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Magnetoelectric and multiferroic properties of ternary copper chalcogenides Cu$_{2}$M$^{II}$M$^{IV}$S$_{4}$

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Abstract

We investigate theoretically the ternary copper chalcogenides with the general formula Cu$_{2}$M$^{II}$M$^{IV}$S$_{4}$. This family of compounds can crystallize in two different non-centrosymmetric structures, $I42m$ or $Pnm2_1$. We show that all the reported members of Cu$_{2}$M$^{II}$M$^{IV}$S$_{4}$ having the $Pnm2_1$ symmetry exhibit a large spontaneous polarization. This result suggests that several of these materials are likely to be multiferroics since they order magnetically at low temperature. We discuss in detail in the framework of Landau theory the members Cu$_{2}$MnSnS$_{4}$ and Cu$_{2}$MnGeS$_{4}$ which should present both a linear magnetoelectric effect and multiferroic behavior.

1. Introduction

In recent years, the coupling between magnetic and dielectric properties in transition metal oxides attracted a lot of attention [1–3]. This interest is governed by the emerging of new fundamental physics and potential technological applications [2, 3].

The search for a strong interplay between magnetic and dielectric properties lead to the discovery of a new class of materials based on the perovskite structure RMnO$_3$ (R = Tb, Dy) and RMn$_2$O$_5$ (R = rare-earth). More recently Sergienko et al [4] demonstrated that E-type antiferromagnetic ordering results in a ferroelectric state below the Néel temperature of orthorhombic HoMnO$_3$ and RNiO$_3$ (R = rare-earth). These series of new materials are called magnetically induced ferroelectrics. The use of symmetry arguments in order to predict new multiferroic or magnetoelectric materials is not new [5, 6].

Recent investigations for new multiferroic and magnetoelectric materials is largely based on oxides [1–3]. While in the old literature the search for multiferroic and magnetoelectric materials has not been dedicated to a particular family of compounds [7], the recent revival is mostly dedicated to perovskite related materials [8]. Since multiferroic and magnetoelectric materials are scarce, there is a need to look for other materials than oxides. We have predicted already several new magnetoelectric materials among the fluorides [9]. Several of them are likely to be multiferroic compounds.

In this contribution, we discuss the symmetry properties of the non-centrosymmetric ternary copper chalcogenides Cu$_{2}$M$^{II}$M$^{IV}$S$_{4}$. We use symmetry arguments and structural considerations to show that among this piezoelectric family, several of the compounds are possible multiferroics with high polarization. In addition, we use the results of group and Landau theory to discuss in detail the compounds Cu$_{2}$MnSnS$_{4}$ and Cu$_{2}$MnGeS$_{4}$. We demonstrate the possibility for a magnetic order induced polarization in Cu$_{2}$MnSnS$_{4}$. Moreover both compounds possess a polarization which can be switched by a magnetic field (linear magnetoelectric effect).

2. Possible new multiferroic materials in Cu$_{2}$M$^{II}$M$^{IV}$S$_{4}$

Polar structures having atomic displacements smaller than 1 Å with respect to a hypothetical non-polar configuration are considered materials with a high probability of having a phase transition into this configuration at higher temperatures. This concept gave rise to the prediction of a large number...
Table 1. Estimated ferroelectric transition temperatures for the candidate multiferroic materials belonging to the Cu2MIIIMIVS4 family. H is the room temperature space group and G is the minimal centrosymmetric supergroup of H.

<table>
<thead>
<tr>
<th>Compound</th>
<th>H</th>
<th>G</th>
<th>d_{rel}^{max} (Å)</th>
<th>T_{c}^{estim} (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu2MnSiS4</td>
<td>Pmn21</td>
<td>Pmmm</td>
<td>1.02</td>
<td>2600(500)</td>
</tr>
<tr>
<td>Cu2MnGeS4</td>
<td>Pmn2</td>
<td>Pmmm</td>
<td>0.942</td>
<td>2250(450)</td>
</tr>
<tr>
<td>Cu2SiS4</td>
<td>Pmn21</td>
<td>Pmmm</td>
<td>0.926</td>
<td>2200(450)</td>
</tr>
<tr>
<td>Cu2GeS4</td>
<td>Pmn21</td>
<td>Pmmm</td>
<td>0.935</td>
<td>2200(450)</td>
</tr>
<tr>
<td>Cu2FeSiS4</td>
<td>Pmn21</td>
<td>Pmmm</td>
<td>1.11</td>
<td>3000(600)</td>
</tr>
</tbody>
</table>

Table 2. Calculated high symmetry of the paraelectric state of Cu2MnSiS4 with G = Pmmm and α = 7.543 Å, b = 6.193 Å and c = 6.446 Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4f</td>
<td>1.0024</td>
<td>0.2501</td>
<td>−0.6780</td>
</tr>
<tr>
<td>Mn</td>
<td>2b</td>
<td>1/4</td>
<td>3/4</td>
<td>−0.8448</td>
</tr>
<tr>
<td>Si</td>
<td>2a</td>
<td>1/4</td>
<td>1/4</td>
<td>−0.1773</td>
</tr>
<tr>
<td>S1</td>
<td>4f</td>
<td>0.9790</td>
<td>0.749</td>
<td>−0.6645</td>
</tr>
<tr>
<td>S2</td>
<td>2a</td>
<td>1/4</td>
<td>1/4</td>
<td>−0.8628</td>
</tr>
<tr>
<td>S3</td>
<td>2b</td>
<td>1/4</td>
<td>3/4</td>
<td>−0.1913</td>
</tr>
</tbody>
</table>

of displacive ferroelectrics [10, 11]. In addition, these candidates order magnetically, we can predict new multiferroic materials. Various materials among the ternary copper chalcogenides crystallize in the polar symmetry Pmn21 (No. 31). Among the Cu2MIIIMIVS4 family, Cu2FeSiS4, Cu2NiGeS4, Cu2CuIIISiS4, Cu2CuIIIISiS4, Cu2MnSiS4 and Cu2MnGeS4 crystallize in this polar structure [12–16]. If these compounds present a pseudosymmetry with a non-polar symmetry, they are likely to be considered as possible multiferroic materials. We use the program PSEUDO [11] for the search of pseudosymmetry in these materials. A detailed description of the principle of this program can be found in [11, 17].

The procedure for the pseudosymmetry search has been applied to the compounds with symmetry H = Pmn21 in the Cu2MIIIMIVS4 family. The search for pseudosymmetry has been performed among all the non-polar minimal supergroups G of H = Pmn21 space group with a tolerance limit \( \Delta_{\text{tol}} = 1.52 \) Å, which restricts the maximal atomic displacement \( d_{\text{max}} \) to be less than 0.76 Å for supergroups of index 2. We present in table 1 our results. All the pseudosymmetry searches give rise to the non-polar G = Pmmm space group as hypothetical high temperature phase. We show in table 2 the description of the structure of Cu2MnSiS4 with G = Pmmm. We give in figure 1 the relationship between the high temperature hypothetical space group G = Pmmm and the room temperature polar H = Pmn21 symmetry.

It is possible to estimate the transition temperature towards the hypothetical high temperature paraelectric phase. For this purpose, we used the relation proposed by Kroumova et al [17]:

\[
T_c = \alpha (d_{\text{rel}}^{\text{max}})^2 + \beta.
\]

In equation (1), \( \alpha = 0.22(4) \times 10^6 \) K Å², \( \beta = 300(100) \) K and \( d_{\text{rel}}^{\text{max}} = d_{\text{max}} - d_{\text{min}} \), \( d_{\text{max}} \) and \( d_{\text{min}} \) are the values of the maximal and the minimal displacements along the polar axis taken with their corresponding signs. The estimated values of the transition temperature for the candidates for proper ferroelectrics with symmetry Pmn21 among the Cu2MIIIMIVS4 family are given in table 1. The high values for the transition temperature corresponding to the compounds suggest that the paraelectric phase will not be reached before melting or decomposition. This is the case for instance for Cu2MnGeS4 where the melting point has been reported to be \( T_m = 1287 \) K [18].

The estimation of the transition temperature is made assuming a ferroelectric–paraelectric phase transition described by a displacive type transition. This hypothetical transition can be also of order–disorder type in which case we can not estimate the transition temperature. Consequently, the transition temperature can be lower than the one estimated in the hypothesis of a displacive type transition. If we estimate the transition temperature for the system LiNbO3, we find a transition temperature of about 2100 K. This is above the melting point which is of 1530 K. This discrepancy can be explained by the fact that LiNbO3 is known to exhibit a order–disorder phase transition towards the ferroelectric phase [19]. Moreover, irrespective of the mechanism for the emergence of spontaneous electrical polarization, the possibility of twinning and domain switching may exist.

Additionally, one of the most studied families among magnetoelectric/multiferroic materials is BaXF4 (X = Mn, Co; Fe, Ni). One of the main characteristics of this family is that its members melt before to reach the transition temperature [20]. Despite the absence of phase transition towards a paraelectric phase, ferroelectric switching has been demonstrated for several members [21]. Moreover several members exhibit rather strong magnetoelectric effect [22]. In light of this family, we can conclude that the melting prior to reach the paraelectric phase does not preclude of the interest and strength of the magnetoelectric coupling. Consequently, the search and investigations of new families of magnetically ordered pyroelectric materials is of prime importance in...
the search for new magnetoelastic/multiferroic materials irrespective of their mechanism for electrical polarization.

One of the most important features for large coupling between the dielectric and magnetic properties in multiferroics is the value of the spontaneous polarization displayed by these materials. The spontaneous polarization can be estimated using an ionic model by simplifying the electric charge of each ion with a point charge [23].

\[ P = \left( \frac{e}{V} \right) \sum_i m_i Q_i \Delta z_i. \]  

(2)

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 discussed already the hypothetical high temperature paraelectric phase, we can estimate the displacement \( \Delta z_i \) for each ion of each material reported in table 1. We present in table 3 the results of these derivations.

The estimation of the spontaneous polarization for the compounds reported in table 3 is very high. These calculated spontaneous polarizations are upper bounds. The ionic model is just a calculated one as reported in the inorganic crystal structure database [15]. For BaAl\(_2\)O\(_4\), the ionic model gives an overestimation of \( P_s \) by a factor of six compared to the experimental value [24]. Sulfur is a softer Lewis base than oxygen, and covalency effects are more dominant than for oxides. This should reduce further the polarization of a ionic crystal. We denote \( N \) by a factor of six compared to the experimental value [24]. Sulfur is a softer Lewis base than oxygen, and covalency effects are more dominant than for oxides. This should reduce further the polarization of a ionic crystal.

\[ P_s = 26 \ \mu \text{C cm}^{-2} \]  

for the pyroelectric materials for the compounds Cu\(_2\)M\(_{III}\)M\(_{IV}\)S\(_4\). family we have, for instance, Cu\(_2\)NiGeS\(_4\) which orders below \( T_N = 36 \ \text{K} \) [27]. However, only two members of the Cu\(_2\)M\(_{III}\)M\(_{IV}\)S\(_4\) family have been investigated in detail both for their magnetic and their structural properties. These members are Cu\(_2\)MnSnS\(_4\) and Cu\(_2\)MnGeS\(_4\) [28, 12, 13]. We will discuss in detail in this section the magnetic properties of Cu\(_2\)MnSnS\(_4\).

Cu\(_2\)MnGeS\(_4\) crystallizes in an orthorhombic wurtzite superstructure type (\( Pmn2_1 \)) while Cu\(_2\)MnSnS\(_4\) crystallizes in a tetragonal sphalerite superstructure type (\( I4_2m \)). Wurtzite (ZnS) is based on a hexagonal closed packed structure of S, while sphalerite (ZnS) is based on a cubic closed packed structure of S. In both structures the metal ions occupy half of the tetrahedral sites. It has been shown that the relation of the sizes of the different tetrahedra plays the most important role with respect to the resulting structure type [14]. In the wurtzite superstructure type, the largest polarization contribution originates from the off-centering of the Cu\(^{2+}\) ion from the barycenter of the coordinating sulfur tetrahedron.

Several authors have investigated the magnetic structure of Cu\(_2\)MnSnS\(_4\) [28, 12, 13]. The compound Cu\(_2\)MnSnS\(_4\) crystallizes in the space group \( I4_2m \) (No. 121) where the Mn\(^{2+}\) ions occupy the Wyckoff position 2a. The compound presents an antiferromagnetic structure characterized by a propagation wavevector \( \vec{k} = (1/2, 0, 1/2) \) (carrying moment \( S_1 \)) and at (1/2, 1/2, 1/2) (carrying moment \( S_2 \)). Consequently, we can define two magnetic vectors:

\[ \vec{M} = S_1 + S_2 \]

\[ \vec{L} = S_1 - S_2. \]  

(3)

The little group of the \( \vec{k} \)-vector can be derived using the program REPREs of the Bilbao Crystallographic Server [29]. The little group contains only two symmetry elements: the identity 1 and a two fold axis along the y axis. We denote them \( \vec{h}_1 \) and \( \vec{h}_2 \), respectively. The expressions of these two

---

**Table 3.** Estimated spontaneous polarization using an ionic model for the pyroelectric materials for the compounds Cu\(_2\)M\(_{III}\)M\(_{IV}\)S\(_4\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>( P_s ) (( \mu \text{C cm}^{-2} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(_2)MnSiS(_4)</td>
<td>76</td>
</tr>
<tr>
<td>Cu(_2)MnGeS(_4)</td>
<td>65</td>
</tr>
<tr>
<td>Cu(_2)SiS(_4)</td>
<td>85</td>
</tr>
<tr>
<td>Cu(_2)GeS(_4)</td>
<td>81</td>
</tr>
<tr>
<td>Cu(_2)FeSiS(_4)</td>
<td>86</td>
</tr>
</tbody>
</table>

---

**Figure 2.** Magnetic structure of Cu\(_2\)MnSnS\(_4\) in the \((a, c)\) plane. Arrows indicate the magnetic moments on the Mn\(^{2+}\) ions.
The magnetic structure below collinear structures described in equation (3) and the magnetic describes the antiferromagnetic ordering below $T$. We can replace $Py$ properties of free energy of our system, we investigate the transformation of point group 2 (see table 4).

In order to write down the general expression of the free energy of our system, we investigate the transformation properties of $L$ and $M$ under the elements of the little group. We present the results of our derivations in table 5.

### 3.2. Magnetically induced polarization in Cu$_2$MnSnS$_4$

#### 3.2.1. Magnetic order induces spontaneous electrical polarization

The results of table 5 allow us to construct the Landau free energy [30]. We use here the notations for collinear structures described in equation (3) and the magnetic modes defined in table 5. The magnetic structure below $T_N$ is described by the irreducible representation $\tau_1$. This irreducible representation is characterized by the magnetic modes $L_z$, $M_x$, and $M_z$. The various coupling terms between the various order parameters are derived from symmetry considerations. Every product of the axial vector components belonging to the same irreducible representation is invariant by time reversal and the crystal symmetry [30]. We call $\eta$, the order parameter which describes the antiferromagnetic ordering below $T_N$. This order parameter $\eta$ has the same transformation properties of the components $L_z$ and $L_x$. From these considerations, we can write the free energy in its simplest form as

$$F = F_0 + \frac{a}{2} \eta^2 + \frac{b}{4} \eta^4 + \sigma \eta M_x + \frac{p^2}{2a} + \beta \eta^2 P_y + \frac{c}{2} M_y^2 + \lambda_1 \eta M_x P_y.$$  

In equation (4) the coefficient $a$ becomes zero at $T_N$. Its temperature dependence is assumed to be $a = a_0(T - T_N)$. The only non-zero magnetization and polarization components are $M_y$ and $P_y$. By minimizing $F$, one can work out the expression of these components. We can replace $P_y$ by its expression in function of $M_y$ and vice versa. We find

$$P_y = \frac{\alpha \eta^2(b - \alpha \beta \lambda_1)}{c - \alpha \lambda_1^2 \eta^2} \quad M_y = \frac{-\eta(\sigma - \alpha \beta \lambda_1 \eta^2)}{c - \alpha \lambda_1^2 \eta^2}.$$  

We notice that $M_y$ varies as $\eta$ as function of temperature while $P_y$ varies as $\eta^2$. In addition, we can check that there is no polarization above $T_N$ in agreement with the non-polar structure of the compound. While a ferromagnetic component is allowed along $y$, this has not been observed in the neutron diffraction experiment and neither by magnetometry. It has been shown that the magnetization along the $c$ axis is lower than perpendicular to it. This result is in agreement with a weak ferromagnetic component perpendicular to the $c$ axis (ferromagnetic component $M_y$ is expected to be along the $b$ axis).

Now that we obtained the expressions for $M_y$ and $P_y$, we can find the expression of $\eta$. For this purpose, we use the results of $\frac{\partial F}{\partial \eta} = 0$ and the expressions of $M_y$ and $P_y$ given in equation (5). We find a complicated expression:

$$\eta[-\alpha \lambda_1^2 \eta^4(b - \alpha \beta \lambda_1) + \eta^2(b c + 2 \alpha \beta^2 c - \alpha \lambda_1(\alpha \lambda_1 + \beta \sigma + \beta \sigma c - \lambda_1 \tau_2)) + ac - \sigma^2] = 0.$$  

From equation (6), we can describe the paramagnetic high temperature phase by $\eta = 0$. Otherwise, we have to solve an equation of the 2nd degree by substituting $x = \eta^2$.

If we assume that $\lambda_1^2$ are small in the equation (5), one can simplify the expression of equation (6). In this hypothesis, we obtain

$$\eta[ac - \sigma^2 + c(b + 2 \alpha \beta^2 \eta^2)] = 0 \quad \eta = 0 \quad \text{or} \quad \eta^2 = \frac{\sigma^2 - ac}{c(b + 2 \alpha \beta^2)}.$$  

In this case (assuming the $\lambda_1$ coupling term negligible), the expressions for the associated polarization $P_y$ and magnetization $M_y$ are

$$P_y = \frac{\alpha \beta \sigma(-ac)}{b + 2 \alpha \beta^2} \quad M_y = \frac{-\sigma}{c} \sqrt{\frac{\sigma^2 - ac}{c(b + 2 \alpha \beta^2)}}.$$  

We see from equations (7) and (8) that $\eta$ varies as $\sqrt{T_N - T}$, like $M_y$ while $P_y$ varies as $(T_N - T)$. We have been describing here the magnetic ordering of Cu$_2$MnSnS$_4$ using symmetry analysis. We have shown that below $T_N$ a polarization along $y$ is allowed. In addition, symmetry allows a ferromagnetic component along $y$ which has not been observed experimentally likely due to a too weak coupling between the order parameter $\eta$ and $M_y$.

#### 3.2.2. Linear magnetoelastic effect in Cu$_2$MnSnS$_4$

In addition to magnetic order, due to the magnetic point group 2, this compound presents magnetoelastic properties. To study theoretically this effect, several coupling terms have to be considered. In particular, one must take into account the possible magnetoelastic coupling terms which are of the type $\eta M_y P_y$. These terms are the couplings between the magnetic order parameter $\eta$, the total magnetization $M_y$ and the electrical polarization $P_y$. For this purpose, one needs to know the transformation properties of the various components of the electrical polarization. It can be shown that $P_y$ and $P_z$ transform like the irreducible representation $\tau_2$ while $P_x$ transforms like the irreducible representation $\tau_1$. In addition, we need to add the term $-\mathbf{M} \cdot \mathbf{H}$ (application of a magnetic

---

**Table 4.** Irreducible representations of the little group where $R$ represents the time-inversion operator.

<table>
<thead>
<tr>
<th>$h_1$</th>
<th>$h_2$</th>
<th>$Rh_1$</th>
<th>$Rh_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table 5.** Basis vectors for the atoms of the 2a site (Mn$^{2+}$ ion site).

<table>
<thead>
<tr>
<th>Basis vectors</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau_1$</td>
<td>$L_1$</td>
<td>$L_1$</td>
<td>$M_1$</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>$L_2$</td>
<td>$M_1$</td>
<td>$M_2$</td>
</tr>
</tbody>
</table>
and the expressions of the minima of $P_x$ and $P_z$ terms since they are different from zero. While the expression for the various components of polarization remain unchanged compared to the case where there is no magnetic field, the expressions for the components of the magnetization change. First we will start by treating the case of the polarization components $P_x$ and $P_z$. We will demonstrate that under the application of a magnetic field, these components become non-zero. For this purpose, we write down the new expressions for $M_x$ and $M_z$ as function of $P_x$ and $P_z$. We find for $M_x$ and $M_z$:

$$M_x = \frac{H_x - \eta(\lambda_2 P_z + \lambda_3 P_x)}{c},$$

$$M_z = \frac{H_z - \eta(\lambda_4 P_x + \lambda_5 P_z)}{c}. \tag{10}$$

After careful derivations, using the results of equation (10) and the expressions of the minima of $P_x$ and $P_z$ ($\frac{\partial P_x}{\partial M} = 0$), we find the rather complicated relationship between these two components:

$$P_x = -\alpha\eta[\lambda_3 H_x + \lambda_5 H_z - \eta P_z(\lambda_2 P_x + \lambda_3 P_z)]$$

$$P_z = -\alpha\eta[\lambda_2 H_x + \lambda_4 H_z - \eta P_x(\lambda_2 P_x + \lambda_3 P_z)]. \tag{11}$$

Using the expressions of equation (11), we find the non-trivial expressions for $P_x$ and $P_z$:

$$P_x = [-\alpha\eta(\lambda_3 H_x + \lambda_5 H_z) - \alpha\eta^2(\lambda_2^2 + \lambda_3^2)]$$

$$P_z = [-\alpha\eta(\lambda_2 H_x + \lambda_4 H_z) - \alpha\eta^2(\lambda_3^2 + \lambda_5^2)]. \tag{12}$$

Despite of the complicated expressions for the polarization components $P_x$ and $P_z$, there are several features that are important. First of all, if there is no applied magnetic field ($H_x = H_z = 0$), $P_x$ and $P_z$ are zero. This demonstrates that these induced polarization components arise from the linear magnetoelectric effect. Second, these components depend on both $H_x$ and $H_z$. Let us consider first the $P_x$ component. If we apply a magnetic field along $x$ ($H_z = 0$), we will have a polarization along the $x$ axis (term $\alpha_{11}$ in the magnetoelectric tensor [7]). If we apply a magnetic field along $z$, we will have also a polarization along $x$. This is the $\alpha_{13}$ term of the magnetoelectric tensor for the magnetic point group 2. On the other hand, let us consider now the $P_z$ component. If we apply a magnetic field along $z$, we have an induced polarization along $x$. This is the $\alpha_{31}$ term. We get an extra term $\alpha_{33}$ resulting from the application of a magnetic field along $x$. This is the $\alpha_{31}$ term. We have treated here the polarization components $P_x$ and $P_z$ but not yet the $P_y$ component. We recall that it is along this direction that a spontaneous polarization may arise below $T_N$. For this purpose, we can take the same approach than for $P_x$ and $P_z$. After simplification and rearranging the different terms, we find

$$P_y = \frac{\alpha\eta^2(\sigma_1 \lambda_1 - \beta c)}{c - \alpha\lambda_1^2\eta^2} - \frac{\lambda_1 \eta}{c - \alpha\lambda_1^2\eta^2} H_y. \tag{13}$$

The temperature dependence of $P_y$ can be modeled using equation (13). Knowing that $\eta$ is proportional to $\sqrt{T - T_c}$, we are able to find the temperature dependence of $P_y$. This is given in figure 3 in the cases of a strong and a weak magnetoelectric coupling.

We notice two features in the expression of $P_y$. First, the spontaneous part (1st term) is unchanged under magnetic field. Second, the application of a magnetic field along $y$ creates some additional polarization along $y$ (2nd term). This second term is the $\alpha_{22}$ term of the magnetoelectric tensor. We show that the magnetic point group below $T_N$ is 2 which is described by the magnetoelectric tensor given in equation (14).

$$\alpha_{ij} = \begin{pmatrix} \alpha_{11} & 0 & \alpha_{13} \\ 0 & \alpha_{22} & 0 \\ \alpha_{31} & 0 & \alpha_{33} \end{pmatrix}. \tag{14}$$

While Cu$_2$MnSnS$_4$ exhibits the magnetic space group $P2_1/a$ and thus the magnetic point group 2, Cu$_2$MnGeS$_4$ orders below $T_N = 8.25 \pm 0.3$ K [31] with the magnetic space group $P2_1/c$ [12]. Consequently the magnetic point group describing the pyroelectric material Cu$_2$MnGeS$_4$ is $m$. By inspection of the table 1.5.8.1 of [6], we see that the magnetic point group $m$ gives rise to the complementary magnetoelectric tensor as in
Cu$_2$MnSnS$_4$ having the expression given in equation (15).  
\[
\alpha'_i = \begin{pmatrix}
0 & \alpha_{12} & 0 \\
\alpha_{21} & 0 & \alpha_{23} \\
0 & \alpha_{32} & 0
\end{pmatrix}.
\]  
(15)

We have shown in section 3.2.2 that terms like $\eta M_z P_z$, $\eta M_z P_y$, $\eta M_z P_y$, $\eta M_z P_z$ were responsible for the linear magneto-electric effect in Cu$_2$MnSnS$_4$. If we call $\xi$ the magnetic order parameter describing the antiferromagnetic ordering in Cu$_2$MnGeS$_4$, the terms responsible for the linear magneto-electric effect given by equation (15) are $\xi M_z P_z$, $\xi M_y P_z$, $\xi M_z P_y$ and $\xi M_z P_z$. We stress that the spontaneous polarization existing along $z$ at room temperature can be controlled below the magnetic ordering temperature trough the term $\xi M_z P_z$.

Using a Landau theoretical approach we are able to describe the magnetic phase transition of CuMnSnS$_4$ below $T_N$. We predict a ferromagnetic component along the $y$ axis which has not been observed experimentally. This is likely due to weak coupling to the order parameter $\eta$. More importantly, we show that a spontaneous polarization along the $y$ axis may arise below $T_N$. This polarization can be tuned via the linear magneto-electric effect. We gave the expressions of the various components of the polarization with and without magnetic field.

4. Conclusion

We show using symmetry arguments that several members of the Cu$_2$Mn$^3$M$^4$S$_4$ family are promising multiferroic candidates. In addition, we discuss in detail Cu$_2$MnSnS$_4$ which can be considered as a new magnetically induced ferroelectric. Moreover we demonstrate that Cu$_2$MnSnS$_4$ and Cu$_2$MnGeS$_4$ are good magneto-electric candidates. This means that the polarization in these materials, magnetically induced and spontaneous respectively, can be tuned by this effect. We expect that this contribution will stimulate further experimental investigations of the Cu$_2$Mn$^3$M$^4$S$_4$ family and in particular of the dielectric properties of Cu$_2$MnSnS$_4$ and Cu$_2$MnGeS$_4$.

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