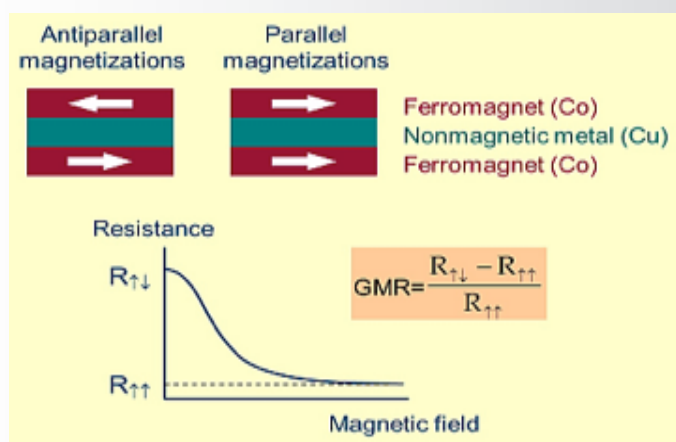


# APPLICATIONS OF MAGNETOELECTRIC MATERIALS FOR SOLID-STATE DEVICES

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In 1947, three men, William Shockley, Walter Brattain, and John Barden, revolutionized the world of electronics by developing the first operational transistor. The transistor made the creation of the computer and other digital electronics possible, ushering in a new era of technology and earning the three men the 1956 Nobel Prize in Physics. Armed with the transistor, scientists and engineers (notably, those from Intel Corporation) developed faster, smaller, and more efficient microprocessors and RAM storage devices throughout the 1980s and 1990s. The development of solid-state storage devices and hard drives is of utmost importance for our increasingly electronic world. Within the last decade, computers have reached unprecedented operation speeds, but we are approaching a plateau. Recently, scientists have found that we cannot overcome this hurdle simply by fitting more and more transistors onto a chip; we must actually change the fabric of the device by creating new materials in a fashion that takes advantage of their inherent quantum electronic properties.

Currently, hard drives operate by using the principle of magnetoresistance. Magnetoresistance describes the phenomenon of a magnetic polarization affecting the resistance of a material.



**Figure 1.** Diagram of parallel and anti-parallel magnetic tunnel junction (MTJ) configurations (Tsymbol, 1999)

In Figure 1, we can see that the magnetic tunnel junction (MTJ) consists of a thin insulator sandwiched by two magnets. The insulator has a thickness on the order of a few nanometers; therefore, electrons

from one magnet can tunnel across the dielectric to the other magnet. Tunneling essentially means that every particle has a non-zero probability of traversing a solid boundary. While the mechanics of tunneling are not well understood, we do know that it is due to the wave-particle duality of matter; thus, tunneling is a purely quantum phenomenon and can only happen to very small particles such as electrons or quarks. When electrons traverse the boundary, they create a current and we can measure a resistance across the MTJ device. The number of electrons that will tunnel across the insulator is dictated by the relative orientations of the two magnets. Suppose that there are only two magnetic orientations: “left” and “right.” If both magnets have the same orientation, we call that the parallel state. If they point in opposite directions, they are in the anti-parallel state. Tunneling is highly encouraged in the anti-parallel state and suppressed in the parallel configuration (Nishimura, 2002). Thus, we can conclude that for a given potential, the anti-parallel state has a very low resistance while the parallel state has a high resistance. In hard disk drives, a read head applies a set voltage over many of these MTJ bits, measuring the resulting resistance of each one. It interprets a high resistance as a “1” state and a low resistance as a “0” state; thus, magnetoresistance directly leads to a digital interpretation.

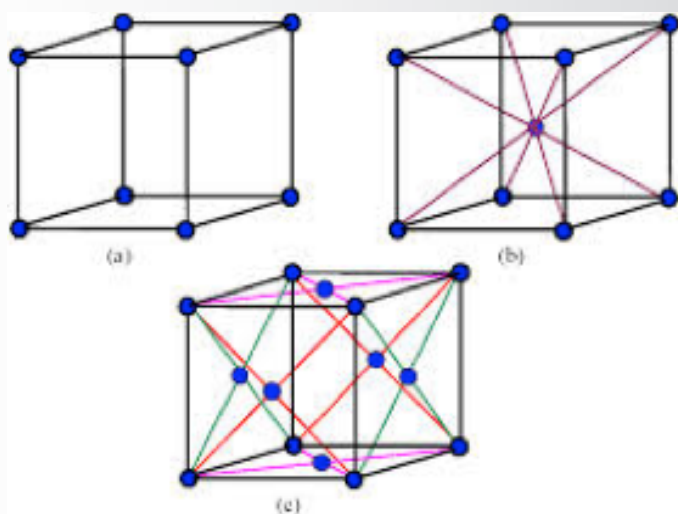
In the case of RAM (random-access memory), these bits are constantly being changed and re-interpreted over and over. The problem is that imparting these magnetic polarizations (a process called writing) utilizes an external magnetic field and is energetically inefficient given how many times the polarization changes. Recently, there has been a huge interest in a new class of materials called multiferroics. These materials exhibit two or more so-called “ferroic parameters”: ferroelectricity, ferromagnetism, and ferroelasticity. Current research suggests that using specific multiferroic materials in place of the magnets in Figure 1 can revolutionize computer memory systems and usher in a new era of quantum electronic technology.

Before we can understand what the different ferroic parameters are and how they occur, we need to understand crystalline materials and crystal structure. When one thinks of crystals, one often pictures

diamond or some other glistening gem. In reality, crystals are much more common than precious stones and the study of crystalline materials constitutes the backbone of solid-state physics and quantum electronics. Crystalline materials are simply those in which the atoms that make up the material are arranged

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in a regular pattern. There are seven different crystal structures: cubic, tetragonal, trigonal, orthorhombic, monoclinic, triclinic, and hexagonal. In cubic crystal systems, the atoms lie on or within a cube; the other 6 systems can be thought of as a normal cube warped along one or more dimension. Crystallographers further break down these seven systems by their spatial symmetry into 14 unique structures known as Bravais lattices. The three Bravais lattices that we will be focusing on are the simple lattice, base-centered lattice, and face-centered lattice. Figure 2 shows these three different Bravais lattices

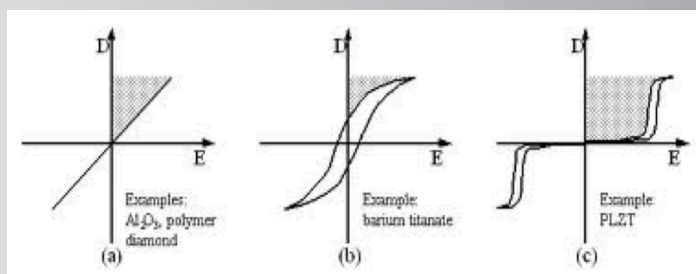


**Figure 2.** (a) simple lattice, (b) base-centered lattice, (c) face-centered lattice. The blue dots represent the constituent (not necessarily the same) atoms of the material (Kotowski, 2002)

From the picture, we can see that the simple structure is the easiest to understand with one atom occupying a vertex position of the cube in each unit cell. A base-

centered structure is the same as the simple structure except for that there is one more atom in the center of the cube. Face-centered lattices share the same framework as simple lattice but also includes an atom at the center of each of the 6 cubic faces. The geometry of a material’s unit cell is called that material’s lattice while the unique atomic makeup is called the material’s crystal motif. A good analogy is to think of the lattice as a blueprint for a building while the motif is what actually fills the building. Many buildings may have the same blueprint (for example, homes built by the same architect) but each building has a different appearance and interior due to what one chooses to fill it with. Similarly, many materials exhibit the same lattice but each material has a unique motif that gives it the properties it possesses.

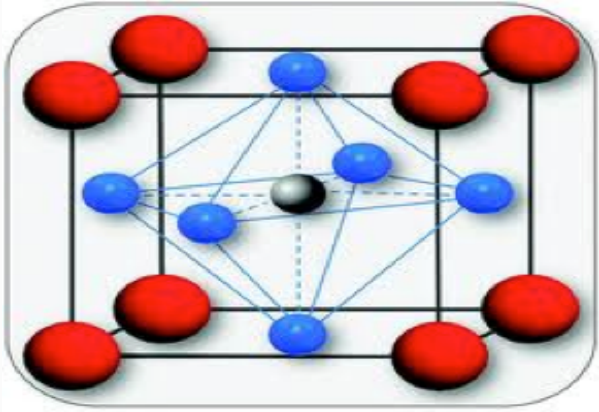
Armed with a basic understanding of crystal structure, we can tackle the electronic ferroic parameter: ferroelectricity. All materials can be grouped into one or more of three electronic categories: dielectric, paraelectric, and ferroelectric. These distinctions are made based on how a material reacts when an external electric field is applied to it. While a material can only be characterized into one electronic category at a time, it can switch between categories with a change in external parameters such as temperature. Figure 3 depicts the three different responses:



**Figure 3.** Graphs of dielectric (a), paraelectric (b), and ferroelectric (c) responses (TRS Technologies, 2014)

Each graph plots the material’s electric displacement field (D) against the applied electric field (E). For the sake of simplicity, we can take the displacement field to be the internal electric polarization of the material. A dielectric material has a linear response to the applied field: as the external field increases in magnitude, so does the material’s polarization. The drastic non-linear response in figure 3(c) shows that a paraelectric material actually acquires a polarization greater than the applied electric field. The most interesting of these, the ferroelectric response, is characterized by a spontaneous, intrinsic electric polarization even in the absence of an externally applied field (there is a non-zero y-value for an applied field of zero in the ferroelectric graph). Furthermore, a ferroelectric material can have the direction of

its intrinsic polarization changed by changing the external electric field. Why do these reactions occur? Dielectrics (often called insulators) are often polymers, glasses, and other non-conducting materials while paraelectrics and ferroelectrics are almost exclusively crystalline materials. Let us observe the unit cell of a generic paraelectric:



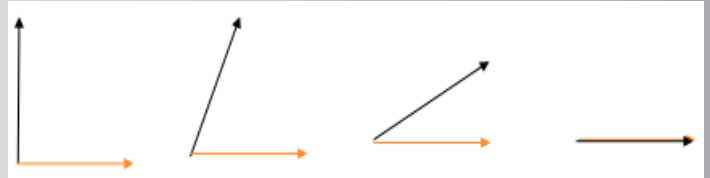
**Figure 4.** Generic paraelectric/ferroelectric FCC crystal unit cell. The black arrows represent each atoms' electric polarization (Strobel, 2009)

The reason why a paraelectric has no intrinsic electronic polarization is because all of these small arrows cancel each other out in the end, resulting in a net polarization of 0. However, when acted upon by an externally applied field, all of these arrows suddenly align in the direction of the applied field and there is a huge spike in the electric polarization of the material as a whole.

Consider the same figure but now take it to be a ferroelectric material. Ferroelectrics come in two different flavors: displacive and order-disorder. In displacive ferroelectrics, each unit cell actually has a net polarization (the arrows do not cancel each other out) and for a certain range of temperature, each unit cell in the material as a whole has a non-zero electric polarization that contributes to a predictable, non-zero intrinsic material polarization. At higher and higher temperatures, displacive ferroelectrics can have more random unit-cell polarizations that lead to an unpredictable and possibly non-existent spontaneous polarization. Order-disorder ferroelectrics are caused by slight ionic displacements that lead to an asymmetry between the nearby ions' electric fields and the elastic restoring force on the unit cell. In particular, the electric field grows faster than the mechanical force, causing a net electric force on the ion. This leads to a net ionic displacement which leads to a net polarization. In the sample unit cell in Figure 4, the center ion is typically the one that is displaced from equilibrium and causes the net electric moment. Scientists have observed that many order-disorder ferroelectrics exhibit Perovskite structure. Perovskite is the common name given

to crystalline materials with the chemical formula  $ABO_3$  where O is oxygen and A and B are two other elements. For example, the best classical example of a ferroelectric material is barium titanate ( $BaTiO_3$ ). Barium ions lie on the 8 cube vertices, one titanium ion sits in the center, and 6 oxygen ions are located at so-called "tetrahedrally coordinated" positions. The titanium ion is permanently displaced from its center equilibrium position and is responsible for causing a net electric moment.

Another important feature of ferroelectric materials is that their electric polarization can be changed by applying an electric field in a different direction. Imagine we have a ferroelectric unit cell with polarization pointing up and we decide to apply an electric field pointing directly to the right. The polarization (black) will move toward the direction of the electric field (orange) over a period of time:



If we were to plot this motion to change the polarization by 180 degrees, reverse the bias, then plot the movement back to the original direction, we would trace out a loop similar to that in Figure 3(b). This is referred to as a hysteresis loop; this name is derived from the fact that the new position of the polarization is guided by its previous position (or history). If we looked at a paraelectric material, the polarization would immediately snap into line with the electric field.

The second and most famous ferroic parameter is called ferromagnetism. Ferromagnetism is completely analogous to ferroelectricity except that ferromagnets have a spontaneous magnetic moment; therefore, much of our discussion of ferroelectricity applies in a similar way to ferromagnetism. Everyday magnets are ferromagnets, including the most famous one, iron, for which the property is named. Similar to electronic categorization, materials also belong to at least one of the following three classes: paramagnets, diamagnets, and ferromagnets. The graphs of the applied magnetic field versus the material magnetization look the same as those shown in Figure 3. Paramagnetic atoms align their magnetic moments with the external field much like paraelectrics do while diamagnets partially cancel out the external and almost stay magnetically neutral. Ferromagnets exhibit a spontaneous magnetic moment similar to how ferroelectrics have an intrinsic electronic polarization. On top of being ferromagnetic, some

materials can also be classified as anti-ferromagnetic or ferrimagnetic. Anti-ferromagnets have alternating magnetic polarizations on each atom, causing them to be magnetically neutral but controllable by external magnetic forces while ferromagnetic materials exhibit unequal alternating moments on their constituent atoms, causing a net magnetization equal to exactly half that of a normal ferromagnetic magnetization.

We can now delve into the heart of multiferroic research: magnetoelectric multiferroic materials. Magnetoelectric multiferroics are those materials that are both ferroelectric and either ferromagnetic or anti-ferromagnetic. Indeed, the most promising of these materials is bismuth ferrite (BiFeO<sub>3</sub>), a perovskite ferroelectric/anti-ferromagnetic multiferroic. At room temperature, BFO has rhombohedral crystal structure, but depending on the substrate it is grown on, it can turn into a monoclinic or tetragonal phase with different electronic and magnetic properties (Catalan, 2009). BFO is composed of equal parts Bi<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>. According to current research, when BFO is grown as a thin-film (nanometer to micron thickness), it retains a nearly 15% higher remnant electric polarization when compared to bulk crystalline BFO (Catalan, 2009). The reason for this and for why thin-film technology is incredibly promising for developing technology is because electrons behave differently when they are interacting within a crystal of thickness approximately equal to the wavelength of the electron wavefunction. The electrons act more or less as if they were in a potential well rather than a free particle. This is to say that electrons in thin-films are essentially trapped; thus, they have very predictable and well-defined behaviors. This makes thin-film nanostructures an exciting prospect for quantum electronics research.

when the ferromagnet CoFe is placed on top of a thin-film of BFO, we observe an exchange coupling interaction between the anti-ferromagnetic moment of BFO and the ferromagnetic moment of CoFe (Martin 2008). Even though an anti-ferromagnet is magnetically neutral, it still has two “orientations.” If the first atom has a “down” polarization, the next must have an “up,” followed by a “down,” and so on until the whole unit cell is magnetically neutral. If we flip the initial condition (i.e. start on an “up”), all of the other atoms also flip their polarizations. To put in simply, this magnetic exchange coupling interaction refers to the CoFe’s ability to “read” the orientation of the antiferromagnetic moment and align its own ferromagnetic moment appropriately (Martin 2008). Suppose the “down” initial condition on BFO corresponds to a “left” magnetic moment on CoFe; if the BFO were to flip for some reason and go into the “up”-starting configuration, the CoFe would read this switch and turn its magnetic moment appropriately to the “right” orientation.

The only question that now remains is: how do we flip BFO’s antiferromagnetic configuration? Fortunately, scientists at UC Berkeley have observed another internal coupling interaction between BFO’s ferroelectric polarization and its antiferromagnetic moments (Martin 2008). As we have established earlier, all ferroelectrics can have their electric polarization changed by an external voltage. Thus, if we apply an electric field to BFO and flip its electric polarization, we also flip its anti-ferromagnetic polarization which is read by the CoFe on top of it, flipping the CoFe’s magnetic moment and allowing us to successfully re-write a magnetic moment without ever having to utilize an energetically expensive magnetic field. This discovery is a huge triumph and forms the basis

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*“In particular, when the ferromagnet CoFe is placed on top of a thin-film of BFO, we observe an exchange coupling interaction between the anti-ferromagnetic moment of BFO and the ferromagnetic moment of CoFe”*

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Earlier we proposed that whatever multiferroic replaced the magnets in Figure 1 could have a tremendous impact on the energetic efficiency of any magnetoresistive device. Since BFO is anti-ferromagnetic, it would seem counterintuitive that it would make a good magnetic component. This is why we would not use just BFO for those magnets; rather, we would replace the magnet with a heterostructure: a stacking of different thin-film materials. In particular,

for new magnetoelectric random access memory (MERAM). MERAM would certainly revolutionize all technology, greatly increasing the speed, decreasing the cost, and stabilizing modern computers as well as phones, microprocessors, and other solid-state devices.

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