Magnetoelectricity via crystallography

L. Fuentes*, M. García, J. Matutes-Aquino, D. Ríos-Jara
Advanced Materials Research Center (CIMA V), Chihuahua, Chih 31109, Mexico

Abstract

Crystal structure conditions for possible existence of magnetoelectric (ME) effect are reviewed, with emphasis on color symmetry and axial nature of related magnitudes. Application of Neumann’s Principle leads to general classification rules. The case of Aurivillius phases is discussed in detail. Measurement of the magnetoelectric coefficient in a Bi$_5$ Ti$_3$ FeO$_{15}$ ceramic is reported.

Keywords: Magnetoelectricity; Multiferroic; Aurivillius; Color symmetry

1. Introduction

Technology demands sensitive and cheap magnetoelectric (ME) sensors, i.e. devices that convert magnetic field variations in electric signals and vice-versa. Consider the case of X-by-wire systems in the automobile industry. “X” means, for example, steering or braking systems. Substitution of present hydraulic servomechanisms by electric motors will lead to 5–10% economy. Implementation of this new technology requires recognition of the steering wheel (brake pedal) movement via detection of variations in magnetic field. (See, for example, present developments described in the web pages of some major manufacturers of automobile electric equipment) [1–3].

There are two principal families of ME materials: magnetostrictive–piezoelectric composites and single-phase crystals and polycrystals. The first report on experimental observation of the ME effect was published by Schmid and co-workers [4] in 1966. The investigated material was nickel-iodine boracite Ni$_3$B$_7$O$_{13}$I, a ferroelectric–ferromagnetic. In 1972 Suchetelene [5], working for the Philips Laboratories, developed the first magnetic field sensor based on ME effect. The sensitive material was a composite of CoFeO$_4$–BaTiO$_3$. This initial period registered other significant papers written in Japan [6,7], Europe [8] and USA [9].

Only recently the ME effect has been detected with intensities of practical interest. Present reports refer mostly to composite materials [10–12]. A reduced number of single-phase ceramics also exhibit the desired property [13,14].

As to theory, the groups of Schmid [15] and Hill [16] may be considered as pioneering the field. The purpose of the present paper is to give a brief review of the crystallographic conditions required for the ME phenomenon to be observable. Emphasis is put on symmetry considerations. A particular case from experimental work at CIMA V is reported.

2. Review of principal and coupling properties: polar and axial tensors

We briefly summarize the macroscopic characterization of reversible thermal, elastic, electric and magnetic interactions. Approach and notation follow the IEEE Standard on piezoelectricity [17].

Independent variables are selected according to the conditions affecting the considered system. The usual experimental setup for observation of ME effect allows control of temperature \( \theta \), stress \( T \), electric displacement \( D \) and magnetic field intensity \( H \). We take these quantities as independent variables. Related dependent variables are, in this case, entropy \( \sigma \), strain \( S \), electric field intensity \( E \) and magnetic induction \( B \).

The behavior of a given material under the considered actions is generally described, using a linear approximation, by relations of the type \( Y = kX \), where \( X \) (a tensor of rank \( m \)) represents a cause and \( Y \) (tensor of rank \( n \)) is the corre-
3. Crystal color symmetry and magnetoelectric effect

A basic law that rules the orientational dependence of a given property in a solid is the Neumann Principle. Application of this principle to magnetic coupling requires consideration of the difference between polar and axial tensors as well as of color symmetry. Color symmetry is a generalized representation that considers the "anti" or "time inversion" operation, denoted $\theta$. Inverting a characteristic parameter to its opposite is described as changing from "white" to "black". Depending on the way the "anti" operation appears, color symmetry groups are classified as given further.

1. Ordinary or single-color groups (the 32 classical crystallographic point groups).
2. Gray symmetry (concurrent manifestation of white and black events, 32 groups).
3. Black and white point groups (58 B&W).

B&W point groups are formed as follows. $G$ is an ordinary group, of order $g$. $H$ is a subgroup of $G$, of order $g/2$. Multiply $(G−H)$ by the time inversion operation and build the black and white group $M = H + (G−H)$. It is denoted as $G:H$.

The Neumann Principle for crystal physics may be expressed as follows: color symmetry operations of any macroscopic physical property forms a group that contains as a sub-group the color point group of the considered crystal structure.

Mathematically, the tensor of any physical property satisfies Eqs. (1) or (2), depending on the nature of the tensor, with $G$ scanning all the symmetry operations of the structural color point group.

$$P_{ij\ldots m} = \pm G_{ij\ldots m} G_{ij\ldots m}$$ (1)

$$A_{ij\ldots m} = \pm G_{ij\ldots m} A_{ij\ldots m}$$ (2)

$P_{ij\ldots m}$ is a polar tensor and $A_{ij\ldots m}$ is axial. $G_k$ is a matrix representing the rotations of the structural color point group. Plus sign corresponds to ordinary symmetry and minus to anti-symmetry. The determinant $|G|$ equals +1 for proper rotations and −1 for rotations that include the inversion operation. Sum over repeated indexes $(i, j, \ldots, n = 1\ldots3)$ is assumed.

Application of the condition (2) to the magnetoelectric tensor, with consideration of the 122 crystallographic color point groups leads to the following: 18 ordinary and 40 B&W groups are privileged by the possibility of exhibiting ME effect. No gray group is allowed to show the phenomenon. Table 2 presents a resume of magnetoelectric groups.

To fix the ideas, we discuss in some detail a particular case. Our model crystal is $\text{Bi}_2\text{Ti}_3\text{FeO}_5$, a member of so-called Aurivillius ceramics. The atomic motive is composed of four (Ti–Fe) perovskite octahedra, sandwiched between layers of bismuth oxide ($\text{Bi}_2\text{O}_2$). For temperatures above the Curie Point (∼600°C), the symmetry of the “prototype” centro-symmetrical phase is given by $\text{4mm}$ space group. Crystals are neither capable of spontaneous (electric or magnetic) polarization nor to show magnetoelectricity. At room temperature symmetry becomes $\text{Fmm2}$ ($\text{18}$), polar, with magnetoelectricity allowed. Fig. 1 represents the crystal structure. Crystallographic axes are chosen as

### Table 1

<table>
<thead>
<tr>
<th>Property</th>
<th>Related magnitudes</th>
<th>Tensor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat capacity $C$</td>
<td>Entropy $P(0)$</td>
<td>$P_0$</td>
</tr>
<tr>
<td>Elasticity $\nu$</td>
<td>Strain $P(2)$</td>
<td>$P_2$</td>
</tr>
<tr>
<td>Impeditivity $\beta$</td>
<td>Electrical intensity $P(1)$</td>
<td>$P_1$</td>
</tr>
<tr>
<td>Permeability $\mu$</td>
<td>Induction $A(1)$</td>
<td>$A_1$</td>
</tr>
<tr>
<td>Dielectricity $\varepsilon$</td>
<td>Electrical intensity $P(1)$</td>
<td>$P_1$</td>
</tr>
</tbody>
</table>

### Table 2

<table>
<thead>
<tr>
<th>Crystal system</th>
<th>Color group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ordinary symmetry</td>
<td>Black-white symmetry</td>
</tr>
<tr>
<td>Triclinic</td>
<td>$C_1$</td>
</tr>
<tr>
<td>Monoclinic</td>
<td>$C_1$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>$D_2$, $D_2$</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>$C_4$, $D_2$, $C_4$</td>
</tr>
<tr>
<td>Hexagonal</td>
<td>$C_6$, $D_3$, $C_6v$</td>
</tr>
<tr>
<td>Cubic</td>
<td>$T$, $O$</td>
</tr>
</tbody>
</table>
Fig. 1. Crystal structure of Bi$_5$Ti$_3$FeO$_{15}$. Spheres: large white → Bi; small green → Ti/Fe; large pink → O. Oxygen atoms at the corners of Ti/Fe-coordination octahedra omitted for clarity. Space group Fmm.2. Lattice parameters: \( a = 41.149 \) Å, \( b = 5.4118 \) Å, \( c = 5.4681 \) Å.

follows: axis \( x \) (vector \( \mathbf{a} \)) is normal to \((\text{Bi}_2\text{O}_2)_2^+\) layers; axis \( z \) (vector \( \mathbf{c} \)) is taken along the electric polarization direction and axis \( y \) (vector \( \mathbf{b} \)) is normal to \( x \) and \( c \). The planes \((0, y, z)\) and \((x, 0, z)\) are ordinary mirrors. Macroscopic symmetry corresponds to ordinary point group \( C_{2v} = \text{mm}2 \). Eq. (3) represents the form of the ME (axial) tensor for a Bi$_5$Ti$_3$FeO$_{15}$ crystal at room temperature.

\[
m = \begin{pmatrix}
0 & m_{12} & 0 \\
m_{12} & 0 & 0 \\
0 & 0 & 0 
\end{pmatrix}
\]

(3)

Fig. 2 shows the surface representation [19] of the longitudinal ME effect as function of direction \( h = (\phi, \beta) \). The mathematical expression of the surface is:

\[
m(h) = m(\phi, \beta) = (m_{12} + m_{21}) \sin^2 \phi \sin \beta \cos \beta
\]

(4)

Polar angle \( \Phi \) is referred to the \( z \) axis; azimuth \( \beta \) is measured from the \((x, 0, z)\) plane. For \((m_{12} + m_{21}) > 0\), the maximum longitudinal ME effect is along the lines \((x, x, 0)\) and \((x, -x, 0)\), with \( \Delta E \uparrow \Delta H \) in the former and \( \Delta E \downarrow \Delta H \) in the latter.

The generalization of the symmetry of the surface illustrates the Neumann Principle, as applied to \textit{axial} (or \textit{pseudo}) scalars: surface points transformed by (ordinary) mirror planes are converted to opposite sign.

Fig. 2. Surface representation of the longitudinal ME effect for a mm2 Aurivillius crystal. The (second-order rotational symmetry) \( z \) axis points outwards from the figure. Mirror planes are \((x, 0, z)\) and \((0, y, z)\).

Fig. 3. Bi$_5$Ti$_3$FeO$_{15}$ particles obtained by the molten salts method.

4. Experimental results

Bi$_5$Ti$_3$FeO$_{15}$ was obtained at CIMA V and tested for ME effect. Synthesis was performed by the molten salts method. Details of the preparation method are to be published. XRD showed single-phase Bi$_5$Ti$_3$FeO$_{15}$. Fig. 3 shows a scanning electron micrograph of the obtained crystals. Flake shape is apparent. The thinner dimension corresponds to the crystallographic direction perpendicular to the bismuth oxide layers. Spontaneous electric polarization appears in the plane of the flake.

Polycrystalline ceramics were obtained from the powder by sintering at 1000 °C, 5 h in air. Silver plated samples were electrically polarized under a 1 kV/mm electric field, \( T = 100 \) °C, and tested for ME effect. The system for measuring ME response was built according to the suggestion of Kumar et al. [20]. Fig. 4 shows the registered output. Experiment was performed at room temperature, under an applied alternating magnetic field of amplitude 0.61 Oe.

The ME effect in the studied material is weak, but measurable. Hysteresis phenomenon is present. From the intercepts of the curves, an estimate of the longitudinal polycrystal ME coupling coefficient can be given: \( m \sim 7/0.61 \sim 11 \) mV cm$^{-1}$ Oe$^{-1}$. To date, these results are typical for materials investigated at international scale.
5. Conclusions

The field of magnetoelectricity is young and technologically important. Physics behind the ME effect is interesting and poorly explored. New materials need to be obtained and tested, microscopic theory needs to be developed, single crystals need too be grown, texture needs to be optimized. There is plenty of room to be occupied.

Acknowledgements

Support from CONACyT, Project 31234-U, is gratefully acknowledged.

References