Multiferroics – coexistence of ferromagnetism and ferroelectricity

A. Szewczyk, Institute of Physics, Polish Academy of Sciences

- **Multiferroics** – definition
- **Origins of mutual exclusion** of magnetic and electric orderings
- Mechanisms that make such coexistence possible:
  - perovskites: FeBiO₃, TbMnO₃
  - manganites: (Sr,Ba)MnO₃
  - olivines (?)
  - hexagonal manganites
- **Ferrotoroidic** ordering as a new kind of long-range order in multiferroics
- Ideas of application of multiferroics
Multiferroics – coexistence of ferromagnetism and ferroelectricity


**Multiferroics**: materials in which several (at least two) qualitatively different long-range orderings coexist:
- ferromagnetic (or antiferromagnetic)
- ferroelectric
- ferroelastic (ferrodistorsive)

† 2 kwietnia 2015

Multiferroics – coexistence of ferromagnetism and ferroelectricity

- **Multiferroics** – materials in which several long-range orderings coexist (H. Schmid - 1994), e.g.:
  - ferromagnetic (or antiferromagnetic)
  - ferroelectric
  - ferroelastic
  - ferrotoroidic

\[ T = \frac{1}{2} \sum_n r_n \times M_n \neq 0 \]

Toroidal moment
Multiferroics – coexistence of ferromagnetism and ferroelectricity

- **Multiferroics** – materials in which several long-range orderings coexist (H. Schmid - 1994), e.g.:
  - ferromagnetic (or antiferromagnetic)
  - ferroelectric
  - ferroelastic
  - ferrotoroidic

- **Origins of strong interest:**
  - presence of „cross relations”
  - ferromagnetic ferroelectrics: **magnetoelectric effect** (electrically driven magnetic memories!)
  - coding of information in sign of the toroidal moment (no stray field around magnetic vortices, thus, minimization of cross-talking)
  - ferroelectric ferroelastics: (sonar – Peter and Jacob Curie)
  - ferromagnetic ferroelasticsi: (magnetostrictive devices)
Classification of multiferroics

1. **Proper (or of the 1st type)**
   Weak direct coupling between different order parameters, e.g., indirect coupling via elastic properties (BiFeO$_3$).

2. **Improper (or of the 2nd type)**
   Strong coupling between order parameters, e.g., compounds in which an electric order appears as the result of appearance of the magnetic order.

3. **Composites** – multiphase granular materials or multilayers (e.g., if we have a piezomagnetic and a piezoelectric component, the coupling between magnetization and polarization can be accomplished via elastic properties)
Why are there so few magnetic ferroelectrics?


These phenomena appear in materials of different properties and symmetry, thus, they exclude mutually:

- **ferromagnetic ferroelectrics** do not have:
  - time inversion symmetry \((1')\)
  - space inversion symmetry \((1)\).

- **ferroelectrics**
  - dielectrics, \(\mathbf{P}\) is a “normal” vector, no inversion symmetry, invariant to time inversion

- **ferromagnets**:
  - conducting materials or insulators having the inversion symmetry, \(\mathbf{M}\) is a pseudovector (axial vector), which changes sign under time inversion and is invariant to space inversion.

Promising materials: **perovskites** \((\text{ATO}_3)\), \(T\) – transition metal
Why are there so few magnetic ferroelectrics?

**Perovskites – $\text{ATO}_3$**

\(T\) – transition metal; \(A\) – RE, Y, alkaline earth (Ca, Sr, Ba)

Cubic structure of the ideal perovskite \((Pm\bar{3}m)\)

- \(A^{3+\ (2+)}\)
- \(T^{3+\ (4+)}\)
- \(O^{2-}\)

\[
t = \frac{(r_A + r_O)}{\sqrt{2 (r_B + r_O)}}
\]

tolerance factor (Goldschmidt)

\(~ 100\) magnetic perovskites; \(~ 100\) ferroelectric perovskites

**a few perovskites with coexisting magnetic and electric orderings**

\((\text{BiFeO}_3, \text{BiMnO}_3, \text{PbVO}_3)\)
Why are there so few magnetic ferroelectrics?

Perovskites – $\text{ATO}_3$

$T$ – transition metal; $A$ – RE, Y, alkaline earth (Ca, Sr, Ba)

Cubic structure of the ideal perovskite $(Pm\overline{3}m)$

- experimental finding:
  - in **ferroelectric** perovskites, the $d$ shell of the transition metal $T$ is empty ($d^0$)
  - in **ferromagnetic** perovskites, the $T$ ions have a partially filled $d$ shell.
Why are there so few magnetic ferroelectrics?

Perovskites – $\text{ATO}_3$, $T$ – metal przejściowy

- experimental finding:
  - in **ferroelectric** perovskites, $d$ shell of the $T$ ion is empty ($d^0$)
  - w **ferromagnetycznych** - jony $T$ mają częściowo zapełnioną powłokę $d$.

- explanation given by **ab initio calculations** (Spaldin/Hill, Khomski, Ederer):
  - **LSDA + U** – method taking into account Coulomb interactions between some of localized electrons
  - **LSDA + SIC** – method with correction for self interactions
  - for $T$ with $d^0$, displacement of $T$ towards $O^{2-}$ and creation of a covalent bond ($d$ orbitals of $T$ and $p$ orbitals of $O$) is energetically convenient. Thus, nonzero $P$ appears (ferroelectric perovskites with $z$ Ti$^{4+}$, Ta$^{5+}$, W$^{6+}$)

---

*Diagram showing the atomic structure of a perovskite*
Perowskity – ATMO3

\[ J_H = 0 \]

\[ J_H = 0.8 \text{ eV} \]

- for \( T \) with partially filled d shell, intraatomic exchange interaction (Hund’s coupling) eliminates this mechanism of appearance of nonzero polarization and ferroelectric ordering (np. CaMnO\(_3\), RCrO\(_3\))
Why do magnetic ferroelectrics exist at all?

• Perovskites ($A\text{TO}_3$):
  1. „Paramagnetic doping” – G. Smolenskii, Y.Venevtsev, partial replacement of $T \, d^0$ ions with magnetic $d^n$ ions

$$\text{PbFe}^{3+}_{1/2}\text{Nb}^{5+}_{1/2}\text{O}_3 \quad T_{\text{FE}} = 387 \, \text{K}, \quad T_N = 134 \, \text{K}, \quad \text{weak FE-AM coupling}$$
Why do magnetic ferroelectrics exist at all?

- **Perovskites** ($\text{ATO}_3$):

  2. „Lone pair of $s^2$ electrons“ – Bi (dangling bond)

  - $\text{BiMnO}_3 \quad T_{FE} = 760 \text{ K}, \quad T_C = 105 \text{ K}$
  - $\text{BiFeO}_3 \quad T_{FE} = 1100 \text{ K}, \quad T_N = 643 \text{ K}$

- Ionic bonds are made of $6p^3$ electrons of bizmuth
- Remain $6s^2$ electrons that do not participate in bonds
- Hybridization the $s$ states and (empty) $p$ states is the source of a large polarizability of Bi.
- It facilitates distortions of the crystalline structure and the appearance of FE ordering (Spaldin)
- Bi sublattice is responsible for the appearance of FE ordering $P \sim 6 – 150 \mu \text{C/cm}^2$
- $3d$ ions sublattice is responsible for the magnetic ordering.
- Thus, m-e coupling is not especially strong.

- rotation of octahedra around $<111>$ axis by $\pm 13.8^\circ$
- distortion of the octahedra
- displacement of Fe ions from the centers of octahedra
- displacement of Bi ions along $<111>$ axis
- ferroelectric polarization – result of existence of two different Bi-Fe distances along the $<111>$ axis and of electron contribution
Why do magnetic ferroelectrics exist at all?

- **Perovskites** \((ATO_3)\):
  3. „Extension (stretching) of the oxygen octahedron” - \(\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3\)

rattle? (grzechotka)
Why do magnetic ferroelectrics exist at all?

- **Perovskites ($A\text{TO}_3$):**

  3. „Extension (stretching) of the oxygen octahedron” - $\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3$

Results:

- Multiferroic phase (Pm-3m), MF, appears at $\sim 285$ K for $x \geq 0.44$.
- The phase transition ($\sim 400$ K) to the ferroelectric, FE, phase, smeared over ca 30 K, is not noticeable in the temperature dependence of specific heat.
- The phase transition to the antiferromagnetic, AF, phase damps the tetragonal deformation and diminishes the polarization.
Results:

- Multiferroic phase (Pm-3m), MF, appears at $\approx 285$ K for $x \geq 0.44$.
- The phase transition (~400 K) to the ferroelectric, FE, phase, smeared over ca 30 K, is not noticeable in the temperature dependence of specific heat.
- The phase transition to the antiferromagnetic, AF, phase damps the tetragonal deformation and diminishes the polarization.

Perovskites ($A\text{TO}_3$):

3. "Extension (stretching) of the oxygen octahedron"

- Sakai, …, Y. Tokura,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Sakai, …, Y. Tokura,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
- Pratt, …, B. Dabrowski,
Results:

- Multiferroic phase (Pm-3m), MF, appears at ~285 K for $x \geq 0.44$.
- The phase transition (~400 K) to the ferroelectric, FE, phase, smeared over ca 30 K, is not noticeable in the temperature dependence of specific heat.
- The phase transition to the antiferromagnetic, AF, phase damps the tetragonal deformation and diminishes the polarization.

3. „Extension (stretching)“ of the oxygen octahedron
- Sakai, …, Y. Tokura
- Pratt, …, B. Dabrowski

J. Więckowski, M. U. Gutowska, A. Szewczyk i in.
Results:

- Multiferroic phase (Pm-3m), MF, appears at $\sim 285$ K for $x \geq 0.44$.
- The phase transition ($\sim 400$ K) to the ferroelectric, FE, phase, smeared over ca 30 K, is not noticeable in the temperature dependence of specific heat.
- The phase transition to the antiferromagnetic, AF, phase damps the tetragonal deformation and diminishes the polarization.

3. "Extension (stiching)"

- Sakai, …, Y. Tokura
- Pratt, …, B. Dabrowski

Why do magnetic ferroelectrics exist at all?

J. Więckowski, M. U. Gutowska, A. Szewczyk i in.
Results:

- Multiferroic phase (Pm-3m), MF, appears at ~285 K for \(x \geq 0.44\).
- The phase transition (~400 K) to the ferroelectric, FE, phase, smeared over ca 30 K, is not noticeable in the temperature dependence of specific heat.
- The phase transition to the antiferromagnetic, AF, phase damps the tetragonal deformation and diminishes the polarization.

3. „Extension (stretching) of the oxygen octahedron" - Sakai, …, Y. Tokura
   - Pratt, …, B. Dabrowski

Why do magnetic ferroelectrics exist at all?

J. Więckowski, M. U. Gutowska, A. Szewczyk i in.

Perovskites (\(ATO_3\)):
Why do magnetic ferroelectrics exist at all?

- **Perovskites \((ATO_3)\):**
  1. „Paramagnetic doping”
  2. „Lone pair of \(s^2\) electrons”
  3. „Stretching of the oxygen octahedron”
  4. „FE state induced by magnetic ordering”

- \(\text{PbFe}^{3+}_{1/2}\text{Nb}^{5+}_{1/2}\text{O}_3\)
- \(\text{BiFeO}_3\)
- \(\text{Sr}_{1-x}\text{Ba}_x\text{MnO}_3\)
- \(\text{TbMnO}_3\)
TbMnO$_3$

- at room temperature, paraelectric, paramagnetic phase;
- at $T_N = 41$ K – incommensurate, longitudinally modulated, antiferromagnetic, sinusoidal structure; inversion symmetry present, thus, paraelectric phase;

Kenzelmann et al., PRL 95, 87206 (2005).
Cheong et al., Nature Mat. 6, 13 (2007)
TbMnO$_3$

- at room temperature, paraelectric, paramagnetic phase;
- at $T_N = 41$ K – incommensurate, longitudinally modulated, antiferromagnetic, sinusoidal structure; inversion symmetry present, thus, paraelectric phase;
- at $T_{loc}=27$ K, the phase transition to the incommensurate spiral structure without inversion; ferroelectric polarization ($\sim 0.08 \, \mu C/cm^2$ at $T=10$ K) found.

Kenzelmann et al., PRL 95, 87206 (2005).
Cheong et al., Nature Mat. 6, 13 (2007)
TbMnO$_3$

- at room temperature, paraelectric, paramagnetic phase;
- at $T_N = 41$ K – incommensurate, longitudinally modulated, antiferromagnetic, sinusoidal structure; inversion symmetry present, thus, paraelectric phase;
- at $T_{loc} = 27$ K, the phase transition to the incommensurate spiral structure without inversion; ferroelectric polarization ($\sim 0.08 \mu$C/cm$^2$ w T = 10 K) found.

What is a physical mechanism responsible for the appearance of the polarization?

Dzyaloshinski-Moriya coupling

$$\mathbf{D} \cdot \left( \mathbf{S}_i \times \mathbf{S}_j \right)$$

$$\mathbf{D} \sim \mathbf{r}_i \times \mathbf{r}_j$$
Spiral structure is present *per se* in domain walls.
Spiral structure is present *per se* in domain walls

Olivine LiNiPO$_4$

Properties of olivines LiTPO$_4$

- Strong coupling of the $T$ ions in (100) planes (superexchange $T$-O-$T$)
- Weak coupling between (100) planes (superexchange $T$-O-P-O-$T$)
- Strong magnetocrystalline anisotropy (easy axis different for different $T$ ions)
- Quasi – two-dimensional Ising system
- Antiferromagnetic order appears at low temperatures ($T_N < 50$ K)
- Large ionic conductivity due to Li$^+$ (promising cathode materials for Li-ion batteries)

- Very strong linear magnetoelectric effect
  \[ P_a = \alpha_{ab} H_b \quad \text{dla} \quad T = \text{Co} \quad |\alpha_{yx}(4.2 \text{ K})| = 30.6 \text{ [ps/m]}, \]
  but

no spontaneous dielectric polarization was found till now
Olive LiNiPO₄

- Quasi – two-dimensional Isinga system – c is the easy magnetization axis
- Antiferromagnetic order develops in two steps, on lowering temperature:
  - 2nd order transition: paramagnetic – incommensurate phase (modulated, antiferromagnetic) \( T_{N1}=21.8 \) K
  - 1st order transition: incommensurate – antiferromagnetic phase, \( T_{N1}=20.9 \) K
- **Specific heat** studies (M. Gutowska, S. Lewińska, A. Szewczyk, T. Zajarniuk et al.)

Olivine LiNiPO$_4$ specific heat

Magnetic field $\parallel$ to $a$ and to $b$ does not influence position of the anomalies (!)

Field $\parallel$ do $c$
Olivine LiNiPO$_4$ specific heat

Magnetic field $||$ to $a$ and to $b$ does not influence position of the anomalies (!)

Field $||$ do $c$

Are these two coupled transitions in two coupled subsystems?
Olivine LiNiPO$_4$

- Quasi – two-dimensional Isinga system – $c$ is the easy magnetization axis
- Antiferromagnetic order develops on lowering temperature, in two steps:
  - 2$^{nd}$ order transition: paramagnetic – incommensurate phase (modulated, antiferromagnetic) $T_{N1}=21.8$ K
  - 1$^{st}$ order transition: incommensurate – antiferromagnetic phase, $T_{N1}=20.9$ K

- Specific heat studies (*M. Gutowska, S. Lewińska, A. Szewczyk, T. Zajarniuk et al.*)

• Quasi – two-dimensional Ising system
• Antiferromagnetic order develops on lowering temperature, in two steps:
  - 2\text{nd} order transition: paramagnetic – incommensurate phase (modulated, antiferromagnetic) $T_{N_1}=21.8$ K
  - 1\text{st} order transition: incommensurate – antiferromagnetic phase, $T_{N_1}=20.9$ K
• Specific heat studies (M. Gutowska, S. Lewińska, A. Szewczyk, T. Zajarniuk et al.)

A more complicated structure without inversion, presence of the polarization allowed in $B \neq 0$

Slope analysis allows to put forward a hypothesis that the 1st order phase transition to the commensurate antiferromagnetic phase is coupled to a transition to a ferroelectric phase. Thus, LiNiPO$_4$ is a multiferroic.
**Toroidal ordering - olivine LiCoPO$_4$**

- Co$^{2+}$ in „corrugated” (100) planes
- Strong coupling between Co$^{2+}$ ions in (100) planes
- Strong magnetic anisotropy (with $b$ easy axis)
  
  \[ Vaknin \text{ et al.}, \text{Phys. Rev. B} 65, 224414 (2002) \]
- Quasi – two-dimensional Ising system
- Antiferromagnetic order at $T_N = 21.6$ K
- Co$^{2+}$ magnetic moments deflected from the $b$ axis by $4.6^\circ$ (within the $b$-$c$ plane)
  
  \[ Vaknin \text{ et al.}, \text{Phys. Rev. B} 65, 224414 (2002) \]
- A small spontaneous net magnetization exists (directed along the $b$ axis !!!!)
  
  \[ Kharchenko \text{ et al. (among them R. Szymczak)}, \text{Low Temp. Phys.} 28, 646 (2002) \]

**Conclusion:** magnetic symmetry is not orthorhombic but monoclinic - $P12_1'1$
In the P2’_11 symmetry there can exist:

- net magnetization along the $b$ axis
- modulated structures ($\perp b \ M_n$ components)
- nonzero toroidal moment $\mathbf{T} = \frac{1}{2} \sum_n \mathbf{r}_n \times \mathbf{M}_n$
- nonzero dielectric polarization

The nonzero toroidal moment was found based on neutron studies) [Van Aken et al., Nature 449, 702 (2007); Vaknin et al., Phys. Rev. B 65, 224414 (2002)]

Based on the optical studies (second harmonic generation), 4 different domain states were found and interpreted as 2 weakly ferromagnetic domains, each of which is divided into 2 torroidic domains, differing in sign of $\mathbf{T}$. This was claimed to be the first observation of toroidic domains [Van Aken et al., Nature 449, 702 (2007) 120 citations]. Kharchenko, and Schmid (J.Phys. Condens. Matter 20, 434201 (2008)) proved this interpretation to be erroneous!

- Magnetic field sensors (the most advanced idea)

Terfenol-D = alloy $\text{Tb}_x\text{Dy}_{1-x}\text{Fe}_2$ ($x \sim 0.3$)
Ideas of application of magnetoelectrics and multiferroics

- Magnetic field sensors (the most advanced idea)
- „Permanent” magnets switchable by electric field (a structure similar to the electronic paper)
Ideas of application of magnetoelectrics and multiferroics

- Magnetic field sensors (the most advanced idea)
- “Permanent” magnets switchable by electric field (a structure similar to the electronic paper)
- Write/read heads in hard drives
- Magneto-electric memory cells
Ideas of application of magnetoelectrics and multiferroics

- Magnetic field sensors (the most advanced idea)
- "Permanent" magnets switchable by electric field (a structure similar to the electronic paper)
- Write/read heads in hard drives
- Magneto-electric memory cells
- Elements for high frequency devices (modification of the antiferromagnetic resonance frequency with electric field; valves, circulators)
- Elements for magnonics, e.g., amplifiers of spin waves

- Magnetic field sensors (the most advanced idea)
- „Permanent” magnets switchable by electric field (a structure similar to the electronic paper)
- Write/read heads in hard drives
- Magneto-electric memory cells
- Elements for high frequency devices (modification of the antiferromagnetic resonance frequency with electric field; valves, circulators)
- Elements for magnonics, e.g., amplifiers of spin waves
- Suppliers for wireless net of sensors. Idea of an element drawing energy from a variable electromagnetic field and converting this energy into energy of a bank of capacitors.
Conclusions

• Multiferroics are interesting, scarce materials.

• From the classical point of view, conditions necessary for appearance of a ferromagnetic ($d^m$) and of a ferroelectric order ($d^0$) exclude each other.

• However, there are several physical mechanisms leading to the coexistence of these orderings in a one material, i.e., leading to the existence of multiferroics (e.g. multiferroic perovskites).

• Multiferroics in which ferrotoroidic order is one of the long-range orderings are particularly interesting.

• Several ideas of practical application of multiferroics are considered.
Conclusions

• Multiferroics are interesting, scarce materials.

• From the classical point of view, conditions necessary for appearance of a ferromagnetic ($d^n$) and of a ferroelectric order ($d^0$) exclude each other.

• However, there are several physical mechanisms leading to the coexistence of these orderings in a one material, i.e., leading to the existence of multiferroics (e.g. multiferroic perovskites).

• Multiferroics in which ferrotoroidic order is one of the long-range orderings are particularly interesting.

• Several ideas of practical application of multiferroics are considered.

Thank you for your attention!