Phenomenological Landau analysis of predicted magnetoelectric fluorides: KMnFeF$_6$ and Ba$_2$Ni$_7$F$_{18}$

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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 magnetically ordered pyroelectric material 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]. 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 $\theta_T/T_C = 3$. 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 $(x, y, z)$, $\vec{S}_3$ in $(1/2 - x, 1/2 + y, z)$ and $\vec{S}_4$ in $(1/2 + x, 1/2 - y, z)$. The authors defined the
can be shown that the electrical polarization components $P_x$ and $P_z$ of the space group $Pba2$ have to consider the possible terms of the type $\eta \lambda_1 M_x P_y + \lambda_2 M_z P_x = 0$.

The total magnetization of the system is defined by the order parameter $M$. Its components transform like the components of the vector $F$ (tables 1 and 2). Thus $M_x$, $M_y$ and $M_z$ transform like the IRs $\Gamma_4$, $\Gamma_2$ and $\Gamma_3$, respectively.

$\eta$ and $M_z$ both transform as the $\Gamma_4$ IR, thus the lowest coupling term between $\eta$ and $M$ is $\eta M_z$. 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 $F_z$ component of the electrical polarization. Thus the lowest coupling term between the magnetic order parameter $\eta$ and the polarization is $\eta^2 P_z$. For the possible magnetoelastic coupling terms, one has to consider the possible terms of the type $\eta^2 M_z$ [18]. It can be shown that the electrical polarization components $P_x$, $P_y$ and $P_z$ belong, respectively, to the IRs $\Gamma_3$, $\Gamma_4$ and $\Gamma_1$. Looking at the possible $\eta M_z$ and taking into account the above considerations, we can write the free energy for KMnFeF$_6$ in the presence of a magnetic field as:

$$\Phi = \Phi_0 + \frac{a}{2} \eta^2 + \frac{b}{4} \eta^4 + \gamma \eta M_x + \sigma \eta^2 P_z + \sum_{i,j} \frac{\kappa_{ij}}{2} P_j^2$$

$$+ \sum_{i,j} \frac{\epsilon_{ij}}{2} M_j^2 + \lambda_1 \eta P_y M_z + \lambda_2 \eta P_z M_x - \mathbf{M} \cdot \mathbf{H}. \quad (2)$$

We find the partial derivatives of $\Phi$ at the equilibrium conditions:

$$\frac{\partial \Phi}{\partial \eta} = a \eta + b \eta^3 + \gamma M_x + 2 \sigma \eta P_z$$

$$+ \lambda_1 M_x P_y + \lambda_2 M_z P_x = 0$$

$$\frac{\partial \Phi}{\partial P_y} = \kappa_{11} P_y = 0$$

$$\frac{\partial \Phi}{\partial P_z} = \kappa_{22} P_y + \lambda_1 \eta M_z = 0$$

$$\frac{\partial \Phi}{\partial M_x} = c_{11} M_x + \lambda_2 \eta M_z + \gamma \eta - H_z = 0$$

$$\frac{\partial \Phi}{\partial M_y} = c_{22} M_y - H_y = 0$$

$$\frac{\partial \Phi}{\partial M_z} = c_{33} M_z + \lambda_1 \eta P_y - H_z = 0. \quad (3)$$

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 $\frac{\partial \Phi}{\partial P_y}$ and $\frac{\partial \Phi}{\partial P_z}$. We find:

$$P_y = \frac{-\lambda_1}{\kappa_{22}} \eta M_z$$

$$P_z = \frac{-\gamma \eta}{\kappa_{33}} \eta M_z. \quad (4)$$

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

$$M_x = \frac{\kappa_{33} \kappa_{11}}{\kappa_{33} \kappa_{11} - \lambda_2 \eta^2 \gamma} H_z + \eta (\lambda_2 \sigma \eta^2 - \kappa_3 \gamma)$$

$$M_y = \frac{H_y}{c_{22}} \quad (5)$$

$$M_z = \frac{\kappa_{22}}{\kappa_{22} c_{22} - \lambda_1 \eta^2} H_z.$$

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).
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$_2$Ni$_7$F$_{18}$ reported by Lacorre et al. [22], we performed a pseudosymmetry search among all the minimal supergroups of P1 (symmetry exhibited by Ba$_2$Ni$_7$F$_{18}$). Of the minimal supergroups of P1, we determined P$^\top$ was the only pseudosymmetric minimal supergroup. We therefore concluded that the high-temperature paraelectric phase of Ba$_2$Ni$_7$F$_{18}$ 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 $P^\top$ 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$_2$Ni$_7$F$_{18}$. This is can be done using an ionic model by simplifying the electric charge of each ion with a point charge [23].

\[
P_s = \left( \frac{\mu}{V} \right) \sum_{i} m_i Q_i \Delta z_i.
\]

$e$ is the elementary charge, $V$ the unit-cell volume, $m_i$ the multiplicity of the ion, $Q_i$ the ionic charge and $\Delta z_i$ the displacement ion along the polar axis. Having already discussed the hypothetical high-temperature paraelectric phase, we can estimate the displacement $\Delta z_i$ 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 $\| \vec{P} \| \approx 29 \, \mu C \, cm^{-2}$. 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$_2$O$_4$, the ionic model gives an overestimation of $P_z$ by a factor of six compared to the experimental value [24]. Nevertheless, the spontaneous polarization in Ba$_2$Ni$_7$F$_{18}$ 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$_n$Ni$_7$F$_{18}$ ($n = 9$) and Ba$_n$Ni$_7$F$_{18}$ ($n = 21$) which are members of the Ba$_n$M$_n$F$_{12+2n}$ 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$_2$Ni$_7$F$_{18}$ and

1 We notice that this estimation is not possible for K MnFeF$_3$ since in the reported crystal structure [16], the authors fixed the cations on the atomic positions determined in the P$\bar{2}$bc symmetry and not in Pbe2. Consequently a redetermination of the crystal structure of K MnFeF$_3$ is required to investigate properly the coupling between dielectric and magnetic properties.
Table 3. Irreducible representation for the space group $P11'$ associated with $k = (0, 0, 0)$.

| $h_i$ | $h'_i$ |
|-------|--------|
| $\Gamma_1$ | $1$ $-1$ |

Ba$_2$Ni$_4$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 $\eta$ the magnetic order parameter describing the magnetic ordering of Ba$_2$Ni$_4$F$_{18}$. Since there is only one IR (see Table 3) in this case, following similar arguments to those in the case of KMnFeF$_6$, all the coupling terms $\eta M_j$ 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 $\sum_{i,j} \frac{\partial P_j}{\partial \Psi_{1i}}$ and $\sum_i \sigma_i \eta_j P_i$. In addition to these terms, one needs to consider the magnetoelectric coupling terms. All the electrical polarization components transform as the unique $\Gamma_1$ IR. Thus all $\eta P_i M_j$ are allowed. Consequently we can write the free energy for this fluoride as:

$$\Psi = \Psi_0 + \frac{a}{2} \eta^2 + \frac{b}{4} \eta^4 + (\sigma_i P_i + \sigma_x P_x + \sigma_z P_z) \eta^2$$

$$+ \sum_{i,j} \frac{\kappa_{ij}}{2} P_j^2 + \sum_{i,j} \frac{c_{ij}}{2} M_j^2$$

$$+ (\eta_1 M_x + \eta_2 M_y + \eta_3 M_z) \eta + (\lambda_1 P_x M_x + \lambda_2 P_y M_y + \lambda_3 P_z M_z) \eta + (\lambda_4 P_x M_x + \lambda_5 P_y M_y + \lambda_6 P_z M_z + \lambda_7 P_z M_x) \eta$$

$$+ (\lambda_8 P_x M_y + \lambda_9 P_y M_x) \eta - M \cdot H.$$  \hfill (8)

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

$$\frac{\partial \Psi}{\partial \eta} = a \eta + b \eta^3 + 2 \eta (\sigma_x P_x + \sigma_y P_y + \sigma_z P_z)$$

$$+ \eta_1 M_x + \eta_2 M_y + \eta_3 M_z + \lambda_1 P_x M_x + \lambda_2 P_y M_y + \lambda_3 P_z M_z + \lambda_4 P_x M_x + \lambda_5 P_y M_y + \lambda_6 P_z M_z + \lambda_7 P_x M_y + \lambda_8 P_y M_x + \lambda_9 P_y M_x \eta = 0$$

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

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

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

$$\frac{\partial \Psi}{\partial M_x} = c_x M_x + \gamma_1 \eta + (\lambda_1 P_x + \lambda_2 P_y + \lambda_3 P_z) \eta - H_x = 0$$

$$\frac{\partial \Psi}{\partial M_y} = c_y M_y + \gamma_2 \eta + (\lambda_4 P_x + \lambda_5 P_y + \lambda_6 P_z) \eta - H_y = 0$$

$$\frac{\partial \Psi}{\partial M_z} = c_z M_z + \gamma_3 \eta + (\lambda_7 P_x + \lambda_8 P_y + \lambda_9 P_z) \eta - H_z = 0.$$

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:

$$M_x = \frac{H_x - \eta (\gamma_1 P_x + \lambda_1 P_x + \lambda_4 P_y + \lambda_7 P_z)}{c_x}$$

$$M_y = \frac{H_y - \eta (\gamma_2 P_y + \lambda_2 P_y + \lambda_5 P_z + \lambda_8 P_z)}{c_y}$$

$$M_z = \frac{H_z - \eta (\gamma_3 P_z + \lambda_3 P_z + \lambda_6 P_y + \lambda_9 P_x)}{c_z}.$$  \hfill (10)

If we replace the various $M_i$ components in the expressions for $\frac{\partial \Psi}{\partial P_j}$, we will find, for instance, $P_z$ as function of $P_x$ and $P_y$. To determine the expression for $P_z$ as a function of the various components and of the magnetic order parameter $\eta$, we need to express $P_x$ and $P_y$ as a function of $P_z$. After that we can use these results to solve $\frac{\partial \Psi}{\partial P_j} = 0$ as the only function of $P_z$. 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 $\eta$ starting at second order:

$$P_x \cong \left( \frac{-\lambda_2 H_y - \lambda_3 H_z}{c_x k_x} + \frac{\lambda_7 H_z}{c_y k_x} + \frac{\lambda_9 H_z}{c_z k_x} \right) \eta^2$$

$$+ \left( -\alpha_\kappa \frac{k_y}{k_z} + \frac{\lambda_1}{k_x} + \frac{\lambda_8}{k_y} + \frac{\lambda_9}{k_z} \right) \eta^3;$$

$$P_y \cong \left( \frac{-\lambda_4 H_x - \lambda_5 H_z}{c_y k_y} + \frac{\lambda_7 H_x}{c_z k_y} + \frac{\lambda_9 H_x}{c_z k_y} \right) \eta^2$$

$$+ \left( -\alpha_\kappa \frac{k_x}{k_z} + \frac{\lambda_2}{k_y} + \frac{\lambda_3}{k_y} + \frac{\lambda_6}{k_z} \right) \eta^3;$$

and

$$P_z \cong \left( \frac{-\lambda_3 H_x - \lambda_5 H_y}{c_z k_z} + \frac{\lambda_7 H_y}{c_z k_z} + \frac{\lambda_9 H_y}{c_z k_z} \right) \eta^2$$

$$+ \left( -\alpha_\kappa \frac{k_x}{k_z} + \frac{\lambda_2}{k_z} + \frac{\lambda_3}{k_z} + \frac{\lambda_4}{k_z} \right) \eta^3.$$

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 $\frac{\alpha_{i,j}}{\kappa_{i,j}}$. This result is equivalent to the one reported in section 2 in the hypothesis of small value of $\eta$. 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 $H_i \neq 0$ 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 $\frac{\partial \Psi}{\partial M_j} \eta^3$). 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 (\(\equiv\) 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 \(\frac{1}{2} P_i \eta^2\), where \(\eta\) is the magnetic order parameter, \(\kappa\) 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 \(\alpha\). 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 \(P_c\) and \(P_s\) in terms of \(\eta\) to second order, we find analogous expressions for both expressions. While the magnetic order parameter \(\eta\) varies like \(\sqrt{T - T_N}\) (mean field approximation), the additional polarization resulting from the coupling term \(\sigma, P_i \eta^2\) varies linearly with the temperature (it is a function of \(\eta^2\); 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\(_2\)F\(_8\). We use the general expression for the free energy of Ba\(_2\)Ni\(_2\)F\(_8\) 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 \(\sigma, \eta^2 P_i\), where \(\eta\) 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.

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