroic or magnetoelectric materials is not new [7–9].

In this contribution, we use the phenomenological Landau theory to describe the previously predicted magnetoelectric effect in the multiferroic fluorides KMnFeF$_6$ and Ba$_2$Ni$_7$F$_{18}$ [5]. These two materials exhibit a pyroelectric symmetry and thus show spontaneous electrical polarization at room temperature. Here we are interested in the behavior of this electrical polarization at the magnetic ordering temperature. For this reason, we will consider in the free energy expression only the lowest degree term of the electrical polarization which is P^2. The other coupling terms between the various order parameters are derived from symmetry considerations. Every product of the order parameter components belonging to the same irreducible

representation is invariant by time reversal and the crystal symmetry [10].

We use the general case of Ba$_2$Ni$_7$F$_{18}$ (symmetry $P1$) in order to discuss various contributions to the induced polarization. In particular we show that any magnetically ordered pyroelectric materials will display additional electrical polarization below its magnetic ordering temperature. This electric polarization is not related to the linear magnetoelectric effect. We discuss these results in the light of recent reports on magnetoelectric and multiferroic materials [11–15].

2. Study of KMnFeF$_6$

The crystal structure of the fluoride KMnFeF$_6$ has been discussed in detail in the literature [16]. This compound crystallizes in the space group $Pba2$ (no 32), where the Mn and Fe ions order on the 4c Wyckoff position of the structure and occupy statistically the 4b Wyckoff position. KMnFeF$_6$ orders ferrimagnetically below $T_C = 148$ K with a ratio $\frac{\Theta}{T_C} = 3$. The magnetic unit-cell is identical to the chemical unit-cell and thus $\vec{k} = \vec{0}$. A symmetry analysis by Bertaut's method gives rise to the results presented in tables 1 and 2 [16, 17].

For the Wyckoff position 4c, the labeling of the various spins is $\vec{S}_1$ in (x, y, z), $\vec{S}_2$ in $(\overline{x}, \overline{y}, z)$, $\vec{S}_3$ in $(1/2-x, 1/2+y, z)$ and $\vec{S}_4$ in $(1/2 + x, 1/2 - y, z)$. The authors defined the

Table 1. Irreducible representations for the space group $Pba21'$ associated with $\mathbf{k} = 0$ for the Wyckoff position 4c [16].

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_z	$Pb'a'2$
Γ_4	F_x	C_y	A_z	$Pb'a2'$

Table 2. Irreducible representations for the space group $Pba21'$ associated with $\mathbf{k} = 0$ for the Wyckoff position 2b [16].

Modes	x	y	z	Magnetic space groups
Γ_1	—	—	C_z	$Pba2$
Γ_2	C_x	F_y	—	$Pba'2'$
Γ_3	—	—	F_z	$Pb'a'2$
Γ_4	F_x	C_y	—	$Pb'a2'$

following magnetic vectors:

$$\vec{F} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \vec{S}_4$$
$$\vec{G} = \vec{S}_1 - \vec{S}_2 + \vec{S}_3 - \vec{S}_4$$
$$\vec{C} = \vec{S}_1 + \vec{S}_2 - \vec{S}_3 - \vec{S}_4 \quad (1)$$
$$\vec{A} = \vec{S}_1 - \vec{S}_2 - \vec{S}_3 + \vec{S}_4.$$

For the Wyckoff position 2b, the authors defined two magnetic vectors $\vec{F}' = \vec{S}_1 + \vec{S}_3$ and $\vec{C}' = \vec{S}_1 - \vec{S}_3$ where this time $\vec{S}_1$ is in $(0, 1/2, z)$ while $\vec{S}_3$ is in $(1/2, 0, z)$. The decomposition is given in tables 1 and 2. The neutron data show that the best model for the magnetic structure is given by the Γ_4 mode. The various components of the magnetic vectors defined in (1) transform as the reducible representation. The appropriate way is to consider vectors which transform as the irreducible representation (IR) [10]. In order to simplify the expression of the free energy and fulfill the symmetry requirements, we defined the magnetic order parameter η which transform as the Γ_4 IR as observed experimentally. The total magnetization of the system is defined by the order parameter $\vec{M}$. Its components transform like the components of $\vec{F}$ (tables 1 and 2). Thus M_x, M_y and M_z transform like the IRs Γ_4, Γ_2 and Γ_3, respectively.

η and M_x both transform as the Γ_4 IR, thus the lowest coupling term between η and $\vec{M}$ is ηM_x. The crystal structure of KMnFeF$_6$ has an orthorhombic pyroelectric symmetry. Thus this material exhibits a spontaneous electrical polarization along the z axis. All the symmetry elements of the space group $Pba2$ leave invariant only the P_z component of the electrical polarization. Thus the lowest coupling term between the magnetic order parameter η and the polarization is $\eta^2 P_z$. For the possible magnetoelectric coupling terms, one has to consider the possible terms of the type ηMP [18]. It can be shown that the electrical polarization components P_x, P_y and P_z belong, respectively, to the IRs Γ_3, Γ_4 and Γ_1. Looking at the possible ηMP and taking into account the above considerations, we can write the free energy for KMnFeF$_6$ in the presence of a magnetic field as:

$$\Phi = \Phi_0 + \frac{a}{2}\eta^2 + \frac{b}{4}\eta^4 + \gamma \eta M_x + \sigma \eta^2 P_z + \sum_{i,j} \frac{\kappa_{i,j}}{2} P_j^2$$
$$+ \sum_{i,j} \frac{c_{i,j}}{2} M_j^2 + \lambda_1 \eta P_y M_z + \lambda_2 \eta P_z M_x - \mathbf{M} \cdot \mathbf{H}. \quad (2)$$

We find the partial derivatives of Φ at the equilibrium conditions:

$$\frac{\partial \Phi}{\partial \eta} = a\eta + b\eta^3 + \gamma M_x + 2\sigma \eta P_z$$
$$+ \lambda_1 M_z P_y + \lambda_2 M_x P_z = 0$$
$$\frac{\partial \Phi}{\partial P_x} = \kappa_{11} P_x = 0$$
$$\frac{\partial \Phi}{\partial P_y} = \kappa_{22} P_y + \lambda_1 \eta M_z = 0$$
$$\frac{\partial \Phi}{\partial P_z} = \kappa_{33} P_z + \lambda_2 \eta M_x + \sigma \eta^2 = 0 \quad (3)$$
$$\frac{\partial \Phi}{\partial M_x} = c_{11} M_x + \lambda_2 \eta P_z + \gamma \eta - H_x = 0$$
$$\frac{\partial \Phi}{\partial M_y} = c_{22} M_y - H_y = 0$$
$$\frac{\partial \Phi}{\partial M_z} = c_{33} M_z + \lambda_1 \eta P_y - H_z = 0.$$

In order to investigate the linear magnetoelectric coupling, we express the electrical polarization as a function of the magnetic field. For this purpose, we use the expressions for $\frac{\partial \Phi}{\partial P_z}$ and of $\frac{\partial \Phi}{\partial P_y}$. We find:

$$P_y = \frac{-\lambda_1}{\kappa_{22}} \eta M_z$$
$$P_z = \frac{-(\sigma \eta^2 + \lambda_2 \eta M_x)}{\kappa_{33}}. \quad (4)$$

Using the results of equations (3) and (4), we can derive the expression for the various components of the magnetization:

$$M_x = \frac{\kappa_{33}}{\kappa_{33} c_{11} - \lambda_2^2 \eta^2} H_x + \frac{\eta(\lambda_2 \sigma \eta^2 - \kappa_{33}\gamma)}{\kappa_{33} c_{11} - \lambda_2^2 \eta^2}$$
$$M_y = \frac{H_y}{c_{22}} \quad (5)$$
$$M_z = \frac{\kappa_{22}}{\kappa_{22} c_{22} - \lambda_1^2 \eta^2} H_z.$$

From equations (4) and (5), we can find the expression for the linear relationship between the induced polarization and the application of a magnetic field (linear magnetoelectric effect)

for the fluoride $KMnFeF_6$:

$$P_x = 0$$

$$P_y = \frac{-\lambda_1\eta}{\kappa_{22}c_{33} - \lambda_1^2\eta^2}H_z \qquad (6)$$

$$P_z = \frac{-\lambda_2\eta}{\kappa_{33}c_{11} - \lambda_2^2\eta^2}H_x + \frac{(\lambda_2\gamma - \sigma c_{11})\eta^2}{\kappa_{33}c_{11} - \lambda_2^2\eta^2}.$$

From equation (6), we find that there are two non-zero components for the linear magnetoelectric tensor of $KMnFeF_6$: α_{23} and α_{31}. α_{23} takes the value $\frac{-\lambda_1\eta}{\kappa_{22}c_{33} - \lambda_1^2\eta^2}$ and α_{31} is equal to $\frac{-\lambda_2\eta}{\kappa_{33}c_{11} - \lambda_2^2\eta^2}$. We notice that the polarization along x is zero at any temperature even under the application of a magnetic field. Our results suggest that the polarization along y is purely induced by the magnetic field (linear magnetoelectric effect) while the polarization along z would have an additional component arising at the magnetic transition temperature (term in η^2 in equation (6)). We notice that this additional electrical polarization along z arising below T_N is present even in the absence of a linear magnetoelectric effect ($\lambda_i = 0$). We stress that our model describes only what is happening below the magnetic ordering temperature. One should keep in mind that there is already a spontaneous polarization along z at room temperature resulting from the pyroelectric symmetry exhibited by $KMnFeF_6$. We notice that the magnetic point group $m'm2'$ described by the irreducible representation Γ_4 should exhibit two non-zero components for the magnetoelectric tensor according to [19]: α_{23} and α_{32} instead of α_{31}. This difference can be explained by the fact that we have used the same labeling as the authors of [16]. If we inverse $\vec{S}_3$ and $\vec{S}_4$, we find that the total magnetization component M_y transforms like Γ_4 instead of Γ_2 (see tables 1 and 2). Consequently the invariant term responsible for the linear magnetoelectric effect is not $\lambda_2\eta P_z M_x$ but $\lambda_2\eta P_z M_y$, which will give rise to α_{32} instead of α_{31}. In addition to this linear magnetoelectric effect, we notice that a spontaneous magnetization component along x can be displayed below the Néel temperature in the absence of a magnetic field (see equation (5)).

3. Study of $Ba_2Ni_7F_{18}$

3.1. Estimation of the spontaneous polarization[1]

To estimate the spontaneous polarization of a pyroelectric system, one may deduce the possible high-symmetry (or high-temperature) structure from the low-symmetry structure based on a pseudosymmetry analysis. This concept gave rise to the prediction of a large number of displacive ferroelectrics [20, 21]. It has been implemented in the program PSEUDO (Crystallographic Bilbao Server) [21]. When the atomic coordinates of a given structure display an approximate symmetry in addition to the actual space-group symmetry, the

structure can be considered as pseudosymmetric with respect to a supergroup containing this additional symmetry. The existence of pseudosymmetry in a crystal structure indicates a slightly distorted structure of higher symmetry. If the distortion is small enough, one can expect the crystal to acquire this higher symmetry at a higher temperature. Using the crystal structure of $Ba_2Ni_7F_{18}$ reported by Lacorre *et al* [22], we performed a pseudosymmetry search among all the minimal supergroups of $P1$ (symmetry exhibited by $Ba_2Ni_7F_{18}$). Of the minimal supergroups of $P1$, we determined $P\bar{1}$ was the only pseudosymmetric minimal supergroup. We therefore concluded that the high-temperature paraelectric phase of $Ba_2Ni_7F_{18}$ is in this space group. However, this pseudosymmetric minimal supergroup would produce a maximum atomic displacement of 1.3 Å. The high value of the atomic displacement towards $P\bar{1}$ suggests that the paraelectric phase will not be reached before melting or decomposition. However, the possibility of twinning and domain switching may exist. The pseudosymmetric minimal supergroup allows us to estimate the spontaneous polarization in $Ba_2Ni_7F_{18}$. This is can be done using an ionic model by simplifying the electric charge of each ion with a point charge [23].

$$P_s = \left(\frac{e}{V}\right)\sum_i m_i Q_i \Delta z_i. \qquad (7)$$

e is the elementary charge, V the unit-cell volume, m_i the multiplicity of the ion, Q_i the ionic charge and Δz_i the displacement ion along the polar axis. Having already discussed the hypothetical high-temperature paraelectric phase, we can estimate the displacement Δz_i for each ion. In that case, since we have the symmetry $P1$, we have to deal with a spontaneous polarization vector having three non-zero components: P_x, P_y and P_z. Using the point charge model, we estimate that $P_x = 0.246\ \mu C\ cm^{-2}$, $P_y = 10.87\ \mu C\ cm^{-2}$ and $P_z = -26.87\ \mu C\ cm^{-2}$. The total polarization is thus $\|\vec{P}\| \cong 29\ \mu C\ cm^{-2}$. This is a large spontaneous polarization, but this value is an upper bound. The ionic model used is a crude picture which does not take into account the covalency of the bonds. Additionally, the calculation is strongly dependent on the accuracy of the z coordinate. For $BaAl_2O_4$, the ionic model gives an overestimation of P_s by a factor of six compared to the experimental value [24]. Nevertheless, the spontaneous polarization in $Ba_2Ni_7F_{18}$ remains high and comparable to known multiferroic systems such as $YMnO_3$ ($P_s = 5.5\ \mu C\ cm^{-2}$) [25].

3.2. Landau phenomenological description of the linear magnetoelectric effect

In the previous fluorides, the magnetic frustration appeared in corner-sharing octahedra through the existence of interconnected triangles of magnetic ions. This leads to a single type of magnetic exchange interaction. Lacorre and co-workers have also been investigating compounds like $Ba_2Ni_3F_{10}$ ($n = 9$) and $Ba_2Ni_7F_{18}$ ($n = 21$) which are members of the $Ba_6M_nF_{12+2n}$ family [22, 26]. 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 $Ba_2Ni_3F_{10}$ and

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[1] We notice that this estimation is not possible for $KMnFeF_6$ since in the reported crystal structure [16], the authors fixed the cations on the atomic positions determined in the $P4_2bc$ symmetry and not in $Pba2$. Consequently a redetermination of the crystal structure of $KMnFeF_6$ is required to investigate properly the coupling between dielectric and magnetic properties.

Table 3. Irreducible representation for the space group $P11'$ associated with $\mathbf{k} = (0, 0, 0)$.

	h_1	h_1'
Γ_1	1	-1

Ba$_2$Ni$_7$F$_{18}$ compounds. These compounds have been investigated by means of powder neutron diffraction at room and low temperatures.

In order to keep consistency in the notations between the two cases, we will also call η the magnetic order parameter describing the magnetic ordering of Ba$_2$Ni$_7$F$_{18}$. Since there is only one IR (see table 3) in that case, following similar arguments to those in the case of KMnFeF$_6$, all the coupling terms ηM_j are invariant. Since the crystal structure is $P1$, spontaneous electrical polarization components are non-zero for all the three directions x, y and z. Consequently, the invariant terms involving the electrical polarization are $\sum_{i,j} \frac{\kappa_{i,j}}{2} P_j^2$ and $\sum_i \sigma_i \eta^2 P_i$. In addition to these terms, one needs to consider the magnetoelectric coupling terms. All the electrical polarization components transform as the unique Γ_1 IR. Thus all $\eta P_i M_j$ are allowed. Consequently we can write the free energy for this fluoride as:

$$
\begin{aligned}
\Psi = \Psi_0 &+ \frac{a}{2}\eta^2 + \frac{b}{4}\eta^4 + \left(\sigma_x P_x + \sigma_y P_y + \sigma_z P_z\right)\eta^2 \\
&+ \sum_{i,j} \frac{\kappa_{i,j}}{2} P_j^2 + \sum_{i,j} \frac{c_{i,j}}{2} M_j^2 \\
&+ \left(\gamma_x M_x + \gamma_y M_y + \gamma_z M_z\right)\eta \\
&+ \left(\lambda_1 P_x M_x + \lambda_2 P_x M_y + \lambda_3 P_x M_z\right)\eta \\
&+ \left(\lambda_4 P_y M_x + \lambda_5 P_y M_y + \lambda_6 P_y M_z + \lambda_7 P_z M_x\right)\eta \\
&+ \left(\lambda_8 P_z M_y + \lambda_9 P_z M_z\right)\eta - M \cdot H.
\end{aligned}
\tag{8}
$$

$\mathbf{M}$ and $\mathbf{P}$ designate, respectively, the total magnetization and the electrical polarization of the system. Calculating the derivatives of the different variables, we can write the following set of equations:

$$
\begin{aligned}
\frac{\partial \Psi}{\partial \eta} =\; & a\eta + b\eta^3 + 2\eta\left(\sigma_x P_x + \sigma_y P_y + \sigma_z P_z\right) \\
& + \gamma_x M_x + \gamma_y M_y + \gamma_z M_z + \lambda_1 P_x M_x + \lambda_2 P_x M_y \\
& + \lambda_3 P_x M_z + \lambda_4 P_y M_x + \lambda_5 P_y M_y + \lambda_6 P_y M_z \\
& + \lambda_7 P_z M_x + \lambda_8 P_z M_y + \lambda_9 P_z M_z = 0
\end{aligned}
$$

$$
\frac{\partial \Psi}{\partial P_x} = \sigma_x \eta^2 + \kappa_x P_x + \left(\lambda_1 M_x + \lambda_2 M_y + \lambda_3 M_z\right)\eta = 0
$$

$$
\frac{\partial \Psi}{\partial P_y} = \sigma_y \eta^2 + \kappa_y P_y + \left(\lambda_4 M_x + \lambda_5 M_y + \lambda_6 M_z\right)\eta = 0 \tag{9}
$$

$$
\frac{\partial \Psi}{\partial P_z} = \sigma_z \eta^2 + \kappa_z P_z + \left(\lambda_7 M_x + \lambda_8 M_y + \lambda_9 M_z\right)\eta = 0
$$

$$
\frac{\partial \Psi}{\partial M_x} = c_x M_x + \gamma_x \eta + \left(\lambda_1 P_x + \lambda_2 P_y + \lambda_3 P_z\right)\eta - H_x = 0
$$

$$
\frac{\partial \Psi}{\partial M_y} = c_y M_y + \gamma_y \eta + \left(\lambda_4 P_x + \lambda_5 P_y + \lambda_6 P_z\right)\eta - H_y = 0
$$

$$
\frac{\partial \Psi}{\partial M_z} = c_z M_z + \gamma_z \eta + \left(\lambda_7 P_x + \lambda_8 P_y + \lambda_9 P_z\right)\eta - H_z = 0.
$$

Here the dielectric tensor $\kappa_{i,j}$ has nine non-zero terms. To simplify the notation, we write $\kappa_x = \kappa_{11} + \kappa_{12} + \kappa_{13}$, $\kappa_y = \kappa_{21} + \kappa_{22} + \kappa_{23}$ and $\kappa_z = \kappa_{31} + \kappa_{32} + \kappa_{33}$. We use a similar notation for c_x, c_y and c_z. In a similar manner as in the case of KMnFeF$_6$, we can extract from equation (9) the expression for M_i as function of the magnetic field, of the magnetic order parameter and of the polarization. We find the expressions for the various magnetic components:

$$
M_x = \frac{H_x - \eta\left(\gamma_x + \lambda_1 P_x + \lambda_4 P_y + \lambda_7 P_z\right)}{c_x}
$$

$$
M_y = \frac{H_y - \eta\left(\gamma_y + \lambda_2 P_x + \lambda_5 P_y + \lambda_8 P_z\right)}{c_y} \tag{10}
$$

$$
M_z = \frac{H_z - \eta\left(\gamma_z + \lambda_3 P_x + \lambda_6 P_y + \lambda_9 P_z\right)}{c_z}.
$$

If we replace the various M_i components in the expressions for $\frac{\partial F}{\partial P_i}$, we will find, for instance, P_x as function of P_y and P_z. To determine the expression for P_x as a function only of the various constants and of the magnetic order parameter η, we need to express P_y and P_z as a function of P_x. After that we can use these results to solve $\frac{\partial F}{\partial P_x} = 0$ as the only function of P_x. We have in total six equations with six variables. This system is solvable exactly. However, the full expression for the various electrical polarization components is very lengthy and complicated. Consequently, in order to simplify the discussion we made a series expansion of P_x, P_y and P_z in terms of η at the second order:

$$
\begin{aligned}
P_x \cong\; & \left(\frac{-\lambda_1}{c_x \kappa_x} H_x + \frac{-\lambda_2}{c_y \kappa_x} H_y + \frac{-\lambda_3}{c_z \kappa_x} H_z\right)\eta \\
& + \left(\frac{-\sigma_x}{\kappa_x} + \frac{\lambda_1 \gamma_x}{c_x \kappa_x} + \frac{\lambda_2 \gamma_y}{c_y \kappa_x} + \frac{\lambda_3 \gamma_z}{c_z \kappa_x}\right)\eta^2;
\end{aligned}
$$

$$
\begin{aligned}
P_y \cong\; & \left(\frac{-\lambda_4}{c_x \kappa_y} H_x + \frac{-\lambda_5}{c_y \kappa_y} H_y + \frac{-\lambda_6}{c_z \kappa_y} H_z\right)\eta \\
& + \left(\frac{-\sigma_y}{\kappa_y} + \frac{\lambda_4 \gamma_x}{c_x \kappa_y} + \frac{\lambda_5 \gamma_y}{c_y \kappa_y} + \frac{\lambda_6 \gamma_z}{c_z \kappa_y}\right)\eta^2
\end{aligned}
\tag{11}
$$

$$
\begin{aligned}
\text{and} \quad P_z \cong\; & \left(\frac{-\lambda_7}{c_x \kappa_z} H_x + \frac{-\lambda_8}{c_y \kappa_z} H_y + \frac{-\lambda_9}{c_z \kappa_z} H_z\right)\eta \\
& + \left(\frac{-\sigma_z}{\kappa_z} + \frac{\lambda_7 \gamma_x}{c_x \kappa_z} + \frac{\lambda_8 \gamma_y}{c_y \kappa_z} + \frac{\lambda_9 \gamma_z}{c_z \kappa_z}\right)\eta^2.
\end{aligned}
$$

From the results of equation (11), we are able to determine the magnetoelectric tensor $[\alpha_{i,j}]$. All the terms of the tensor are non-zero. This is in agreement with the results of [19]. We find a similar result to the case of KMnFeF$_6$, where the various components of the tensor are equal to $\frac{\lambda_k}{c_i \kappa_j}\eta$. This result is equivalent to the one reported in section 2 in the hypothesis of small value of η. In a similar way, there are three non-zero spontaneous magnetization components along the three directions x, y and z ($M_j \neq 0$ for $H_j \neq 0$ in equation (10)). To this electrical polarization induced by the magnetic field (linear magnetoelectric effect), there is another contribution of the induced electrical polarization which results from the coupling to the magnetic order parameter (terms in $\frac{-\sigma_i}{\kappa_i}\eta^2$). We shall discuss these two induced electrical polarization contributions in section 4.

4. Discussion

Using phenomenological Landau analysis, we have shown that for any magnetically ordered pyroelectric materials (= multiferroics) an additional electrical polarization should arise upon cooling through the magnetic ordering temperature. In previous Landau theoretical treatment of magnetically ordered ferroelectrics [11], terms linear in the electrical polarization and quadratic in the magnetic order parameter were not taken into account. However, this kind of term is allowed for any directions along which a spontaneous polarization exists. In various publications terms quadratic in the polarization and in the magnetic order parameter are considered [11–15]. These kinds of terms are expected to have a lower contribution (due to their lower degree) compared to terms like $\frac{-\sigma_i}{\kappa_i} P_i \eta^2$, where η is the magnetic order parameter, κ the inverse dielectric susceptibility and P_i the direction of the spontaneous electrical polarization.

We believe that this kind of term is responsible for the reported additional electrical polarization for YMnO$_3$ and LuMnO$_3$ below their respective Néel temperatures [27, 28]. Lee *et al* explained their results by claiming that they observed the simultaneous condensation of three order parameters, spin (S), lattice (L) displacement, and electric dipole (D) moment [27]. They claimed that $-\alpha S^2 L^2$ and $-L.D$ terms condense at the same temperature, with $T_L = T_S$ for a sufficiently strong spin–lattice interaction strength α. If one considers the literature [11, 13, 15] and our results, we see that this statement is incorrect.

The results given by equations (4) and (11) are similar. If we make a series expansion of P_x and P_y in terms of η to second order, we find analogous expressions for both expressions. While the magnetic order parameter η varies like $\sqrt{T - T_N}$ (mean field approximation), the additional polarization resulting from the coupling term $\sigma_i P_i \eta^2$ varies linearly with the temperature (it is a function of η^2; see equations (6) and (11)). More importantly, this additional polarization arising in the magnetically ordered phase is a function of the dielectric susceptibility. Consequently, the dielectric susceptibility of the material under consideration will be higher as will the additional electrical polarization in the magnetically ordered phase (see equation (11)). This behavior differs from the linear magnetoelectric effect since it does not depend on the magnetic susceptibility [29]. In the light of these considerations, we claim that the observations made for YMnO$_3$ and LuMnO$_3$ are not isolated cases but should be true for any magnetically ordered pyroelectric materials.

5. Conclusion

In conclusion, we use a phenomenological Landau analysis to describe the linear magnetoelectric effect in two multiferroic fluorides, namely KMnFeF$_6$ and Ba$_2$Ni$_7$F$_{18}$. We use the general expression for the free energy of Ba$_2$Ni$_7$F$_{18}$ to discuss in detail the various contributions to the induced polarization. We show that contrary to previous reports the biggest contribution to the additional polarization below the magnetic ordering temperature arises from a term $\sigma_i \eta^2 P_i$,

where η is the magnetic order parameter and P_i is the direction of spontaneous electrical polarization. This additional polarization arising below the magnetic ordering temperature is characteristic of any magnetically ordered pyroelectric material. We show that this induced electrical polarization is proportional to the dielectric susceptibility of the material. Thus one should see a change in the slope of the temperature behavior of the electrical polarization at the magnetic transition with an increase in its absolute value. We expect that this work will stimulate experimental investigations of the above reported fluorides but also of the crystal structure of the magnetoferroelectric materials below their magnetic ordering temperature.

Acknowledgments

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