Chapter 6

Predictions for new magnetoelectrics/multiferroics

6.1 Introduction

In the recent years, there has been a renewed interest in the coexistence and interplay of magnetism and electrical polarization [1, 2, 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. In the Landau theory framework, multiferroics which are not magnetoelectric present at least a coupling of the type $P^2M^2$ ($P$: polarization, $M$: total magnetization) while linear magnetoelectrics are characterized by terms like $PM^2$ or LMP ($L$: antiferromagnetic order parameter) [4]. Terms like $P^2M^2$ are of higher degree than $PM^2$ or LMP terms. Consequently, we expect a stronger interplay between dielectric and magnetic properties in linear magnetoelectrics than in multiferroics. Other coupling terms can also characterize the magnetoelectric effect. They are discussed by Harris [5].

In the search for materials presenting a strong coupling of magnetism and polarization, the most promising ones are multiferroics materials presenting linear magnetoelectric properties. These materials are scarce. Thus, it is also of interest to look for new magnetoelectric materials by itself.

The recent efforts have been concentrated on two main ideas: magnetic frustration and breaking of the inversion center due to an antiferromagnetic ordering. These approaches have been generated by the ideas on one side of Katsura [6] and of Sergienko [7] and on the other side of Mostovoy [8]. They 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 Dzialoshinskii-Moriya (DM) interaction contrary to typical magnetoelectric compound such as Cr$_2$O$_3$ [9]. Most of the recent research on multiferroics concerns centrosymmetric oxides [11]. These materials present a breaking of the symmetry giving rise to a spontaneous polarization which may be reversible by application of a magnetic field. However, the investigation of possible polar structures induced by antiferromagnetic ordering is known since about 35 years [13]. The authors of ref. [13] proposed already BiMn$_2$O$_5$ as possible multiferroic which is nowadays one of the most studied families. The idea of using symmetry analysis to predict magnetoelectric compounds is not new. The first reported magnetoelectric compound Cr$_2$O$_3$ was predicted to be magnetoelectric prior to any experimental evidence [12]. Nevertheless, we use symmetry analysis in order to illustrate the usefulness of it by predicting several materials exhibiting possible multiferroic and magnetoelectric properties.

In addition, one can notice that the magnetic point groups do not give information regarding magnetic frustration. The magnetic frustration is strongly correlated to the crystal structure. This is an important and obvious point, however often overlooked. The inversion center breaking due to antiferromagnetic ordering is intrinsic to the symmetry properties of the spins. Thus, the fact that the structure remains centrosymmetric in the magnetically ordered phase is also strongly related to the crystal structure. This will be illustrated in section 6.4.

In the present chapter, we present a symmetry analysis of selected materials. All these materials should present 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 a selection of this list.

### 6.2 Study of selected fluorides

We present in this part our investigation of selected fluorides. We chose this family as an illustration for magnetic frustration as an important component for magnetoelectricity. Moreover, we cannot have polarization in conducting materials. Thus, the high charge transfer in these materials make them good candidates for experimental investigations. Several fluorides were reported to crystallize in a polar structure. Consequently, in addition to magnetoelectric properties, several fluorides are potentially ferroelectric. Experimental examples of magnetic frustration [14] are still rather scarce [15]. Among them, the most common case is provided by the triangular plane lattice with antiferromagnetic interactions, which has been extensively studied, from a theoretical point of view. This geometry leads to three antiferromagnetic
sublattices oriented at 120° to each other. Among these materials, several fluorides have shown to exhibit magnetic frustration. We focus here on several of them. They have been the subject of detailed crystallographic and magnetic studies by means of neutron diffraction. Depending on their structure, they present a high or low degree of magnetic frustration. Several of these fluorides are possibly magnetoelectric multiferroic materials based on symmetry analysis.

### 6.2.1 Study of $\alpha$-KCrF$_4$

$\alpha$-KCrF$_4$ is the first in the selected fluorides we are going to present on magnetically frustrated fluorides with possible magnetoelectric properties. The crystal structure of $\alpha$-KCrF$_4$ is orthorhombic (space group $Pnma$ (n°62), $a = 15.76$ Å, $b = 7.43$ Å, $c = 18.38$ Å). It consists of infinite columns of CrO$_6$ octahedra sharing edges along the $b$ axis (see figure 6.1) [16].

![Crystal structure of KCrF$_4$ projected along b (left) and c axis (right).](image)

This compound is the most frustrated of the fluorides. It orders antiferromagnetically only under $T_N = 4$ K with a quasi 1D behavior. We present in figure 6.2 a representation of the magnetic structure as determined from neutron scattering [17].

There are three inequivalent Cr$^{3+}$ ions per unit cell and occupying 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):
Lacorre and collaborators have investigated also the transformation properties of the different components of the magnetic vectors. We reproduce in table 6.1 the results of their derivations [17].

Let’s have a look at the possible LMP terms allowed by symmetry. These terms are the signature of the linear magnetoelectric effect. For this, we need to know what are the transformation properties of the polarization components. Here once more, it is sufficient to look at the effect of the generators of the space group. In table 6.2, we present the transformation properties of the polarization components.

According to the tables 6.1 and 6.2, 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

$$\vec{M} = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \vec{S}_4 + \vec{S}_5 + \vec{S}_6 + \vec{S}_7 + \vec{S}_8$$
$$\vec{L}_1 = \vec{S}_1 - \vec{S}_2 + \vec{S}_3 - \vec{S}_4 + \vec{S}_5 - \vec{S}_6 + \vec{S}_7 - \vec{S}_8$$
$$\vec{L}_2 = \vec{S}_1 + \vec{S}_2 - \vec{S}_3 - \vec{S}_4 + \vec{S}_5 + \vec{S}_6 - \vec{S}_7 - \vec{S}_8$$
$$\vec{L}_3 = \vec{S}_1 - \vec{S}_2 - \vec{S}_3 + \vec{S}_4 + \vec{S}_5 - \vec{S}_6 - \vec{S}_7 + \vec{S}_8$$
$$\vec{L}_4 = \vec{S}_1 + \vec{S}_2 + \vec{S}_3 + \vec{S}_4 - \vec{S}_5 - \vec{S}_6 - \vec{S}_7 - \vec{S}_8$$
$$\vec{L}_5 = \vec{S}_1 - \vec{S}_2 + \vec{S}_3 - \vec{S}_4 + \vec{S}_5 + \vec{S}_6 - \vec{S}_7 + \vec{S}_8$$
$$\vec{L}_6 = \vec{S}_1 + \vec{S}_2 - \vec{S}_3 - \vec{S}_4 - \vec{S}_5 + \vec{S}_6 + \vec{S}_7 + \vec{S}_8$$
$$\vec{L}_7 = \vec{S}_1 - \vec{S}_2 - \vec{S}_3 + \vec{S}_4 - \vec{S}_5 + \vec{S}_6 + \vec{S}_7 - \vec{S}_8$$

(6.1)

Figure 6.2: Magnetic structure of KCrF$_4$ in the (a,c) plane. Arrows indicate the magnetic moments on the chromium atoms with a quasi-120° configuration.
6.2. Study of selected fluorides

Table 6.1: Magnetic components classified by IR.

<table>
<thead>
<tr>
<th>IR</th>
<th>Magnetic components</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_1)</td>
<td>(L_{1x}, L_{2y}, L_{3z})</td>
</tr>
<tr>
<td>(\Gamma_2)</td>
<td>(M_x, L_{3y}, L_{2z})</td>
</tr>
<tr>
<td>(\Gamma_3)</td>
<td>(L_{2x}, L_{1y}, M_z)</td>
</tr>
<tr>
<td>(\Gamma_4)</td>
<td>(L_{3z}, M_y, L_{4z})</td>
</tr>
<tr>
<td>(\Gamma_5)</td>
<td>(L_{5x}, L_{6y}, L_{7z})</td>
</tr>
<tr>
<td>(\Gamma_6)</td>
<td>(L_{4x}, L_{7y}, L_{6z})</td>
</tr>
<tr>
<td>(\Gamma_7)</td>
<td>(L_{6x}, L_{5y}, L_{4z})</td>
</tr>
<tr>
<td>(\Gamma_8)</td>
<td>(L_{7x}, L_{4y}, L_{5z})</td>
</tr>
</tbody>
</table>

Table 6.2: Transformation properties of the polarization components for the space group Pnma1' associated to \(k = 0\).

<table>
<thead>
<tr>
<th></th>
<th>(2_{1x})</th>
<th>(2_{1z})</th>
<th>(T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(P_x)</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(P_y)</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>(P_z)</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

6.2.2 Study of KMnFeF\(_6\)

The fluoride KMnFeF\(_6\) presents 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 [18]. The family of tetragonal tungsten bronze and related ones have been extensively investigated due to their ferroelectric properties [19]. This compound crystallizes in the space group Pba2 (n°32), where 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 \(ab\) plane, Mn and Fe ions alternate along the \(c\) axis. The magnetic structure is presented in figure 6.3 [18]. Although the ferroelectricity transition has not been investigated to our knowledge, this compound should present a multiferroic character below...
Although presenting magnetic frustration, the compound KMnFeF$_6$ orders ferromagnetically below $T_C = 148$ K with a ratio $\Theta/T_C = 3$. 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 6.5 [18, 20].

<table>
<thead>
<tr>
<th>Modes</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Magnetic space groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td>$G_x$</td>
<td>$A_y$</td>
<td>$C_z$</td>
<td>$Pba2$</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>$C_x$</td>
<td>$F_y$</td>
<td>$G_z$</td>
<td>$Pba'2'$</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>$A_x$</td>
<td>$G_y$</td>
<td>$F_y$</td>
<td>$Pb'a'2$</td>
</tr>
<tr>
<td>$\Gamma_4$</td>
<td>$F_x$</td>
<td>$C_y$</td>
<td>$A_y$</td>
<td>$Pb'a2'$</td>
</tr>
</tbody>
</table>

Table 6.3: Irreducible representations for the space group $Pba2'$ associated to $k=0$.

The neutron data show that the best model for the magnetic structure is given by the $\Gamma_4$ mode. The corresponding magnetic space group is thus $Pb'a2'$ which has the magnetic point group $m'm2'$. According to table 2.4, we have a linear magnetoelectric effect which is allowed having the following allowed terms (after transformation of the coordinates system):

$$[\alpha_{ij}] = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{23} \\ 0 & \alpha_{32} & 0 \end{pmatrix}$$
6.2. Study of selected fluorides

We remind that KMnFeF$_6$ presents a polar structure and is likely to be ferroelectric. Consequently, KMnFeF$_6$ is a multiferroic material which presents 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 presenting such properties. Under 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 $\alpha_{23}$) and vice versa (term $\alpha_{32}$).

6.2.3 Study of 2 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. P. Lacorre and coworkers 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 [21, 22]. 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 Ba$_2$Ni$_7$F$_{18}$ compounds. These compounds have been investigated by means of powder neutron diffraction at room and low temperatures.

Let’s have a look first at the Ba$_2$Ni$_3$F$_{10}$ material. This compound crystallizes in the space group $C2/m$ ($n^\circ12$) containing 3 different Ni$^{2+}$ per unit cell. 2 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 wave-vector $\overrightarrow{k}=(0,0,1/2)$. All the (hkl) magnetic reflections do not satisfy the C-centering of the chemical cell but a primitive lattice. P. Lacorre and collaborators have shown that the magnetic space group is $P2/m'$ where 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 table 2.4, a linear magnetoelectric effect is allowed having the following expression:

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

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$_2$Ni$_7$F$_{18}$ crystallizes in the polar space group P1 ($n^\circ1$) 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 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 present magnetic frustrations, it is not the case in this compound. We mean there is no competition between next nearest neighbors. However, we have a non collinear magnet most probably due to the allowed DM interaction. All the new magnetic reflections can be indexed in the same cell as the chemical one. Consequently, the star of the magnetic wave-vector has only one arm. Thus, we have the following IR:

$$
\begin{array}{c|c}
\Gamma_1 & h_1 \\
\end{array}
$$

Table 6.4: *Irreducible representation for the space group P11’ associated to $k=(0, 0, 0)$.*

According to the table 6.4, there is only one possibility for the magnetic space group which is P1. Following the table 2.4, a linear magnetoelectric effect is allowed with non-zero components:

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

Consequently, Ba$_2$Ni$_7$F$_{18}$ 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 $T_C$.

### 6.2.4 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-4c2 (n°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 wave-vector $\vec{k} = 0$ [23]. This structure is also magnetically frustrated due the presence of ferromagnetic interactions within an antiferromagnetic plane as described in figure 6.4.

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$\textsubscript{4}$ is I-4$'$. The corresponding magnetic point group is -4$'$. If one compares this magnetic point group with the ones listed in table 2.4, we observe that a linear magnetoelectric effect is possible along several directions:

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

Here a probable DM is responsible for the magnetoelectric effect although it has not been reported experimentally. This is probably due to the too low deviation from collinearity along the c axis.

In conclusion, we have shown from symmetry analysis that several fluorides may present a multiferroic character coupled to an induced polarization under the application of a magnetic field. Most of them present 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. While the mechanism for potential ferroelectricity remains to be investigated, the associated magnetoelectric effect is presumably due to the DM interaction (including the non multiferroic cases).
6.3 Other materials of interest

6.3.1 Introduction

We present in this section, compounds already known as potential materials of technological importance. LiFeP$_2$O$_7$ is a material considered for Li battery while Sr$_2$CoSi$_2$O$_7$ is considered as a good candidate for lasers. We want to emphasize with these two examples the possibility for additional interesting properties (i.e. magnetoelectricity) in already known materials.

6.3.2 LiFeP$_2$O$_7$

Introduction

Compositions with general formula LiMX$_2$O$_7$ (M = Fe, V; X = P, As) have been widely investigated in the 90’s but also nowadays for their interesting crystal chemistry and more recently for their potential application as electrode materials. The transition metal ion is surrounded by six oxygens forming an octahedron [27]. In LiFeP$_2$O$_7$, iron atoms are connected through super-super exchange paths involving diphosphate groups which may present interesting magnetic properties. LiFeP$_2$O$_7$ crystallizes in a polar structure described by the space group P2$_1$. It is a remarkable feature since most of the AMP$_2$O$_7$ family members crystallizes in the non-polar space group P2$_1$/c. Many of these materials experience a transition from P2$_1$/c to P2$_1$/c with an enlargement of the unit cell above RT. Thus, we can reasonably expect that LiFeP$_2$O$_7$ may undergo a phase transition towards a centrosymmetric structure. Depending on the IR involved in the transition we will have a proper or an improper ferroelectric. While the magnetic properties of the parent compound NaFeP$_2$O$_7$ have been widely studied, LiFeP$_2$O$_7$ has been the subject of few studies. Among these ones, G. Rousse and collaborators have been investigating the magnetic structure using neutron diffraction on a powder sample [27]. The magnetic structure is presented in figure 6.5.

Magnetic ordering

The compound LiFeP$_2$O$_7$ crystallizes in the space group P2$_1$ (n°4) where there is only one Fe$^{3+}$ per asymmetric unit cell occupying the Wyckoff position 2a. Consequently, there are two Fe atoms per unit cell at (x, y, z) (carrying $S_1$ moment) and (-x, y+1/2, -z) (carrying $S_2$ moment).

Consequently, we can define 2 magnetic vectors:
Figure 6.5: Crystal and magnetic structures of LiFeP$_2$O$_7$ in the (a,c) plane. Arrows indicate the magnetic moments on the iron atoms (mostly along the a axis). The iron atoms are represented in black within oxygen octahedra. The dimers with corner shared oxygen contain the phosphorus atoms.

The space group P2$_1$ contains only two symmetry elements: the identity 1 and a 2 fold screw axis 2$_1$ that we will denote $h_1$ and $h_2$, respectively. The expressions of these two symmetry elements are:

\[
\begin{align*}
M &= S_1 + S_2 \\
L &= S_1 - S_2
\end{align*}
\]

The magnetic order appearing under $T_N = 22$K is described by $\vec{k} = 0$. Consequently, the irreducible representations associated with this wave-vector are the same as the ones of point group 2 (see table 6.5).

In order to know which components of the different magnetic vectors belong to which IR, we need to look at the effect of the symmetry elements on the position of the atoms.
Table 6.5: Irreducible representations for the space group \(P2_11'\) associated to \(k=0\).

\[
\begin{array}{cccc}
\Gamma_1 & h_1 & h_2 & \text{Rh}_1 \\
1 & 1 & -1 & -1 \\
\Gamma_2 & 1 & -1 & -1 & 1
\end{array}
\]

From the example described above, we can find all the transformations properties of the atoms. These results are presented in table 6.6. Using tables 6.5 and 6.6, we can determine to which IR belong each magnetic compounds. We present the results in table 6.7.

Table 6.6: Transformation properties of the symmetry elements on the Wyckoff positions 2a in the space group \(P2_1\).

<table>
<thead>
<tr>
<th>(h_1)</th>
<th>(h_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>((x, y, z))</td>
<td>((-x, y+1/2, -z))</td>
</tr>
<tr>
<td>((-x, y+1/2, -z))</td>
<td>((x, y, z))</td>
</tr>
</tbody>
</table>

The results of table 6.7 allow us to construct the Landau free-energy, separating the exchange and magnetic anisotropy energies. Due to the magnitude of the two contributions, we write the exchange terms up to the fourth degree and the relativistic terms up to the second degree (see equation 6.4).

Table 6.7: Components of the \(\mathbf{M}\) and \(\mathbf{L}\) vectors which form a basis for the IR of \(P2_11'\) at \(k=0\).

<table>
<thead>
<tr>
<th>(\Gamma_1)</th>
<th>(L_x, L_z, M_y)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_2)</td>
<td>(L_y, M_x, M_z)</td>
</tr>
</tbody>
</table>

\[
F = F_0 + \frac{a}{2} L^2 + \frac{b}{4} L^4 + \frac{c}{2} M^2 + \frac{d}{4} M^4 \\
+ \frac{1}{2} \sum_{i=x,y,z} (\nu_i L_i^2 + \beta_i M_i^2) \\
+ \delta L_x L_z + \gamma M_x M_z \\
+ \sigma_1 L_x M_y + \sigma_2 L_z M_y + \sigma_3 L_y M_z + \sigma_5 L_y M_x \\
+ \frac{\alpha}{2} P^2 + \beta L_x L_z P_y 
\] (6.4)
The first line in equation 6.4 represents the exchange energy. It is formed from the scalar products $ \mathbf{L}^2 = \mathbf{L} \cdot \mathbf{L} $ and $ \mathbf{M}^2 = \mathbf{M} \cdot \mathbf{M} $. The other lines correspond to the relativistic terms. We have separated in the magnetic anisotropy term the $ \delta $ which couples different antiferromagnetic components $ L_i $, from the $ \sigma_j $ terms which couple the total magnetization components $ M_i $ to the $ L_i $. $ \gamma $ term couples the total magnetization components $ M_x M_z $. The last line corresponds to the polar state of the structure. We are now able to discuss in a complete manner the type and nature of the magnetic order which arise below $ T_N $.

- First approximation: we neglect the coupling terms involving the total magnetization. This approximation is justified by the fact that no ferromagnetic component has been observed experimentally. We can rewrite the free energy as:

$$ F = F_0 + \frac{a}{2} L_x^2 + \frac{b}{4} L_z^4 + \frac{1}{2} \sum_{i=x,y,z} (\nu_i L_i^2) + \frac{\alpha}{2} P^2 + \beta L_x L_z P_y $$

Minimization of $ F $ gives:

$$ \frac{\partial F}{\partial L_x} = a L_x + b L_x^3 + \nu_x L_x + \beta L_z P_y = 0 $$
$$ \frac{\partial F}{\partial L_z} = a L_z + b L_z^3 + \nu_z L_z + \beta L_x P_y = 0 $$
$$ \frac{\partial F}{\partial P_y} = \alpha P_y + L_x L_z = 0 $$

From the last line of equation 6.6, we find that $ P_y = -\frac{1}{\alpha} L_x L_z $. Replacing $ P_y $ by its expression in $ L_x $ and $ L_z $, we find the magnetic structure observed by G. Rousse et al. [27]:

$$ L_x^2 = \frac{ab}{\alpha} + ab + b \nu_x + \nu_z $$
$$ L_z^2 = \frac{ab}{\alpha} + ab + b \nu_z + \nu_x $$

Magnetoelectric properties

Now that we have described the magnetic ordering, we will have a look at the possible magnetoelectric properties. In order to determine LMP coupling terms allowed by symmetry, we derive table 6.8. Table 6.8 is
### Table 6.8: Transformation properties of the components of the different vectors of interest for the space group $P2_11'$ associated to $k=0$. 

<table>
<thead>
<tr>
<th></th>
<th>$h_1$</th>
<th>$h_2$</th>
<th>Rh$_1$</th>
<th>Rh$_2$</th>
</tr>
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<tbody>
<tr>
<td>$L_x$</td>
<td>1</td>
<td>1</td>
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<td>-1</td>
</tr>
<tr>
<td>$L_y$</td>
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</tr>
<tr>
<td>$L_z$</td>
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</tr>
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<td>$P_x$</td>
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<td>$P_z$</td>
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</tbody>
</table>

From Table 6.8, we notice that a certain number of terms of LMP type are allowed. Keeping in mind that the magnetic structure is described by magnetic components along $x$ and $z$, the terms of interest are: $L_xM_xP_x$, $L_xM_yP_y$ and $L_zM_zP_z$. Consequently, we can write a new expression for the free energy including the magnetoelectric coupling terms given in eq. 6.8. We do not include term like $P^4$ since we are interested here in the magnetic ordered phase.

$$F = F_0 + a \frac{L^2}{2} + b \frac{L^4}{4} + \lambda_1 L_xM_xP_x + \lambda_2 L_xM_yP_y + \lambda_3 L_zM_zP_z$$

(6.8)

Bilinear terms like $L_iM_j$ are not considered because they cannot give rise to polarization. If we minimize equation 6.8, we find:
\[
\frac{\partial F}{\partial L_x} = a L_x + b L_x^3 + \lambda_1 M_x P_x + \lambda_2 M_y P_y \\
\frac{\partial F}{\partial L_y} = a L_y + b L_y^3 \\
\frac{\partial F}{\partial L_z} = a L_z + b L_z^3 + \lambda_1 M_z P_z \\
\frac{\partial F}{\partial M_x} = \lambda_1 L_x P_x + \frac{M_x}{\chi_{xx}} \\
\frac{\partial F}{\partial M_y} = \lambda_2 L_x P_y + \frac{M_y}{\chi_{yy}} \\
\frac{\partial F}{\partial M_z} = \lambda_3 L_x P_z + \frac{M_z}{\chi_{zz}} \\
\frac{\partial F}{\partial P_x} = \lambda_1 L_x M_x + \frac{P_x}{\kappa_{xx}} \\
\frac{\partial F}{\partial P_y} = \lambda_2 L_x M_y + \frac{P_y}{\kappa_{yy}} \\
\frac{\partial F}{\partial P_z} = \lambda_3 L_x M_z + \frac{P_z}{\kappa_{zz}}
\]

From equation 6.9, we can find two series of equalities:

\[
P_x = -\kappa_{xx} \lambda_1 L_x M_x \\
P_y = -\kappa_{yy} \lambda_2 L_x M_y \\
P_z = -\kappa_{zz} \lambda_3 L_x M_z
\]

and

\[
M_x = -\chi_{xx} \lambda_1 L_x P_x \\
M_y = -\chi_{yy} \lambda_2 L_x P_y \\
M_z = -\chi_{zz} \lambda_3 L_x P_z
\]

Using eq. 6.11 to put in eq. 6.10, we find that there is no polarization possible irrespective of the magnetic order (paramagnetic or antiferromagnetic):

\[
P_x(1 - \kappa_{xx} \chi_{xx} \lambda_1^2 L_x^2) = 0 \\
P_y(1 - \kappa_{yy} \chi_{yy} \lambda_2^2 L_x^2) = 0 \\
P_z(1 - \kappa_{zz} \chi_{zz} \lambda_3^2 L_x^2) = 0
\]

However, we shall see that equation 6.12 is true only in the absence of a magnetic field. Let’s imagine that one applies a magnetic field $H$ on cooling
trough \( T_N \). In this case, we can take back the equation 6.8 to which we are going to add a \( \mathbf{M} \cdot \mathbf{H} \) term. This is given in eq. 6.13.

\[
F = F_0 + \frac{a}{2} L^2 + \frac{b}{4} L^4 + \lambda_1 L_x M_x P_x + \lambda_2 L_x M_y P_y + \lambda_3 L_z M_z P_z + \frac{M^2}{2\chi} + \frac{P^2}{2\kappa} - M \cdot H
\]  

(6.13)

This time, if we minimize 6.13, we find a different expression for the minima:

\[
\frac{\partial F}{\partial L_x} = a L_x + b L_x^3 + \lambda_1 M_x P_x + \lambda_2 M_y P_y
\]
\[
\frac{\partial F}{\partial L_y} = a L_y + b L_y^3
\]
\[
\frac{\partial F}{\partial L_z} = a L_z + b L_z^3 + \lambda_1 M_z P_z
\]
\[
\frac{\partial F}{\partial M_x} = \lambda_1 L_x P_x + \frac{M_x}{\chi_{xx}} - H_x
\]
\[
\frac{\partial F}{\partial M_y} = \lambda_2 L_x P_y + \frac{M_y}{\chi_{yy}} - H_y
\]
\[
\frac{\partial F}{\partial M_z} = \lambda_3 L_z P_z + \frac{M_z}{\chi_{zz}} - H_z
\]
\[
\frac{\partial F}{\partial P_x} = \lambda_1 L_x M_x + \frac{P_x}{\kappa_{xx}}
\]
\[
\frac{\partial F}{\partial P_y} = \lambda_2 L_x M_y + \frac{P_y}{\kappa_{yy}}
\]
\[
\frac{\partial F}{\partial P_z} = \lambda_3 L_z M_z + \frac{P_z}{\kappa_{zz}}
\]  

(6.14)

From 6.13, we get new values for the total magnetization components while the polarization components are unchanged:

\[
P_x = -\kappa_{xx} \lambda_1 L_x M_x
\]
\[
P_y = -\kappa_{yy} \lambda_2 L_x M_y
\]
\[
P_z = -\kappa_{zz} \lambda_3 L_z M_z
\]  

(6.15)

and

\[
M_x = -\chi_{xx} \lambda_1 L_x P_x + H_x
\]
\[
M_y = -\chi_{yy} \lambda_2 L_x P_y + H_y
\]
\[
M_z = -\chi_{zz} \lambda_3 L_z P_z + H_z
\]  

(6.16)
Using 6.16 to put in 6.15, we find that there is an induced polarization possible if a magnetic field is applied along a given direction:

\[
P_x = \frac{-\kappa_{xx} \chi_{xx} \lambda_1 L_x}{1 - \kappa_{xx} \chi_{xx} \lambda_1^2 L_x^2} H_x \\
P_y = \frac{-\kappa_{yy} \chi_{yy} \lambda_2 L_y}{1 - \kappa_{yy} \chi_{yy} \lambda_2^2 L_y^2} H_y \\
P_z = \frac{-\kappa_{zz} \chi_{zz} \lambda_3 L_z}{1 - \kappa_{zz} \chi_{zz} \lambda_3^2 L_z^2} H_z
\]

From equation 6.17, we can predict the appearance of a finite polarization along the three direction of the crystal under the application of a magnetic field. This induced polarization by a magnetic field is the characteristic of linear magnetoelectricity. We develop a Landau theoretical model where we investigate the couplings of the induced polarization in the multiferroic LiFeP$_2$O$_7$ system below $T_N=22$K. Experiments are required to investigate the likely ferroelectric state at RT and study the interplay between polarization and magnetism.

### 6.3.3 Sr$_2$CoSi$_2$O$_7$

**Introduction**

During the last years, several studies investigated the 3d$^2$ transition metal ions in tetrahedral environment [28]. These compounds are particularly interesting for their potential application for infrared Lasers ($\lambda = 1$-1.5 $\mu$m). In a tetrahedral coordination, the probability of radiative transition of these ions is significantly increased by the absence of crystallographic inversion center. There are several possible approaches in order to stabilize 3d$^2$ ions in tetrahedral coordination. The ideal situation would be realized by a structure consisting of only tetrahedra. The melilite family with the general formula $X_2T^1T^2_2O_7$ ($X = Na, Ca, Sr$ or Ba; $T^1 = Mg, Co, Fe$ or Al; $T^2 = Al, Si$ or Ge) is very close to this optimal situation ($T^2_2O_7$ dimers linked between each other by $T^1$O$_4$ tetrahedra). These compounds present particularly rich magnetic and structural properties. One of the few magnetic studies which have been carried out in this family concerns the compound Sr$_2$CoSi$_2$O$_7$. This compound crystallizes in the non polar space group $P-42_1m$ (n’113). An antiferromagnetic order of the Co$^{2+}$ ions appears below $T_N = 7.5$ K and is characterized by a magnetic wave-vector $\vec{k} = (0,0,0)$ [29]. Many models for the magnetic structure have been tested. The best model to describe the neutron data measured at 1.5 K consists of an antiferromagnetic ordering with moments along the $c$ crystallographic axis. We
will show that the magnetoelectric effect is allowed in the proposed anti-ferromagnetic model. The crystal and magnetic structures are presented in figure 6.6

![Crystal and magnetic structures](image)

Figure 6.6: Crystal and magnetic structures of $\text{Sr}_2\text{CoSi}_2\text{O}_7$ in the (a,b) and (a,c) planes. Arrows indicate the magnetic moments on the cobalt atoms (along the c axis). Dark grey atoms represent cobalt atoms linked by tetrahedral dimers of $\text{Si}_2\text{O}_7^{6+}$. Sr atoms are not represented for sake of clarity.

**Representation analysis of the magnetic structures**

There are 2 magnetic atoms Co$^{2+}$ per unit cell occupying the Wyckoff position 2a. There are 2 Co atoms per unit cell at (0,0,0) and at (1/2,1/2,0). As stated previously, below $T_N=7.5\text{K}$, the magnetic structure is characterized by $\vec{k} = \vec{0}$. In other words, the magnetic and chemical cells are identical. Consequently, the wave-vector associated with the magnetic structure $\vec{k} = \vec{0}$ has the full point group symmetry of the point group of $P-42_{1}m$. The underlying point group is -42m ($D_{2d}$). Table 6.9 reproduces the characters of this point group.

<table>
<thead>
<tr>
<th>$\Gamma$</th>
<th>E</th>
<th>$C_2$</th>
<th>$2S_4$</th>
<th>$2C'_{2}$</th>
<th>$2\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_2$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_3$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\Gamma_4$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_5$</td>
<td>2</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 6.9: Irreducible representations for the space group $P-42_{1}m$ associated with $k=0$.

We will first determine the directions of the spins associated with each IR. For that we need to derive the axial and permutational representations
of each symmetry element. The symmetry elements are the following of \( P-42 \_1m \):

\[
1 = \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}, \quad -4^+ = \begin{pmatrix} 0 & 1 & 0 & 0 \\ -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}
\]

\[
2_{1z} = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad -4^- = \begin{pmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \end{pmatrix}
\]

\[
m_{xy} = \begin{pmatrix} 0 & 1 & 0 & 1/2 \\ 1 & 0 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \\ -1 & 0 & 0 & 1/2 \end{pmatrix}, \quad 2_{1y} = \begin{pmatrix} -1 & 0 & 0 & 1/2 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & 0 & -1 \end{pmatrix}
\]

\[
m_{xy} = \begin{pmatrix} 0 & -1 & 0 & 1/2 \\ -1 & 0 & 0 & 1/2 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}, \quad 2_{1x} = \begin{pmatrix} 1 & 0 & 0 & 1/2 \\ 0 & -1 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \end{pmatrix}
\]

We are dealing here with atoms at \((0,0,0)\) (atom 1) and \((1/2,1/2,0)\) (atom 2). Consequently, all the symmetry elements having a non-zero translation part will send atom 1 on atom 2 and vice-versa. This is not the case for the other symmetry elements which will not exchange atoms. The permutation representations \( \Gamma_{\text{perm}}(h_j) \) of half of the different symmetry elements is common. We have:

\[
\Gamma_{\text{perm}}(1) = \Gamma_{\text{perm}}(-4^+) = \Gamma_{\text{perm}}(2_{1z}) = \Gamma_{\text{perm}}(-4^-) \quad \text{and} \quad \Gamma_{\text{perm}}(m_{xy}) = \Gamma_{\text{perm}}(m_{xy}) = \Gamma_{\text{perm}}(2_{1x}) = \Gamma_{\text{perm}}(2_{1y})
\]

The corresponding expression for the permutation representations \( \Gamma_{\text{perm}}(h_j) \) is given below:

\[
\Gamma_{\text{perm}}(1) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}, \quad \text{and} \quad \Gamma_{\text{perm}}(m_{xy}) = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}
\]

If \( g_i \) is a symmetry operation of a crystallographic space group \( G \), we can describe the action of \( g_i \) on a spin vector (axial vector) \( S_j \) as:

\[
g_i S_j = \sum_k D_{kj}(g_i) S_k
\]

Here the matrix \( D(g_i) \) is the transpose of the transformation matrix of the spins. The set of matrices \( D(g_i) \) of the crystallographic space group \( G \) form a representation \( \Gamma \) of the space group \( G \). \( \Gamma \) of dimension \( 3n \) is generally reducible. After reduction, we can use the technique of the projection
operators in order to determine the basis vectors of the irreducible representations $\Gamma^{(\nu)}$ according to:

$$a^{(\nu)} = d^{-1} \sum_{G_i} \chi^\Gamma(G_i) \chi^{(\nu)*}(G_i)$$

$$\Psi^{(\nu)}_{ij} = \sum_{G_i} D^{(\nu)}_{ij}(G_i) G_i \Psi$$  \hspace{1cm} (6.21)

Applying this approach to our case, we find:

$$\Gamma = \Gamma_1 + \Gamma_2 + 2\Gamma_5$$

One needs now to work out the base vectors of each of these IR's. Using the projector technique, we find the following $P^j_i$ projectors associated to the $\Gamma_i$ IR:

$$P^1 = (1) + (-4^+)(2_{1z}) + (-4^-) + (m_{xy}) + (2_{1y}) + (m_{xy}) + (2_{1x})$$
$$P^2 = (1) + (-4^+)(2_{1z}) + (-4^-) - (m_{xy}) - (2_{1y}) - (m_{xy}) - (2_{1x})$$
$$P^5_{11} = (1) + i(-4^+) - (2_{1x}) - (-4^-)$$
$$P^5_{12} = (m_{xy}) - i(2_{1y}) - (m_{xy}) + i(2_{1x})$$
$$P^5_{21} = (m_{xy}) + i(2_{1y}) - (m_{xy}) - i(2_{1x})$$
$$P^5_{22} = (1) - i(-4^+) - (2_{1z}) + i(-4^-)$$  \hspace{1cm} (6.23)

Applying the projection operators of 6.23, we find the possible different magnetic orders. For the $\Gamma_1$ IR, we have an antiferromagnetic ordering with the magnetic components along the $c$ axis. For the $\Gamma_2$ IR, we have a ferromagnetic ordering with the magnetic components along the $c$ axis. And finally, the $\Gamma_5$ IR describes an antiferromagnetic ordering with the magnetic components in the $ab$ plane. Consequently, we can say that the magnetic ordering appearing under $T_N$ is described by the $\Gamma_1$ IR.

Knowing the IR characterizing the magnetic ordering, we need now to find out about the magnetic space group in order to determine if a linear magnetoelectric effect is possible. The space group $P-42_1m$ contains 8 symmetry elements. However, it is more convenient to consider only the generators of this space group. We have several possibilities to choose the generators. We chose the simplest ones which are the ones associated with the Hermann-Mauguin symbols: $-4^+//[001], 2_{1z}//[100]$ and $m//[110]$. Looking at the characters associated to the $\Gamma_1$ IR in table 6.9, we can see that the magnetic space group associated to it is $P-42_1m$. The associated magnetic point group is thus $-42_1m$. Consequently, a linear magnetoelectric effect is allowed with only two non zero components $\alpha_{11} = -\alpha_{22}$. Here, this materials is not multiferroic but simply magnetoelectric.
6.4 Inversion center breaking due to antiferromagnetic ordering

6.4.1 Introduction

Various groups looked for magnetically induced ferroelectrics. The main idea is that antiferromagnetic ordering may break the inversion center of a given structure [13]. Until very recently the magnetically induced ferroelectrics exhibited low polarization values. It has been proposed that the ferroelectric displacements should not rely on the presence of spin orbit coupling alone in order to have a significant polarization [10]. We treat here the case where the inversion center is broken by the antiferromagnetic ordering. We predict a new antiferromagnetic induced ferroelectric due to a non E type antiferromagnetism contrary to the orthorhombic HoMnO$_3$ and in RNiO$_3$ (R = rare-earth) [10].

6.4.2 Cu$_2$MnSnS$_4$

Introduction

The title compound has been studied in the search for new dilute magnetic semiconductors (DMS’s). Most of the new designed DMS have been based on Mn-II-VI compositions with a zinc-blende or wurtzite crystal structure. However, the main issue in these materials in the light of application is the difficulty to align the Mn spins even with a high magnetic field. In this type of materials, it has been demonstrated that the necessity for a high magnetic field to align the spins is directly related to the amount of Mn in the structure. In order to investigate more in details the relationship between the critical field to align the spins and the structure of recent DMS’s, T. Fries and coworkers investigated the magnetic structure of Cu$_2$MnSnS$_4$. This compound crystallizes in the space group $I-42m$ (n°121) where only the manganese atoms carry a spin since the copper atoms here are Cu$^+$ ions. The Mn$^{2+}$ ions occupy the Wyckoff position 2a. This compound presents an antiferromagnetic structure characterized by a propagation wave-vector $\vec{k}$ = (1/2,0,1/2) below $T_N$=8.8K. A representation of the magnetic structure is presented in figure 6.7.

Magnetic ordering

The little group of $\vec{k}$ describing the magnetic structure of Cu$_2$MnSnS$_4$ is identical to the one describing the magnetic structure of LiFeP$_2$O$_7$ (see section 6.3.2). Consequently, we can write a similar expression for the free-energy:
Figure 6.7: Magnetic structure of Cu$_2$MnSnS$_4$ in the (a,c) plane. Arrows indicate the magnetic moments on the manganese atoms.

\[
F = F_0 + \frac{a}{2} L^2 + \frac{b}{4} L^4 + \frac{c}{2} M^2 + \frac{d}{4} M^4 \\
+ \frac{1}{2} \sum_{i=x,y,z} (\nu_i L_i^2 + \beta_i M_i^2) \\
+ \delta L_x L_z + \gamma M_x M_z \\
+ \sigma_1 L_x M_y + \sigma_2 L_z M_y + \sigma_3 L_y M_z + \sigma_5 L_y M_x
\]  

(6.24)

We will not discuss here the free-energy and the different magnetic symmetries since there are the same as for LiFeP$_2$O$_7$. Experimentally, it has been observed that the structure orders magnetically in the magnetic structure described by 2 antiferromagnetic components (L$_x$ and L$_z$). The magnetic ordering is described by the magnetic space group P2$_1$.

**Magnetic ordering induces polarization**

We will have a look at the possible breaking of the inversion center. In other words, can we have appearance of spontaneous polarization while the compound orders magnetically? In order to determine the extra terms susceptible to appear, we investigated the transformation properties of the different magnetic components. We present the results in table 6.10.

From table 6.10, we notice an interesting term L$_x$L$_z$P$_y$. Consequently, we can write a simplified expression for the free energy including this new term:
Inversion center breaking due to antiferromagnetic ordering

<table>
<thead>
<tr>
<th></th>
<th>h₁</th>
<th>h₂</th>
<th>Rh₁</th>
<th>Rh₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lₓ</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>Lᵧ</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>Lₚ</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>Mₓ</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>Mᵧ</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>Mᵢ</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>Pₓ</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>Pᵧ</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Pᵢ</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

Table 6.10: Transformation properties of the components of the different vectors of interest for the magnetic space group I-42m associated to \( \mathbf{k} = (1/2, 0, 1/2) \).

\[
F = \frac{a}{2} L_x^2 + \frac{b}{4} L_y^4 + \frac{\alpha}{2} P^2 + \beta L_x L_z P_y + \frac{1}{2} \sum_{i=x,y,z} \nu_i L_i^2
\]  

(6.25)

If we minimize 6.25, we find:

\[
\begin{align*}
\frac{\partial F}{\partial L_x} &= aL_x + bL_x^3 + \beta L_z P_y + \nu_x L_x \\
\frac{\partial F}{\partial L_y} &= aL_y + bL_y^3 + \nu_y L_y \\
\frac{\partial F}{\partial L_z} &= aL_z + bL_z^3 + \beta L_x P_y + \nu_z L_z \\
\frac{\partial F}{\partial P_x} &= \alpha P_x \\
\frac{\partial F}{\partial P_y} &= \alpha P_y + \beta L_x L_z \\
\frac{\partial F}{\partial P_z} &= \alpha P_z
\end{align*}
\]  

(6.26)

From 6.26, we can find two series of equalities:
\[ P_x = P_z = 0 \]
\[ P_y = -\frac{\beta}{\alpha} L_x L_z \]

\[ L_x = 0 \quad \text{or} \quad L_x = \frac{-(a + \nu_x + \frac{\beta^2}{\alpha} L_z^2)}{b} \]  
\[ (6.27) \]

\[ L_y = 0 \quad \text{or} \quad L_y = \frac{-(a + \nu_y)}{b} \]

\[ L_z = 0 \quad \text{or} \quad L_z = \frac{-(a + \nu_z + \frac{\beta^2}{\alpha} L_x^2)}{b} \]

Consequently, we have different magnetic ordering patterns possible. However, from experiment we know that we have the situation \((L_x, L_z) \neq (0, 0)\).

Above \(T_N\), we have \(L_x = L_z = 0\) and consequently \(P_y = 0\). However, below \(T_N\), we have (replacing the expression of \(L_x\) in \(L_z\) and vice-versa):

\[ L_x = -\alpha \frac{(aba^2 + a\beta^2 + \beta^2 \nu_z + \alpha \beta \nu_x)}{\alpha^2 b^2 - \beta^4} \]  
\[ (6.28) \]

Using 6.28 to put in 6.27, we find that there is a spontaneous polarization possible while going in the magnetic ordered state:

\[ P_y = -\frac{\beta}{\alpha} L_x L_z \]
\[ = -\frac{\beta}{\alpha} \times \frac{-(a + a\beta^2 + \beta^2 \nu_z + \alpha \beta \nu_x)}{\alpha^2 b^2 - \beta^4} \times \frac{-(a + a\beta^2 + \beta^2 \nu_z + \alpha \beta \nu_x)}{\alpha^2 b^2 - \beta^4} \]  
\[ (6.29) \]

If we assume that the relativistic components \(\nu_j\) have a negligible effect on the value of the spontaneous polarization, we can rewrite 6.29 as:

\[ P_y \approx -a^2 \alpha \beta \frac{(ba^2 + \beta^2)^2}{(\alpha^2 b^2 - \beta^4)^2} \]  
\[ (6.30) \]

From 6.30, we see that the spontaneous polarization appearing below \(T_N\) is proportional to \(a^2\). This is the first time to our knowledge that a non-oxide material exhibits such property.
6.4. Inversion center breaking due to antiferromagnetic ordering

Magnetoelectric properties

We have been describing in the previous section, the spontaneous polarization susceptible to arise going through the antiferromagnetic ordering. However, this is not the only polarization possible. We have to deal here with the same point group than in the case of LiFeP$_2$O$_7$ (see section 6.5). Consequently, under the application of a magnetic field, we will have the following polarization components which will appear:

$$
\begin{align*}
P_x &= \frac{-\kappa_{xx}\lambda_1 L_x}{1 - \kappa_{xx}\chi_{xx}\lambda_1^2 L_x^2} H_x \\
P_y &= \frac{-\kappa_{yy}\lambda_2 L_x}{1 - \kappa_{yy}\chi_{yy}\lambda_2^2 L_x^2} H_y \\
P_z &= \frac{-\kappa_{zz}\lambda_3 L_z}{1 - \kappa_{zz}\chi_{zz}\lambda_3^2 L_z^2} H_z
\end{align*}
$$

(6.31)

From 6.31, we can predict the appearance of some polarization along the three direction of the crystal under the application of a magnetic field. This induced polarization by a magnetic field is the characteristic of magnetoelectricity. However, here we have to deal with a structure giving rise to some spontaneous polarization along y under T$_N$. Consequently, we will have an increase of this polarization under magnetic field by an amount of:

$$
\Delta P_y = -\frac{\beta}{\alpha} \times \frac{-\alpha(ab\alpha^2 + a\beta^2 + \beta^2\nu_x + \alpha\beta\nu_x)}{\alpha^2b^2 - \beta^4} \\
\times \frac{-\alpha(ab\alpha^2 + a\beta^2 + \beta^2\nu_x + \alpha\beta\nu_x)}{\alpha^2b^2 - \beta^4} \\
- \frac{-\kappa_{yy}\lambda_2 L_x}{1 - \kappa_{yy}\chi_{yy}\lambda_2^2 L_x^2} H_y \\
\simeq -a^2\alpha\beta \frac{(bo\alpha^2 + b^2)^2}{(\alpha^2b^2 - \beta^4)^2} - \frac{-\kappa_{yy}\lambda_2 L_x}{1 - \kappa_{yy}\chi_{yy}\lambda_2^2 L_x^2} H_y
$$

(6.32)

We show using Landau and group theory that Cu$_2$MnSnS$_4$ can be considered as a new magnetically induced ferroelectric. In addition to a spontaneous polarization, we show that a linear magnetoelectric effect is allowed. Moreover, the ferroelectric displacements are not expected to rely on the presence of spin-orbit coupling. Consequently, the polarization should be quite strong as in the predicted orthorhombic HoMnO$_3$ and in RNiO$_3$ [10]. Contrary to these compounds, the polarization should be tunable by electric and magnetic fields.
References

6.4. Inversion center breaking due to antiferromagnetic ordering


Chapter 6. Predictions for new magnetoelectrics/multiferroics