

# **Ferroelectricity, Magnetism, and Multiferroicity**

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# Magnetism, Ferroelectricity, and Multiferroics

## *Magnetism*

- Spontaneous magnetic ordering.
- Microscopic nature of magnetic ordering, in principle, same in most strong magnets → *an exchange interaction between mostly localized magnetic moments.*

## *Ferroelectricity*

- There are many disparate mechanisms that lead to FE ordering.
- In many cases, the microscopic mechanisms of FE are not as well understood as magnetism.

## *Multiferroics*

- Two or more ferroic states coexist in the same material
- It could be any combination of FE, magnetism, ferroelasticity, etc.
- We are mostly interested in FE and magnetic multiferroics

*When discussing multiferroics, the main problem lies in the FE part of the story.*

# Discord between Magnetism and FE

To achieve greater functionality, it is desirable that the **electric and magnetic ordering** be **coupled**.

*Not an easy task!*

- $(\mathbf{P}, \mathbf{E})$  change sign under spatial inversion ( $\mathbf{r} \rightarrow -\mathbf{r}$ ) but remain unaltered under time inversion ( $t \rightarrow -t$ )
- $(\mathbf{M}, \mathbf{H})$  change sign under time inversion ( $t \rightarrow -t$ ) but remain unaltered under spatial inversion ( $\mathbf{r} \rightarrow -\mathbf{r}$ )



Linear coupling between is possible only when these vectors vary both in time and space!

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

Linear coupling between  $\mathbf{E}$  and  $\mathbf{B}$   
(one of the four Maxwell's equations)

# Discord between Magnetism and FE

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t}$$

Linear coupling between **E** and **B**  
(one of the four Maxwell's equations)

Not desirable in materials intended to be used in device application.

Devices require a coupling between STATIC **P** and **M**.

- Coupling between static **P** and **M** can only be non-linear.
- Non-linear results from interplay between spin, charge, orbital, and lattice degrees of freedom.
- This complicates the problem significantly (both synthesis and analysis part)

*How do we achieve coupling between static **P** and **M**?*

# General observations on FE and magnetic materials

A comprehensive list of hundreds of ferroelectric [1] and magnetic [2] perovskites can be found at:

[1] T. Mitsui, et al., Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, vol.16(1), Springer, Berlin, 1981

[2] J.B. Goodenough, J.M. Longo, Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology, New Series, vol. III.4, Springer, Berlin, 1970, p. 126.

- Comparison of these list shows that there is no overlap between the two sets of materials.
- Ferroelectricity and magnetism in perovskites seem to exclude one another.
- Comparison between these two sets also reveals general characteristics of FE and magnetic perovskites.

# General observations on FE and magnetic perovskites

- Most ferroelectric are transition metal oxide
- Transition metals ions have empty  $d$ -shells.
- These +ve ions like to form “molecules” with neighboring –ve oxygen ions.
- This leads to collective shifts of +ve and –ve ions inside the material → induces bulk electric polarization.
- The mechanism of covalent bonding (electronic pairing) in such materials is virtual hopping of electrons from filled oxygen shells to the empty  $d$ -shells of the transition metal ions.

**Magnetism, on the other hand, requires partially filled  $d$ -shells.**

Since total moment of completely filled shells adds to zero.

Exchange interaction between uncompensated spins → long-range magnetic ordering

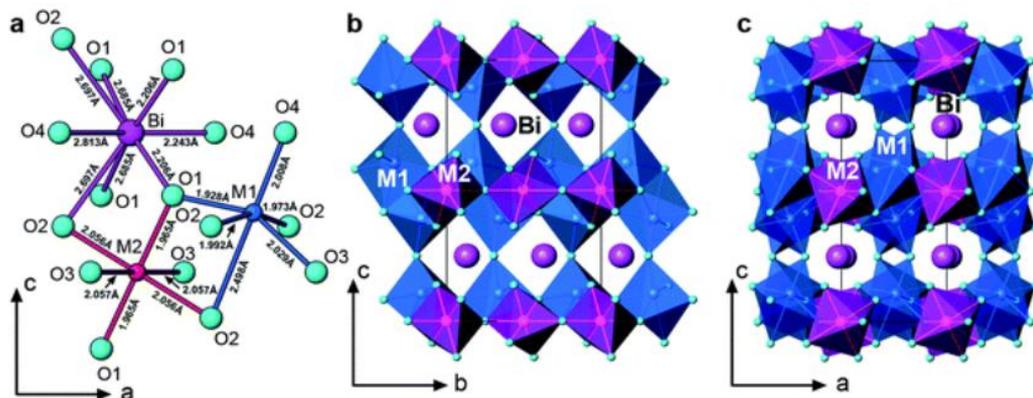
*However, there seem to be two exceptions to these empirical rules!*

# Bi (and Pb) perovskites: Role of lone pairs

BiMnO<sub>3</sub> and BiFeO<sub>3</sub> are multiferroic systems where FE and FM coexist

**BiFeO<sub>3</sub>:**  $T_{FE} = 1100$  K,  $T_M = 643$  K

**BiMnO<sub>3</sub>:**  $T_{FE} = 760$  K,  $T_M = 105$  K



(a) Local coordination environments of metal cations; (b) structure view along the a-axis; (c) structure view along the b-axis.

- Both have transition metal ions Fe<sup>3+</sup> ( $d^4$ ) and Mn<sup>3+</sup> ( $d^4$ ).
- These materials seem to violate the  $d^0$  requirement in the perovskite family.

***Not really!***

**A careful study shows that FE in these compounds do not stem from transition metal ions.**

FE is driven by A-site ions

# Bi (and Pb) perovskites: Role of lone pairs

- Bi<sup>3+</sup> and Pb<sup>2+</sup> ions have lone pairs – two valence electrons.
- Such pairs usually participate in chemical bonds through *sp*-hybridizations (*sp*<sup>2</sup> or *sp*<sup>3</sup>).

***But not in these systems!***

Particular orientation of these lone pairs (or dangling bonds) may create local dipoles



Increases energy of the system, and hence, make the structure unstable.



This instability induces distortion so that dipoles order in FE or anti-FE fashion.  
(This is achieved through displacement of Bi<sup>3+</sup> ions.)

Calculations show that *Bi* lone pairs are predominantly responsible for FE in these materials.

# Co-existence of FE and Magnetism

- One way to achieve this is by having ions of different species responsible for magnetism and FE individually.
- But, then, how do we achieve the coupling between magnetic and electric order parameters?

**Allow non-linear interplay between spin, charge, orbital, and lattice degrees of freedom.**

In my next presentation, I'll talk about the ways these non-linear couplings can be achieved and also some materials that exhibit such couplings.

## References:

- [1] D.I. Khomskii, Journal of Magnetism and Magnetic Materials 306 (2006) 1–8
- [2] S.-W. Cheong, M. Mostovoy, Nature Materials | VOL 6 | JANUARY 2007
- [3] P. W. Anderson, Physical Review, Volume 115, Number 1, 1959
- [4] T. Moriya, Physical Review, Volume 120, Number 1, 1960

*Thank you!*

# Multiferroic hexagonal manganites

( $\text{RMnO}_3$ , R = Y or small rare-earth ion)

## *h*- $\text{RMnO}_3$

- $\text{Mn}^{3+}$  ions are in 5-fold coordination environment in the center of the  $\text{O}_5$  trigonal bipyramids.
- R ions are in a 7-fold coordination
- Crystal field splitting of d-electrons: Two doublets and an upper singlet
- Four d-electrons of  $\text{Mn}^{3+}$  occupy the two lowest-lying doublets
- No orbital degeneracy left, hence,  $\text{Mn}^{3+}$  is not a Jahn-Teller ion in these compounds

## *o*- $\text{RMnO}_3$

- $\text{Mn}^{3+}$  ions are in 6-fold coordination environment in the center of the  $\text{O}_6$  octahedra.
- R ions are in a 12-fold coordination
- Crystal field splitting of d-electrons: Triple  $t_{2g}$  and a double  $e_g$
- Orbital degeneracy left