Chapter 5

Interplay between polarization and dielectric properties

5.1 Magnetodielectric coupling in an organic-inorganic hybrid

5.1.1 Introduction

While both organic and inorganic materials can be polar or magnetic, the combined properties rarely occur in either class of materials. Here, we introduce a hybrid material in which the polar symmetry originates from the organic component, while the magnetism comes about from the 3d transition metal ions \( \text{Cr}^{2+} \). Using such hybrid materials is a significant new approach in which the dielectric and magnetic properties can be tuned individually. Thus, this also provides a new method to tune the magnetodielectric coupling in a systematic manner.

\( \text{Cr}[(\text{H}_3\text{N}-(\text{CH}_2)_2\text{PO}_3)](\text{Cl})(\text{H}_2\text{O}) \) (I) is a rare polar organic-inorganic hybrid example. I contains \( \text{Cr}^{2+} \) ions which order magnetically at low temperature. It crystallizes in the polar space group \( \text{P}_2_1 (n^4) \) with \( a=5.249(1)\text{Å}, b=14.133(3) \text{Å}, c=5.275(1)\text{Å}, \) and \( \beta=105.55(2)^\circ \) [1] (see figure 5.1). Electrostatic interactions as well as hydrogen bonds ensure the cohesion of the 3D structure. The magnetic susceptibility data in the temperature range from 300 to 50 K show Curie-Weiss behavior, with \( C=2.716 \text{ cm}^3\text{K.mol}^{-1} \) and a Weiss constant \( \theta=-2.2 \text{ K} \). Hysteresis loops taken at different temperatures show that I behaves as a canted antiferromagnet below \( T_N=5.5 \text{ K} \) with a coercive field and a remnant moment of 30 Oe and 0.08 \( \mu_B \), respectively at 4.5K [1]. Two main reasons have motivated this work: the first one is that polar molecule based materials may show some interesting phenomena (pyroelectricity, non linear optical effect, etc) [2]. The second one resides in the fact that magnetodielectric coupling studies of polar materials
are focused mainly on inorganic multiferroic metal-oxides [3, 4, 5, 6, 7, 8]. Our aim here is twofold: to investigate the magnetodielectric coupling in a polar organic-inorganic hybrid material and to discuss our results in comparison with some well known magnetodielectric compounds. Indeed, this is particularly of interest since YMnO$_3$ like I presents one unique polar axis, both are antiferromagnetic but with a small ferromagnetic component for the latter. In addition, we use a Landau approach which explains the temperature dependence of the dielectric constant ($\varepsilon$). It is similar to previous studies [7]. The other features of the magnetodielectric coupling are explained using classical mechanics. We derive a relationship that quantifies the decrease of $\varepsilon$ below $T_N$. In addition, we show that the departure from a quadratic dependence in magnetic field of $\varepsilon$ is not necessarily due to magnetic fluctuations. This is in disagreement with recent claims [5].

5.1.2 Experimental section

I has been synthesized according to a previous published paper [1]. The resulting light-blue microcrystalline solid was finely ground under inert atmosphere. The fine blue powder was then introduced in a stainless-steel die (Perkin Elmer) and pressed under vacuum ($10^{-2}$ mm Hg) at a pressure of 12 t. A cylindrical shaped blue pellet of 1.5 mm thickness and 8 mm radius was obtained and stored under inert atmosphere$^1$.

Complex impedance measurements were performed using an Agilent AG4284A LCR meter. In order to measure the dielectric constant in the presence of a magnetic field, a home made sample holder with four coaxial cables was used. The sample holder fits inside a commercial Quantum Design PPMS apparatus, allowing measurements of the dielectric constant in

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$^1$The sample was provided by Elvira M. Bauër, Carlo Bellitto and Guido Righini from the CNR-Istituto di Struttura della Materia, Monterotondo Stazione, Roma, Italy.
the presence of a magnetic field up to 9T and at different temperatures. The ac-voltage applied to the sample was set at 1 Volt. The dielectric constant can be extracted from the value of capacitance using the sample dimensions.

5.1.3 Results and Discussion

The dielectric constant of a pellet of I was measured as a function of temperature, T, and of frequency, f, with 0.25 K step. We observed a shift towards higher value of the dielectric constant for f = 1kHz while the two other frequencies (f = 10kHz and f = 100kHz) do not show noticeable difference. In addition, we see that the measurement with f = 1kHz is significantly more noisy than for the other frequencies. For all the studied frequencies, the loss is quite low (\(\tan(\delta) < 0.01\)). The loss for f = 1kHz is more noisy than for the other frequencies.

Based on the frequency dependence studies, we chose to use a 10kHz frequency for our measurement. We present in figure 5.2 the temperature dependence of \(\varepsilon\) measured with 0.25K step. We observe clearly an anomaly at the Néel temperature. The anomaly is evidenced by a decrease below the Néel temperature. This anomaly demonstrates for the first time, to our knowledge, the existence of a magnetodielectric coupling in a polar organic-inorganic hybrid material. We notice that the anomaly is significantly less pronounced than in other magnetodielectric compounds (see table 5.1). In order to compare our data, we have normalized the variation of \(\varepsilon\) to the magnetic transition temperature.

Figure 5.2: Dielectric constant measured versus temperature. A clear anomaly is observable below \(T_N\) (f = 10kHz).
In order to investigate the magnetic field dependence of the magnetodielectric coupling, we have performed magnetocapacitance measurement under a magnetic field up to 5T below and above $T_N=5.5$K. The results are presented in figure 5.3. We show that both magnetocapacitive responses below and above $T_N$ follow a quadratic dependence in magnetic field, at least up to a field of 3T. The significant difference in the magnetocapacitive responses below ($T=4.2$K) and above $T_N$ ($T=10$K) can be explained by the onset of the magnetic ordering (see section 5.1.4). The increase of the magnetocapacitive response below $T_N$ is almost one order in magnitude between 4.2 and 10K ($\Delta\varepsilon/\varepsilon(H=0) = a + bH^2$, $b_{T<T_N}/b_{T>T_N} = 2.1\times10^{-2}/2.4\times10^{-3} = 8.75$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta\varepsilon$ at $H = 5T$</th>
<th>$\Delta\varepsilon$ per K</th>
<th>$b_{T&lt;T_N}$</th>
<th>$T_N$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EuTiO$_3$ [4]</td>
<td>$\approx$6%</td>
<td>1%</td>
<td>2.74x$10^{-3}$</td>
<td>5.5</td>
</tr>
<tr>
<td>$\varepsilon$-Fe$_2$O$_3$ [6]</td>
<td>0.26%</td>
<td>0.05%</td>
<td>5.2x$10^{-2}$</td>
<td>110</td>
</tr>
<tr>
<td>YMnO$_3$ [8]</td>
<td>0.005%</td>
<td>9.1%</td>
<td>$\approx$ 2x$10^{-4}$</td>
<td>77</td>
</tr>
<tr>
<td>this work</td>
<td>0.0275%</td>
<td>0.0085%</td>
<td>2.1x$10^{-2}$</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 5.1: Different relevant magnetodielectric parameters for several compounds compared to Cr$^{II}$ organophosphonate. $\Delta\varepsilon$ at $H = 5T$ is given below the magnetic ordering temperature. $\Delta\varepsilon$ per K is the variation of the $\varepsilon$ normalized to $\Delta T = T_N - T_{\text{low}}$ where $T_{\text{low}}$ is the lowest measured temperature. $b_{T<T_N}$ corresponds to the curvature of $\Delta\varepsilon/\varepsilon(H=0) = a + bH^2$.

In I the magnetic field response of $\varepsilon$ below $T_N$ is almost one order of magnitude larger than above $T_N$. This is not the case in YMnO$_3$ where the magnetocapacitive response is almost constant below and above $T_N$ [8]. We will show in the section 5.1.4 that this increase in the magnetodielectric coupling is due to the arising of the magnetic ordering below $T_N$. While the field dependence of our sample is quite small above $T_N$, the magnetodielectric constant $b_{T<T_N}$ in the magnetically ordered phase is larger by two orders of magnitude than for YMnO$_3$ or EuTiO$_3$ (see table 5.1). We notice also from table 5.1 that b is not related to the magnetic transition temperature.
5.1. Magnetodielectric coupling in an organic-inorganic hybrid

5.1.4 A phenomenological description

In this section, we develop a phenomenological approach based on symmetry analysis and in the framework of Landau theory [9]. We will show that we can describe the main features of $\varepsilon$ as function of magnetic field and temperature:
- Quadratic dependence of $\varepsilon$ in magnetic field
- $b$ coefficient higher below $T_N$ ($\varepsilon = a + bH^2$)
- Decrease of $\varepsilon$ below $T_N$

$I$ crystallizes in the space group $P2_1$ (n°4) where there is only one Cr$^{2+}$ per asymmetric unit cell occupying the general Wyckoff position 2a. Consequently, there are two Cr atoms per unit cell at $(x, y, z)$ (carrying $\vec{S}_1$) and at $(-x, y+1/2, -z)$ (carrying $\vec{S}_2$ moment).

Consequently, we can define 2 magnetic vectors:

\begin{align*}
\vec{M} &= \vec{S}_1 + \vec{S}_2 \\
\vec{L} &= \vec{S}_1 - \vec{S}_2
\end{align*} \quad (5.1)

The space group $P2_1$ contains only two symmetry elements the identity 1 and a two fold screw axis 2, that we will denote $h_1$ and $h_2$, respectively. The matrix expressions of these two elements of symmetry are:

Figure 5.3: Magnetocapacitance measured below and above $T_N = 5.5K$ ($f = 10kHz$). In black, we present the field dependence at 4.2K and at 10K. In grey, we show the fit with $\Delta\varepsilon / \varepsilon (H=0) = a + bH^2$. 
The magnetic ordering which develops below \( T_N = 5.5 \text{K} \) is characterized by the presence of a ferromagnetic component giving rise to a canted antiferromagnet. Although the magnetic structure has not been studied by neutron diffraction, we can consider the simplest case where the magnetic cell is identical to the chemical one. Indeed having two \( \text{Cr}^{2+} \) sites per unit cell, one can easily imagine an antiferromagnetic coupling between these two sites. Consequently, the irreducible representations (IR) associated with this wave-vector \( (\vec{k} = 0) \) are the same as the ones of point-group 2 (see table 5.2).

\[
\begin{align*}
\Gamma_1 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\
\Gamma_2 &= \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}
\end{align*}
\]

\[
\begin{align*}
h_1 &= \begin{pmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \\
h_2 &= \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix}
\end{align*}
\]

Table 5.2: Irreducible representations for the space group \( P2_11' \) associated with \( k=0 \).

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.

\[
h_2 = \begin{pmatrix} -1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 1/2 \\ 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 1 \end{pmatrix} \times \begin{pmatrix} x \\ y \\ z \\ 1 \end{pmatrix} = \begin{pmatrix} -x \\ y + 1/2 \\ -z \\ 1 \end{pmatrix}
\]

Since \( h_1 \) keeps the whole system invariant, we can simply write the following table (see table 5.3)

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

Table 5.3: Transformation properties of the symmetry elements on the Wyckoff positions 2a in the space group \( P2_1 \).

Table 5.3 gives us the permutational representations of the two symmetry elements \( h_1 \) and \( h_2 \). In order to be able to write down the free-energy, we need to determine the axial representations of the group. We can derive
this representation by using the matrix representations of the different symmetry elements (see above). For this purpose, we use $\tilde{V}(h_i) = \text{Det}(h_i) \times h_i$, where Det is the determinant of the matrix representation of the rotational part of the symmetry element. Since for $h_1$ and $h_2$ the determinant is 1, the axial representations are given by:

$$\tilde{V}(h_1) = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}; \tilde{V}(h_2) = \begin{pmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$$

Thanks to the table 5.3 and the expressions of $\tilde{V}(h_i)$, we can associate to each magnetic component an IR. The results are presented in table 5.4.

<table>
<thead>
<tr>
<th>$\Gamma$</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>

Table 5.4: Components of the $\mathbf{M}$ and $\mathbf{L}$ vectors which form a basis for the IR of $P2_11'$ at $k=0$.

The results of table 5.4 allow us to construct the Landau free-energy, separating the exchange and magnetic anisotropy energies. We write the exchange terms up to the fourth degree and the relativistic terms up to the second degree:

$$F = F_0 + \frac{a}{2} L^2 + \frac{b}{4} L^4 + \frac{c}{2} M^2 + \frac{d}{4} M^4$$

$$+ \frac{1}{2} \sum_{i=x,y,z} (\nu_i L_i^2 + \beta_i M_i^2)$$

$$+ \delta L_x L_z + \gamma M_x M_z$$

$$+ \sigma_1 L_x M_y + \sigma_2 L_z M_y + \sigma_3 L_y M_z + \sigma_5 L_y M_x$$

(5.3)

The first line in equation 5.3 represents the exchange energy. It is formed from the scalar products $\overline{L}^2 = \overline{L} \cdot \overline{L}$ and $\overline{M}^2 = \overline{M} \cdot \overline{M}$. The other lines in equation 5.3 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 $L_i$ and $\gamma$ which couples the total magnetization components $M_x$ and $M_z$. We are now able to discuss in a complete manner the type and nature of the magnetic order which arise below $T_N$.

Most of the magnetic phase transitions involve only one IR. We know that below $T_N$, we have antiferromagnetic interactions. Thus, looking at table 5.4, there are two possibilities for the antiferromagnetic ordering, either with magnetic moments in the $(ac)$ plane or along the $b$ axis. Since the
closest next neighbors of Cr$^{II}$ are within the ($ac$) plane, the strongest magnetic coupling will be in this plane. However, it is not sufficient to decide what is the most likely direction of the spins. It can be shown that the discussion will not be much changed irrespective of the spin directions. Thus, we decide arbitrarily to assume that the antiferromagnetic components are in the ($ac$) plane. In this hypothesis, we can rewrite the free-energy in its simplest form as:

$$F = F_0 + \frac{a}{2} L_x^2 + \frac{b}{4} L_y^4 + \frac{1}{2} \sum_{i=x,y,z} \nu_i L_i^2 + \delta L_x L_z + \sigma_1 L_x M_y + \sigma_2 L_z M_y + \frac{c}{2} M^2$$

(5.4)

Minimization of $F$ gives:

$$\frac{\partial F}{\partial L_x} = a L_x + b L_x^3 + \nu_x L_x + \delta L_z + \sigma_1 M_y = 0$$

$$\frac{\partial F}{\partial L_y} = a L_y + b L_y^3 + \nu_y L_y = 0$$

$$\frac{\partial F}{\partial L_z} = a L_z + b L_z^3 + \nu_z L_z + \delta L_x + \sigma_2 M_y = 0$$

$$\frac{\partial F}{\partial M_y} = \sigma_1 L_x + \sigma_2 L_z + c M_y = 0$$

(5.5)

Below $T_N$, we see from the expression of the free energy (equation 5.5) that the minimum of $F$ arises for non zero value of $M_y$. Thus an induced magnetization can occur. A detailed neutron study below $T_N$ could give more informations on the origin of the ferromagnetic component in $I$. Now that we have described a possible origin of the weak ferromagnetic properties of $I$, we will have a look at the decrease of the capacitance at $T_N$.

We present in figures 5.2 and 5.3, the magnetodielectric measurement of a pellet of $I$. Let’s try to justify the above point that we observed experimentally. For this purpose, we note the ferromagnetic component $M$ and $L_s$ the antiferromagnetic vector describing the antiferromagnetic ordering below $T_N$. We use only relevant terms as derived above. Thus, we can write the free-energy to investigate the magnetodielectric coupling as:

$$F = F_0 + \frac{a}{2} L_s^2 + \frac{b}{4} L_s^4 + \sigma_1 L_s M_y + \frac{1}{2 \chi_p} P^2 - PE + \gamma_1 L_s^2 P^2 + \gamma_2 M_y^2 P^2$$

(5.6)
\( \chi_p \) is the dielectric tensor of the polar paramagnetic phase of the material. We do not put term like \( P^4 \) since we are not interested in the ferroelectric transition. If we differentiate \( F \) respect to \( P \), we have:

\[
\frac{\partial F}{\partial P} = \frac{P}{\chi_p} + 2\gamma_1 L_s^2 P + 2\gamma_2 M_y^2 P - E = 0
\]

\[
\iff \frac{1}{\chi_p} \frac{\partial P}{\partial E} + 2\gamma_1 L_s^2 \frac{\partial P}{\partial E} + 2\gamma_2 M_y^2 \frac{\partial P}{\partial E} - 1 = 0
\]

\[\iff \frac{\partial P}{\partial E} = \frac{1}{\chi_p} + 2\gamma_1 L_s^2 + 2\gamma_2 M_y^2
\]

We note that the equation 5.7 assumes that \( L_s \) does not depend on the electric field \( E \). The total dielectric susceptibility is defined as \( \chi_e = \frac{\partial P}{\partial E} \) and the dielectric constant as \( \varepsilon = 1 + \chi_e \). Consequently:

\[
\begin{align*}
- T > T_N (L_s = 0 \text{ and } M_y = 0) & \quad \frac{\partial P}{\partial E} = \chi_p \\
- T < T_N (L_s \neq 0 \text{ and } M_y \neq 0) & \quad \frac{\partial P}{\partial E} = \frac{\chi_p}{1 + 2\gamma_1 \chi_p L_s^2 + 2\gamma_2 \chi_p M_y^2} 
\end{align*}
\]

We can define the variation of the dielectric constant \( \Delta \varepsilon \) as function of temperature:

\[
\Delta \varepsilon = \frac{\partial P}{\partial E (T > T_N)} - \frac{\partial P}{\partial E (T < T_N)} = \chi_p - \frac{\chi_p}{1 + 2\gamma_1 \chi_p L_s^2 + 2\gamma_2 \chi_p M_y^2}
\]

\[= \frac{2\gamma_1 \chi_p^2 L_s^2 + 2\gamma_2 \chi_p^2 M_y^2}{1 + 2\gamma_1 \chi_p L_s^2 + 2\gamma_2 \chi_p M_y^2}
\]

Since we have a weak ferromagnetic component, we can express \( L_s \) as function of \( M_y \). This is given in equation 5.10.

\[
\frac{\partial F}{\partial M_y} = \sigma_1 L_s + 2\gamma_2 M_y P^2 = 0 \quad \rightarrow \quad L_s = \frac{-2\gamma_2 M_y P^2}{\sigma_1}
\]

Using the results of equation 5.10 to put in equation 5.9, we obtain the following expression:
\[ \Delta \varepsilon = \frac{\gamma_2 \chi_p M_y^2 (8 \gamma_1 \gamma_2 P^4 + 2 \sigma_1^2)}{\sigma_1^2 + \gamma_2 \chi_p M_y^2 (8 \gamma_1 \gamma_2 P^4 + 2 \sigma_1^2)} \]

if we assume that \( 8 \gamma_1 \gamma_2 P^4 \ll 2 \sigma_1^2 \)

\[ \Delta \varepsilon \sim \frac{2 \gamma_2 \chi_p M_y^2}{1 + 2 \gamma_2 \chi_p M_y^2} \]

Using the last expression of equation 5.11, we can explain all the characteristics of \( \varepsilon \) as function of temperature and magnetic field. Assuming that \( \gamma_2 > 0 \) and taking into account that \( \mathbf{M} = \chi_{\text{mag}} \mathbf{H} \), we see that \( \varepsilon \) varies for low magnetic field (\( 1 \gg 2 \gamma_2 \chi_p M_y^2 \)) as \( H^2 \) in agreement with our experimental observations. Moreover, the \( b \) coefficient in \( \varepsilon = a + b H^2 \) is proportional to \( \chi_{\text{mag}}^2 \). \( \chi_{\text{mag}} \) is higher below \( T_N \) than above \( T_N \). Therefore we can explain the increase of \( b \) below \( T_N \).

We see that the variation of the dielectric constant is directly related to the square of the magnetic moment. Consequently if one plots \( \Delta \varepsilon \) as function of the square of the magnetic moment, we will find a linear dependence for magnetic field. This behavior has been reported for various compounds such as EuTiO\(_3\) [4], \( \varepsilon - Fe_2 O_3 \) [6] and YMnO\(_3\) [8]. However, it is not the case for compounds presenting large magnetic fluctuations such as \( R_2 Ti_2 O_7 \) [5]. Katsufuji et al. show that the relationship above is not fulfilled below the temperature where the magnetic fluctuations start to develop. This is justified by the fact that \( \langle S_i S_j \rangle \) (pair correlation of neighboring spins) cannot be replaced by the square of the spin moments \( |\langle S \rangle|^2| \) if magnetic fluctuations are present. However, as shown from Landau theory, the quadratic dependence in magnetic field is an approximation. A fuller expression would include term like \( 1 + \gamma_2 \chi_p M_y^2 \) in the denominator of \( \varepsilon \). Consequently, a deviation from the quadratic dependence in magnetic field of the magnetocapacitance response can arise if a more complete expression is taken into account. Consequently, the deviation from quadratic dependence in magnetic field may not be systematically due to magnetic fluctuations.

\section*{5.1.5 Conclusion}

We have investigated the magnetodielectric coupling of polar organic-inorganic hybrid material. We show that the magnetodielectric response is enhanced by almost one order of magnitude below \( T_N \) between 4.2 and 10K due the appearance of long range magnetic ordering. We discuss the common and different features with well-known magnetodielectric compounds. In addition to these experimental observations, we elaborate a Landau approach.
5.2 Magnetoelectricity in \( \text{Ho}_2\text{BaNiO}_5 \) Haldane gap system

5.2.1 Introduction

Interest in low dimensional magnetism was greatly renewed by the theoretical work of Haldane, who predicted that an integer-spin Heisenberg antiferromagnetic chain should have a singlet ground state, and a gap in the magnetic spectrum \cite{12}. Several examples of quasi-one dimensional systems with a Haldane gap have been studied by now (see ref. \cite{13} and references therein). Most of the work has been carried out on organometallic compounds \cite{14}.

Darriet and Regnault \cite{15} and DiTusa et al. \cite{16} were the first to observe a Haldane gap in a metal oxide compound, namely, \( \text{Y}_2\text{BaNiO}_5 \). The \( \text{R}_2\text{BaNiO}_5 \) (R = rare-earth or Y) oxides present interesting structural and magnetic properties due to the fact that their structure posses a strong 1D character \cite{17, 18}. As a function of R and the synthesis conditions, the \( \text{R}_2\text{BaNiO}_5 \) family can crystallize in two different polymorphs: \( Pnma \) (n°62) and \( I\text{mmm} \) (n°71) \cite{19, 20}. The members in which we are interested have the \( I\text{mmm} \) symmetry. The main structural feature is the presence of 1D chains of \( \text{NiO}_6 \) octahedra along the \( a \)-axis. The octahedra are strongly distorted with a very short Ni-O\text{apical} distance (\( \approx 1.88\text{Å} \)), and a longer Ni-O\text{basal} distance (\( \approx 2.18\text{Å} \)) (see figure 5.4).

In particular, the \( \text{R}_2\text{BaNiO}_5 \) family is of interest from a magnetic point of view, due to the fact that the onset of 3D long-range magnetic order does not eliminate the Haldane-like behavior above and below the \( \text{Néel} \) temperature \cite{21}. Our motivation in studying the Ho member of this family was triggered by two reasons: the existence of two field induced phase transitions at low temperature and the possible existence of magnetoelectricity. We will show in a first part that we predicted the presence of a linear magnetoelectric effect based on symmetry analysis. From this prediction, we have synthesized the compound and studied its magnetic properties. We finally demonstrate experimentally the presence of an induced polarization by application of a magnetic field (linear magnetoelectric effect) on a polycrystalline sample. We discuss the magnetic field behavior of the induced polarization in the light of the two unusual field induced phase transitions.

which enables us to describe the main characteristics of the magnetodielectric response: quadratic dependence in the magnetic field, increase of the magnetodielectric coupling below \( T_N \) and the decrease of the dielectric constant below \( T_N \).
Space-group: Immm (#71)

\( a = 3.8 \text{Å}, \quad b = 5.8 \text{Å}, \quad c = 11.7 \text{Å} \)

Figure 5.4: Crystallographic structure of the \( \text{R}_2\text{BaNiO}_5 \) in the space group Immm. The cell parameters are \( a \approx 3.8 \text{Å} \), \( b \approx 5.8 \text{Å} \), and \( c \approx 11.3 \text{Å} \) for small \( R \) and \( c \approx 11.7 \text{Å} \) for large \( R \).

### 5.2.2 Magnetic symmetry analysis

E. García-Matres et al. have studied the magnetic structures of most of the members of the \( \text{R}_2\text{BaNiO}_5 \) family using neutron powder diffraction (\( R = \text{Nd, Tb, Dy, Ho, Er and Tm} \)) [23]. Below \( T_N \), \( \text{Ho}_2\text{BaNiO}_5 \) orders magnetically with a magnetic wave-vector \( \mathbf{k} = (1/2, 0, 1/2) \). The Ni atoms occupy the Wyckoff position 2a and the Ho atoms occupy the Wyckoff position 4j with \( z \approx 0.202 \). The authors determined the point-group of the little group \( G_k = 2/m \). Using methods presented in chapter 2, they determined that \( \text{Ho}_2\text{BaNiO}_5 \) could be described by the \( B_g \) representation of the little group \( 2/m \). Consequently, the magnetic moments of Ni and Ho ions are within the \( ac \)-plane. Let’s have a look which terms are primed or unprimed. The easiest way is to describe the magnetic structure in the enlarged unit cell. Using the program ISOTROPY [24], an enlargement of the unit cell by a vector \((1/2, 0, 1/2)\) gives rise to the space group \( C\text{mmm} \) (\( \text{n}^\circ65 \)) with \( \overrightarrow{a'} = 2 \overrightarrow{c}, \quad \overrightarrow{b'} = 2 \overrightarrow{a} \), and \( \overrightarrow{c'} = \overrightarrow{b} \). The new Wyckoff positions for Ni are (in \( C\text{mmm} \) setting) 2a, 2b, and 4f. The new Wyckoff positions for Ho are 8p, and 2 times 4h with different \( x \) coordinate in \( C\text{mmm} \) setting.

We know from the work of E. García-Matres et al. [23, 25] that the magnetic moments of Ni and Ho at 1.5K are \( \overrightarrow{S_{\text{Ni}}} = (0.58(9), 0, -1.26(4)) \) and \( \overrightarrow{S_{\text{Ho}}} = (0.12(5), 0, 9.06(4)) \), respectively. We consider only one propagation vector which defines the magnetic structure. Thus, we can relate...
any magnetic moment in the structure by:

\[ \vec{S}_n = \vec{S}_k \exp(-i2\pi \vec{k} \cdot \vec{R}_n) \]  

(5.12)

where \( \vec{S}_n \) is the magnetic moment of the atom considered attached to the lattice point \( \vec{R}_n \) for a magnetic wave-vector \( \vec{k} \). We investigate the 8 axial vector representations of the symmetry elements (we deal here with spins) of the space group \( C_{mmm} \) (in the enlarged unit cell). We find out that the only symmetry elements which remain are the two fold axis along \( y \) (in \( C_{mmm} \) symmetry) and the mirror \( m_{xy} \) (in \( C_{mmm} \) symmetry) which is primed. Consequently, the magnetic point-group describing the magnetic order under \( T_N \) is \( 2/m' \). According to table 2.4, this compound may present a linear magnetoelastic effect. This prediction has been the motivation for an experimental investigation of \( \text{Ho}_2\text{BaNiO}_5 \).

### 5.2.3 Synthesis and characterization

The synthesis of \( \text{Ho}_2\text{BaNiO}_5 \) was already reported [20, 23, 25]. We follow a similar procedure for the synthesis of our sample. \( \text{Ho}_2\text{BaNiO}_5 \) was prepared as polycrystalline material by solid state reaction from stoichiometric mixtures of analytical grade \( \text{Ho}_2\text{O}_3 \) (dried at 1000°C overnight prior to use), \( \text{NiO} \) (99.999%) and \( \text{BaCO}_3 \). The sample was ground, pelletized and heated in air overnight at 900°C, 950°C, 1050°C and 1100°C until reaching X-ray pure sample. After each thermal treatment, the reaction products were reground and repelletized before starting the next treatment.

The quality of the sample was checked by means of powder X-ray diffraction using a Bruker D8 Advance diffractometer with an energy dispersive detector. Refinement of the powder data has been carried out using the program GSAS [22]. We use the peak profile function of type 2 in GSAS. Only three parameters have been used to describe the peaks shape with one Gaussian parameter, one Lorentzian parameter and the shift. The results of the refinement are presented in figure 5.5 and in table 5.5. We obtain very good refinement of the structure with the following statistics: GoF = 1.51, \( wR_p=3.28\% \) and \( R_p=3.94\% \) with cell parameters \( a = 3.76010(5)\text{Å}, b = 5.75871(7)\text{Å}, c = 11.3275(1)\text{Å} \).

### 5.2.4 Magnetic properties

The magnetic properties have been investigated for two reasons: the magnetoelastic effect is dependent on the magnetic properties and two field induced phase transitions have been reported for \( \text{Ho}_2\text{BaNiO}_5 \). Checking for the existence of such transition is a good way to further investigate the quality of the sample, especially in terms of phase purity.
Figure 5.5: Refinement of the crystal structure of Ho$_2$BaNiO$_5$ on a powder sample. The refinement was carried with Immm symmetry giving rise to the following statistics: GoF = 1.51, wR$_p$ = 3.28% and R$_p$ = 3.94%. Cell parameters: a = 3.76010(5)Å, b = 5.75871(7)Å, c = 11.3275(1)Å.

Table 5.5: Crystallographic coordinates extracted from the refinement carried out on X-ray powder diffraction.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>U$_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho</td>
<td>4j</td>
<td>0.5</td>
<td>0</td>
<td>0.7977(1)</td>
<td>0.0473(7)</td>
</tr>
<tr>
<td>Ba</td>
<td>2c</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.0490(8)</td>
</tr>
<tr>
<td>Ni</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.049(1)</td>
</tr>
<tr>
<td>O$_1$</td>
<td>8l</td>
<td>0</td>
<td>0.766(1)</td>
<td>0.8500(5)</td>
<td>0.058(2)</td>
</tr>
<tr>
<td>O$_2$</td>
<td>2b</td>
<td>0</td>
<td>0.5</td>
<td>0.5</td>
<td>0.041(5)</td>
</tr>
</tbody>
</table>

We present in figure 5.6, the magnetic field dependence of the magnetization measured at T = 5K in order to confirm the experimental observations [20, 23, 25]. We confirm the two field induced phase transitions at a slightly different value for H$_{C2}$ (5.2T versus 5.4T) and exactly the same for H$_{C1}$ (2.9T).

The magnetization for Ho$_2$BaNiO$_5$ reaches $\approx 1\mu_B$ at H$_{C1}$ and $\approx 4.5\mu_B$ at H$_{C2}$ per formula unit. From neutron measurements in zero magnetic field [25], the Ni moments are rotated 26° from the c-axis to the a-axis, and the Ho moment is almost collinear with the c-axis at 1.5K (0.7°). The Ni and Ho moments reach 1.4$\mu_B$ and 9$\mu_B$ at 1.5K, respectively. Thus, we observe that even at H$_{C2}$, we are still far from the saturated value of the magnetic moment of Ho. This is in contrast with Nd$_2$BaNiO$_5$. In this material, a full saturation of the rare-earth moment is reached at H$_{C2}$ [26] while this is not
5.2. Magnetoelectricity in Ho$_2$BaNiO$_5$: Haldane gap system

Figure 5.6: Magnetic field dependence of the magnetization measured on a pellet of Ho$_2$BaNiO$_5$ at 5K. Two noticeable magnetic induced transitions are at $H_{C1}=2.9T$ and at $H_{C2}=5.2T$.

the case for Ho in Ho$_2$BaNiO$_5$. From neutron diffraction, we expect that the scenario for Nd will also hold for Ho since both rare-earths order along the $c$ axis. Experiments on single crystal of Ho$_2$BaNiO$_5$ could clarify the reasons for this discrepancy. In addition to the magnetization versus magnetic field, we measure also the temperature dependence of the magnetic susceptibility of a Ho$_2$BaNiO$_5$ pellet. The results are presented in figures 5.7 and 5.8.

Figure 5.7: Magnetic susceptibility measured on a Ho$_2$BaNiO$_5$ pellet in zero field cooled mode function for different applied magnetic fields: 0.1T (triangles), 4T (circles) and 6T (squares).

The magnetic susceptibility data present the common features of the R$_2$BaNiO$_5$ family. There is a broad maximum at around 30K characteristic for all the family. Indeed, this broad maximum (maximum at $\chi_{max}$) is
always present below $T_N$ for any R (e.g. Er$_2$BaNiO$_5$, $T_{\text{max}} = 16$K and $T_N=33$K) [27]. From neutron diffraction, it has been shown that there is a change of slope versus temperature in the Ho magnetic moment around 30K corresponding to $\chi_{\text{max}}$ in the magnetic susceptibility data [25]. In low-dimensional magnetic systems a maximum in magnetic susceptibility is not related to the 3D antiferromagnetic ordering.

In figure 5.8, we present the inverse susceptibility of a polycrystalline sample of Ho$_2$BaNiO$_5$ measured in zero field cooled mode with a magnetic field of 0.01T. We could fit the data in the paramagnetic phase using a Curie-Weiss dependence defined by $\frac{1}{\chi} = \frac{T + \theta}{C}$ between 200 and 300K. We find that Ho$_2$BaNiO$_5$ exhibits ferromagnetic interactions since $\theta$ is positive ($\theta=10.8$K). In addition, the value of the Curie constant $C=27.8$ emu.K.mol$^{-1}$ is in good agreement with the theoretical value of 28. It should be noted that at all temperatures the magnetic susceptibility is dominated by the contribution of the Ho$^{3+}$ moments ($p_{\text{eff}}=10.4\mu_B$, $C_{2\text{Ho}^{3+}}=27$ emu.K.mol$^{-1}$) being much larger than the contribution of the Ni$^{2+}$ moments ($p_{\text{eff}}=2.8\mu_B$, $C_{\text{Ni}^{2+}}=1$ emu.K.mol$^{-1}$). This means that in the paramagnetic regime the Ni$^{2+}$ contribution is only about 4% of the total susceptibility.

Figure 5.8: Inverse magnetic susceptibility measured on a pellet of Ho$_2$BaNiO$_5$ in zero field cooled mode with 0.01T. The line is a fit of the Curie-Weiss function using $\frac{1}{\chi} = \frac{T + \theta}{C}$.

Considering the derivative $d\chi/dT$, we notice an anomaly around 50K in agreement with the reported Néel temperature of $T_N=53$K [23, 25, 27] (see figure 5.9). Consequently, we ascribe this anomaly as the signature for the Néel temperature. The insufficient accuracy of our data for higher
magnetic fields does not allow, even by plotting $d\chi/dT$, the determination of the magnetic ordering temperature. In first approximation, we assume that $T_N$ does not change.

Figure 5.9: $d\chi/dT$ versus temperature for an applied field of 0.01 Tesla. The arrow indicates the Néel temperature in agreement with the literature [23, 25, 27].

In figure 5.7, we can observe that the decrease below $\chi_{\text{max}}$ disappears when applying a magnetic field of 6T. As the susceptibility is dominated by the Ho-contribution, this decrease should be associated with the magnetic behavior of the Ho-spins. There can be several reasons for this decrease: 1) the magnetic ordering of the Ho-sublattice; 2) the low-dimensional behavior of the Ho-sublattice or 3) a coupling of the Ho$^{3+}$-spins to the Ni$^{2+}$-Haldane system. We consider the first possibility unlikely because this would not lead to a suppression below 30K but already below $T_N \approx 53K$ [25]. The second option arises from the large moment for Ho for which a field of 6T represents a significant magnetic energy compared with the magnetic interactions. Nevertheless, we adopt the suggestion by Zheludev et al. [28]. They argue that there exists significant coupling of local crystal field excitations of the rare-earth ions to the Haldane-gap excitations of the Ni-sublattice. In such case the low-temperature behavior of the susceptibility may be determined by excitations of the Ho-sublattice, being coupled to the Ni-sublattice system, which exhibits excitations across the Haldane gap $\Delta$. Modelling the magnetic susceptibility by a temperature independent term and a Haldane-gap term $\exp(-\Delta/T) \sqrt{T}$ [29], we extract from our magnetic susceptibility data below 15K a value of $\Delta \approx 42K$ which is significantly lower than the value reported for Nd$_2$BaNiO$_5$ ($\Delta=127K$) [21] or for Y$_2$BaNiO$_5$ ($\Delta=100K$) [15].
The dependence of the Néel temperature of this family as function of temperature of the ionic radius suggests the influence of the volume, as well as the value of gJ, in the magnetic order [23]. For a Haldane system, a value of the gap $\Delta$ is function of J. The value of the gap for Ho$_2$BaNiO$_5$ is reduced by a factor 2 compared to other known R$_2$BaNiO$_5$. Such reduction of the gap could be due to different reasons:

- a significant difference in the Ni-Ni distances for Ho$_2$BaNiO$_5$ compared to the other rare-earth.
- an interchain coupling much larger in Ho$_2$BaNiO$_5$ which would renormalize the value of the gap.

The first possibility is unlikely due to the fact that the Ni-Ni distance (cell parameter $a = d$(Ni-Ni)) varies only by few percents over the different ionic radius (see figure 5.11).

If we assume that J does not change much between different members of the R$_2$BaNiO$_5$ family, which is true at least for Tb, Dy, Ho, Er and Tm [23], the value of the Haldane gap $\Delta$ should vary in an opposite fashion to the Néel temperature. We see in figure 5.11 that the Néel temperature increases linearly between Yb and Dy. Thus we believe that the reason for a reduced Haldane gap in Ho$_2$BaNiO$_5$ is likely due to a renormalization originating from the onset of a long range magnetic ordering.

We believe that for $T \ll \Delta$, the magnetic susceptibility exhibits Haldane
behavior (see figure 5.10) originating from the Ho-spins, being coupled by exchange to the Ni-sublattice. Thus the disappearance of the decrease in \( \chi \) below \( \chi_{\text{max}} \) can be associated with the closure of the Haldane gap by a magnetic field, or with a change in the coupling of the Ho-spins to the Ni-spins. We do not know the influence of the external magnetic field on the staggered exchange field acting on the Ni chains due to the Ho sublattice magnetization. In zero field, the staggered exchange field is about 35T [30]. Therefore, we believe that an external magnetic field of 6T \( \ll \) 35T does not close the Haldane gap.

5.2.5 Magnetoelectricity

Now that we have investigated the magnetic properties of Ho\(_2\)BaNiO\(_5\), we will show that we could induce a finite polarization in a magnetic field. The polarization was measured in a magnetic field. For each measurement, we cooled down the sample to 5K starting from 90K (\( T \gg T_N \)). During the cooling process, we applied the magnetic field perpendicular to the electric field (magnetoelectric annealing). We used two different electric fields: 3.15kV/cm (175V) and 4.5kV/cm (250V). At 5K, we removed the electric field and kept the magnetic field. The induced polarization was measured upon heating by integrating the pyroelectric current. The electric field was generated using a Keithley 237 high voltage source measure unit. The pyroelectric current was measured using a Keithley 617 programmable electrometer. We show in figure 5.12 the sample holder that we used. The sample used was a sintered pellet polished down to 0.55 mm thickness with
First, we measure our sample applying an electric field of 3.15kV/cm (175V). We show the induced polarization in figure 5.13 under the application of a 1T magnetic field. We observe that the induced polarization has a broad maximum around 30K. Above $T \approx 30K$, the polarization decreases almost linearly and becomes zero near 70-75K. The linear magnetoelectric effect is observable only in the magnetically ordered phase. Thus, it is surprising that the polarization disappears near 70-75K while $T_N$ is about 55K. Thus, we measure the induced polarization under $H=1T$ for a higher electric field. We show for comparison in the same figure, the induced polarization under 1T magnetic field when applying a 4.5kV/cm (250V) electric field. The temperature behavior is similar for both electric fields. However, the polarization for a 4.5kV/cm electric field becomes zero at a lower temperature around 60K. Moreover, we notice a significant higher value of the induced polarization for the 4.5kV/cm electric field. Thus we believe that the apparent transition temperature to the paramagnetic paraelectric phase is related to the electric domains structure of our polycrystalline sample. One possible reason could be the presence of strong low dimensional interactions below $T_N$. This is known to occur in Nd$_2$BaNiO$_5$ [28]. The magnetic interactions could couple to the polarization and thus being affected by the strength of the electric field. Therefore the onset of the polarization does not coincide exactly with $T_N$.

Attempts of measurement with higher electric fields than 4.5kV/cm were not possible due to the closeness to the electrical breakdown of the sample. Consequently in the remaining part of our investigation, we made a magnetic field dependence study using a 4.5kV/cm electric field. We present in figure 5.14 the magnetic field dependence of the induced polarization.

There are common features of the induced polarization independently of the applied magnetic field. These common features are a linear dependence of the induced polarization close to $T_N$ and a broad maximum around 30K.
In first approximation, we know that the induced polarization close to $T_N$ is proportional to the magnetic order parameter [31]. From neutron diffraction [25], we know that the Ho magnetic moment below $T_N$ and over a quite large range of temperature has a quasi linear temperature dependence. The Ni moments saturate very quickly below $T_N$. Thus, we ascribe the linear temperature dependence of the polarization below $T_N$ as a result of the magnetic order parameter. In this temperature range, this magnetic order parameter is mostly governed by the Ho magnetic moment and thus we are not sensitive to the Haldane gap to which the Ni moments contribute. Another common feature is the broad maximum around 30K which is almost magnetic field independent. This broad maximum is also present in the magnetic susceptibility (see figure 5.7) as a result of the one dimensional character of the magnetic order. Thus, we observe that the temperature dependence of the polarization reflects the 1D character of the magnetic order. Applying a magnetic field, we observe a decrease of the induced polarization from 1 to 5T. At $H=6T$, we observe a jump in the induced polarization. This jump in the polarization cannot be related to the eventual closing of the Haldane gap as discussed earlier. We know from susceptibility data that at $H_{C2}$, we have a new magnetic phase. Thus, in the hypothesis of a higher magnetization, one can expect a higher induced polarization. If the gap is closed thus the total magnetic moment of the system would increase and thus the induced polarization would be increased too. However the decrease from 1 to 5T followed by the increase at 6T of the polarization remains to be explained in its details. However the observation of a finite

Figure 5.13: Influence of the applied voltage on the induced polarization with $H=1T$
polarization at any magnetic fields give us the indication that the three magnetic phases observed in figure 5.6 are magnetoelectric and thus magnetically ordered. This is surprising since the second metamagnetic phase transition at $H_C^2$ would typically gives rise to a paramagnetic phase for a simple 1D-Heisenberg system. Additional measurements and neutron diffraction under magnetic field could clarify the magnetic field dependence of the structural and magnetic properties.

5.2.6 Conclusion

Using symmetry arguments, we predict a linear magnetoelectric effect in $\text{Ho}_2\text{BaNiO}_5$. We investigate the magnetic and magnetoelectric properties of this Haldane gap system. We confirm the existence of two metamagnetic phase transitions at $H_C^1=2.9\text{T}$ and at $H_C^2=5.2\text{T}$. We show that this system presents a linear magnetoelectric effect which exhibits the 1D character of its magnetic order. In addition, we demonstrate the unusual magnetic behavior of this Heisenberg system through its magnetoelectric response. Further investigations are necessary to interpret the relationships between magnetic and structural properties.
5.2. Magnetoelectricity in Ho$_2$BaNiO$_5$, Haldane gap system

References


