

# Introduction on Multiferroic Materials

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## Abstract

A brief introduction on the concept of Multiferroic Materials is present with a simple review on the recent research discoveries related to this topic. In this presentation, we will first explain what is so called Multiferroic Materials and then set some popular ones as examples. What's more, we are going to explore the important physical properties of these materials and have a look at the phase diagrams.

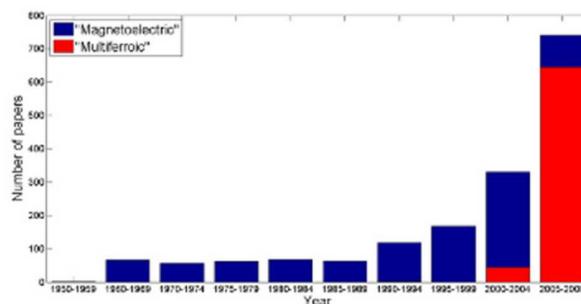
## I. THE CONCEPT OF MULTIFERROICS

### A. History

Electric and magnetic fields and related phenomenas have been considered to be important since Maxwell, and they were clearly shown to be unified in the special theory of relativity. However, people used to think that ferroelectricity and magnetism are exclusive to each other and can only have weak coupling when they coexist.

The term multiferroic was first used by H. Schmid in 1994<sup>4</sup>. His original definition referred to multiferroics as single phase materials which simultaneously possess two or more primary ferroic properties among the 4 in the following subsection. Today people extend the definition to include other long-range orders, such as antiferromagnetic. In this extended definition, we can say that this research field was born in the 60's even the 50's. From then people started to do related studies under the name magnetoelectric.

From the figure it is clear that there is a burst in the number of papers at the beginning of this century. The direct reason is that in 2003, people discovered large ferroelectric polarization in the epitaxially grown  $BiFeO_3$ <sup>6</sup> thin film and strong magnetoelectric coupling in  $TbMnO_3$ <sup>3</sup> and  $TbMn_2O_5$ <sup>8</sup>. Especially in the so called frustrated multiferroics, the electric dipole moments are very sensitive to the applied magnetic fields, although its magnitude is still much smaller than typical ferroelectrics. These new discoveries broke the traditional thinking about multiferroics and opened a new gate for industry: if charge can be controlled by external magnetic fields and spins can be controlled by applied voltage, new devices with varieties of functions may be designed.<sup>5</sup>



**FIG. 1:** The number of papers using the keywords *Magnetoelectric* and *Multiferroic* from 1950 to 2008, this picture is taken from: <http://en.wikipedia.org>

## **B. Ferroics**

There are four types of ferroics:

*Ferroelectric* materials possess a spontaneous polarization that is stable and can be switched hysteretically by an applied electric field; antiferroelectric materials possess ordered dipole moments that cancel each other completely within each crystallographic unit cell.

*Ferromagnetic* materials possess a spontaneous magnetization that is stable and can be switched hysteretically by an applied magnetic field; antiferromagnetic materials possess ordered magnetic moments that cancel each other completely within each magnetic unit cell.

*Ferroelastic* materials display a spontaneous deformation that is stable and can be switched hysteretically by an applied stress.

*Ferrotoroidic* materials possess a stable and spontaneous order parameter that is taken to be the curl of a magnetization or polarization. By analogy with the above examples, it is anticipated that this order parameter may be switchable. Ferrotoroidic materials have evaded unambiguous observation.

## **C. Order Parameter Couplings**

The order parameter couplings are described by:

*Magnetolectric* describes the influence of a magnetic (electric) field on the polarization (magnetization) of a material.

*Piezoelectricity* describes a change in strain as a linear function of applied electric field, or a change in polarization as a linear function of applied stress.

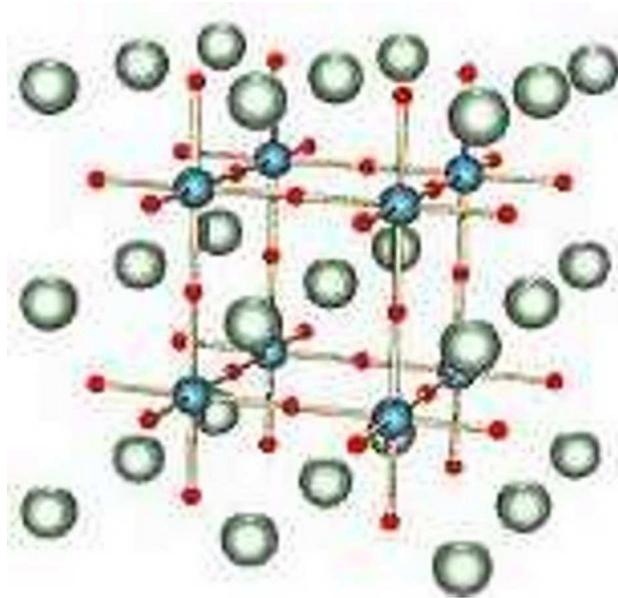
*Piezomagnetism* describes a change in strain as a linear function of applied magnetic field, or a change in magnetization as a linear function of applied stress.

*Electrostriction* describes a change in strain as a quadratic function of applied electric field.

We will focus on the ferromagnetic and ferroelectric because they are of most physical concern.

#### D. Examples of Multiferroics

Typical multiferroics belong to the group of the perovskite (*Fig.2*) transition metal oxides, and include rare-earth manganites and ferrites such as  $TbMnO_3$ ,  $YMn_2O_5$  and  $LuFe_2O_4$ . Other examples are the bismuth compounds  $BiFeO_3$  and  $BiMnO_3$ , and non-oxides such as  $BaNiF_4$  and spinel chalcogenides like  $ZnCr_2Se_4$ .



**FIG. 2:** Perovskite structure

## II. PROPERTIES OF MULTIFERROICS

### A. Types and Possible Mechanisms

1. Charge ordering is one way leads to ferroelectricity. When the ions are also magnetic, multiferroic is formed. A famous example is  $LuFe_2O_4$ <sup>9</sup>, the ordering of  $Fe^{2+}$  and  $Fe^{3+}$  provides ferroelectricity. Meanwhile, site-centered and bond-centered charge ordering in  $R_xCa_{1-x}MnO_3$ <sup>10</sup> can also provide ferroelectricity.

2. Geometrical multiferroic is another type. The mechanism of ferroelectricity is consid-

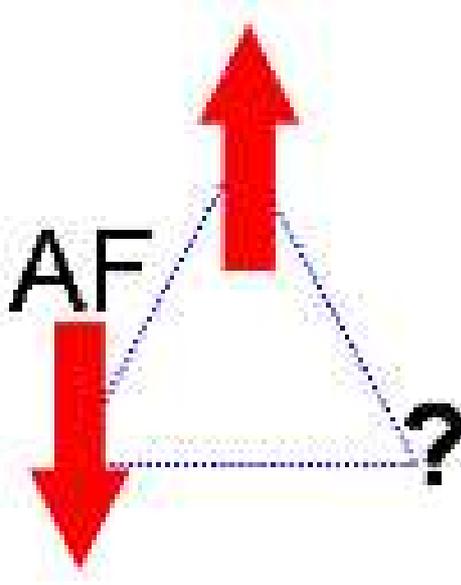


**FIG. 3:** Left:site-centered charge ordering. Mid:bond-centered charge ordering. Right:ferroelectricity by Charge Ordering. This picture is taken from ref.10.

ered as nonlinear couplings between different lattice distortions, suggested by first principle calculations<sup>11</sup>. A proper example of this compound would be hexagonal  $RMnO_3$ , in which the coupling of different phonon modes creates ferroelectricity. Geometrical reasons also produce magnetical induced ferroelectricity.

3. In some systems, Heisenberg spin-spin coupling with ferromagnetic for nearest neighbour and antiferromagnetic for next nearest neighbour will provide spiral spin phase. And this phase may come with ferroelectricity via the coupling  $\vec{P} = \gamma \times (\vec{M} \cdot \nabla \vec{M} - \vec{M} \nabla \cdot \vec{M})$ <sup>12</sup> (obtained from thermodynamics). The microscopic mechanism maybe explained as the relativistic correction of the Heisenberg term, which is called Dzyaloshinskii-Moriya interaction  $\vec{D}_{ij} \cdot \vec{S}_i \times \vec{S}_j$ . Moreover, in certain systems Ising type spin-spin (also ferromagnetic for nearest neighbour and antiferromagnetic for next nearest neighbour) interaction will lead to the  $\uparrow\uparrow\downarrow\downarrow$  ground state, which will also cause a lattice distortion.

Let us discuss more about the DM interaction here. First of all, what is the origin of it? The

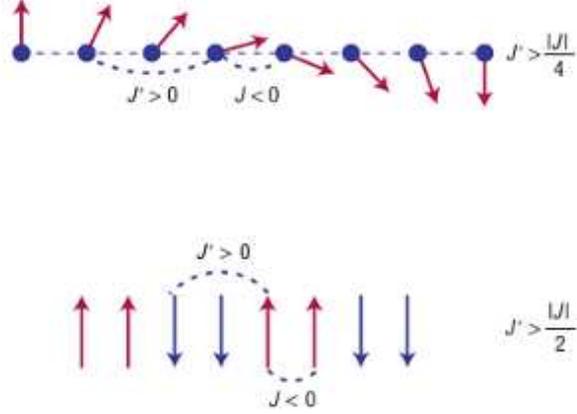


**FIG. 4:** An illustration of geometrical frustration. The spin on the third site can be in any direction, but then the interaction between this site and the other 2 will be different. As a consequence, the third site will move closer to one site and away from another, which will break the symmetry and induce ferroelectricity. This picture is gained from: <http://en.wikipedia.org>

answer is the relativistic correction to the Hamiltonian up to the order of  $\frac{1}{c^2}$ . As well known, the Heisenberg super exchange interaction is due to the second order virtual hopping of the electrons, and the spin of every electron is conserved during the hoppings. However, in relativistic quantum mechanics, the z component of spin is no longer a good quantum number: it may flip once during the second order virtual hopping (It may also flip twice, of course. But that will be at the order of  $\frac{1}{c^4}$  and can be neglected here). These virtual hoppings with one time spin flip will lead to the DM interaction in the same way as non-relativistic virtual hoppings lead to the Heisenberg interaction.

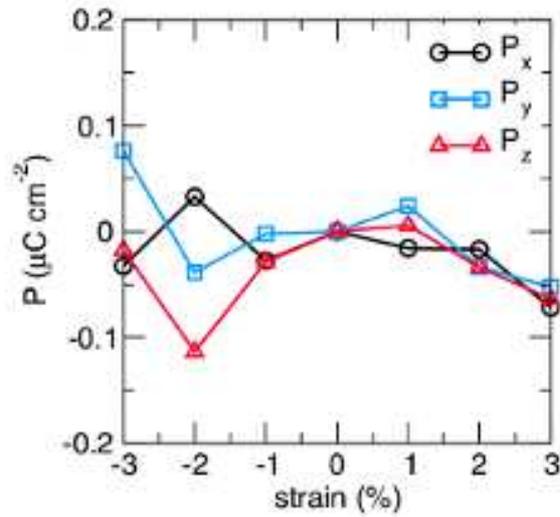
Secondly, how does the DM interaction lead to ferroelectricity? Intuitively, people can argue that the relativistic correction can be expressed by the spin-orbital interaction, which will try to rotate the atomic orbitals in order to align them with the spins. This rotation of the atomic orbitals, obviously, will repulse the oxygen ion between the 2 sites via Coulomb force, and result in ferroelectricity. Mathematically, the vector  $\vec{D}_{ij}$  is found to be proportional to  $\vec{R}_{ij} \times \vec{x}_{ij}$ , where  $\vec{R}_{ij}$  is the position difference of the 2 sites and  $\vec{x}_{ij}$  is the displacement of the oxygen ion.

4. Lone pair multiferroics: in some perovskite materials, the  $6p$  orbital of the A site and the



**FIG. 5:** Spin frustration structures appear under certain range of  $J'/J$  in both Heisenberg model (spiral spin) and Ising model ( $\uparrow\uparrow\downarrow\downarrow$ ). This picture is taken from ref.5.

$2p$  orbital of the O atoms will have a hybridization due to strain from surfaces, which leads to the distortion of the A sites so that ferroelectricity appears<sup>7</sup>. Ferromagnetic structure is due to the B sites.



**FIG. 6:** Induced polarization induced by strain on the (111) plane of  $BiMnO_3$  as indicated by ref.7.

## B. Reversal symmetry

Ferromagnetic and ferroelectric have the same reversal symmetries as magnetic and electric field. From the Maxwell equations

$$\begin{aligned}\nabla \cdot \vec{E} &= 4\pi\rho \\ \nabla \times \vec{E} &= -\frac{\partial \vec{B}}{\partial t}\end{aligned}\tag{1}$$

it is clear that electric fields are invariant under time reversion but will get a minus sign under spatial reversion, while magnetic fields are invariant under spatial reversion but will get a minus sign under time reversion. And this totally opposite property in symmetry is one of the reasons for people to think ferromagnetism and ferroelectricity exclude each other.

Characteristic symmetry	Spatial-inversion symmetry?	Time-reversal symmetry?
Ferroelastic	Yes	Yes
Ferroelectric	No	Yes
Ferromagnetic	Yes	No

**FIG. 7:** Reversal symmetries table for ferroics from ref.5.

## C. Difficulty of Traditional Landau Theory

Traditional materials under external fields  $\vec{E}, \vec{H}$  have free energies expressed by the Landau phase transition theory

$$\begin{aligned}-F(E, H) &= \frac{1}{2}\epsilon_{ij}E_iE_j + \frac{1}{2}\mu_{ij}H_iH_j + \alpha_{ij}E_iH_j \\ &+ \beta_{ijk}E_iH_jH_k + \gamma_{ijk}H_iE_jE_k + \dots\end{aligned}\tag{2}$$

and one easily obtains

$$\begin{aligned}P_i &= \alpha_{ij}H_j + \beta_{ijk}H_jH_k \\ M_i &= \alpha_{ji}E_j + \beta_{ijk}E_jE_k\end{aligned}\tag{3}$$

However, these expressions are not preferred in the research of multiferroics. The reason is that those coupling parameters will display field hysteresis, which make them dependent

on the history of the material. People are trying to use the resultant field, instead of the external one, to describe the state of multiferroics.

Another challenge arise from the higher order terms. These non-linear terms will dominate in large fields while the magnetoelectric coupling is already complicated. What's more, the effects of strain, which is not included in the above equation, can also be significant.

All of the above strongly desire a microscopic and quantum mechanical, instead of macroscopic and thermodynamical, model in order to study ferroics theoretically. However, it seems to be very difficult to establish a simple but accurate enough microscopic model for all the ferroics.

#### D. Microscopic Double-Exchange Model

A complete microscopic model should contain:

1. Electron hopping between sites.
2. Coulomb interaction between electrons.
3. Super-exchange coupling between spins.
4. Electron-phonon coupling.

Bad news: these 4 kinds of interactions do not mean that there are only 4 terms in the Hamiltonian. The complexity increases rapidly with the number of orbitals, and 2 body interaction should be expressed by 4 Fermion operators in a many body basis. For example, although there is only one term for the Coulomb interaction in the single orbital problems (Hubbard model), we need 4 terms in a two orbital problem:

$$U \sum_{i,\alpha} n_{i\alpha\uparrow} n_{i\alpha\downarrow} + U' \sum_{i,\alpha\neq\beta} n_{i\alpha} n_{i\beta} + J \sum_{i,\alpha\neq\beta} \vec{S}_{i\alpha} \cdot \vec{S}_{i\beta} + J' \sum_{i,\alpha\neq\beta} c_{\alpha\uparrow}^\dagger c_{\alpha\downarrow}^\dagger c_{\beta\downarrow} c_{\beta\uparrow} \quad (4)$$

The similar thing happens to the super-exchange coupling. As stated above, the multiferroics are mainly transition metal oxides, and multiorbital problems are really common.

Good news: there are particular systems in which the multiorbital problems can be easier. Manganites, in which the 5 d orbitals are split into 3 degenerate t2g orbitals with lower energy and 2 degenerate eg orbitals with higher energy, is a system that can be studied by significantly simplified model. People found that in such systems, first of all, the Coulomb interaction between electrons are so strong that any orbital is hardly double occupied. Secondly, the Hund coupling (in fact one part of the Coulomb interaction) is also much stronger

than the hopping, and then one can make the approximation that all electrons on the same site must have the "same" spin. The most dramatic thing is that numerical calculations showed that for spin-3/2, quantum spin and classical spin give very close results, so that the t2g spin can be treated classically (the 3 electrons form a spin-3/2 state by the infinite Hund coupling) in the super-exchange coupling.

Finally, we obtain the so called double-exchange model for manganites:

$$\begin{aligned}
H = & \sum_{i,j,\alpha,\beta,\sigma} t_{i,j,\alpha,\beta} \Omega_{i,j} c_{i,\alpha,\sigma}^\dagger c_{j,\beta,\sigma} + \sum_{i,j} J_{AF} \vec{S}_i \cdot \vec{S}_j \\
& + \sum_i [\lambda(-Q_{1,i} I_{2 \times 2} + Q_{2,i} \tau_i^x + Q_{3,i} \tau_i^z) + \frac{1}{2}(\gamma Q_{1,i}^2 + Q_{2,i}^2 + Q_{3,i}^2)] \\
& + \sum_{i,j} \vec{D}_{ij} \cdot \vec{S}_i \times \vec{S}_j
\end{aligned} \tag{5}$$

Where  $\Omega_{i,j}$  is called berry phase, comes from the fact that the hopping amplitude will be dependent on the spin directions of the 2 sites due to infinite Hund coupling. The  $Q$ 's are normal modes of the so called Jahn-Teller phonon (there are other 3 modes with no significance), and the gamma, which is usually taken as 2, appears due to the  $Q_1$  mode has a spring constant different from  $Q_2$  and  $Q_3$ .

### E. The Phase Diagrams

Now let us pay attention to some phase diagrams of the multiferroics.

### F. The Future

1.The first challenge is to find a efficient mechanism via which electric polarization can induce magnetic structures. Although an external magnetic field can strongly affect the electric properties of a multiferroic material, external electric fields have rare effect on the magnetic properties of the material. Because electric polarization does not break the time reversal symmetry, it can not produce magnetical order in the same way as how magnetic frustrations induce ferroelectricity.

2.For practical applications, it is important to find more and more room temprature multiferroics. However, the magnetic coupling is ususally not strong enough to hold at room temprature (but it is not impossible, for example, hexaferrite  $Ba_{0.5}Sr_{1.5}Zn_2Fe_{12}O_{22}$ ).

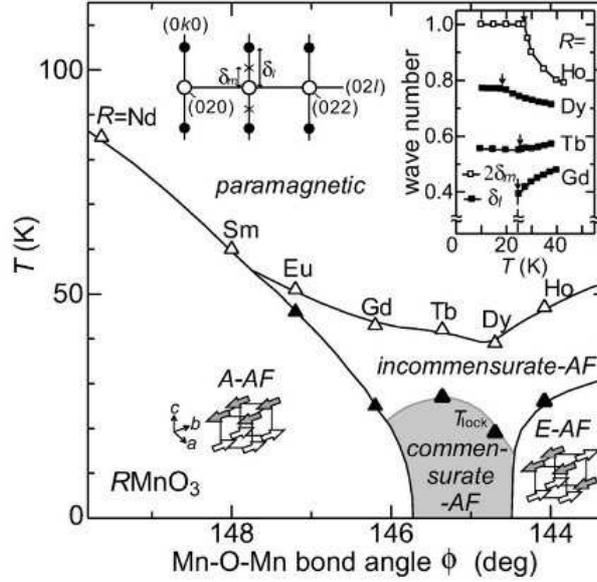


FIG. 8

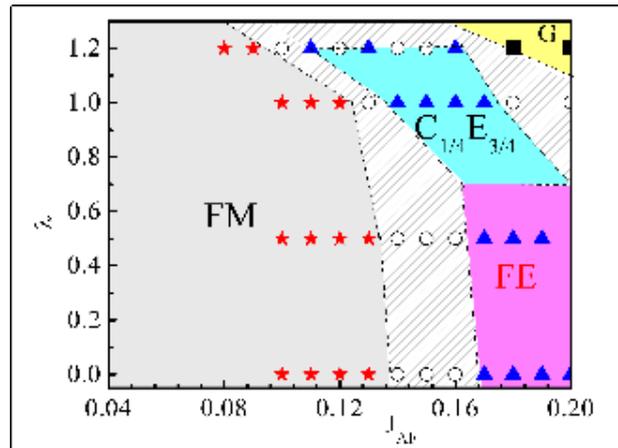
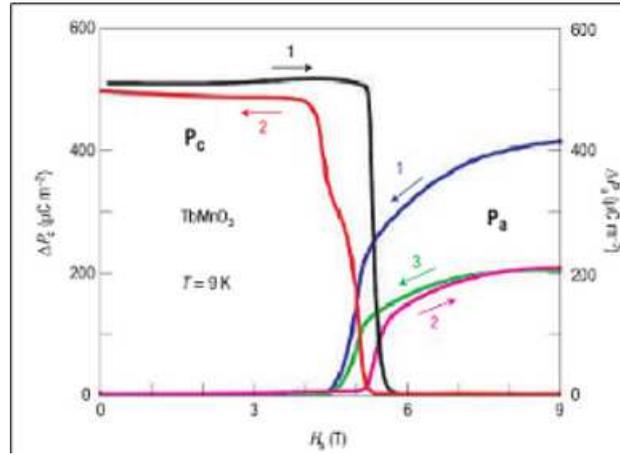
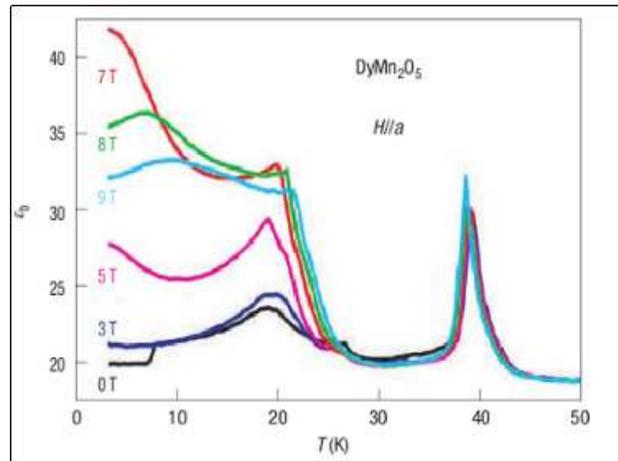


FIG. 9: New phase found in large JAF by Shuai Dong appears to be ferroelectric.

3. For theoretical physics, more detailed and comprehensive understanding to the microscopic mechanism and dynamics of the magnetoelectric coupling is desired. This requires both a more detailed study via double-exchange model on the lucky systems and a development of brilliant ideas to explore what we can do for the more complicated systems. An alternative way is to develop more advanced numerical methods in order to calculate multiorbital many body problems more accurate and efficient, which is always important, not only for



**FIG. 10:** Polarization of  $TbMnO_3$  under external magnetic field along the b axis. A critical field  $5T$  turns the polarization from c axis to a axis.(ref.5)



**FIG. 11:** Dielectric constant of  $DyMn_2O_5$  along the b axis under applied magnetic field along the a axis. Under  $25T$ , the dielectric constant is strongly field-dependent, but then it becomes almost field-independent and a peak appears at  $38T$ .(ref.5)

multiferroics but also for all the other problems in computational physics.

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