**CHAPTER THREE**

**Magnetoelectricity**

L.E. Fuentes-Cobas\(^1\), J.A. Matutes-Aquino\(^1\) and M.E. Fuentes-Montero\(^2\)

**Contents**

1. Historical Introduction: Magnetoelectricity and Multiferroicity 130
2. Fundamentals 134
   2.1. Physical quantities, their symbols and units 134
   2.2. Thermodynamics and tensor properties of materials 136
   2.3. Space symmetry, electricity and magnetism 140
   2.4. Space–time symmetry and magnetoelectric multiferroics 144
   2.5. The NP and magnetoelectric tensors via group theory 147
   2.6. Microscopic approach and classification of magnetoelectric multiferroics 154
   2.7. Theoretical calculations 156
3. Measurement of Magnetoelectric Properties 159
   3.1. Experimental techniques for measuring magnetoelectric coupling coefficients and multiferroic nature of materials 159
   3.2. Theory of measurement in a dynamic magnetic field 161
   3.3. Theory of measurement in pulsed magnetic field 164
   3.4. Magnetoelectric measurements by the dynamic method 167
   3.5. Magnetoelectric measurements by the pulsed dynamic method 168
4. Single-Phase Magnetoelectric Multiferroics 171
   4.1. Cr\(_2\)O\(_3\) 171
   4.2. Ni\(_3\)B\(_2\)O\(_{13}\) 174
   4.3. Olivine phosphates 175
   4.4. Perovskites—BiFeO\(_3\) and BiMnO\(_3\) 179
   4.5. Bi\(_2\)FeCrO\(_6\) 186
   4.6. Hexagonal manganites YMO\(_3\), HoMnO\(_3\) 187
   4.7. Orthorhombic manganites RMnO\(_3\) (R = Gd, Tb, Dy) 190
   4.8. Half-doped manganites 193
   4.9. Layered perovskites 195

\(^*\) Corresponding author. Tel.: (52 614) 439 11 59
E-mail address: luis.fuentes@cimav.edu.mx

1 Advanced Materials Research Center, Chihuahua, Mexico
2 Autonomous University of Chihuahua, Chihuahua, Mexico

*Handbook of Magnetic Materials, Volume 19* © 2011 Elsevier B.V.
ISSN 1567-2719, DOI: 10.1016/S1567-2719(11)19003-4 All rights reserved.
1. HISTORICAL INTRODUCTION: MAGNETOELECTRICITY AND MULTIFERROICITY

Magnetoelectricity, in a wide sense, means interaction between the magnetic and electric subsystems in a given material. Several reported events related with variations in the dielectric constant (Kanamadi et al., 2005) or the electrical resistivity (Patankar et al., 2001) produced by magnetic fields, or about nonlinear magnetoelectric coupling (Jia and Berakdar, 2009; Miyamoto, 1994), are considered today as magnetoelectricity. From this point of view, the Hall effect may be considered as magnetoelectricity (Jiang and Hu, 2006). A much more narrow conception refers to linear changes of the electric polarization induced by magnetic fields, or the inverse: linear changes in magnetization induced by electric fields.

Hundreds of single-phase and composite materials are currently being investigated in the search for large magnetoelectric responses. As general view, bulk composites show orders of magnitude larger effects. However, understanding and improving magnetoelectricity in single-phase materials are considered one of the hottest challenges of present-day materials physics. Furthermore, nanometric magnetoelectric structures should become the path to a next generation of nanospintronics and other low-dimensional technologies.

Multiferroicity is the simultaneous manifestation of at least two of the so-called ferroic conditions (Aizu, 1972). Following a narrow criterion,
ferroelectric, ferroelastic and ferromagnetic ordering are the ones to be considered. The candidate material must be single-phased. Widening the scope, ferri-, antiferro- and weakly ferro-ordering schemes also tend to be included. Composites are accepted. The overwhelming majority of materials regarded today as multiferroics are ferroelectric–antiferromagnetic (Font et al., 2008).

In principle, electromagnetic multiferroicity is a sufficient condition for magnetoelectricity. In real-world single-phase materials, even among multiferroics, magnetoelectric responses generally are weak and require low temperatures. The hunt for magnetoelectric materials, in many practical cases, coincides with the investigation of multiferroics. The search for large magnetoelectric coupling focuses frequently on the study of magnetically induced rotation or inversion of ferroelectric domains polarization.

The history of magnetoelectricity somehow resembles that of the Sleeping Beauty. After its birth in the prolific imagination of Pierre Curie (1894), it has been “sleeping” (better “hidden”) for approximately one century. Magnetoelectricity was not awakened by a prince, but by the accumulative work of several talented researchers that, during the whole twentieth century, delivered significant contributions. Among the pioneers and developers of the science of magnetoelectricity, some key contributors of the earlier periods are listed below:

- **Debye (1926)** introduced the term “magnetoelectricity” for the effect that was at that time unsuccessfully searched for.
- **Wigner (1932)** distinguished magnetic quantities from electric ones in relation to space inversion and proposed the consideration of time inversion as a symmetry criterion.
- **Van Vleck (1932)** clarified the role of external magnetic field on the appearance of the magnetoelectric effect.
- **Landau (1937)** established the theory of phase transitions and the dependence of physical properties on the symmetry of internal charge and current distribution.
- **Zeldovich (1957)** initiated theoretical studies of toroidal current distributions as sources of non-dipolar, non-quadrupolar magnetic fields. Considered systems, at that time named “anapoles”, formed the embryo of the present-day concept of ferrotoroidic magnetoelectrics.
- **Dzyaloshinskii (1959)** predicted theoretically, on magnetic symmetry grounds, that magnetoelectric effect should be observable in antiferromagnetic Cr$_2$O$_3$.
- **Astrov (1960)** confirmed experimentally Dzyaloshinskii’s prediction of electric-field induced magnetization in Cr$_2$O$_3$.
- **Rado and Folen (1961)** observed magnetically induced electric signals in Cr$_2$O$_3$. 

---

**Author's personal copy**

*MagnetoElectricity*
Shubnikov (1951) introduced symmetry-antisymmetry relationships. Shubnikov and Belov (1964) established all the possible bicolor point groups.

Ascher (1966, 1974) identified three types of electromagnetic vectors, according to their space–time symmetry relationships. Table 3.1 resumes the Ascher classification and presents an updated notation.

Al’shin and Astrov (1963) observed magnetoelectric response in Ti$_2$O$_3$ and Rado (1964) reported the phenomenon in GaFeO$_3$.

The groups of Ascher and Schmid at the Battelle Institute in Geneva and of Newnham at the Pennsylvania State University discovered an important number of magnetoelectric boracites (Ascher et al., 1966) and phosphates (Santoro et al., 1966). Magnetoelectric coupling coefficients were not as high as desired, but the number of new magnetoelectric materials grew significantly (Schmid, 1973).

In the mid 1970s, scientific production about magnetoelectric phases reached a kind of saturation. Researchers felt that single-phase magnetoelectrics were unpractical because the coupling was weak, the required temperatures were low and theory did not show a path towards significant improvements. During the 1980s, research continued (e.g., Tabares-Munoz et al., 1985), but at a lower rate.

The situation started changing for the good in the late 1990s. Some factors that promoted the renaissance of magnetoelectricity were the following:

- The “magnetoelectricity” concept found a conjunction with “multiferroicity” (Schmid, 1994). As will be discussed below, the simultaneous occurrence of ferromagnetism and ferroelectricity is highly favourable for magnetoelectricity. The search for magnetoelectrics has evolved into a search for multiferroics with magnetoelectric coupling, see Fig. 3.1.
- Development of theoretical tools, basically *ab initio* calculations (Hill, 2000; Spaldin and Fiebig, 2005), opened new and promising routes for designing potential magnetoelectric materials.
- Solution–combustion (Morán et al., 2008) and other preparative techniques (Kanatzidis et al., 2008) have made possible the synthesis of new families of compounds.
- Advances in thin-films growth methods (Wang et al., 2003) have opened a new field of experimentation. This new physical dimensionality has produced nanomaterials with surprising magnetoelectric properties.

### Table 3.1 Classification of electromagnetic vectors.

<table>
<thead>
<tr>
<th>Vectors</th>
<th>Ascher</th>
<th>Present</th>
</tr>
</thead>
<tbody>
<tr>
<td>E, P, D</td>
<td>Polar</td>
<td>i-Polar</td>
</tr>
<tr>
<td>j</td>
<td>Axio-polar</td>
<td>c-Polar</td>
</tr>
<tr>
<td>B, M, H</td>
<td>Axial</td>
<td>c-Axial</td>
</tr>
</tbody>
</table>
– Last but not least, the requirements of nanotechnology (Martin et al., 2008), the need for new methods for writing and reading (by means of electrical signals) information (as magnetic entities) at the nanoscale, have promoted a high level of research activity on magnetoelectric multiferroics.

During the last years of the past century and the beginnings of the present one, magnetoelectricity has received a tremendous impulse. The discoveries of Catalan (2006), Ederer and Fennie (2008), Eerenstein et al. (2006), Fiebig (2005), Katiyar et al. (2010), Ramesh and Spaldin (2007), Rivera (2009), Schmid (2008), Scott (2007), Spaldin et al. (2008), Zheng et al. (2004), their collaborators and others, have converted magnetoelectricity into one of the hottest fields of present-day materials science. Today, magnetoelectricity research is well awake; it is like a young and gorgeous princess with plenty of mysteries and promises.

A number of detailed reviews about the state of the art in magnetoelectric multiferroics have been published recently. Some representative papers on this line are the following:

– Eerenstein et al. (2006)
2. FUNDAMENTALS

2.1. Physical quantities, their symbols and units

The International System of Units (SI) will be used in the presentation of the various topics in this Handbook Chapter. For practical reasons, results of case studies from the literature will be cited in the units used in the original articles.

2.1.1. Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>area</td>
</tr>
<tr>
<td>( B )</td>
<td>magnetic induction</td>
</tr>
<tr>
<td>( C )</td>
<td>heat capacity, capacitance</td>
</tr>
<tr>
<td>( D )</td>
<td>electric displacement</td>
</tr>
<tr>
<td>( E )</td>
<td>electric-field intensity</td>
</tr>
<tr>
<td>( G )</td>
<td>Helmholtz free energy</td>
</tr>
<tr>
<td>( \mathbf{G} )</td>
<td>space transformation operator</td>
</tr>
<tr>
<td>( H )</td>
<td>magnetic field intensity</td>
</tr>
<tr>
<td>( i )</td>
<td>electric current intensity</td>
</tr>
<tr>
<td>( j )</td>
<td>current density</td>
</tr>
<tr>
<td>( M )</td>
<td>magnetization</td>
</tr>
<tr>
<td>( P )</td>
<td>electric polarization</td>
</tr>
<tr>
<td>( p )</td>
<td>pyroelectric vector</td>
</tr>
<tr>
<td>( Q )</td>
<td>electric charge</td>
</tr>
<tr>
<td>( r )</td>
<td>position vector</td>
</tr>
<tr>
<td>( \mathbf{R} )</td>
<td>rotation matrix</td>
</tr>
<tr>
<td>( R_x, R_y, R_z )</td>
<td>generic pseudovector bases</td>
</tr>
<tr>
<td>( S )</td>
<td>strain</td>
</tr>
<tr>
<td>( T )</td>
<td>stress</td>
</tr>
<tr>
<td>( \mathbf{T} )</td>
<td>toroidal moment</td>
</tr>
<tr>
<td>( t )</td>
<td>thickness</td>
</tr>
<tr>
<td>( u )</td>
<td>energy density</td>
</tr>
<tr>
<td>( x, y, z )</td>
<td>coordinates, generic vector bases</td>
</tr>
<tr>
<td>( \mathbf{a} )</td>
<td>linear magnetoelectric coupling tensor</td>
</tr>
<tr>
<td>( \mathbf{a}^{EH} )</td>
<td>linear EH magnetoelectric coupling</td>
</tr>
<tr>
<td>( \beta, \gamma )</td>
<td>bilinear magnetoelectric tensors</td>
</tr>
<tr>
<td>( \chi_c )</td>
<td>generic component of a hypervector</td>
</tr>
<tr>
<td>( \mu )</td>
<td>permeability</td>
</tr>
<tr>
<td>( \mu^{rel} )</td>
<td>relative permeability</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>permittivity</td>
</tr>
<tr>
<td>( \varepsilon^{rel} )</td>
<td>relative permittivity = dielectric const</td>
</tr>
<tr>
<td>( \epsilon_{ijk} )</td>
<td>Levi–Civita symbol</td>
</tr>
<tr>
<td>( \Theta )</td>
<td>time inversion operator</td>
</tr>
<tr>
<td>( \eta )</td>
<td>thermal expansion</td>
</tr>
<tr>
<td>( \chi_M )</td>
<td>magnetic susceptibility</td>
</tr>
<tr>
<td>( \chi_p )</td>
<td>magnetic susceptibility</td>
</tr>
</tbody>
</table>

 Scalars are denoted with *italic* symbols, vectors with **Bold-Times New Roman** and tensors (rank \( \geq 2 \)) with **Bold-Arial**.
2.1.2. Acronyms

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>AFM</td>
<td>antiferromagnetic</td>
</tr>
<tr>
<td>BFO</td>
<td>BiFeO$_3$</td>
</tr>
<tr>
<td>DFT</td>
<td>density functional theory</td>
</tr>
<tr>
<td>EMF</td>
<td>electronic magnetic ferroelectric</td>
</tr>
<tr>
<td>FE</td>
<td>ferroelectric</td>
</tr>
<tr>
<td>FM</td>
<td>ferromagnetic</td>
</tr>
<tr>
<td>ME</td>
<td>magnetoelectric</td>
</tr>
<tr>
<td>MF</td>
<td>multiferroic</td>
</tr>
<tr>
<td>MEMF</td>
<td>magnetoelectric multiferroic</td>
</tr>
<tr>
<td>NP</td>
<td>Neumann Principle</td>
</tr>
<tr>
<td>SMF</td>
<td>structural magnetic ferroelectric</td>
</tr>
<tr>
<td>TM</td>
<td>transition metal</td>
</tr>
</tbody>
</table>

2.1.3. Some important relations between electric and magnetic quantities (SI)

Definition of electric displacement: $D = \varepsilon_0 E + P$ (1)

Linear dielectric effect: $P = \varepsilon_0 \chi^P \cdot E$ (2)

Dielectric constitutive equations: $D = \varepsilon_0 (\mathbf{I} + \chi^P) \cdot E = \varepsilon_0 \mathbf{e}_{ref} \cdot E = \varepsilon E$ (3)

Magnetic induction → intensity: $B = \mu_0 (H + M)$ (4)

Linear diamagnetism: $M = \chi^M \cdot H$ (5)

Paramagnetic constitutive equations: $B = \mu_0 (\mathbf{I} + \chi^M) \cdot M = \mu_0 \mu^\text{ref} \cdot H = \mu H$ (6)

$\varepsilon_0 = 8.9 \times 10^{-12} \text{F/m}$ and $\mu_0 = 4\pi \times 10^{-7} \text{H/m}$ are vacuum permittivity and permeability, respectively. $\mathbf{I} = || \delta_{ij} ||$ is the identity tensor. $c = (\varepsilon_0 \mu_0)^{-1/2}$ is the velocity of light in vacuum. $\mu_B = e\hbar /2m_e = 9.27400915 \times 10^{-24} \text{J/T}$ is the Bohr magneton.

Table 3.2 Some Gaussian → SI conversion factors.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Non-rationalized Gaussian</th>
<th>SI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E$</td>
<td>1 statvolt/cm</td>
<td>$3 \times 10^4$</td>
</tr>
<tr>
<td>$D$</td>
<td>1 statcoulomb/cm$^2$</td>
<td>$1/(12\pi \times 10^5)$</td>
</tr>
<tr>
<td>$B$</td>
<td>1 Gauss</td>
<td>$1/10^4$</td>
</tr>
<tr>
<td>$H$</td>
<td>1 Oe</td>
<td>$1000/(4\pi)$</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>1</td>
<td>$1/(3 \times 10^8) = c^{-1}$</td>
</tr>
<tr>
<td>$\beta$</td>
<td>1/Oe</td>
<td>$4\pi/(3 \times 10^{11})$</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>1 cm statvolt</td>
<td>$1/(9 \times 10^{13})$</td>
</tr>
</tbody>
</table>
2.1.4. Units

2.2. Thermodynamics and tensor properties of materials

We briefly summarize the macroscopic characterization of reversible thermal, elastic, electric and magnetic interactions. Irreversible processes (e.g., resistive electrical conduction) are not included. The energy per unit volume of a sample under actions of the considered types is given by Eq. (7):

\[ du = \theta d\sigma + T_{ij} dS_{ij} + E_{m} dD_{m} + H_{n} dB_{n} \]  

(7)

The scalars \( \theta \) and \( \sigma \) are, respectively, the temperature and entropy. \( T = \| T_{ij} \| \) and \( S = \| S_{ij} \| \) are second-rank polar tensors associated with stress and strain. \( E = \| E_{m} \| \) and \( D = \| D_{m} \| \), polar vectors, are the electric field intensity and electric displacement. \( H = \| H_{n} \| \) and \( B = \| B_{n} \| \), magnetic field intensity, induction and magnetization, are axial vectors (see below). Einstein convention, indicating the sum over repeated indexes \((i, j, \text{ etc.}) = 1, 2, 3\), is applied.

In Eq. (7), independent variables are the entropy, strain, electric displacement and magnetic induction. In symbols: \( u = u(\sigma, S, D, B) \). On the other hand, experiments with \( \theta, T, E \) and \( H \) as independent variables are frequent. Exchanging dependent–independent variables is performed by means of Legendre transformations, as follows.

The generalized Helmholtz free energy \( G = G(\theta, T, E, H) \) is defined by Eq. (8):

\[ G = u - \sigma \theta - S_{ij} T_{ij} - D_{m} E_{m} - B_{n} H_{n} \]  

(8)

\[ dG = -\sigma d\theta - S_{ij} dT_{ij} - D_{m} dE_{m} - B_{n} dH_{n} \]  

(9)

The exact differential nature of \( dG \) leads to the following identifications:

\[ \sigma = -\left( \frac{\partial G}{\partial \theta} \right)_{T, E, H} \quad S_{ij} = -\left( \frac{\partial G}{\partial T_{ij}} \right)_{\theta, E, H} \]

\[ D_{m} = -\left( \frac{\partial G}{\partial E_{m}} \right)_{\theta, T, E} \quad B_{n} = -\left( \frac{\partial G}{\partial H_{n}} \right)_{\theta, T, E} \]  

(10)

(\( \sigma, S, D, B \)) are considered responses to the stimuli \((\theta, T, E, H)\):

\[ d\sigma = \left( \frac{\partial \sigma}{\partial \theta} \right) d\theta + \left( \frac{\partial \sigma}{\partial T_{ij}} \right) dT_{ij} + \left( \frac{\partial \sigma}{\partial E_{m}} \right) dE_{m} + \left( \frac{\partial \sigma}{\partial H_{n}} \right) dH_{n} \]  

(11)

\[ dS_{ij} = \left( \frac{\partial S_{ij}}{\partial \theta} \right) d\theta + \left( \frac{\partial S_{ij}}{\partial T_{kl}} \right) dT_{kl} + \left( \frac{\partial S_{ij}}{\partial E_{m}} \right) dE_{m} + \left( \frac{\partial S_{ij}}{\partial H_{n}} \right) dH_{n} \]  

(12)
Magnetoelectricity

\[ \frac{\partial D_n}{\partial \theta} \] 
\[ \frac{\partial D_m}{\partial T_{ij}} \] 
\[ \frac{\partial D_n}{\partial E_n} \] 
\[ \frac{\partial D_n}{\partial H_n} \] 
\[ dD_m = \left( \frac{\partial D_m}{\partial \theta} \right) d\theta + \left( \frac{\partial D_m}{\partial T_{ij}} \right) dT_{ij} + \left( \frac{\partial D_m}{\partial E_n} \right) dE_n + \left( \frac{\partial D_m}{\partial H_n} \right) dH_n \] (13)

\[ dB_m = \left( \frac{\partial B_n}{\partial \theta} \right) d\theta + \left( \frac{\partial B_n}{\partial T_{ij}} \right) dT_{ij} + \left( \frac{\partial B_n}{\partial E_n} \right) dE_n + \left( \frac{\partial B_n}{\partial H_n} \right) dH_n \] (14)

The second-order derivatives of \( G \) are material's properties, according to the following definitions, Eqs. (15)–(24). Generally speaking, they are tensors. Their ranks \( r \) and polar/axial characters (see below) are included. Supra-indexes denote the independent variables that are held constant during the determination of a given property. \( \rho \) is material’s density.

\[ \rho \frac{\partial C_{\text{TEH}}^{\text{TEH}}}{\partial \theta} = \left( \frac{\partial \sigma}{\partial \theta} \right) \frac{\partial C_{\text{TEH}}^{\text{TEH}}}{\partial \theta} = \text{heat} - \text{capacity (scalar, } r = 0) \] (15)

\[ P_{\text{TEH}} = \left( \frac{\partial \sigma}{\partial E_n} \right) \frac{\partial P_{\text{TEH}}}{\partial \theta} = \text{pyroelectricity (polar, } r = 1) \] (16)

\[ \eta_{\text{TEH}} = \left( \frac{\partial \sigma}{\partial T_{ij}} \right) \frac{\partial \eta_{\text{TEH}}}{\partial \theta} = \text{pyromagnetism (axial, } r = 1) \] (17)

\[ \eta_{\text{TEH}}^{ij} = \left( \frac{\partial \sigma}{\partial T_{ij}} \right) \frac{\partial \eta_{\text{TEH}}^{ij}}{\partial \theta} = \text{thermo-expansion (polar, } r = 2) \] (18)

\[ \epsilon_{\text{TEH}}^{ij} = \left( \frac{\partial D_k}{\partial E_j} \right) \frac{\partial \epsilon_{\text{TEH}}^{ij}}{\partial \theta} = \text{permittivity (polar, } r = 2) \] (19)

\[ \mu_{\text{TEH}}^{ij} = \left( \frac{\partial B_n}{\partial H_n} \right) \frac{\partial \mu_{\text{TEH}}^{ij}}{\partial \theta} = \text{permeability (polar, } r = 2) \] (20)

\[ \chi_{\text{T}}^{ij} = \left( \frac{\partial D_k}{\partial H_j} \right) \frac{\partial \chi_{\text{T}}^{ij}}{\partial \theta} = \text{magnetoelectricity (axial, } r = 2) \] (21)

\[ \delta_{\text{ij}}^{H} = \left( \frac{\partial S_k}{\partial H_j} \right) \frac{\partial \delta_{\text{ij}}^{H}}{\partial \theta} = \text{piezoelectricity (polar, } r = 3) \] (22)

\[ \delta_{\text{ijk}}^{E} = \left( \frac{\partial S_k}{\partial E_j} \right) \frac{\partial \delta_{\text{ijk}}^{E}}{\partial \theta} = \text{piezomagnetism (axial, } r = 3) \] (23)

\[ \chi_{\text{ijkl}}^{\text{EH}} = \left( \frac{\partial S_k}{\partial T_{ij}} \right) \frac{\partial \chi_{\text{ijkl}}^{\text{EH}}}{\partial \theta} = \text{elasticity (polar, } r = 4) \] (24)

The definitions presented above allow writing the so-called constitutive equations in their standard form, Eqs. (25)–(28). Following usual conventions, differential symbols corresponding to mechanical and electromagnetic properties are omitted.
Besides electric displacement and magnetic induction, polarization and magnetization are familiar to physical perception. We rewrite the electromagnetic constitutive equations, setting \( \mathbf{P} \) and \( \mathbf{M} \) as dependent variables. Combining Eqs. (1)–(3) with Eq. (27), we obtain Eq. (30). Supra-indexes denoting constant magnitudes are simplified.

\[
\begin{align*}
D_m &= \varepsilon_0 E_m + \varepsilon_m d\theta + \varepsilon_m T_{yj} + \varepsilon_m E_m + \chi_{mm} H_m \\
&= p_m d\theta + d_{mij} T_{yj} + \varepsilon_0 \left( \delta_{mm} + \chi_{mm}^P \right) E_m + \chi_{mm} H_m \\
&= p_m d\theta + d_{mij} T_{yj} + \varepsilon_0 E_m + \varepsilon_0 \chi_{mm}^P E_m + \chi_{mm} H_m \\
P_m &= p_m d\theta + d_{mij} T_{yj} + \varepsilon_0 \chi_{mm}^P E_m + \chi_{mm} H_m
\end{align*}
\]

Combining Eqs. (4)–(6) with Eq. (28), Eq. (32) is established.

\[
\begin{align*}
B_m &= \mu_0 H_m + \mu_0 M_m = i_m d\theta + b_{mij} T_{yj} + \mu_{mm} H_m + \chi_{mm} E_m \\
&= a_m d\theta + b_{mij} T_{yj} + \mu_0 \left( \delta_{mm} + \chi_{mm}^M \right) H_m + \chi_{mm} E_m \\
&= a_m d\theta + b_{mij} T_{yj} + \mu_0 H_m + \mu_0 \chi_{mm}^M H_m + \chi_{mm} E_m \\
&= a_m d\theta + b_{mij} T_{yj} + \mu_0 \chi_{mm}^M H_m + \chi_{mm} E_m
\end{align*}
\]

To schematically describe the considered interactions, the concentric tetrahedrons in Fig. 3.2 have been suggested (Fuentes, 1998). Outer spheres represent causes while inner ones correspond to effects. Broad coloured lines are associated with so-called principal interactions, relating magnitudes of the same subsystem (e.g., electric field intensity and polarization: \( \mathbf{P} = \varepsilon_0 \mathbf{E} \)). Coupling relations, linking different subsystems in the same object, are represented by discontinuous lines (piezoelectricity, \( \mathbf{S} = d\mathbf{E} \)). Continuous black lines denote “cause–cause” and “effect–effect” links (corresponding to the considered selection of independent variables).

The present description of the magnetoelectric effect can be naturally expanded to take into account nonlinearity. The so-called bilinear magnetoelectric coefficients, \( \beta \) and \( \gamma \), characterize the magnetoelectric effect second-order approximation in Eqs. (33) and (34):

\[
\begin{align*}
P_m &= \chi_{mm} H_m + \gamma_{mm} H_m E_i + \frac{1}{2} \beta_{mm} H_i H_j \\
&= \mu_0 E_m + \beta_{mm} H_i E_j + \frac{1}{2} \gamma_{mm} E_i E_j.
\end{align*}
\]
The magnetoelectric coupling is also (frequently) characterized by means of a “practical” coefficient \( \alpha_{EH} \equiv \delta E/\delta H \). The relationship between \( \alpha \) (Eqs. (21), (31) and (32)) and \( \alpha_{EH} \) is easily obtained by consideration of a parallel-plate capacitor formed by a thin disk-shaped magnetoelectric material with its faces plated. Thickness is \( t \) and face area is \( A \). Voltage is \( V = Et \) and capacitance is \( C = \varepsilon A/t \). Then

\[
\alpha_{EH} = \frac{\delta E}{\delta H} = \frac{\delta V}{t \delta H} = \frac{\delta Q}{C \cdot t \delta H} = \frac{\delta Q}{A \cdot \varepsilon \delta H} = \frac{\delta P}{P \cdot \delta H}
\]

\[
\alpha = \varepsilon \cdot \varepsilon_{EH} = \varepsilon_{rel} \cdot \varepsilon_{EH}
\]

(35)

In SI units, \( \alpha \) is given in second/metre (s/m, inverse of velocity) and \( \alpha_{EH} \) in V/A. Gaussian (dimensionless) and mixed (\( \alpha_{EH} \rightarrow \text{V/m Oe} \)) units are also utilized.

Values of \( \alpha \) of the order of 10–100 ps/m are considered as “high” in single-phase magnetoelectrics. As demonstrated by Brown et al. (1968), the magnetoelectric coefficients have an upper bound related with the values of the electric permittivity and the magnetic permeability:

\[
\varepsilon_{mn}^2 \ll \varepsilon_{mn} \mu_{mn} = \varepsilon_0 \mu_0 \varepsilon_{rel} \mu_{rel} = \varepsilon_{rel} \mu_{rel} \frac{\mu_{mn}}{\varepsilon^2}
\]

(36)
\( c = (\varepsilon_0 \mu_0)^{-1/2} \) is the speed of light in vacuum. For ferroelectric–
antiferromagnetic materials, \( \varepsilon_{\text{rel}} \) is of the order of 100 and \( \mu_{\text{rel}} \) is close to 1. Putting numbers in Eq. (36), one finds

\[
\alpha_{mn} \approx \frac{\sqrt{\mu_{\text{rel}} \varepsilon_{\text{rel}}}}{c} \approx \frac{10^{-8}}{3 \times 10^8} \approx 3 \times 10^{-8} \text{m}^{-1} = 3 \times 10^4 \text{ps/m} \quad (36a)
\]

For single-phase materials, currently observed \( \alpha \)s are a couple of orders
below their theoretical limit. Composite magnetoelectrics give rise to better figures.

2.3. Space symmetry, electricity and magnetism

Electric and magnetic vectors, the physical magnitudes linked by magne-
toelectricity, differ in the manner in which they respond to symmetry.
Differences concern symmetry with respect to space as well as symmetry
with respect to time. To establish consistent criteria for the study of
magnetoelectric crystals, we start with this section devoted to the study of
the charge/current ↔ electro/magnetic field relationship, from the point
of view of spatial symmetry.

A basic idea, known as The Neumann’s Principle (NP), provides one
with the most important tools to investigate the cause–effect relationships in
crystal physics. Qualitatively, this law may be stated as follows:

The symmetry of the effect is, at least, equal to the symmetry of the cause.

In electromagnetic theory, \textit{causes} are charges and currents; \textit{effects} are
electric and magnetic fields. Application of the NP to electromagnetism
requires clarifying the behaviour of different kinds of magnitudes under
symmetry operations.

Electric fields \( \mathbf{E} \), \( \mathbf{D} \), \( \mathbf{P} \) and current density \( \mathbf{j} \) are \textit{polar} vectors. Their
behaviour under point-group \textit{ordinary symmetry operations} \( \mathbf{R} \) (rotations,
inversion and mirrors) is described by Eq. (37):

\[
\mathbf{E}(\mathbf{R} \cdot \mathbf{r}) = \mathbf{R} \cdot \mathbf{E}(\mathbf{r})
\]

This is different from the behaviour of a scalar field \( \Omega(\mathbf{r}) \): \( \Omega(\mathbf{R} \cdot \mathbf{r}) = \Omega(\mathbf{r}) \).
Under symmetry: scalars are invariant; vectors transform as position vectors
(Fig. 3.3(a)).

\textit{Antisymmetry operations}, denoted with a star (*), convert a magnitude into
its opposite. \( \mathbf{R}^* \) [white] = [black]. Application of the anti-symmetry oper-
tor to a positive electric charge produces a negative one: \( \mathbf{R}^* \cdot Q = -Q \).
Figure 3.3(b) shows the transformation of a dipolar charge distribution and
its electric field under an anti-mirror \( m^* \).

\( \mathbf{B} \) and \( \mathbf{H} \) fields, as well as magnetization density \( \mathbf{M} \) \( (B = \mu_0 H + \mu_0 M) \),
are axial- or pseudovectors. The reason for this is that their basic equations
(Ampere and Biot–Savart laws) involve vector cross products. Under
coordinate’s inversion, the cross product of vectors $\mathbf{V}_1$ and $\mathbf{V}_2$ does not undergo inversion: $(-\mathbf{V}_1) \times (-\mathbf{V}_2) = \mathbf{V}_1 \times \mathbf{V}_2$. The equation that describes the behaviour of an axial vector under a symmetry operation is

$$\mathbf{B}(m \cdot \mathbf{r}) = |\mathbf{R}| \mathbf{R} \cdot \mathbf{B}(\mathbf{r})$$

(38)

$|\mathbf{R}| = \pm 1$ is the determinant of matrix operator $\mathbf{R}$.

**Figure 3.4** Magnetic field of an electric current ring with axial vector symmetry plane.

**Figure 3.3** Symmetry and antisymmetry of the scalar “electric charge” and polar vector “electric field intensity”. The (generalized) symmetry of the effect follows that of its cause. The shown configurations are independent of time.
(an axial vector, the “effect”) also exhibits mirror symmetry—the magnetic way—with respect to the equatorial plane. Curiously, even though this system shows magnetic north and south poles, respectively, in its upper and lower semi-spaces, it shows mirror and inversion symmetries. That is the way magnetic (pseudovectorial) magnitudes fulfil the NP.

Table 3.3 resumes the characteristics of polar and axial vectors under the considered spatial transformations.

Electromagnetic configurations, in general, show symmetry and anti-symmetry properties. The collection of all the symmetry and anti-symmetry operations of a system forms a group, its magnetic, black-and-white (B&W) or “colour”-symmetry group. The subject of “colour symmetry” has been introduced by Shubnikov (1951) and further systematized by Shubnikov and Belov (1964).

To illustrate the behaviour of polar- and axial-vectors under B&W symmetry operations, we now comment a few electric and magnetic configurations—related with magnetoelectricity—from the point of view of symmetry. All the considered charge–current-fields distributions are observed at a fixed time. B&W symmetry groups are denoted by the extended Hermann–Mauguin notation. Inside parentheses, a generalized Schoenflies notation (to be explained below) is included. Observe differences in the behaviour of scalar (charge), polar vectors (E, j) and axial vector (B). All systems fulfil the NP.

**Case 1**: Electric dipole, Fig. 3.3(b). B&W symmetry group:
\[ \mathcal{S}_{m} \times \mathcal{S}_{m} \times \mathcal{S}_{m} (= \mathcal{D}_{2h} : \mathcal{C}_{2h}) \]. Fibre symmetry (invariance with respect to azimuthal angle) of charges and currents. On the equatorial plane, the electric field intensity is perpendicular to the anti-mirror. Vertical planes are mirrors.

**Case 2**: Magnetic dipole, Fig. 3.4. B&W symmetry group:
\[ \mathcal{S}_{m} \times \mathcal{S}_{m} \times \mathcal{S}_{m} (= \mathcal{D}_{2h} : \mathcal{C}_{2h}) \]. Fibre symmetry. On the equatorial plane, magnetic induction is perpendicular to the mirror. Vertical planes are anti-mirrors.

**Case 3**: Electric quadrupole, Fig. 3.5. B&W symmetry group:
\[ \mathcal{S}_{m} \times \mathcal{S}_{m} \times \mathcal{S}_{m} (= \mathcal{D}_{4h} : \mathcal{D}_{2h}) \]. Symmetry and anti-symmetry two-fold axes in the plane of the drawing. Mirror and anti-mirror vertical (out of the drawing) planes.

**Case 4**: Coaxial magnetic quadrupole, Fig. 3.6: B&W symmetry group:
\[ \mathcal{S}_{m} \times \mathcal{S}_{m} \times \mathcal{S}_{m} (= \mathcal{D}_{2h} : \mathcal{C}_{2h}) \].

**Case 5**: Current-carrying long wire and toroid, Fig. 3.7: B&W (rotational) symmetry group:
\[ \mathcal{S}_{m} \times \mathcal{S}_{m} \times \mathcal{S}_{m} (= \mathcal{D}_{2h} : \mathcal{C}_{2h}) \]. The symmetry of these configurations is different from that of the magnetic quadrupole. Antiparallel magnetic dipoles in Fig. 3.6 are collinear, while magnetization in Fig. 3.7, if present, would show loop (“toroidal”) character.

In Figure 3.7, if an external magnetic field B pointing from right to left was applied, the following phenomena would happen. (a) In the long wire, Hall effect would move up the charge carriers, creating a vertical polarization. (b) In the toroid, the magnetic dipoles associated with current rings close to position 1 would be in a high-energy, unfavourable condition. Dipoles near position 2 would be in an energetically favourable condition. The system of Fig. 3.7b is the circuit analog of ferrotoroidic materials.
Table 3.3  Electrostatic and magnetostatic magnitudes under space rotations

| Symmetry $R$ | $|R| = 1$ | $|R| = -1$ | $R = i$ | $r \in m$ | Antisymmetry $R^*$ | $|R^*| = 1$ | $|R^*| = -1$ | $R^* = i^*$ | $r \in m^*$ |
|-------------|-----------|------------|---------|-----------|-------------------|-----------|------------|----------|-----------|
| Scalar: $\rho$ | $\rho(R \cdot r) = \rho(r)$ | $\rho(-r) = \rho(r)$ | $\rho(r)$ | $\rho(R^* \cdot r) = -\rho(r)$ | $\rho(-r) = -\rho(r)$ | $\rho = 0$ |
| Polar vectors: $E, P, D, j, T$ | $E(R \cdot r) = R \cdot E(r)$ | $E(-r) = -E(r)$ | $E \in m$ | $E(R^* \cdot r) = -R^* \cdot E(r)$ | $E(-r) = E(r)$ | $E \perp m^*$ |
| Axial vectors: $B, M, H, S$ | $B(R \cdot r) = R \cdot B(r)$ | $B(-r) = B(r)$ | $B \perp m$ | $B(R^* \cdot r) = -R^* \cdot B(r)$ | $B(-r) = -B(r)$ | $B \in m^*$ |

Matrices $R$ ($R^*$) associated with proper rotations have positive determinant ($|R| = 1$) while improper rotations (roto–inversions) have a negative one ($|R| = -1$). Symbols represent the following magnitudes: $\rho$: electric charge density; $E$: electric field intensity; $P$: polarization; $D$: electric displacement; $j$: current density; $T$: toroidal moment; $B$: magnetic induction; $M$: magnetization; $H$: magnetic field intensity; $S$: spin. $E$ represents the behavior of polar vectors; $B$ characterizes axial ones. The Table includes some particular cases: The columns $R = i$ and $R^* = i^*$ are associated with the space inversion ($r \rightarrow -r$). The columns $r \in m$ and $r \in m^*$ describe the characteristics of polar and axial vectors on points that belong to mirror and anti–mirror planes.
In ferrotoroids, the presence of an external magnetic field alters the atomic-currents pattern and the associated charges and fields distributions. As discussed by Gorbatsevich et al. (1994), mentioned phenomena lead to the appearance of an induced electric dipole, which is magnetoelectricity.

**2.4. Space–time symmetry and magnetoelectric multiferroics**

In crystal physics, material’s crystallographic and electronic structures are considered the *cause* and physical properties are the *effects.*
The application of the NP to magnetoelectricity requires the consideration of so-called time reversal \((t \rightarrow -t)\). This transformation, denoted \(\Theta\), consists of virtually reversing velocities, electric currents, spins and other motions.

Electrostatic vectors \((E, P, D)\) are invariant with respect to time inversion, they are given the category of polar \(i\)-vectors.

Polar \(j\) and axial \(B, H, M\) vectors reverse their senses if we switch a battery to invert its circuit polarity, or if we imagine that time starts running in the opposite sense. If the transformation \(t \rightarrow -t\) takes place in the magnetic dipole of Fig. 3.4, all the drawn vectors start pointing in the opposite direction \([j(-t) = -j(t); B(-t) = -B(t), \ldots]\). This kind of vector magnitudes is denoted as \(c\)-vectors.

The combination of time inversion and a space transformation \((\Theta \cdot \mathbf{R} = \mathbf{R'} \cdot \Theta)\), denoted as \(\mathbf{R'}\), affects the \(i\)- and \(c\)-vectors differently. The following scheme resumes the resultant effects:

\[
\mathbf{R'} = \Theta \cdot \mathbf{R} = \begin{cases} \mathbf{R} & \text{\(i\)-magnitudes \((\rho, E, P, D)\)} \\ \mathbf{R}^* & \text{\(c\)-magnitudes \((j, B, M, H)\)} \end{cases}
\] (39)

Among the interesting peculiarities that build the fascination of magnetoelectricity, we recall that this phenomenon links polar- and axial-vectors, time-independent and time-reversible magnitudes, symmetry and antisymmetry.

The symmetry system required for the study of electromagnetic properties of materials, taking into account time reversal, is Shubnikov’s “coloured symmetry” representation. The application of this subject to functional materials has been discussed in detail by Litvin (2003, 2005, 2009).
The magnetic (B&W) point groups are classified as follows:

1. Ordinary or single-colour groups (the 32 classical crystallographic point groups).
3. “B&W” point groups (58 B&W groups). B&W point groups are formed as follows. $G$ is an ordinary group, of order $g$. $H$ is a sub group of $G$, of order $g/2$. Multiply $(G - H)$ by the time inversion operation and build the B&W group $M = H + \Theta (G - H)$. In the Schoenflies notation, it is denoted as $G:H$. International symbols of the generating elements are most frequently employed.

Meso- and macroscopic properties are conditioned by the structures at the level of several unit cells. Symmetry–properties relationships, at meso- and macroscopic scales, are determined by the magnetic point group.

To exemplify the important role of colour symmetry, we compare the structural and magnetic symmetries of “BCC” iron. Figure 3.8 shows one unit cell of an iron crystal. If we ignore the (time reversible) atomic currents and limit our observation to the spatial distribution of atoms, we find that the structure is “cubic”, with space group $Im\bar{3}m$. This would be a good structural description for an investigation about elasticity, for example. But if we are looking for an explanation of Fe magnetic properties, we must take into account its internal microscopic currents. In the figure, each atom shows a curved arrow that represents the electric current generated by its spin. All atomic magnetic dipoles are parallel, because the crystal is ferromagnetic. Magnetization along $z$ axis breaks the cubic symmetry and transforms the crystal to tetragonal. The magnetic space group, the one that defines its magnetism, is $I4/\text{mm}m'/m'$.

Fe (A2)

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paramagnetic</td>
<td>$Im\bar{3}m$</td>
</tr>
<tr>
<td>Ferromagnetic</td>
<td>$I4/\text{mm}m'/m'$</td>
</tr>
<tr>
<td>Moment direction</td>
<td>(001)</td>
</tr>
<tr>
<td>$\mu_F=2.218 \mu_B/\text{atom}$</td>
<td></td>
</tr>
<tr>
<td>$T_c=1043 K$</td>
<td></td>
</tr>
<tr>
<td>$a=2.932 \text{Å}$</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 3.8** Conventional and magnetic symmetries of BCC iron. Courtesy of Laughlin (2000).
2.5. The NP and magnetoelectric tensors via group theory

The NP leads to powerful analytical tools by means of the Theory of Irreducible Representations (irreps) of Groups. This subject has been presented at different levels of abstraction. Some representative contributions are those given by Nowick (1995), Zheludev (1987) and Litvin (2005). We now give a bird’s eye view of the irreps’ implementation of the NP. Examples will be used to facilitate the understanding of somewhat abstract concepts and methods.

Consider the macroscopic property $K$, that fulfils $Y = K \cdot X$. To establish whether $K$ may be non-null in a given crystal, the following procedure holds:

- Identify the sample’s magnetic-symmetry point group.
- Determine the characters’ table and the irreps’ functional bases.
- In the previous table, identify whether there exists a linear relationship between irreps of $X$ and $Y$. In particular, determine which irreps are common to $X$ and $Y$, according to the tensor’s characteristics.
- If this relationship exists, then the considered property may be present in the investigated material.

Figure 3.9, taken from Eerenstein et al. (2006), resumes the space–time symmetry conditions for the possible occurrence of electric, magnetic and magnetoelectric spontaneous polarizations.

Figure 3.9, taken from Eerenstein et al. (2006), resumes the space–time symmetry conditions for the possible occurrence of electric, magnetic and magnetoelectric spontaneous polarizations.
As a first illustration of the mentioned methodology, the case of magnetoelectricity in crystals of magnetic point group \( C_{2v} = 2mm \) is discussed. The analysis of this group is relatively simple, because it does not include antisymmetries. Table 3.4 shows the irreps of the considered point group.

Group \( C_{2v} \), of order \( g = 4 \), is Abelian (commutative), so each element defines its proper class. The irreps \( A_1 \ldots B_2 \) are one-dimensional and their characters are \( \pm 1 \). The right-hand part of the table presents the bases of the different irreps. Variables \( x, y \) and \( z \) represent polar vectors, \( R_x, R_y \) and \( R_z \) are components of axial-vectors and \( a_i \) are components of second-rank tensors (expressed as hypervectors). In this treatment, electric polarization is represented by the \((x, y, z)\) basis and magnetic field intensity corresponds to the \((R_x, R_y, R_z)\) basis. By inspection, it is observed that \( [x \text{ and } R_y; y \text{ and } R_x] \) belong, respectively, to irreps \( B_1 \) and \( B_2 \). No other coincidence in an irrep of polar and axial vector components is found. The identified conjunctions imply that the magnetoelectric tensor for crystals belonging to point group \( C_{2v} \) is of the form given in Eq. (40):

\[
\mathbf{a} = \begin{bmatrix} 0 & x_{12} & 0 \\ x_{21} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}
\]  

(40)

We now analyze a somewhat more complicated case: magnetoelectricity in \( \text{Cr}_2\text{O}_3 \). The corresponding colour symmetry point group is a B&W one. Figure 3.10 represents the crystal structure of \( \text{Cr}_2\text{O}_3 \). The structure is characterized in ICSD report #250078. The \( \text{Cr}^{3+} \) ions occupy the centres of inclined \( \text{O}^{2-} \) octahedrons. The octahedrons are paired vertically, sharing one face. There is an inversion centre on the octahedrons shared face, at the intersection point of the two spin arrows in Fig. 3.10b. The international space group symbol of the crystal structure is (number 167): \( \text{R}3\tilde{2}/\iota = R3\iota = D_{3d}^6 \). The structural point group is \( 32/m = 3\overline{m} = D_{3d} \).

If the analysis is limited to material distribution in the unit cell, \( D_{3d} \) crystals do not allow magnetoelectricity. Table 3.5 shows the irreducible representations (irreps) of the conventional point group.

<table>
<thead>
<tr>
<th>( C_{2v} )</th>
<th>( E )</th>
<th>( C_2 )</th>
<th>( \sigma_{xx} )</th>
<th>( \sigma_{yy} )</th>
<th>( \mathbf{a}_1; \mathbf{a}_2; \mathbf{a}_3 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>( Z )</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>( R_z ) ( a_6 )</td>
</tr>
<tr>
<td>( B_1 )</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>( x; R_y ) ( a_5 )</td>
</tr>
<tr>
<td>( B_2 )</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>( y; R_x ) ( a_4 )</td>
</tr>
</tbody>
</table>
Considering the magnetic intensity $\mathbf{H}$ as the “cause” and electric polarization $\mathbf{P}$ as the “effect”, we focus attention on the irreps associated with $R$ bases: $R_z$ belongs to the $A_{2g}$ irrep and $(R_x, R_y)$ belong to the $E_g$ irrep. None of these irreps coincides with the ones $(A_{2u}, E_u)$ corresponding to polar vectors $(\mathbf{E}, \mathbf{P}, \mathbf{D})$. That is why magnetoelectricity is a forbidden effect for crystals belonging to this symmetry.

Let us now take spins, time inversion and magnetic symmetry into account. According to Brown et al. (2005), the magnetic symmetry point group of $\text{Cr}_2\text{O}_3$ is:

\[ \tilde{3} \tilde{m} = 1, 3, \tilde{3}, 1; 2, 2, m', m', \ell, \ell', \tilde{\ell}, \tilde{\ell}', \tilde{\ell} \tilde{\ell}' \]
\[ = D_{3d} : D_3 = D_3 + \Theta (D_{3d} - D_3) = E, 2C_3, 3C_2, \ell, 3\sigma_d / 2S_6' \]

**Figure 3.10** A simplified structural diagram of $\text{Cr}_2\text{O}_3$. (a) Cell view, with inclined $\text{CrO}_6$ octahedrons; (b) Details of opposite spins. Figure 3.10b adapted from Brown et al. (2005).

**Table 3.5** Irreps of point group $D_{3d} = \tilde{3}2/m = \tilde{3}m$.

<table>
<thead>
<tr>
<th>$D_{3d}$</th>
<th>$E$</th>
<th>$2C_3$</th>
<th>$3C_2$</th>
<th>$i$</th>
<th>$2S_6$</th>
<th>$3\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$x_1 + x_2; x_3$</td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
<td>1</td>
<td>1</td>
<td>$R_z$</td>
</tr>
<tr>
<td>$E_u$</td>
<td>2</td>
<td>$-1$</td>
<td>0</td>
<td>2</td>
<td>$-1$</td>
<td>$(R_x, R_y)$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
<td>$-1$</td>
<td>1</td>
<td>$x_1 - x_2, x_3$</td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>1</td>
<td>1</td>
<td>$-1$</td>
<td>$-1$</td>
<td>1 $Z$</td>
<td></td>
</tr>
<tr>
<td>$E_u$</td>
<td>2</td>
<td>$-1$</td>
<td>0</td>
<td>$-2$</td>
<td>1</td>
<td>$(x, y)$</td>
</tr>
</tbody>
</table>
Cr$_2$O$_3$ is antiferromagnetic. The magnetic moments (the spins) of neighbouring cations are anti-parallel, as shown in Fig. 3.10b. According to Table 3.3, taking into account that spin is an axial vector, the inversion centre is an anti-symmetry element. Concerning the symmetry associated with vertical planes, it is observed that the spins belong to these planes, so the planes are anti-mirrors.

According to Eq. (39), polar $i$-vectors, say $\mathbf{P}$, continue (in $D_{3d}:D_3$) being represented according to the $D_{3d}$ irreps table. The following discussion refers to the representation of axial and $c$-polar vectors, affected by time inversion.

The first row of Table 3.6 shows, grouped according to their classes, the elements of $D_{3d}$. The second line describes the generation of $D_{3d}:D_3$ starting from $D_3$. The plus (+) sign means preservation of the symmetry element and the minus sign (−) represents conversion of symmetry to antisymmetry.

The irreps of $D_{3d}:D_3$ are complementary irreps of $D_{3d}$. They are obtained from the $D_{3d}$ irreps by applying the signs given in Table 3.6 to the respective characters. Focusing attention on $A_{2g}$ and $E_u$ (the irreps linked with $\mathbf{H}$) and performing the mentioned sign transformations one finds for the $D_{3d} \rightarrow D_{3d}:D_3$ conversion the $\text{irrep} \rightarrow \text{co-irrep}$ correspondence shown in Table 3.7.

Now we can analyze the $\mathbf{P} = \alpha \mathbf{H}$ relationship from the point of view of representation theory. For a given component of $\mathbf{P}$ to be non-zero, the irreps of the linked components in $\mathbf{P}$ and $\mathbf{H}$ must coincide. Taking into account the different nature of $\mathbf{P}$ and $\mathbf{H}$ (i-polar or c-axial), the irreps to be taken into account are, respectively, the ones for $D_{3d}$ and the ones for $D_{3d}:D_3$. By inspection, $P_z$ and $H_z$ are represented by $A_{2g}$ and $(P_x, P_y)$ and $(H_x, H_y)$ are represented by $E_u$. Magnetoelectricity is possible in Cr$_2$O$_3$ and the magnetoelectric tensor has the following structure, characteristic of a longitudinal, plane-isotropic effect:

\[
\alpha = \begin{bmatrix}
\alpha_{11} & 0 & 0 \\
0 & \alpha_{11} & 0 \\
0 & 0 & \alpha_{33}
\end{bmatrix}
\] (41)
By application of the just-presented procedure, the form of the magnetoelectric tensor $\alpha$ may be determined for all the magnetic point groups. Here we include, as Table 3.8, the result of such an investigation. Linear magnetoelectric effect is possible in 58 magnetic-symmetry point groups. Methodical presentations of polar- and axial-tensor properties for tensor ranks up to $r = 4$ can be found in the treatises by Nowick (1995) and Zheludev (1987). The theoretical contributions by Ascher (1974), Schmid (2001, 2008) and Litvin (2009) systematize the symmetry–properties relationships in the field of electromagnetic coupling interactions.

Table 3.9 resumes the possible electric and magnetic coupling effects in the 32 crystallographic point groups. To find out whether a magnetic

<table>
<thead>
<tr>
<th>Table 3.8 Magnetoelectric matrices for the magnetic point groups.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1, C_1, C_1$</td>
</tr>
<tr>
<td>$\begin{bmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
</tr>
<tr>
<td>$C_{2\perp}, D_{2\perp}, C_{2\perp}, D_{2\perp}$</td>
</tr>
<tr>
<td>$\begin{bmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
</tr>
<tr>
<td>$C_{4}, C_4, C_{4\perp}, C_{4\perp}, C_{3\perp}, S_6, C_{3\perp}, C_6, C_{3\perp}, C_{3\perp}, C_{6\perp}$</td>
</tr>
<tr>
<td>$\begin{bmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
</tr>
<tr>
<td>$C_{2\perp}, C_{2\perp}, D_{2\perp}, S_4$</td>
</tr>
<tr>
<td>$\begin{bmatrix} 1 &amp; 0 &amp; 0 \ 0 &amp; 1 &amp; 0 \ 0 &amp; 0 &amp; 1 \end{bmatrix}$</td>
</tr>
<tr>
<td>$T_\perp, T_\perp, T_\perp, T_\perp, O, O, O, O$</td>
</tr>
</tbody>
</table>
property is possible in a given crystal, the ordinary symmetry elements of its magnetic point group must be taken into account. For example, Cr$_2$O$_3$ must be classified as $D_3$ (not as $D_{3d}$). The full magnetic point group determines the forms of the properties tensors.
Figure 3.11 shows a Venn diagram of single-phase insulating materials, classified according to the magnetic symmetry dependence of the considered properties.

In electric as well as in magnetic cases, ferroic materials are a subset of pyro-ones and pyro- are a subset of piezo-susceptible materials.

All isolating materials are polarizable both electrically (dielectrics) and magnetically (at least, diamagnetics or paramagnetics). Electric and magnetic susceptibilities link, respectively, polar \( \mathbf{P} \) or axial \( \mathbf{M} \) vectors. The irreps of cause and effect are the same for any symmetry group. The property always exists.

*Multipiezo* materials, those that show simultaneously piezoelectricity and piezomagnetism, tend to show magnetoelectricity via elasticity. If a given piezoelectric is stimulated by an electric field, it will become stressed. As a piezomagnetic material, if stressed, it will show a variation in its magnetization. The global result is magnetoelectricity. This reasoning is valid and works well for all but two of the crystallographic point groups, as described in Table 3.9. Crystals belonging to point groups \( C_{3h} \) and \( D_{3h} \) are both piezoelectric and piezomagnetic. But in these groups, the stress produced by an electric field acts in directions that do not coincide with the ones required to produce piezomagnetization.
Figure 3.11 includes magnetoelectric multiferroics, materials that show simultaneously some kind of electric and magnetic ferroic orders. Most frequent cases, for example, BiFeO$_3$, are ferroelectric–antiferromagnetic. From the point of view of symmetry, all the crystallographic point groups associated with simultaneous pyroelectricity and pyromagnetism (multiferroics included) allow magnetoelectricity. Cubic point group $O = 432$ is neither pyro- nor piezo-, but may be magnetoelectric. The Venn diagram of Fig. 3.11 describes the mentioned sets–subsets relations.

2.6. Microscopic approach and classification of magnetoelectric multiferroics

The search for “high-$\alpha$” magnetoelectrics has evolved to the search for intimately linked multiferroics. Such systems are expected to bring the desired magnetoelectric coupling. In this section, we analyze the behaviour of magnetoelectric multiferroics at the atomic level. A first, important question that has been investigated in detail since Nicola Hill/Spaldin (2000) started the discussion is: “why are there so few magnetic ferroelectrics?” (Spaldin and Fiebig, 2005; Ederer and Spaldin, 2004, 2005a, 2005b).

Experience shows crystals that are good for magnetism are not good for ferroelectricity and vice versa. The investigation of FE perovskites has led researchers to the clue: the overwhelming majority of known FE perovskites (PbTiO$_3$, BaTiO$_3$, PZTs, etc.) contains in the octahedral position a TM cation with an empty d-shell (Ti$^{4+}$, Ta$^{5+}$, W$^{6+}$). Formally, this condition is described as “$d^0$ configuration”. In a ferroelectric perovskite cell, say of BaTiO$_3$, electronic interaction between Ti and O (see Fig. 3.12)

![Figure 3.12](image-url) Ligand field stabilization of empty cation d orbitals by oxygen p electrons. Courtesy of Spaldin (2010).
gives rise to orbitals hybridization that results in the oxygen atom “pulling up” the titanium, breaking the inversion symmetry and producing ferroelectricity. For this phenomenon to occur, the central “B” cation must be in a d⁰ condition.

On the other hand, magnetic cations [Fe³⁺ (d⁵), Mn³⁺ (d⁴)] are essential for magnetism, but do not tend to form ferroelectric perovskites.

So, the search for ME frequently evolves to the search for a by-pass to the “d⁰-ness rule”.

There are two well-known ferroelectric perovskites with magnetic “B” cations: BiFeO₃ and BiMnO₃. Both these cases are valid examples of ways to circumvent the rule.

In these materials, ferroelectricity does not come from displacement of the “B” cation, but from phenomena associated with the “A” ions. Bi³⁺ (as well as Pb²⁺) differs from Ba²⁺ in the symmetry of the electronic structure. Ba²⁺ has the Xe electronic structure and Bi³⁺ has the so-called “lone pair” of valence electrons. In a crystal, the lone pair introduces a certain asymmetry into the electron cloud distribution inside the unit cell and these effects lead to the appearance of local electric dipoles. The crystal is ferroelectric.

Next we give a classification of MEMF that follows the treatment of Picozzi and Ederer (2009).

BiFeO₃ is the prototype of so-called structural magnetic ferroelectrics (SMF). BiFeO₃ and BiMnO₃ are SMF due to the role of the stereochemically active lone pair cations Bi³⁺. There is another subgroup of SMF, represented by YMnO₃. In these materials, named geometric ferroelectrics, ferroelectricity is due to size effects (space filling) and other geometrical constraints (ionic coordination, Van Aken et al., 2004).

The second group of MEMF refers to electronic magnetic ferroelectrics (EMF). In this family, ferroelectricity is driven by electronic degrees of freedom such as spin-, charge-, or orbital-ordering. Rare-earth manganites are prototypes. In EMFs, the primary order parameter is the electronic non-centrosymmetric configuration (Cheong and Mostovoy, 2007). Polarization is a secondary effect of the electronic phase transition. It is considered a “secondary” order parameter. In this group of MEMFs, electrons by themselves give rise to ferroelectricity. Furthermore, ions are susceptible to the non-centrosymmetric charge-redistribution and consequently generate an ionic contribution to the total polarization.

Ferroelectricity in EMFs is driven by correlation effects and in SMFs by covalency.

Due to its origin, it is to be expected that magnetoelectric coupling in EMFs must be intense. Temperature dependences of electric and magnetic orderings coincide.

Figure 3.13 (after Picozzi and Ederer, 2009) represents a classification of EMFs according to currently identified mechanisms to induce ferroelectricity.
2.7. Theoretical calculations

Computer-aided Density Functional Theory (DFT; Hohenberg and Kohn, 1964; Kohn and Sham, 1965) is the framework that supports magnetoelectric multiferroics theoretical investigations. Despite some limitations of DFT in the presence of magnetic fields, it has made decisive contributions to the impressive advance that is apparent in the field of magnetoelectricity. Here we list some representative computational approaches that have played and/or play important roles in the mathematical characterization of magnetoelectricity and multiferroicity. For details, see Martin (2004):

- **LDA** = local density approximation
  - The functional depends only on the density at the coordinate where the functional is evaluated.
- **GGA** = generalized gradient approximation
  - The density functional depends on the up and down spin densities.
  - Includes the density gradient for the higher order correction
- **PAW** = projector augmented wave
  - Only valence electrons are taken into account.
  - The interaction between valence electrons and the ionic core is taken into account within a pseudopotential, without norm constraint.
  - Two bases are mixed: local orbitals and plane waves.
- **GW** = Green’s function plus screened interaction potential
  - A natural extension beyond Hartree–Fock formalism leading to self-energy correction.

Figure 3.13 Schematic classification of EMFs, in terms of different mechanisms (left side) and compounds (right side). Reproduced with permission from Picozzi and Ederer (2009).
- LDA + $U$
  - A Hubbard-like Hamiltonian including effective on-site interactions. It gives a better description of electronic correlations.


DFT gives access to the total energy and, by means of the energy’s derivatives, first principles methods allow the calculation of diverse physical properties (Ghosez et al., 1994; Veithen et al., 2004).

Figure 3.14 (Ghosez and Junquera, 2006) shows schematically a kind of results obtainable by DFT techniques. The crystal energy $U$ is a determinable function of the central cation displacement $\xi$ from the inversion centre. The calculated double-well explains the occurrence of the electrical hysteresis loop.

As illustration, we compare the calculated structures of BiFeO$_3$ and BiMnO$_3$.

**Figure 3.14** (a) Crystal structure of BaTiO$_3$ in its high temperature paraelectric cubic perovskite structure and in its room-temperature tetragonal structure (for “up” and “down” polarization states). (b) Typical double-well shape for the internal energy of BaTiO$_3$ in terms of displacement $\xi$. (c) Hysteresis behaviour of the polarization-electric field curve. Reproduced with permission from Ghosez and Junquera (2006).
Figure 3.15 shows the theoretical structure of BiFeO$_3$, with details of the electron localization function (ELF; Neaton et al., 2005). Observe how the Bi <em>stereochemically active lone pairs</em> introduce an important charge asymmetry around the black Bi atoms. BiFeO$_3$ is a good ferroelectric. Pity, from the magnetic point of view, it is almost antiferromagnetic.

Consider now the calculated structure of BiMnO$_3$. This case is a focus of attention, because published descriptions of the BiMnO$_3$ crystal structure and of its ferroelectric properties, are somewhat paradoxical (see section 4.4.4). Calculations by Baettig et al. (2007) were performed using the PAW method (Blöchl, 1994; Kresse and Joubert, 1999) of density functional theory as implemented in the VASP code (Kresse and Furthmüller, 1996). The exchange–correlation functional was treated using the LDA + $U$ model in the around mean field limit. Default VASP PAW potentials were employed. Polarizations were calculated by means of the Berry-phase method (King-Smith and Vanderbilt, 1993; Resta, 1993, 1994).

Figure 3.16 shows the theoretical output and the experimental data (Atou et al., 1999) for the electron distribution around Bi atoms in BiMnO$_3$. 

![Figure 3.15](image)

**Figure 3.15** Calculated electron localization function for BiFeO$_3$. The structure has been optimized with space group R3c. The yellow lobes are the lone pairs on the black Bi ions. BiFeO$_3$ is non-centrosymmetric, ferroelectric. Courtesy of Spaldin (2010).
In the theoretical (C2/c) structure, the lone pairs cancel perfectly, whereas in the experimental (C2) structure, there is imperfect cancellation, leading to a small net polarization along \( b \). Comparison between BiFeO\(_3\) and BiMnO\(_3\) shows a striking difference regarding multiferroicity: BiFeO\(_3\) is a good ferroelectric and a weak ferromagnetic, whereas BiMnO\(_3\) is a good ferromagnetic and it is not clear whether it is ferri- or antiferroelectric. We shall see reports, in the experimental sections, of its multiferroic properties. BiFeO\(_3\) and BiMnO\(_3\) require more investigation.

3. Measurement of Magnetoelectric Properties

3.1. Experimental techniques for measuring magnetoelectric coupling coefficients and multiferroic nature of materials

At present, there are four key methods for the measurement of the magnetoelectric practical coefficient \( \varepsilon_{\text{EH}} \). In any one of these methods, the sample should be completely polarized. In the methods for measuring the magnetoelectric coefficient, charge migration depends on the impedance of the measuring system. Next, we will briefly describe the different measuring
methods. In particular, we will illustrate with examples the dynamic and the pulsed dynamic methods.

### 3.1.1. Static method

In the static method, the magnetoelectric response (charge or voltage) is measured as a function of the applied magnetic field variations using a high input impedance electrometer.

During the polarization of the sample, charge is accumulated at the grain boundaries and later, during the measurement process, the charge moves slowly to the electrodes until the output signal becomes stabilized. This charge accumulation at the grain boundaries can lead to measurement errors with respect to the real material response (Kumar et al., 1988).

### 3.1.2. Quasistatic method

In the quasi-static method, the magnetoelectric response is measured by using a high impedance electrometer during half a minute and in the absence of an applied magnetic field. Later, a magnetic field is increased linearly with time from zero until a given maximum value $H_{\text{max}}$ is reached and is applied during half a minute. Finally, the applied magnetic field is decreased linearly to zero and soon after that the magnetoelectric response is measured. This way charge draining, usually linear with time, can be corrected. The measurement should be made at a constant and carefully stabilized temperature. This method allows an appropriate determination of the linear magnetoelectric coefficient without the error brought about by the charge draining.

### 3.1.3. Dynamic method

In the dynamic method, the magnetoelectric response voltage, $V_{\text{ME}}$, is measured with a phase-sensitive technique using a lock-in amplifier. A DC magnetic bias field is applied with an electromagnet together with a small constant-amplitude ($h_0 \approx 1$ Oe) sinusoidal magnetic field using a pair of Helmholtz coils. As the DC magnetic field from the electromagnet is changing, the curve of the magnetoelectric coefficient as a function of this DC field is obtained. This small sinusoidal magnetic field allows the measurement of the magnetoelectric coefficient for different values of the DC magnetic bias field.

Figure 3.17 shows the experimental set-up for the measurement of the cross-sectional magnetoelectric coefficient with the dynamic method.

### 3.1.4. Pulsed dynamic method

This is a recently established method for measuring the magnetoelectric coefficient (Elizalde-Galindo et al., 2005; Bueno-Baques et al., 2006a). In the dynamic pulsed method, the sample is inserted in a specially designed
probe for measuring the magnetoelectric response voltage ($V_{ME}$) as a function of the pulsed applied magnetic field. The pulsed applied magnetic field and the voltage response signals are simultaneously measured and digitalized with analogic to digital converters. During the 20 ms pulse duration, it is possible to measure up to 6144 values of pulsed applied magnetic field and of the magnetoelectric voltage response signal using an NI-6110E National Instruments data acquisition card with four 12-bits 5 MS/s simultaneous successive approximation ADC. With this method, one obtains a relatively high response voltage for magnetoelectric composites that can be measured directly (Fig. 3.18). However, in single-phase magnetoelectric materials that have a very low level of the magnetoelectric voltage signal, it would be necessary to add a small sinusoidal magnetic field and phase-sensitive lock-in amplification (Bueno-Baques et al., 2006b).

3.2. Theory of measurement in a dynamic magnetic field

In an electrically polarized magnetoelectric material, a response voltage is obtained when a magnetic field is applied. In general, there is a nonlinear dependence between the applied magnetic field and the magnetoelectric response voltage (Matutes-Aquino et al., 2003):
Expanding the voltage in Taylor power series of the total magnetic field:

\[ V = f(H) \]

\[ V = \sum_{n=0}^{\infty} \frac{1}{n!} \frac{d^n V}{dH^n} H^n = V(H)|_{H=0} + \frac{dV}{dH}|_{H=0} H + \frac{1}{2} \frac{d^2 V}{dH^2} H^2 \]

\[ + \frac{1}{6} \frac{d^3 V}{dH^3} H^3 + \frac{1}{24} \frac{d^4 V}{dH^4} H^4 + \cdots \]

Making

\[ \text{Const.} = V(H)|_{H=0}; \quad \alpha' = \frac{dV}{dH}|_{H=0}; \quad \beta' = \frac{1}{2} \frac{d^2 V}{dH^2}; \quad \gamma' = \frac{1}{6} \frac{d^3 V}{dH^3}; \quad \delta' = \frac{1}{24} \frac{d^4 V}{dH^4} \]

We have

\[ V = \text{Const.} + \alpha' H + \beta' H^2 + \gamma' H^3 + \delta' H^4 + \cdots \]

In the dynamic measurement method, a constant magnetic field, \( H_0 \), is applied with an electromagnet together with a small sinusoidal magnetic field, \( h_0 \sin \omega t \), of amplitude \( h_0 \) and angular frequency \( \omega \) using a pair of Helmholtz coils, so that the total applied magnetic field \( H \) is the sum of the constant magnetic field \( H_0 \) plus the small sinusoidal magnetic field:

\[ H = H_0 + h_0 \sin \omega t \]
Replacing this expression for the total applied magnetic field in the power series:

\[ V = \text{Const.} + \alpha' (H_0 + h_0 \sin \omega t) + \beta' (H_0 + h_0 \sin \omega t)^2 + \gamma' (H_0 + h_0 \sin \omega t)^3 + \delta' (H_0 + h_0 \sin \omega t)^4 + \cdots \] (46)

After expanding the expressions for second, third and fourth powers and grouping conveniently, we obtain

\[ V = \frac{1}{8} \left[ (\text{Const.} + 4\beta' h_0^2 + 3\delta' h_0^4 + 8\alpha' h_0 + 12\gamma' h_0^2 h_0 + 8\beta' H_0^2 + 24\delta' h_0^2 h_0^2 + 8\gamma' h_0^4 + 8\delta' H_0^4) + (8\alpha' h_0 + 6\gamma' h_0^3 + 16\beta' h_0 h_0 + 24\delta' h_0^3 h_0) + 24\gamma' h_0 H_0^2 + 32\delta' h_0 H_0^2 (\sin \omega t - 4\delta' h_0^3 - 12\gamma' h_0^2 H_0 - 24\delta' h_0^2 H_0^4) \right] \]

\[ \cos 2\omega t + (-2\gamma' h_0^3 - 8\delta' h_0^2 H_0) \sin 3\omega t + (\delta' h_0^3) \cos 4\omega t \] (47)

Now, as at the output of the amplifier lock-in amplifier, we only have the voltage \( V' \) of the sinusoidal component, with the same frequency \( \omega \) as the reference, we are left with

\[ V' = \frac{1}{8} (8\alpha' h_0 + 6\gamma' h_0^3 + 16\beta' h_0 H_0 + 24\delta' h_0^3 H_0 + 24\gamma' h_0 H_0^2 + 32\delta' h_0 H_0^3) \] (48)

Multiplying and dividing this equation by \( H_0^4 \), we obtain

\[ V' = \frac{H_0^4}{8} \left[ \left( \frac{8\alpha'}{H_0^2} \left( \frac{h_0}{H_0} \right) + 6\gamma' \left( \frac{h_0}{H_0} \right)^3 + 16\beta' \left( \frac{h_0}{H_0} \right) + 24\delta' \left( \frac{h_0}{H_0} \right)^3 \right) + \frac{24\gamma'}{H_0^2} \left( \frac{h_0}{H_0} \right) + 32\delta' \left( \frac{h_0}{H_0} \right) \right] \] (49)

Neglecting the terms of higher order in \( \left( \frac{h_0}{H_0} \right) \) for \( \left( \frac{h_0}{H_0} \right) < 1 \), we have

\[ V' = \frac{H_0^4}{8} \left[ \frac{8\alpha'}{H_0^2} \left( \frac{h_0}{H_0} \right) + 16\beta' \left( \frac{h_0}{H_0} \right) + 24\gamma' \left( \frac{h_0}{H_0} \right) + 32\delta' \left( \frac{h_0}{H_0} \right) \right] \] (50)

\[ V' = h_0 (\alpha' + 2\beta' H_0 + 3\gamma' H_0^2 + 4\delta' H_0^3) \]

But \( (\alpha' + 2\beta' H_0 + 3\gamma' H_0^2 + 4\delta' H_0^3) \) is the sum of the first four terms of the derivate of the function \( V = \text{Const.} + \alpha H + \beta H^2 + \gamma H^3 + \delta H^4 + \cdots \), then

\[ V' = h_0 \left( \frac{dV}{dH_0} \right) \] (51)
Dividing this expression by the amplitude $h_0$ of the sinusoidal magnetic field, and by the thickness $d$ of the sample, we get the magnetoelectric coefficient $\alpha^{EH}$ of Eq. (35):

$$\alpha^{EH} = \frac{E_{\text{out}}}{h_0} = \frac{1}{h_0} \frac{V}{d} = \frac{1}{d} \frac{dV}{dH_0}$$  \hspace{1cm} (52)

### 3.3. Theory of measurement in pulsed magnetic field

Figure 3.19 represents magnetoelectric measurements under pulsed magnetic fields. (a) A magnetic field pulse is applied. (b) Synchronously, the magnetoelectric response voltage is measured and digitized (BuenoBaques et al., 2006a, 2006b; Botello-Zubiate et al., 2006a, 2006b).

In pulsed field magnetoelectric measurements, the sample can be represented by its equivalent circuit formed by a capacitor $C_S$ in parallel to a resistor $R_S$, as shown in Fig. 3.20. This sample equivalent electric circuit is connected to the input resistance of the measuring system $R_i$.

It is important to understand that in the magnetoelectric measurement with an applied pulsed magnetic field, the sample equivalent resistance $R_S$ is much greater than the input resistance of the measuring circuit ($R_i \sim 1 \text{ M\Omega}$), and then the generated current from the capacitor voltage is almost completely discharged through the internal resistance $R_i$ of the measurement equipment. Applying Ohm’s law:

$$i = \frac{dQ}{dt} = \frac{V}{R_i}$$  \hspace{1cm} (53)

As shown in Fig. 3.21, the sample capacitance $C_S$ behaves like a parallel plates plane capacitor with plate area $A$ and dielectric thickness $d$.

The capacitance of this capacitor is

$$C = \varepsilon^{\text{rel}} \varepsilon_0 \frac{A}{d}$$  \hspace{1cm} (54)

where $\varepsilon^{\text{rel}}$ is the sample relative dielectric permittivity and $\varepsilon_0$ is vacuum permittivity. The capacitance definition gives

$$C = \frac{Q}{V} \Rightarrow Q = CV$$  \hspace{1cm} (55)

The voltage and the electric field in a plane capacitor are related by the equation:

$$V = Ed$$  \hspace{1cm} (56)
replacing

\[ Q = e^\text{rel} \frac{A}{d} Ed = e^\text{rel} Ae \]  

(57)

As the measured charge, \( Q \), is a function of the magnetic field pulse, and the last magnitude is a function of time, \( Q = (H(t)) \), then deriving and applying the chain rule:

**Figure 3.19** Magnetoelectric measurements under pulsed magnetic fields. (a) 20 ms magnetic-field pulse waveform measured and digitalized. (b) Magnetoelectric response voltage measured and digitalized.
Differentiating the equation \( Q = \varepsilon_r \varepsilon_0 AE \) with respect to the magnetic field \( H \), we obtain \( \frac{dQ}{dH} = \varepsilon_r \varepsilon_0 A \frac{dE}{dH} \), and replacing in Eq. (59):

\[
\frac{dQ}{dH} = \frac{V}{R_i \frac{dH}{dt}}
\]  

Rearranging terms, we finally obtain the magnetoelectric coefficient

\[
\alpha_{EH} = \frac{dE}{dH} = \frac{V}{R_i \varepsilon_0 \varepsilon_0 A} \frac{1}{\frac{dH}{dt}}
\]  

The magnetoelectric output voltage is detected by an analog-to-digital converter. In order to ensure the reproducibility of the measurements, a
zero signal without sample is always taken and then subtracted to the signal of the sample. The magnetoelectric effect can be measured during the application of a magnetic field pulse when the voltage appearing on the sample is directly recorded. The recorded voltage is proportional to the current in the circuit which is the first derivative of the charge $dQ/dt$ generated by the induced polarization due to the deformation caused by the magnetic field pulse. Considering that the sample resistance is much bigger than the input resistance of the measurement circuit, the charge can be obtained from

$$Q = \frac{1}{R_i} \int V_{out} dt$$

(62)

where $R_i$ is the input resistance of the measurement circuit and $V_{out}$ is the voltage measured on the sample. In this way, considering the sample as a plane parallel capacitor with an area $A$, the electric field will be

$$E = \frac{1}{R_i \varepsilon_0 \varepsilon_{rel} A} \int V_{out} dt$$

(63)

where $\varepsilon_0$ is the relative permittivity of the material and $A$ is the area of the silver-plated surface of the sample. Then, the magnetoelectric voltage coefficient can be obtained from this equation and the magnetic field $H(t)$, taking time as a parameter, according to the relation:

$$\alpha_{ME} = \frac{dE}{dH} = \frac{d}{dH(t)} \left[ \frac{1}{R_i \varepsilon_0 \varepsilon_{rel} A} \int V_{out} dt \right]$$

(64)

The above derivative should be done numerically starting from the sample-recorded voltage and from the recorded magnetic field. It is desirable a highly accurate and sensitive electronics to obtain smooth experimental data in order to minimize the numerical noise generated during the data processing. In this simple model, another problem arises from the fact that in some samples, there is a possibility that charges get accumulated at the grain boundaries during poling. These charges may move towards the electrodes during the measurement (Rivera, 1994). An estimation and a study of this effect can be performed by changing the input impedance of the electronic circuitry to known values.

### 3.4. Magnetoelectric measurements by the dynamic method

Figure 3.22 shows the nonlinear dependence of the magnetoelectric coefficient as a function of the applied magnetic DC field measured by the dynamic method for three different compositions of BaTiO$_3$–CoFe$_2$O$_4$ composites. The 25% BaTiO$_3 + 75%$ CoFe$_2$O$_4$ composite has the
largest magnetoelectric coefficient (1.97 mV/cm Oe), while the 50% BaTiO₃ + 50% CoFe₂O₄ and 75% BaTiO₃ + 75% CoFe₂O₄ composites have magnetoelectric coefficients of 1.67 and 1.23 mV/cm Oe, respectively. One can observe a hysteretic behaviour when increasing and then decreasing the applied magnetic field.

3.5. Magnetoelectric measurements by the pulsed dynamic method

Figure 3.23 shows the time behaviour of the pulsed magnetic field in the field coil, and Fig. 3.24 shows the time behaviour of the magnetoelectric response voltage for three different composite compositions measured by the pulsed field method. We can observe a correspondence between the behaviour of the pulsed magnetic field and the magnetoelectric voltage: when the pulsed magnetic field values go from negative to positive, so does the magnetoelectric voltage, and again when the pulsed magnetic field values go from positive to negative, so does the magnetoelectric voltage.

Figure 3.25 shows the response voltage for three different composite compositions as a function of the pulsed magnetic field. From these curves, the values of the magnetoelectric coefficient were calculated as described above. The calculation was made only with data between points 1 and 2 in each curve. The remaining values were not taken into account since they involve related values of magnetic and electrical hysteresis.
Figure 3.26 shows the results of the measurement of magnetoelectric coefficient for the three BaTiO$_3$–CoFe$_2$O$_4$ composite compositions. Values of 1.67, 1.45 and 1.20 mV/cm Oe were obtained for 25%, 50% and 75% of BaTiO$_3$, respectively.
The results of the magnetoelectric coefficients of the different composites obtained by the pulsed dynamic method were calculated on the basis of the theory of measurement in pulsed magnetic fields. Table 3.10 compares

<table>
<thead>
<tr>
<th>Voltage (V)</th>
<th>-2000</th>
<th>-4000</th>
<th>-6000</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.10</td>
<td>0.00</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>-0.08</td>
<td>0.02</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>-0.06</td>
<td>0.04</td>
<td>0.06</td>
<td>0.08</td>
</tr>
<tr>
<td>-0.04</td>
<td>0.06</td>
<td>0.08</td>
<td>0.10</td>
</tr>
<tr>
<td>-0.02</td>
<td>0.08</td>
<td>0.10</td>
<td>0.12</td>
</tr>
<tr>
<td>0.00</td>
<td>0.10</td>
<td>0.12</td>
<td>0.14</td>
</tr>
<tr>
<td>0.02</td>
<td>0.12</td>
<td>0.14</td>
<td>0.16</td>
</tr>
<tr>
<td>0.04</td>
<td>0.14</td>
<td>0.16</td>
<td>0.18</td>
</tr>
<tr>
<td>0.06</td>
<td>0.16</td>
<td>0.18</td>
<td>0.20</td>
</tr>
<tr>
<td>0.08</td>
<td>0.18</td>
<td>0.20</td>
<td>0.22</td>
</tr>
<tr>
<td>0.10</td>
<td>0.20</td>
<td>0.22</td>
<td>0.24</td>
</tr>
</tbody>
</table>

**Figure 3.25**  Response voltage of three different composite compositions as a function of the pulsed magnetic field.

**Figure 3.26**  Magnetoelectric coefficients for three composite compositions measured by the pulsed field method.

The results of the magnetoelectric coefficients of the different composites obtained by the pulsed dynamic method were calculated on the basis of the theory of measurement in pulsed magnetic fields. Table 3.10 compares
the magnetoelectric coefficients as obtained by the dynamic and the pulsed dynamic methods. One can observe that the measurements follow a similar trend.

## 4. Single-Phase Magnetoelectric Multiferroics

The following sections describe the characteristics of representative magnetoelectrics. The analysis of some particular materials will be employed as a basis for the discussion of noteworthy topics.

### 4.1. Cr\(_2\)O\(_3\)

As described in the Historical Introduction, Cr\(_2\)O\(_3\) was the object of pioneering theoretical (Dzyaloshinskii, 1959) and experimental (Astrov, 1960) discoveries on magnetoelectricity. The results obtained by Rado’s group completed a systematic characterization of magnetoelectricity in Cr\(_2\)O\(_3\). Figure 3.27 (Folen et al., 1961) shows the temperature dependence of the magnetoelectric tensor components allowed by \(D_{3d}\) symmetry (recall Eq. (41)). The results shown in this Figure, expressed in Gaussian units, were obtained by measurement of magnetic response to electrical stimulus. In SI, the values would be of the order of units, in ps/m.

Rado and Folen (1961) confirmed experimentally the reciprocity of the effects \(E \rightarrow M\) and \(H \rightarrow P\) (Eqs. (30) and (32)) and gave evidence of the presence of domain structures in antiferromagnetic crystals. Rado (1961) proposed a phenomenological description of magnetoelectricity in Cr\(_2\)O\(_3\) and a statistical theory for magnetoelectricity in antiferromagnets Rado (1962). Rado’s model is based on the microscopic idea of an external electric field deforming the electron cloud of the magnetic cation. This deformation affects, via spin–orbit coupling, the spin configuration, and as a result, the ion changes its magnetic moment.

Rado’s (1962) model has been recently upgraded and computer-aided revitalized by Delaney and Spaldin (2009). By application of a simple non-collinear Zeeman term introduced into the Kohn–Sham energy functional,
these authors were able to calculate the magnetoelectric susceptibility tensor of Cr$_2$O$_3$. Their calculations, for $T = 0$ K, lead to $\alpha_{\parallel} = 0$, as in Folen’s experiment. For $\alpha_{\perp}$, the authors take spin–orbit interaction into consideration, apply the Berry-phase approach to estimate the magnetic-field-induced electric polarization and obtain the value $\alpha_{\perp} = 1.43$ ps/m, in excellent agreement with experiment.

Recently, a new series of investigations has refocused the attention on Cr$_2$O$_3$. Interestingly, when this material is exposed to an intense magnetic field, a “spin-flop” effect takes place, and consequently, its magnetic symmetry and magnetoelectric tensor change (Popov et al., 1999). Figure 3.28 describes schematically the mentioned effect.

Under the condition of moderate external magnetic field, symmetry and magnetoelectric properties follow the already mentioned description of Astrov (1960), and Rado and Folen ((1961) Fig. 3.28a, Eq. (41)). If an intense magnetic field is applied, the spin-flop effect leads to the magnetic
configurations of Fig. 3.28b and c. According to Table 3.8, magnetoelectric tensors transform, as shown in Fig. 3.28. Krotov et al. (2001) have investigated the magnetoelectric response of Cr₂O₃ under magnetic fields about two orders of magnitude more intense than those of Astrov (1960) and Rado (1961). The results so obtained are reproduced in Fig. 3.29. The appearance of measurable off-diagonal components in the tensor, signal of spin-flop effect, is clearly visible.

The asymmetric nature ($\alpha_{31} \neq \alpha_{13}$) of the observed $\alpha$ is interpreted as a manifestation of the toroidal character in the magnetic structure of Cr₂O₃.
The toroidal moment $T$ of a magnetoelectric configuration is a measurable polar-\(c\) vector given by the antisymmetric part of the magnetoelectric axial-c tensor $\alpha$. The basic equation is

$$T_i = e_{ijk} \alpha_{jk}$$

where $e_{ijk}$ is the Levi–Civita symbol [1 if \((i, j, k)\) is an even permutation of \((1,2,3)\); −1 if it is an odd permutation; 0 if any index is repeated].

The data in Fig. 3.29 reveal that $\text{Cr}_2\text{O}_3$ is toroidically ordered, with an observable toroidal moment component $T_2 = \frac{1}{2}(\alpha_{31} - \alpha_{13})$.

4.2. **Ni$_3$B$_7$O$_{13}$I**

Figure 3.30 shows the anthological $\text{Ni}_3\text{B}_7\text{O}_{13}$I magnetoelectric hysteresis loop obtained by Ascher et al. (1966). Nickel iodine boracite is rich in electromagnetic properties. For $T$ above $\sim 120$ K, it is piezoelectric–paramagnetic, for
64 < T < 120 K, it is piezoelectric–antiferromagnetic and below 64 K, it becomes ferroelectric–weak ferromagnetic. The low-temperature phase has $2\text{m}'\text{m} = C_{2v}\cdot C_s$ magnetic symmetry, with the magnetoelectric coupling tensor:

$$
\alpha = \begin{bmatrix}
\cdot & \cdot & \cdot \\
\cdot & \cdot & z_{23} \\
\cdot & z_{32} & \cdot
\end{bmatrix}
$$

Only the transverse linear magnetoelectric effect is observable for this material. In the experiment of Fig. 3.30, the electric polarization was measured along the $z$ axis and the magnetic field was applied in the $xy$ plane. Material response showed a linear interval for low fields and a dramatic (nonlinear) inversion of polarization at $H = \pm 6 \text{ KOe}$.

**4.3. Olivine phosphates**

The study of magnetoelectricity in olivine phosphates LiMePO$_4$ (Me = Ni, Co, Fe, Mn) has been constant since the pioneering works of Santoro and Newnham (1967). Here, we refer relevant information from some recent representative articles (Jensen et al., 2009; Kornev et al., 2000; Li et al., 2006; Vaknin et al., 2002, 2004; Yamauchi and Picozzi, 2009) on this family.
The crystal symmetry of considered phases is orthorhombic, space group $Pnma = D_{2h}^{16}$. The magnetic symmetry groups in general differ from phase to phase. LiFePO$_4$ and LiMnPO$_4$ belong to the magnetic space group $Pn'm'a'$. LiCoPO$_4$ and LiNiPO$_4$ correspond, respectively, to $Pnma$ and $Pnnma$. Figure 3.31, adapted from Brown et al. (2005), describes the structures of representative unit cells, with the orientations of ionic magnetic dipoles shown. B&W symmetry elements are sketched.

To facilitate the geometrical understanding of magnetic symmetries, we recall the behaviour of magnetic vectors with respect to mirrors and anti-mirrors:

- Magnetic dipole vectors (or components) perpendicular to a mirror are invariant under reflection. These vectors undergo inversion under antireflection.
- Magnetic dipole vectors (components) parallel to a mirror undergo inversion under reflection. These vectors are invariant under antireflection.

**Figure 3.31** Crystal and magnetic structures of magnetoelectric olivine phosphates. Reproduced with permission from Brown et al. (2005).
As an example of B&W symmetry, consider the transformation of ion numbered “1” in the LiNiPO$_4$ cell, in the group $Pmnm'a$. The following operations occur:

- Ion “1” transforms into ion “2” under glide mirror $n$
- Ion “1” transforms into itself under anti-mirror $m'$
- Ion “1” transforms into ion “3” under glide mirror $a$.

In LiMnPO$_4$ and in LiFePO$_4$, anti-parallel moments form coaxial chains, while in LiCoPO$_4$ and LiNiPO$_4$, they show a tendency to form toroidal loops. According to Table 3.8, the magnetoelectric effect is mostly longitudinal (matrix $x$ is diagonal) for LiMnPO$_4$ and LiFePO$_4$, whereas for LiCoPO$_4$ and LiNiPO$_4$, the magnetoelectric effect is transverse. For LiCoPO$_4$, non-null coefficients are $\alpha_{12}$ and $\alpha_{21}$, while for LiNiPO$_4$, non-zero coefficients are $\alpha_{13}$ and $\alpha_{31}$.

Figure 3.32 shows the results of measurements performed by the group of Rivera (1994), on a single crystal of LiNiPO$_4$. Magnetoelectricity is only detected at very low temperatures. The observation confirmed that only two (off-diagonal) tensor coefficients are different from zero. Both $\alpha_{xz}$ and $\alpha_{zx}$ show maxima, $\alpha \approx 2$ ps/m, a few K before the magnetic phase transition at $T \approx 21$ K.

According to Jensen et al. (2009), the microscopic origin of magnetoelectricity in LiNiPO$_4$ can be explained as a cooperative effect of

![Figure 3.32](image-url) Magnetoelectric coefficients of LiNiPO$_4$ versus temperature measured by the dynamic technique. The ME coefficients, $xz$ and $zx$, were measured under 5 kOe magnetic field along the $c$ axis and the $a$ axis, respectively. Reprinted with permission from Vaknin et al. (2004).
super-exchange, Dzyaloshinsky–Moriya spin interactions and elastic distortions. Figure 3.33 describes the magnetically induced ionic shifts, giving rise to polarization changes in the model of Jensen and collaborators.

LiCoPO$_4$ has been characterized by Rivera (1994). Figure 3.34 describes experimental and calculated (Kornev et al., 2000) results for this phase. The magnetoelectric coefficients are about 10 times higher for LiCoPO$_4$ than for LiNiPO$_4$. The temperature domain for magnetoelectricity in both phases is practically the same.

From the theoretical point of view, Kornev et al. (2000) developed the phenomenological representation, based on the free energy expansion, which leads to the calculated curve of Fig. 3.34. Vaknin et al. (2002) present a neutron diffraction study of LiCoPO$_4$ that suggests a change in the microscopic description of the magnetic properties of this phase. According

![Diagram](image)

**Figure 3.33** (a) Positions of Ni (large blue (dark) circles), O (small yellow (bright) circles) and the PO$_4$-tetrahedra (triangles) in zero field. (b) Same as (a), but for $H||c$. PO$_4$-tetrahedra are assumed to shift downwards with $x$ (arrows), giving an electric polarization $P_x$ and changing the superexchange interaction. (c) Measured (circles) and calculated ME coefficient $\alpha_{xz}$ for $H||c$, assuming identical spin lengths (dashed line) and different spin lengths (solid line). (d) Same as (c) for $\alpha_{zx}$ with $H||a$. Insets in (c) and (d) show the assumed angles between spins $S_1$, $S_2$, $S_3$ and $S_4$. Reproduced with permission from Jensen et al. (2009).
to Vaknin et al., the magnetic moments are not strictly aligned along the $b$ axis, but are uniformly rotated from this axis by a small angle ($\approx 4.6^\circ$). This rotation breaks the mirror symmetry along the orthorhombic $b$ axis. The proposed magnetic symmetry is monoclinic point group $2\overline{1}$. The mentioned considerations are consistent with the appearance of weak ferromagnetism and with the magnetoelectricity of LiCoPO$_4$.

4.4. Perovskites—BiFeO$_3$ and BiMnO$_3$

4.4.1. Synthesis of BiFeO$_3$

By far, BiFeO$_3$ (BFO) is today the most extensively studied ME multi-ferroic. We devote this section to this prototype material.

The first report on the synthesis of BFO is the one by Royen and Swars (1957). The Bi$_2$O$_3$–Fe$_2$O$_3$ phase diagram has been established by Koizumi et al. (1964) and refined by Morozov and Gusarov (2002). Monodomain single crystals of BFO were obtained by Kubel and Schmid (1990). Kim et al. (2005) describe the synthesis of high-purity BFO powders by the sol–gel method, using bismuth nitrate and iron nitrate as sources. These authors detect, by differential thermal analysis, a reversible phase transformation of
the BFO R-phase at 836 °C. Jiang et al. (2006) report the preparation of Bi_{1-x}La_xFeO_3 by a modified Pechini approach. The La modification of BiFeO_3 has a beneficial effect on the ferroelectric and magnetic properties. Prado-Gonjal et al. (2009) compare the following methods for preparing BiFeO_3 polycrystals: hydrothermal synthesis, microwave heating in the solid state and the combination of both, that is a hydrothermal method using microwave heating. The best materials, without high-purity reactants, are obtained in few minutes by the last procedure.

Multiferroic bismuth ferrite (BiFeO_3) nanotubes have been synthesized by Park et al. (2004) using a modified template methodology. Figure 3.35 shows elements of structural characterization of the obtained nanotubes.
4.4.2. The crystal and magnetic structures of BFO

Figure 3.36 shows various features of the crystalline and magnetic structures of BiFeO₃. Structural and magnetic symmetries are trigonal, point group $C_{3v} = 3m$. The structural report by Reyes et al. (2007) is the following:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>R3c (hexagonal system description)</td>
</tr>
<tr>
<td>Cell parameters (Å)</td>
<td>$a = 5.57414(4)$; $c = 13.8588(1)$</td>
</tr>
<tr>
<td>Atomic parameters</td>
<td></td>
</tr>
<tr>
<td>$x$</td>
<td>Bi: 0.00000; Fe: 0.00000; O: 0.895(1)</td>
</tr>
<tr>
<td>$y$</td>
<td>Bi: 0.00000; Fe: 0.00000; O: 0.206(1)</td>
</tr>
<tr>
<td>$z$</td>
<td>Bi: 0.00000; Fe: 0.7207(3); O: 0.628(1)</td>
</tr>
<tr>
<td>$B$ (Å$^2$)</td>
<td>Bi: 1.00(2); Fe: 0.68(7); O: 0.2(2)</td>
</tr>
<tr>
<td>Occupation</td>
<td>Bi: 6.000; Fe: 6.000; O: 18.000</td>
</tr>
</tbody>
</table>

**Electromagnetic data of BFO**

Ferroelectric, Curie temperature: 1103 K, $P_c \sim 50 \mu$C/cm$^2$.

G-type Antiferromagnetism, Néel Temperature: 643 K

The antiferromagnetism in BiFeO₃ is caused by superexchange interaction via the oxygen atoms connecting Fe cations. The antiparallelism of the Fe spins is not perfect because the Dzyaloshinskii–Moriya interaction

**Figure 3.36** Crystal and magnetic structures of BiFeO₃. (a) Hexagonal unit cell. (b) Oxygen octahedron around Fe. (c) Canted antiferromagnetism between Fe cations (intermediate oxygen not shown). (d) Incommensurate cycloidal distribution of resultant magnetic dipoles. (d). Reproduced with permission from Lebeugle et al. (2008).
produces a slight canting of the magnetic moments. Thus, weak ferromagnetism appears. The average–bulk-magnetism tends to zero because their resultant magnetic moments generate an incommensurate cycloid where dipoles cancel each other. Interruption of this cycloid by doping or other agents favours ferromagnetism and magnetoelectricity in BiFeO$_3$.

4.4.3. Properties of BiFeO$_3$ and its variants

Yu et al. (2001) investigated the interruption of the cycloidal magnetic structure of BiFeO$_3$ by a high magnetic field, the onset of a linear magnetoelectric effect and the appearance of a toroidal moment. A group-theoretical approach to the mentioned effects has been given by Kadomtseva et al. (2004).

Bhattacharjee et al. (2009) studied 0.73BiFeO$_3$–0.27PbTiO$_3$ in the temperature range from 300 to 600 K. They detected a monoclinic distortion of the ferroelectric phase. Catalan et al. (2009) have investigated BFO ceramics doped with Ca. Ca acted as a proxy for hydrostatic pressure, at a rate of 1% Ca $= 0.3$ GPa. The magnetic Neel temperature increases as Ca concentration increases, at a rate of 0.66 K per 1%Ca (molar). Le Bras-Jasmin et al. (2009) report characterization of the multiferroic series Bi$_{1-x}$La$_x$FeO$_3$ for $0 \leq x \leq 0.25$. La reduces the threshold magnetic field for cancelling the magnetic spiral phase. Maximum magnetocapacitance occurs for $x = 0.15$. Palkar et al. (2004) reported the finding of magnetoelectric coupling in Bi$_{0.92-x}$R$_x$La$_{0.1}$FeO$_3$ (R = Gd, Tb, Dy) at room temperature. Seidel et al. (2009) reported the observation of room-temperature electronic conductivity at ferroelectric domain walls in the insulating multiferroic BiFeO$_3$.

Wang et al. (2006) reported on the characterization of multiferroic BiFeO$_3$ doped with Ba. Their samples exhibited magnetism and ferroelectricity simultaneously at room temperature. The magnetoelectric coupling was evidenced by an increase of the dielectric constant with the increasing applied magnetic field. See Figs. 3.37–3.39.

Naik and Mahendiran (2009) presented systematic studies of substituted BFO that are resumed in Fig. 3.40. The divalent cation A (=Sr, Ba and Sr$_{0.5}$Ba$_{0.5}$) substitutes Bi in Bi$_{1-x}$A$_x$FeO$_3$, with ($x = 0$ and 0.3). Longitudinal ($z^\parallel_{EH}$) and transverse ($z^\perp_{EH}$) magnetoelectric coefficients were measured using a dynamic lock-in technique. The maximum $z^\perp_{EH} = 2.1$ mV/cm Oe in the series was found for $A = Sr_{0.15}Ba_{0.15}$.

The paper by Wang et al. (2003a) has become a reference on multiferroicity and magnetoelectricity in BiFeO$_3$ thin films. The crystal structure of the film is monoclinic in contrast to the bulk, which is rhombohedral. The films display a room-temperature spontaneous polarization almost an order of magnitude higher than that of the bulk. The films also exhibit enhanced thickness-dependent magnetism compared with the bulk. Initial ME measurement showed a maximum value of $z_{EH} \sim 3$ V/cm Oe.

Beautiful and illustrating images in the work by Zhao et al. (2006) demonstrated the electrical control of the antiferromagnetic domain
Figure 3.37 Magnetic hysteresis loops of Bi$_{1-x}$Ba$_x$FeO$_3$ ($x = 0.15$, 0.25). Reproduced with permission from Wang et al. (2006).

Figure 3.38 (a) Frequency dependence of the dielectric constant of Bi$_{1-x}$Ba$_x$FeO$_3$ ($x = 0.15$, 0.25); (b) magnetic field-induced change in dielectric constant of Bi$_{1-x}$Ba$_x$FeO$_3$ ($x = 0.15$, 0.25) measured at 80, 120, and 300 K. Reproduced with permission from Wang et al. (2006).
structure in a single-phase multiferroic material at room temperature. The ferroelectric structure was measured using piezo force microscopy (PFM), whereas the antiferromagnetic configuration was detected by means of X-ray photoemission electron microscopy (PEEM; see Figs. 3.41–3.44).

4.4.4. BiMnO$_3$

BiMnO$_3$ is also the object of interest as low-temperature MEMF perovskite. Collinear ferromagnetic ordering, attributed to orbital-ordering, is well established for temperatures below $T_c = 105$ K (Moreira dos Santos et al., 2002a). The low-temperature phase crystallizes in the monoclinic space group C2 with unit-cell parameters $a = 9.5317(7)$ Å, $b = 5.6047(4)$ Å, $c = 9.8492(7)$ Å and $\beta = 110.60(1)$ Å. The spin direction is along [010] and the magnetic moment per formula unit is 3.2 $\mu$B (close to 4 $\mu$B expected for the fully saturated FM state; Atou et al., 1999).

Figure 3.39  Ferroelectric hysteresis loop of Bi$_{1-x}$Ba$_x$FeO$_3$ ($x = 0.15, 0.25$) at room temperature. Reproduced with permission from Wang et al. (2006).
The scenario is not so clear regarding ferroelectricity. A generally accepted idea is that the structure of BiMnO$_3$ is polar (see the mentioned space group) and that the ferro-paraelectric transition occurs at a temperature of approximately 450 K (Moreira dos Santos et al., 2002b). The electrical conductivity of BiMnO$_3$ is relatively high and this factor adds difficulties to basic measurements, as well as to applications. Figures 3.45–3.47 show the multiferroic characteristics of BiMnO$_3$, reported by Grizalez et al. (2009).

Recent experimental results indicate that the room-temperature structure is more symmetric than the usual representation. According to Belik et al. (2007), at 300 K, BiMnO$_3$ crystallizes in the centrosymmetric space group $C2/c$. The crystallographic data are $a = 9.5415(2)$ Å, $b = 5.61263(8)$ Å, $c = 9.8632(2)$ Å and $\beta = 110.6584(12)$ Å. At 550 K, $a = 9.5866(3)$ Å,
$b = 5.59903(15) \ \text{Å}, \ \epsilon = 9.7427(3) \ \text{Å} \ \text{and} \ \beta = 108.601(2) \ \text{Å}, \ \text{space group} \ C2/c$. A centrosymmetric structure is compatible with antiferroelectricity, but not with ferroelectricity. Solovyev and Pchelkina (2009) agree with this model and discuss the temperature dependency of inversion symmetry with multiferroicity. Further work on the synthesis of BiMnO$_3$, the unification of diffraction analysis, hysteresis loops and \textit{ab initio} results is still required.

4.5. Bi$_2$FeCrO$_6$

Nechache et al. (2006) report the structural and physical properties of epitaxial Bi$_2$FeCrO$_6$ (BFCO) thin films on epitaxial SrRuO$_3$ grown on (100)–oriented SrTiO$_3$ substrates by pulsed-laser ablation. The 300-nm
thick films exhibit both ferroelectricity and magnetism at room temperature with a maximum dielectric polarization of $2.8 \mu\text{C}/\text{cm}^2$ at $E_{\text{max}} = 82 \text{kV/cm}$ and a saturated magnetization of 20 emu/cm$^3$ ($\sim 0.26 \mu\text{B}$ per rhombohedral unit cell), with a coercive field below 100 Oe. See Figs. 3.48 and 3.49.

4.6. Hexagonal manganites YMnO$_3$, HoMnO$_3$

Nugroho et al. (2007) studied the magnetoelectric coupling in YMnO$_3$ single crystal, in which a part of the Mn$^{3+}$ ions is substituted by non-magnetic Ga$^{3+}$ ions. While the antiferromagnetic ordering temperature is...
gradually suppressed by Ga doping, the magnetocapacitance is enhanced by two orders of magnitude, which is attributed to the lifting of frustration of interlayer spin interactions in doped samples. The authors also find that the dielectric constant anomaly below magnetic ordering temperature is strongly anisotropic, which is explained using a phenomenological Landau description of ferroelectric antiferromagnets. See Figs. 3.50 and 3.51.

Hur et al. (2009) present an example of a giant magnetoelectric effect in a conventional multiferroic HoMnO$_3$, where the polarization is very large ($\sim 56$ mC/m$^2$) and the ferroelectric transition temperature is higher than the magnetic ordering temperature by an order of magnitude. The authors attribute the characteristic of the giant magnetoelectric effect to the ferroelectricity induced entirely by the off-centre displacement of rare-earth ions with large magnetic moments. This finding suggests an avenue to design multiferroics with large polarization and higher ferroelectric transition temperature as well as large magnetoelectric effects. The results are shown in Figs. 3.52 and 3.53.

Figure 3.43 PEEM and in-plane PFM images taken in the same area of an as-grown BiFeO$_3$ film. (a, b) PEEM images. (a) Before and (b) after 90° in-plane rotation between the two images. The arrows show the direction of X-ray polarization relative to the domain structure. (c,d) In-plane PFM images. (c) Before and (d) after 90° in-plane rotation. The arrows show the direction of the in-plane component of ferroelectric polarization. Reproduced with permission from Zhao et al. (2006).
Figure 3.44  PEEM and in-plane PFM images of the same area of a BiFeO$_3$ film before and after electrical poling. (a, b) PEEM images. (a) Before and (b) after poling. The arrows show the X-ray polarization direction during the measurements. (c, d) In-plane PFM images. (c) Before and (d) after poling. The arrows show the direction of the in-plane component of ferroelectric polarization. Regions 1 and 2 (marked with green
4.7. Orthorhombic manganites RMnO$_3$ (R = Gd, Tb, Dy)

Kimura et al. (2005) have investigated the magnetoelectric phase diagrams of rare-earth manganites with orthorhombically distorted perovskite structure, RMnO$_3$ (R = Gd, Tb, and Dy). A variety of magnetic and electric phases emerge with varying R-site ion, temperature, and magnetic field in these systems. The magnetoelectric phase diagram varies sensitively with the direction of a magnetic field relative to the crystallographic axes. Although the ground state of GdMnO$_3$ with the largest ionic radius of $R(r_R)$ is not ferroelectric in zero magnetic fields, a ferroelectric phase with electric polarization along the $a$ axis appears by applying $H (>\sim 1$ T) along the $b$ axis. Both TbMnO$_3$ and DyMnO$_3$ show a ferroelectric order with $P$ along the $c$ axis even at $H = 0$ below a lock-in transition temperature where non-zero wave vectors for magnetic and lattice modulations become nearly constant. These systems also exhibit a flop of the ferroelectric polarization ($P||c$ to $P||a$) when $H$ is applied along the $a$ or $b$ axis. By contrast, the application of $H$ above $\sim 10$ T along the $c$ axis completely suppresses the ferroelectricity in TbMnO$_3$ (Figs. 3.54–3.61).

![Figure 3.45](image)


and red circles, respectively) correspond to 109° ferroelectric switching, whereas 3 (black-and-yellow circles) and 4 (white circles) correspond to 71° and 180° switching, respectively. In regions 1 and 2, the PEEM contrast reverses after electrical poling. (c) A superposition of in-plane PFM scans shown in (c) and (d) used to identify the different switching mechanisms. Reproduced with permission from Zhao et al. (2006).
**Figure 3.46** Magnetization ($M$ vs. $H$) hysteresis loops at 5 and 120 K on BiMnO$_3$/SrTiO$_3$ grown in oxygen pressure of $5 \times 10^{-2}$ mbar. Inset displays $H_c \sim 28$ Oe. Reproduced with permission from Grizalez et al. (2009).

**Figure 3.47** Conductivity versus Temperature for a BiMnO$_3$ bulk sample. Reproduced with permission from Grizalez et al. (2009).
Figure 3.48  Ferroelectric properties of a 300-nm-thick BFCO film. (a) ferroelectric hysteresis loop at room temperature; (b) local remanent piezoresponse hysteresis. Inset shows a PFM image scan size of 10 × 10 μm² after writing oppositely polarized domains using the AFM tip as a top electrode (black/white contrast represents polarization oriented upwards/downwards). Reproduced with permission from Nechache et al. (2006).
4.7.1. TbMnO$_3$

Fig. 3.55 and 3.56

4.7.2. DyMnO$_3$
See Fig. 3.57–3.59

4.7.3. GdMnO$_3$
See Fig. 3.60 and 3.61

4.8. Half-doped manganites

Efremov et al. (2004) report on a possible way to avoid the ferroelectric–ferromagnetic incompatibility, and show that in charge-ordered and orbitally ordered perovskites, it is possible to make use of the coupling between magnetic and charge ordering to obtain ferroelectric magnets. In particular, in manganites that are less than half doped, there is a type of charge ordering that is intermediate between site-centred and bond-centred. Such a state breaks the inversion symmetry and is predicted to be magnetic and ferroelectric. The idea is represented in Figs. 3.62–3.64.

Karmakar et al. (2009) have carried out measurements of the magnetization, magnetoresistance and magnetodielectricity of the half-doped
charge-ordered manganite, Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. The low-temperature state is found to be strongly dependent on the oxygen stoichiometry, whereas the high-temperature state remains almost unaltered. A disorder–driven phase separation in the low-temperature state is noticed in the magnetic, magnetoresistance and dielectric measurements, which is attributed to the oxygen deficiency in the compound. A considerable magnetodielectric (MD) effect is noticed close to room temperature at 280 K which is fascinating for technological applications. The strongest MD effect observed in between 180 and 200 K is found to be uncorrelated with magnetoresistance, but it is suggested to be due to a number of intricate processes occurring in this temperature range which includes paramagnetic to antiferromagnetic transition, incommensurate to commensurate charge ordering and orbital

Figure 3.50  (a) Magnetocapacitance effect of 30% Ga doping level of YMnO$_3$ at 5 K for $E \parallel c$ in magnetic field applied along $H \parallel c$ and $H \perp c$. (b) field dependence of magnetization for $x = 0.3$ with magnetic field applied along $H \parallel c$ and $H \perp c$. Reproduced with permission from Nugroho et al. (2007).
ordering. The strongest MD effect seems to emerge from the high sensitivity of the incommensurate state to the external perturbation such as external magnetic field. The results propose a possible magnetoelectric coupling in the charge-ordered compound (see Figs. 3.65 and 3.66).

4.9. Layered perovskites

$\text{Bi}_x\text{FeTi}_3\text{O}_{15}$ and $\text{Bi}_y\text{Fe}_2\text{Ti}_3\text{O}_{18}$ are members of the Aurivillius family of compounds (Fuentes-Montero et al., 2008; Montero-Cabrera et al., 2008; Srinivas et al., 1999a, 2004a) having simultaneous electrical and magnetic ordering. Magnetoelectric measurements carried out by Srinivas et al. (1999b) in a linear time-varying magnetic field with an

Figure 3.51 (a) Magnetic-field dependence of the in-plane dielectric constant at 10, 60, and 90 K. (b) Magnetization of YMnO$_3$ along the c axis as a function of the magnetic field at 10, 60 and 90 K. Reproduced with permission from Nugroho et al. (2007).
Figure 3.52  (a) $T$ dependence of $P$ (solid circle) and $\varepsilon$ (open circle) for HoMnO$_3$ in zero $H$. Vertical dashed lines indicate magnetic phase boundaries. (b) $T$ dependence of $\varepsilon$ along the $c$ axis in various $H$ applied along the $c$ axis. (c) $T$ dependence of $P$ along the $c$ axis in $H$. Reproduced with permission from Hur et al. (2009).
alternating-current field superimposed yielded a nonlinear signal. The shift from linearity, which is not usually observed for antiferromagnetic materials, may be due to the tilt in the octahedra. The variation of the magneto-electric output with temperature for Bi$_5$FeTi$_3$O$_{15}$ and Bi$_6$Fe$_2$Ti$_3$O$_{18}$ indicated magnetic anomalies with enhanced sensitivity, corresponding to those in magnetization data. The results of magnetoelectric measurements are given in Figs. 3.67 and 3.68.

Srinivas et al. (2004b) report that bismuth iron titanate, Bi$_8$Fe$_4$Ti$_3$O$_{24}$, also belongs to the Aurivillius family of compounds. This material was synthesized by a solid-state route and showed a ferroelectric transition around 776 °C. Magnetization measurements carried out from 14 to 300 K showed a slope change around 220 K. Hysteresis loops observed at room temperature and at 14 K showed narrow loops, indicating

**Figure 3.53**  $H$ dependence of the field-induced $P$ and the $\varepsilon$ change at (a) 18 K; (b) 4.5 K; (c) 3.0 K; (d) 2.5 K. The field-induced $P$ was obtained by measuring the magnetoelectric current as a function of $H$, which was varied linearly with time at the uniform rate of 100 Oe/s. (e) $T$ and $H$ phase diagram for HoMnO$_3$ overlaid with $\varepsilon$ change versus $H$ for each $T$. Dashed lines indicate phase boundaries and hatched regions are the intermediate phase ($> 5$ K) and the field hysteresis region ($< 5$ K). Note that the $T$ scale is expanded below 5 K. Reproduced with permission from Hur et al. (2009).
antiferromagnetic behaviour. Dynamic magnetoelectric measurements carried out at room temperature and at 77 K indicated a nonlinear output signal. A temperature scan of ME output was performed from 77 to 300 K and showed an anomaly at 200 K, which can be corroborated to the slope change observed in the magnetization data (see Figs. 3.69 and 3.70).

Prasad and Kumar (2000) report work on five-layered compounds of Bi$_5$RFe$_2$Ti$_3$O$_{18}$, (where R = La, Sm, Gd, Dy). Magnetic and magnetoelectric measurements were performed on all the samples at room temperature. Magnetic measurements were also performed at low temperature in the case of the DyBi$_5$Fe$_2$Ti$_3$O$_{18}$ compound. From the magnetic measurements, the compounds were found to be of weak ferromagnetic/antiferromagnetic nature depending upon the temperature. The magnetoelectric coefficient $z^{EH}$ was found to be higher in the case of DyBi$_5$Fe$_2$Ti$_3$O$_{18}$. The results are plotted in Fig. 3.71.
Figure 3.55 Temperature profiles of electric polarization along the \(a\), \(b\) and \(c\) axes at various magnetic fields up to 9 T along the \(a\), \(b\) and \(c\) axes for TbMnO\(_3\) crystals. Reproduced with permission from Kimura et al. (2005).
Figure 3.56 Temperature profiles of $\varepsilon$–dielectric constant and $P$–electric polarization along the $c$ axis at high magnetic fields 9–14 T along the $a$, $b$, and $c$ axes for TbMnO$_3$ crystals. Reproduced with permission from Kimura et al. (2005).
Figure 3.57  Temperature profiles of electric polarization along the a and c axes at various magnetic fields up to 9 T along the a, b and c axes for DyMnO$_3$ crystals. Reproduced with permission from Kimura et al. (2005).
Figure 3.58  Magnetic-field-induced change in $a$ dielectric constant and $b$ electric polarization along the $a$ axis at selected temperatures for a DyMnO$_3$ crystal. Magnetic fields are applied along the $b$ axis. Reproduced with permission from Kimura et al. (2005).

Figure 3.59  $P$–$E$ curves obtained at magnetic fields of 0 T (red) and 6 T (blue) for a DyMnO$_3$ crystal. The measurements were done at 4.2 K and 100 Hz. Magnetic and electric fields are applied along the $b$ and $a$ axes, respectively. Reproduced with permission from Kimura et al. (2005).
**Figure 3.60** Temperature profiles of electric polarization along the \( a \) axis at various magnetic fields up to 8 T along the \( b \) axis for a GdMnO\(_3\) crystal. Except for the data denoted by black dots 0 T-A, all the data were taken at zero electric fields after poling the crystal. The measurements for the 0 T-A data black were done while always applying an electric field 200 V/mm. The inset shows a magnified view. Reproduced with permission from Kimura et al. (2005).

**Figure 3.61** \( P-E \) curves obtained at magnetic fields of 0 T (red) and 6 T (blue) for a GdMnO\(_3\) crystal. The measurements were done at 4.2 K and 10 Hz. Magnetic and electric fields are applied along the \( b \) and \( a \) axes, respectively. Reproduced with permission from Kimura et al. (2005).
Figure 3.62  Three types of charge ordering. (a) Site-centred charge order; (b) bond-centred charge order (the Zener polaron state); and (c) a ferroelectric intermediate state. The charge-ordered structure in (c) lacks inversion symmetry. Thin green arrows indicate the dipole moments of horizontal and vertical dimers, and the diagonal arrow is the total ferroelectric moment. Reproduced with permission from Efremov et al. (2004).

Figure 3.63  Concomitant magnetic order of the three charge-ordered phases in Fig. 3.62. (a) The magnetic CE-phase ($\Phi = 0$); (b) the orthogonal magnetic phase ($\Phi = \pi/2$); and (c) the magnetic structure of a ferroelectric intermediate state ($\Phi$; where $0 < \Phi < \pi/2$). Reproduced with permission from Efremov et al. (2004).

Figure 3.64  Schematic representation of the orbital order in the three charge-ordered phases. (a) Site-centred ordering; (b) bond-centred ordering; and (c) the ferroelectric intermediate state. Reproduced with permission from Efremov et al. (2004).
Figure 3.65 (a) Temperature variation of the real part of dielectric permittivity at \( f = 1 \text{ kHz} \) in the heating cycle in three different modes viz, without field, at \( H = 30 \text{ kOe} \) with zero-field cooled heating (ZFCH) and field-cooled heating (FCH) modes for the oxygen deficient sample. Inset shows the variation of the magnetodielectric (MD) effect as a function of temperature. (b) \( T \)-dependence of \( \tan \delta \) at \( f = 1 \text{ kHz} \) in the heating cycle with zero field, ZFCH and FCH modes for the oxygen-deficient sample. Inset shows the \( T \) variation of \( \tan \delta \) for the oxygen annealed sample at \( f = 1 \text{ kHz} \) and \( H = 0 \text{ Oe} \). Reproduced with permission from Karmakar et al. (2009).
Figure 3.66 Magnetic-field ($H$) dependence of the magnetoresistance (MR) at 150, 180 and 210 K, respectively. Inset shows the resistivity as a function of temperature in zero field, ZFCH and FCH modes with different fields. In the right axis, $\rho$ at $H = 0$ and in ZFCH mode with 30 kOe field are shown by the semilogarithmic plot. In the left axis, $\rho$ in field-cooled cooling (FCC) and FCH modes with 50 kOe field are shown by the linear plot. All the results are given for the oxygen-deficient sample. Reproduced with permission from Karmakar et al. (2009).

Figure 3.67 The variation of the magnetoelectric output with field for Bi$_5$FeTi$_3$O$_{15}$ at room temperature and 77 K (the curves are fits to the data points). Reproduced with permission from Srinivas et al. (1999b).
Figure 3.68  The variation of the magnetoelectric output with field for Bi$_6$Fe$_2$Ti$_3$O$_{18}$ at room temperature and 77 K (the curves are fits to the data points). Reproduced with permission from Srinivas et al. (1999b).

Figure 3.69  ME output for Bi$_6$Fe$_2$Ti$_3$O$_{24}$. (a) $E$ versus $H$ at 300 K, (b) $E$ versus $H$ at 77 K. Reproduced with permission from Srinivas et al. (2004b).

Figure 3.70  ME output versus $T$ of Bi$_6$Fe$_2$Ti$_3$O$_{24}$. Reproduced with permission from Srinivas et al. (2004b).
Figure 3.71 (a–d) Electric versus magnetic field for different rare-earth-substituted (R = La, Sm, Gd and Dy) Bi$_5$RFe$_2$Ti$_3$O$_{18}$ compounds at room temperature. (e) Magnetoelectric field ($E$) versus magnetic field of DyBi$_5$Fe$_2$Ti$_3$O$_{18}$ compound at 80 K. Reproduced with permission from Frasad and Kumar (2000).
5. Magnetolectric Composites

5.1. The extrinsic magnetolectric effect in composite systems

As it was explained above, the magnetolectric effect in single-phase magnetolectric multiferroic materials is an intrinsic property that originates from the coupling of the electric and magnetic subsystems. From the quantitative point of view, the linear ME effect in traditional single-phase bulk materials is generally not very intense. Materials with $\varepsilon_{EH}$ higher than a few tens mV/cm Oe are just starting to be discovered. Nano-single-phase magnetoelastics show better performance than bulk ones. The majority of high-$\varepsilon$ materials shows their best performances at low temperatures. Ryu et al. (2002a) has pointed out that single-phase multiferroics may show a tendency to suffer degradation under cyclic conditions.

Magnetolectric effect in composite materials is an extrinsic property that does not exist in the separated component phases, and it originates from the elastic coupling between a piezoelectric phase and a piezomagnetic (or magnetostrictive) phase (Chang and Carman, 2007; De Frutos et al., 2007; Nersessian et al., 2004). The magnetolectric effect, in composite materials, can also be realized by coupling the thermal interaction in pyroelectric–pyromagnetic composites. The magnetolectric coefficients of composites may be one or two orders of magnitude higher than those corresponding to the majority of present-day single-phase bulk magnetoelastics.

Ferromagnetic materials like cobalt ferrite ($\text{CoFe}_2\text{O}_4$), $\text{SmFe}_2$ and Terfenol-D are not piezomagnetic, but they show a highly nonlinear hysteretic magnetostrictive effect proportional to the square of the magnetic-field strength which makes them different to the linear behaviour in single-phase multiferroic magnetolectric materials. The nonlinear behaviour of the magnetolectric effect in composite materials makes difficult their applications as linear devices. A DC bias magnetic field has to be applied across the magnetolectric composite materials in order to obtain a linear behaviour in a short range around this DC bias magnetic field (Ryu et al., 2002a).

Some key points should be taken into account when working with magnetolectric composite materials (Ryu et al., 2002b; Van den Boomgaard and Born, 1978):

a) The two individual phases should be in equilibrium.
b) The mismatching between grains should not be present.
c) The magnitude of the magnetostriction coefficient of the piezomagnetic or magnetostrictive phase and the magnitude of the piezoelectric coefficient of the piezoelectric phase must be as great as possible.
d) The accumulated charge must not leak through the piezomagnetic or magnetostrictive phase.

e) A deterministic strategy applies for poling of the composites.

At present, various composites, such as Ni(Co, Mn)Fe$_2$O$_4$–BaTiO$_3$, CoFe$_2$O$_4$–BaTiO$_3$, NiFe$_2$O$_4$–BaTiO$_3$, LiFe$_5$O$_8$–BaTiO$_3$, and CoFe$_2$O$_3$–Bi$_4$Ti$_3$O$_12$, have been reported. (Bokhan and Laletin, 1996; Botello-Zubiate et al., 2006a, 2006b; Corral-Flores et al., 2006; De Frutos et al., 2007; Lupeiko et al., 1991a, 1991b, 1994, 1995; Matutes-Aquino et al., 2009; Van den Boomgaard et al., 1974, 1976; Van den Boomgaard and Born, 1978; Van Suchetelene, 1972; Van Run et al., 1974).

5.2. The magnetoelectric effect and the composite connectivity: laminates (2-2), particulate composites (3-0), fibrous composites (3-1) and interpenetrating composites

The concept of connectivity in magnetoelectric composites deserves special attention because the magnetoelectric effect depends on the type of connectivity of each component phase. The different types of connectivities of the phases in a composite have already been established (Mazur, 1995; Newnham et al., 1980, 1978). Each phase in a composite can be self-connected in zero, one, two or three dimensions. For the case of a two-phase composite, like the magnetoelectric composites, 10 different types of connectivities are possible: 0-0, 1-0, 2-0, 3-0, 1-1, 2-1, 3-1, 2-2, 3-2 and 3-3. For the general case of $n$ phases, the number of connectivity patterns is equal to $(n+3)!/3!n!$. Figure 3.72 shows four common and important types of connectivity for the case of a two-phase composite.

![Figure 3.72](image)

**Figure 3.72** Four common and important types of connectivity in two-phase composites.
In the 0-0 type of connectivity, we can see that the “cubic particles” of each phase (in different colours) are not connected with each other. In the 3-0 type of connectivity, the blue phase is not connected, but the matrix phase is connected in three dimensions. In the 3-1 type of connectivity, the blue phase is connected in one direction and the matrix is connected in three dimensions. Finally, in the 2-2 type of connectivity (laminate type), each phase is connected in two dimensions. Particulate magnetoelectric composites can be modelled either with 0-0 or 3-0 connectivity according to their microstructure. Magnetoelectric composites composed by a matrix and a fibrous second phase can be modelled with a 3-1 connectivity. Finally, laminate composites with two or more layers can be modelled with a 2-2 connectivity.

5.3. Laminate composites

Magnetoelectric laminate composites are a recent development that has the potential to revolutionize the field of electroceramics. We are going to review the exciting developments achieved for different types of material, including all-ceramic, metal-ceramic and metal-polymer composites. The advancements in this field since the turn of the millennium has opened up many possibilities in new and unique applications of sensors, transformers, non-reciprocal couples, tunable microwave filters and microwave devices (Bichurin et al., 1997; Dong et al., 2003, 2004, 2006a, 2006b; Srinivasan et al., 2005, 2006a, 2006b; Zhai et al., 2006a, 2006b, 2007, 2008).

5.3.1. Cosintered piezoelectric perovskites/magnetostrictive ferrite laminates

(Zhai et al., 2004) fabricated a PZT/NiFe$_2$O$_4$ laminate by cosintering. But, they obtained a low mechanical coupling between the phases because the interface between the PZT and NiFe$_2$O$_4$ layers is not smooth and, besides that, they also found porosity near the interface, as could be observed by optical and scanning electron microscopy. They reported a magnetoelectric coefficient $\varepsilon^{EH} = 160$ mV/cm Oe that is significantly smaller than the value predicted by theoretical calculations, which can be attributed to the residual porosity and a poor mechanical coupling across the interface as mentioned above (Zhai et al., 2008).

A giant transverse magnetoelectric effect of $\varepsilon^{EH} = 460$ mV/cm Oe was first reported by Srinivasan in the bilayer composites of PZT and NiFe$_2$O$_4$ thick films (thicknesses range of 14–200 nm) fabricated by tape casting (Fig. 3.73). Without a bias magnetic field, they obtained $\varepsilon = 0$, because in composites, a biasing magnetic field is necessary to achieve a piezomagnetic behaviour. In their experiments, the $\varepsilon^{EH}$ coefficient first increased with the bias magnetic field to reach a maximum value for a bias magnetic field of about 80 Oe. After that, the $\varepsilon^{EH}$ coefficient decreased with the bias
magnetic field. According to Srinivasan et al., the data on the dependence of \( \varepsilon_{EH} \) with the volume fraction of the two phases and with the bias magnetic field are in excellent agreement with a theoretical model for a perfectly bonded bilayer. For multilayers, a higher transverse magnetoelectric effect of \( \varepsilon_{EH} = 1500 \text{ mV/cm Oe} \) was measured (Srinivasan et al., 2002a, 2002b; Zhai et al., 2008).

5.3.2. Ceramic piezoelectric perovskite/magnetostrictive Terfenol-D or Galfenol alloys laminates

Dong et al. (2003) realized that a further increase of the magnetoelectric coefficient may be achieved by using materials like Terfenol-D or Galfenol alloys that have a higher magnetostriction coefficient than ferrites. But neither Terfenol-D nor Galfenol can be cosintered with ceramic piezoelectric perovskites because the high sintering temperature of PZT would oxidize Terfenol-D or Galfenol and would also reduce PZT in the process. Dong et al. found the solution to this dilemma by simply using a low-cost epoxy layer between the PZT and Terfenol-D to bond them together. According to these authors, the epoxy layer should be as thin as possible because otherwise the viscoelastic nature of the epoxy would relax the

Figure 3.73  Transverse magnetoelectric coefficient at room temperature as a function of static magnetic field \( H \) for a two-layer structure consisting of 200-mm films of NiFe\(_2\)O\(_4\) and Pb(Zr,Ti)O\(_3\). The DC and the small 1-kHz AC magnetic fields were applied parallel to the plane of the sample and the magnetoelectric voltage was measured perpendicular to the plane of the sample. Reproduced with permission from Zhai et al. (2008).
mechanical coupling between the layers. A magnetoelectric voltage coeffi- 
cient of Terfenol-D/PZT laminates as high as $a_{EH} = 4.6 \text{ V/cm Oe}$ was 
reached, which is nearly an order of magnitude higher than the giant 
magnetoelectric effect in cosintered ferrite/PZT laminates (Ryu et al., 
2001; Dong et al., 2005a). Figure 3.74 shows the experimental results for 
a Terfenol-D/PZT/Terfenol-D trilayer.

Dong et al. also showed that the magnetostrictive Fe–Ga alloy (Galfenol) 
can be substituted for Terfenol-D. The Galfenol/PZT laminates have lower 
magnetoelectric properties than the corresponding Terfenol-D/PZT laminates, with $a_{EH} = 0.3 \text{ V/cm Oe}$ in the low (quasistatic) frequency range. 
They also found that a long-type magnetostrictive Fe–20 atm.%Ga crystal 
plate has a higher magnetostrictive strain at lower fields than a disk-type 
sample. Furthermore, this long-type laminate of Fe–20%Ga and PZT has 
been found to have (i) a large longitudinal–longitudinal (L–L) magnetoelec-
tric voltage coefficient (larger than 345 mV/Oe) under modest DC mag-
netic biases; (ii) a dramatic enhancement of the magnetoelectric response 
near the resonance frequency; and (iii) a high sensitivity to minute mag-
netic-field variations. These results demonstrate the feasibility of fabricating 
low-cost, highly sensitive magnetic field and/or electric current sensors 
using Fe–20 atm.%Ga/PZT laminates (Dong et al., 2005b, 2005c).

![Figure 3.74](image)

**Figure 3.74** Induced magnetoelectric (ME) voltages as a function of dc magnetic field of Terfenol-D/PZT/Terfenol-D trilayers. The polarization direction of PZT and is 
along the longitudinal direction. Reproduced with permission from Zhai et al. (2003).
5.3.3. Resonant magnetoelectric laminate composites

Investigations by Zhai et al. (2008) in Terfenol-D/PZT laminates revealed a dramatic enhancement of $a_{EH}$ near the electromechanical resonance frequency of the piezoelectric phase of the laminate. These findings are illustrated in Fig. 3.75 and demonstrate that $a_{EH}$ is enhanced by a factor of nearly 10 under resonance excitation at the electromechanical resonance frequency (Zhai et al., 2008).

5.3.4. Metglas-based laminate composites

Zhai et al. (2008) noted that it is actually not the magnetostriction coefficient that is important for the value of $a_{EH}$, but rather the fact of how much magnetostrictive strain is induced per unit magnetic field applied. It is the effective linear piezomagnetic coefficients that are important. The material with the known highest piezomagnetic coefficient is Metglas. The total magnetostriction of Metglas 2605 is small (~40 ppm) compared with Terfenol-D magnetostriction. However, the maximum value of the piezomagnetic constant of Metglas is 4 ppm/Oe, which is four times larger than the maximum value for Terfenol-D under its optimum magnetic bias conditions.

5.3.4.1. Metglas/polyvinylidene difluoride (PVDF) magnetoelectric laminate

Zhai et al. (2008) studied thin flexible magnetoelastic composites (thickness < 100 μm) consisting of Metglas (high-$\mu$ magnetostriction)
and polyvinylidene-fluoride (piezopolymer) layers laminated together. Because of the high permeability of Metglas, the required DC bias was only $H_{DC} < 8$ Oe. Although polyvinylidene-fluoride (PVDF) has a very small piezoelectric charge constant, it has a relatively high piezoelectric voltage. Both unimorph and three-layer configurations have been studied. These Metglas/PVDF laminates have notable advantages in some applications; as they are flexible and can readily be fabricated in thin film form, they could be used in conformal surfaces (Fig. 3.76). The authors found that these magnetoelectric laminates require DC magnetic biases as low as 8 Oe to induce giant magnetoelectric coefficients of 7.2 V/cm Oe at low frequencies, and up to 310 V/cm Oe under resonant drive (Zhai et al., 2006c, 2008).

5.3.4.2. Metglas/(1-3) PZT-fibre magnetoelectric laminate  Dong et al. (2006c) reported the highest magnetoelectric properties for a Metglas layer that is epoxied together with a (1-3) PZT-fibre composite: a three-phase composite with a net (2-1) phase connectivity. The magnetoelectric coefficient of this laminate has been reported to be as high as $\alpha_{EH}^{H1} = 22$ V/cm Oe at low frequencies for a long-type composite, and up to $\alpha_{EH}^{H1} = 750$ V/cm Oe at the electromechanics resonance conditions. These results are very exciting, as the values are nearly 50 times higher than those of the initial reports of giant magnetoelectricity in laminated composites. Compared with a PZT plate, fibres are easier to elongate and

![Figure 3.76](image-url)  
*Figure 3.76*  DC magnetic-field dependence of the magnetoelectric coefficient and phase for a Metglas/PVDF three-layer laminate, measured at 1 kHz and $H_{ac} = 1$ Oe. Reproduced with permission from Zhai et al. (2008).
shrink under application of force. The thicknesses of the Metglas and PZT-fibre layers were only 25 and 100–250 mm, respectively. In addition, the giant permeability of Metglas not only decreases the required magnetic bias field, \(H_{DC}\), but also increases the anisotropy of the magnetoelectric coefficient (Dong et al., 2006c; Zhai et al., 2008).

It is also important to note that (i) under low magnetic biases, the induced voltage was near-linearly proportional to the DC magnetic bias field, \(H_{DC}\); (ii) no hysteretic phenomena were observed that would result in a dependence of the induced voltage on \(H_{DC}\) history; and (iii) when the direction of the magnetic DC bias was changed, a 180° phase shift occurred, which will enable the determination of the direction of the magnetic field. These are all potentially useful attributes to magnetic field and electric current sensors (Zhai et al., 2007).

5.4. Nanostructured magnetoelectric composites: superlattices and nanopillars

Magnetoelectric nanostructures have become an important topic of ever-increasing interest in the last few years, since they, especially magnetoelectric thin films, are easy to on-chip integration, which is a prerequisite for incorporation into microelectronic devices (Nan et al., 2008).

Materials made in the form of superlattice structure yielded unusual transport properties that cannot be obtained by classical solid-state chemistry route. Thus, it is possible to construct superlattices whose structure consists of alternating ferroelectric and ferromagnetic layers, and then it is possible to investigate the coupling between the two properties. However, these types of superlattice structures have rarely been investigated. Murugavel et al. (2004) investigated multiferroic superlattices composed of ferromagnetic Pr_{0.85}Ca_{0.15}MnO_{3} and ferroelectric Ba_{0.6}Sr_{0.4}TiO_{3} made by pulsed-laser deposition. The magnetization and the dielectric constant measured as a function of temperature indicates that the superlattice could have the coexistence of both ferromagnetic and ferroelectric properties. The magnetoresistance of 40% was observed at 80 K for the superlattice with high Ba_{0.6}Sr_{0.4}TiO_{3} layer thickness, which could be attributed to the associated magnetoelectric effect.

A magnetoelectric effect has been observed in two-phase nanocomposite epitaxial films (Zheng et al., 2004). In the case of two-phase epitaxial films of piezoelectric BaTiO_{3} and magnetostrictive CoFe_{2}O_{4} grown on SrTiO_{3} substrates, one can either grow nano-thin layers of alternating phases in a laminate structure, or as single layer consisting of both phases. For nano-thin laminate composites, the constraint imposed by the substrate restricts the in-plane deformation of both layers, resulting in weak magnetoelectric properties compared with thicker film or
bulk laminate composites (He et al., 2007; Liu et al., 2007). However, investigations have shown that a single layer consisting of BaTiO$_3$ and CoFe$_2$O$_4$ phases has a unique nanostructure (Zheng et al., 2004), where magnetostrictive nanopillars are imbedded in a piezoelectric matrix, as shown in Fig. 3.77. In this case, the phases are free to deform in the direction perpendicular to the film. Accordingly, large ME effects occur due to coupling between the strictions of the magnetic and polar subsystems. Two-phase nanocomposites offer much of the same opportunities and enhanced properties of laminated bulk composites, but on a miniaturized scale. They offer much promise with regard to integration with Si and other microelectronic materials (Zhai et al., 2008).

5.5. Effective properties of magnetoelectric composites.
Green’s function and the magneto-electro-elastic Eshelby tensor techniques

The physical properties of composite can be divided into sum, combined and product properties (Ryu et al. 2002a; Mazur, 1995; Nan et al., 2008). As an example of a sum property, the stiffness of a composite is determined by the elastic properties of the phases in a composite, together with the rule
of mixing (that depends on the geometry of the phases). But, if some property involves two or three coefficients, then it cannot be described as a sum property. In these cases, we have a combined property. In some composites besides the sum property existing in the separated phases, there is also a product property which does not exist in the separated phases. For example, the magnetoelectric effect is a product property that exists in the composite, but it is not present in any of the separated phases. These product properties depend on the involved phases, their connectivity and processing of the composite.

The magnetoelectric linear constitutive equations for an elastically coupled piezoelectric–piezomagnetic composite are

\[
\bar{p}_m = \langle d_{ij} \rangle \bar{T}_{ij} + \varepsilon_0 \langle \chi_m^P \rangle \bar{E}_n + \langle \alpha_{mn} \rangle \bar{H}_n \tag{66}
\]

\[
\mu_0 \bar{M}_m = \langle b_{ij} \rangle \bar{T}_{ij} + \mu_0 \langle \chi_m^M \rangle \bar{H}_n + \langle \alpha_{mn} \rangle \bar{E}_n \tag{67}
\]

The symbols in Eqs. (66) and (67) represent the same magnitudes as in Eqs. (30) and (32), adapted to composite materials. This means

- Stimuli \((\bar{T}, \bar{E}, \bar{H})\) and materials responses \((\bar{P}, \bar{M})\) are now mean values, averaged over the volume of interest.
- Composite properties, say \(\langle \alpha_{mn} \rangle\), are now effective values. Frequently, the mean is a good approximation to the effective value. But, in general, mean values do not coincide exactly with effective ones (see “the Average problem”, Bunge, 1982). Specifically, a piezoelectric–piezomagnetic composite may exhibit \(\langle \alpha_{mn} \rangle \neq 0\), even though both components have \(\alpha = 0\) (Camacho-Montes et al., 2006, 2009).

\(\langle \alpha_{mn} \rangle\) depends on the composite microstructure: the properties of the component phases, the volume fractions and shape of each phase, their connectivity, etc.

The effective material properties of magnetoelectric composites have been determined by solving the constitutive equations with the Green’ function technique. The constitutive equations have also been solved using micromechanics methods based on the eigenstrain formulation, the Mori–Tanaka theory and the magneto-electro-elastic Eshelby tensors. Using the Green’ function technique, expressions for the magnetoelectric coupling properties coefficients in magnetoelectric composites with different kinds of connectivities have been deduced. On the other side, using micromechanics simple and closed-form solutions for the magnetoelectric coupling properties coefficients have been derived when both the matrix and inclusions of the composite are transversely isotropic with different magneto-electro-elastic moduli, and the inclusions are either elliptical cylinder, circular cylinder, disk or ribbon. See Nan (1994), Nan and Clarke, 1997, Nan et al., 2008, Wu and Huang (2000) and Huang et al. (2000).
6. Applications

6.1. Spintronics

Twenty years ago, research on magnetic multilayers gave birth to spintronics with the discovery of giant magnetoresistance which is used in read heads in computer hard drives and in magnetic-field sensors (Baibich et al., 1988). Today, single-phase multiferroics are intensively investigated for spintronics applications. For instance, when used as a tunnel barrier, BiFeO$_3$ allows the observation of a large tunnel magnetoresistance with Co and (La, Sr)MnO$_3$ ferromagnetic electrodes. Also, its antiferromagnetic and magnetoelectric properties have been exploited to induce an exchange coupling with a ferromagnet. The mechanisms of such an exchange coupling open ways to electrically control magnetization and possibly the logic state of spintronics devices. Recently, ferromagnetic and ferroelectric (La, Bi)MnO$_3$ have been used as an active tunnel barrier in magnetic tunnel junctions with Au and (La, Sr)MnO$_3$ electrodes. A four-resistance-state device has been obtained, with two states arising from a spin filtering effect due to the ferromagnetic character of the barrier and two resulting from the ferroelectric behaviour of the (La, Bi)MnO$_3$ ultrathin film. These results show that the additional degree of freedom provided by the ferroelectric polarization brings novel functionalities to spintronics either as an extra order parameter for multiple-state memory elements or as a handle for gate-controlled magnetic memories (Béa et al., 2008).

Bibes and Barthélémy (2008) discussed a possible MagnetoElectric Random Access Memory (MERAM) as an alternative solution to reduce drastically the writing energy of Magnetic Random Access Memories (MRAM). This MERAM would use a writing procedure based on the application of a voltage rather than large currents. The basic operation of the MERAM combines the magnetoelectric coupling with interfacial exchange coupling between a multiferroic and a ferromagnet to switch the magnetization of the ferromagnetic layer by using a voltage (Fig. 3.78). In the MERAM, the magnetoelectric coupling enables an electric field to control the exchange coupling at the interface of the multiferroic with the ferromagnet. Then, the exchange coupling across the interface controls the magnetization of the ferromagnetic layer and the magnetization can be switched by the electric polarization of the multiferroic (Bibes and Barthélémy, 2008).

6.2. Magnetoelectric sensors

Because of the large coupling between the magnetic and electric properties, laminate composites with giant magnetoelectricity are potentially useful for applications in magnetic and electric current sensors, amongst other devices (Prieto et al., 2000; Zhai et al., 2008).
According to Zhai et al., all low-frequency magnetic sensors face the problem of how to reduce self-noise in the sensor, and how to reject environmental noise from the signal to be detected. The largest sources of environmental noise for a magnetoelectric sensor are thermal noise induced from pyroelectric currents in the piezoelectric layer and vibration noise induced via piezoelectricity (Zhai et al., 2008).

By modifying the composite structure, the noise can be rejected. In particular, a bimorph mode was developed (Fig. 3.79) to decrease the pyroelectric noise, by using differential detection (Zhai et al., 2006a).

Compared with a unimorph mode, a bimorph is fabricated by first epoxying two PZT layers together with reverse polarization directions. Subsequently, this PZT bilayer is then epoxied to a Terfenol-D one.
In this case, under temperature fluctuations, the two PZT layers elongate and/or shrink by the same amount. Correspondingly, the signals at the two electrodes have the same sign and magnitude; thus, they cancel out on differential detection. However, on the contrary, an applied magnetic field causes the bimorph structure to bend or flex. In this case, one PZT layer elongates and the other shrinks. Consequently, the signals at the two electrodes have the same magnitude but different signs. The signals do not cancel on differential detection! Bimorph magnetoelectric laminate structures have been studied as magnetic-field sensors. They have been shown to be effective in the rejection of low-frequency noise from thermal fluctuations, and have been demonstrated to be effective in significantly improving the signal-to-noise ratio (Zhai et al., 2008).

6.3. Magnetoelectric gyrator

The gyrator is an electric four-port network that inverts an impedance (it can make a capacitive circuit behave inductively and a bandpass filter behave like a band-stop filter). The gyrator was invented by Tellegen (1948).

Zhai et al. (2009) developed three trilayer gyrators structures based on Terfenol-D/PZT/Terfenol-D, Nickel/PZT/Nickel and Metglas/PZT/Metglas operating at the electromechanical resonance frequency ($f \approx 86$, $64$ and $15$ kHz, respectively). These magnetoelectric gyrators can convert not only active and reactive impedances, but also current and voltage (Zhai et al., 2009).

Figure 3.80 shows the magnetoelectric laminate with a transversely poled piezoelectric layer sandwiched between two longitudinally magnetized Ni or Terfenol-D layers, that is, the longitudinal-magnetization and transverse polarization (L–T) mode configuration. To make this structure work as a gyrator, it is necessary to wrap a coil tightly around the laminate. When a current is applied, the coil generates a magnetic field which elongates or shrinks the magnetostrictive layers. Then, the transmitted strain...
between the layers generates charge or voltage from the piezoelectric layer. Or, vice versa, an applied voltage to the piezoelectric layer will induce a current from the coil.

**Figure 3.80** Gyrator (L–T mode) of a magnetoelectric laminate composite consisting of longitudinally poled PZT layer between two Ni or Terfenol-D layers. Inspired from Zhai et al. (2009).

**Figure 3.81** Frequency dependence of ME voltage coefficient for Ni/PZT composite. Reproduced with permission from Zhai et al. (2009).

**Figure 3.81** shows the magnetoelectric voltage coefficient for Ni/PZT laminates as a function of frequency. At resonance frequency, the magnetoelectric coefficient is enhanced by a factor of 100× which produces a strong magnetoelectric coupling with a low energy dissipation.
6.4. Magnetoelectric gradiometer

While a magnetometer measures the magnetic-field intensity at a specific point, a magnetic gradiometer measures the changes of the magnetic-field intensity between two specific points. Gradiometer is commonly used in the location of underground objects that have magnetic properties. They are also used in magnetic measurements with SQUID. While single-axis gradiometers measure the magnetic gradient in only one direction, three-axis gradiometers measure the magnetic gradient in the $x$, $y$ and $z$ directions.

Bedekar et al. (2009) developed the magnetoelectric gradiometers represented in Fig. 3.82. The device uses magnetoelectric composites with ring–dot piezoelectric transformer structure working near electromechanical resonance (in the range of 91–94 kHz), where ring acts as the input while dot acts as the output.

In these magnetoelectric gradiometers, the generated magnetic field, due to the converse magnetoelectric effect, interacts with the externally applied magnetic field producing a flux gradient which is detected through the frequency shift and the output voltage change of gradiometer. The measurements clearly illustrate that the proposed design has high sensitivity and it can be used for detecting magnetic-field gradients (Bedekar et al., 2009).

**ACKNOWLEDGEMENTS**

Support from Consejo Nacional de Ciencia y Tecnología, México, Projects CONACYT 102171, CONACYT 25380 and FONCICYT 94682, is gratefully acknowledged.
REFERENCES

Debye, P., 1926. Z. Phys. 36, 300.
Karmakar, A., Majumdar, S., et al., 2009. Possible Magnetoelectric Coupling in the Half Doped Charge Ordered Manganite, Pr_0.5Ca_0.5MnO_3 - d. arXiv:0904.4309v1 [cond-mat.str-el].