Multiferroics: Past, present, and future

Nicola A. Spaldin

The following article is based on a Symposium X (Frontiers of Materials Research) presentation given by Nicola A. Spaldin at the 2016 MRS Fall Meeting in Boston, Mass.

This article provides a personal guided tour of multiferroic materials, from their early days as a theoretical curiosity, to their position today as a focus of worldwide research activity poised to impact technology. The article begins with the history of, and the answer to, the question of why so few magnetic ferroelectric multiferroics exist, then gives a survey of the mechanisms and materials that support such multiferroicity. After discussing the tremendous progress that has been made in the magnetoelectric control of magnetic properties using an electric field, some unusual applications of multiferroics in high-energy physics and cosmology are outlined. Finally, the most interesting open questions and future research directions are addressed.

Introduction

Multiferroics are defined to be materials that combine two or more of the primary ferroic order parameters simultaneously in the same phase. The established primary ferroics are ferromagnets (materials with a spontaneous magnetization that is switchable by an applied magnetic field), ferroelectrics (materials with a spontaneous electric polarization that is switchable by an applied electric field), and ferroelastics (materials with a spontaneous deformation that is switchable by an applied stress).[1]

The primary ferroic phenomena are illustrated by the vertices of the triangle in **Figure 1**, where the ferromagnetic, ferroelectric, and ferroelastic switching are indicated by blue, yellow, and purple arrows, respectively. The most interesting aspect of multiferroics is the cross-coupling between the order parameters, represented by the sides of the triangle. Piezoelectricity, resulting from the coupling between polarization and deformation in ferroelectric ferroelastics (left edge of the triangle), is well established and widely exploited (e.g., in sonar detectors). Likewise, magnetism and structure are often strongly coupled (bottom edge of the triangle) leading to piezomagnetism, which can be used in magnetomechanical actuation or magnetic sensing. The multiferroics that combine ferromagnetism and ferroelectricity are represented by the right edge of the triangle and are much less common. They are appealing, however, since their coupling produces the so-called magnetoelectric effect, in which an electric field can induce or modify the magnetization, and a magnetic field affects the electrical polarization (green arrows in Figure 1). Electric-field control of magnetism in particular is highly appealing for potential devices, since electric fields can be engineered to be far smaller and to use less power than their magnetic counterparts.

Why are there so few magnetic ferroelectrics?

A Web of Science search returns a paper entitled *Why are there so few magnetic ferroelectrics?*[2,3]* as the earliest result for "multiferroic." The answer to the question is simple. The chemistries of ions that tend to be magnetic in solids are different from those that tend to form electric dipoles.

For an ion to carry a magnetic moment, its electrons, each of which have 1 Bohr magneton (μ_B) of spin-magnetic moment, must be arranged such that their magnetic moments do not cancel each other. This excludes all completely filled orbitals, so core electrons do not contribute to magnetism, and also, closed-shell ions are not magnetic. Among valence electrons in partially filled shells, the band energy is optimized when the lowest energy levels are occupied by nonmagnetic pairs of antiparallel electrons. This competes with Hund's magnetic coupling, which favors parallel electrons to optimize the exchange energy. The magnetic state tends to win the competition when the electrons are localized, which in solids occurs for transition metals with partially filled $3d$ shells or lanthanides with partially filled $4f$ shells.

For ferroelectricity, there is a philosophically similar competition (known as the second-order Jahn–Teller effect), although the chemical constraints are entirely different. In this case,

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**For the story behind how I arrived at this question, see Reference 3.*

Nicola A. Spaldin, ETH Zürich, Switzerland; nicola.spaldin@mat.ethz.ch
doi:10.1557/mrs.2017.86

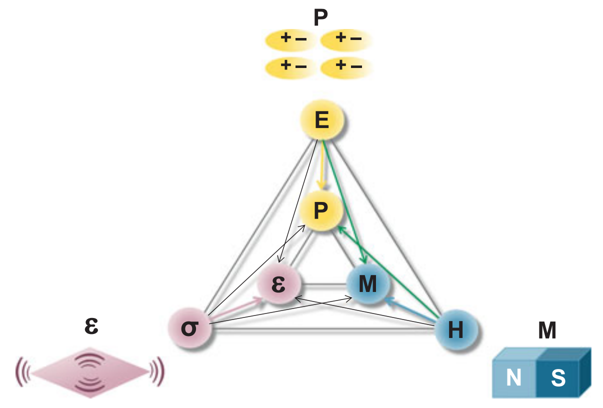

Figure 1. The primary ferroic orders, ferromagnetism (M), ferroelectricity (P), and ferroelasticity (ε); their conjugate magnetic (H), electric (E), and stress (σ) fields; and the cross-couplings between them (black and green arrows).[1]

covalent bonds between neighboring cations and anions provide the stabilizing mechanism for the oppositely charged ions to shift toward each other and form a local dipole. Competing with this bond formation that favors ferroelectricity is the repulsive overlap of the electron clouds as the ions approach; this tends to push the ions apart, back to a nonpolar arrangement.

Many ferroelectric materials are transition-metal oxides, and for this particular chemistry, the ferroelectric state is favored when the transition-metal cations have empty *d* orbitals. Oxygen ions can form stable dative bonds with such "d^0" cations, whose Coulomb repulsion with the oxygen electrons is small (for a detailed analysis, see Reference 4). Therefore, "d^0-ness" favors ferroelectricity, but it is in direct contraindication with the partially filled *d* shells that favor magnetism.

Some history

This contraindication between ferromagnetism and ferroelectricity has frustrated attempts to develop materials with a strong magnetoelectric response for more than half of a century. The first mention of the magnetoelectric effect was made in 1958 in the classic book *Electrodynamics of Continuous Media* by Landau and Lifshitz,[5] which states, "Let us point out two more phenomena, which, in principle, could exist. One is piezomagnetism. The other is a linear coupling between magnetic and electric fields in a media, which would cause, for example, a magnetization proportional to an electric field." The authors continue, "We will not discuss these phenomena in more detail because it seems that till present, presumably, they have not been observed in any substance."[5] Soon after this rather discouraging statement, the magnetoelectric effect was demonstrated in Cr$_2$O$_3$, first theoretically,[6] then experimentally,[7] and the field of magnetoelectrics was born. While the research community was at first tiny, it was sustained by a series of now-legendary conferences, entitled "Magnetoelectric Interaction Phenomena in Crystals," whose proceedings provide historical insight into the development of this nascent field. A lively account of the excitement and frustrations of those early days is given by one of the pioneers, Hans Schmid, in Reference 8.

The field continued to struggle throughout the 20th century due to a lack of magnetoelectric materials. While magnetoelectric materials are not necessarily multiferroic, all multiferroics are magnetoelectric. As a result, the discovery of high-quality practical multiferroic materials at the start of the 21st century caused a simultaneous explosion in research activity on the magnetoelectric effect.

The first modern multiferroic material: BiFeO$_3$

Our first real success in developing a useful multiferroic material was the perovskite-structured oxide, bismuth ferrite, BiFeO$_3$.[9] The perovskite structure contains two different cations: a large one on the so-called A site, and a smaller one, often a transition metal, on the B site. The B site is octahedrally coordinated by anions, in this case, oxygen. Our idea was to use a magnetic transition-metal cation on the B site, which we knew would not be the driver for ferroelectricity, and introduce ferroelectricity using the A site.

Fe^{3+} is a particularly good choice for the magnetic cation, since it has five 3*d* electrons, each of which occupies its own *d* orbital and aligns parallel to the others, giving the largest possible spin moment of $5\mu_B$. Bi^{3+} has a stereochemically active lone pair of electrons, that is, its $6s^2$ valence electrons localize and generate a polar structural distortion around the A site. This is illustrated in the calculated electron localization function shown in **Figure 2**a.[10] Here, the black spheres are the Bi ions, and the yellow "umbrella shapes" are the lone pairs

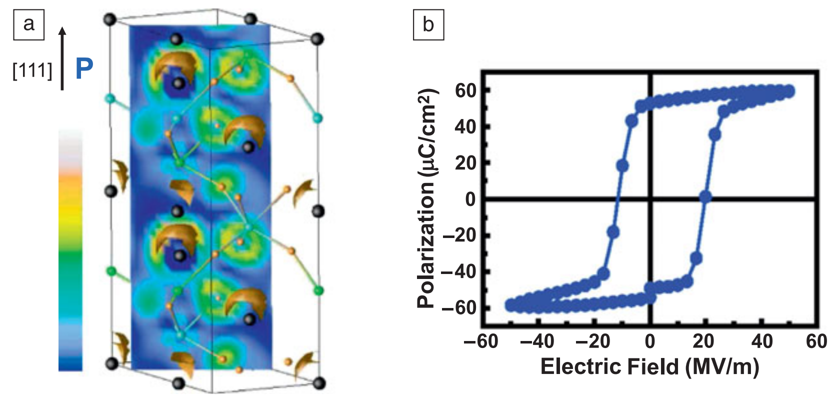

Figure 2. (a) Electron localization function calculated for ferroelectric BiFeO$_3$ within the local spin-density approximation using the Stuttgart tight-binding linear muffin tin orbital (TB-LMTO) density functional theory code.[10] The color scale runs from highly localized (white) to completely delocalized (dark blue). The yellow umbrella-shaped lobes are regions of high electron localization associated with the lone pairs of electrons on the Bi ions (black spheres). **P** indicates the ferroelectric polarization, Fe and O atoms are shown in green and yellow, respectively. (b) The first measurement of ferroelectric polarization as a function of applied electric field on BiFeO$_3$ thin films.[9]

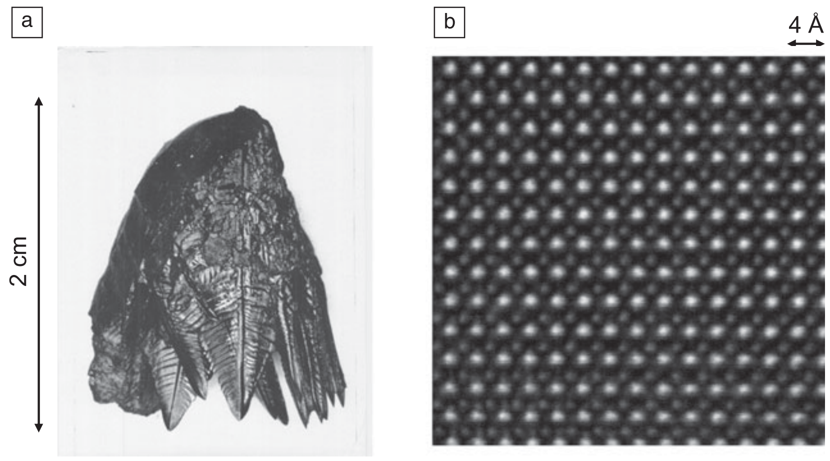

Figure 3. (a) A “fern-like” crystal of bismuth ferrite containing many twin boundaries and defects. The length of the crystal is ~2 cm. Image courtesy of Hans Schmid and Cristobal Tabares-Muñoz. (b) High-resolution transmission electron microscope image of a $BiFeO_3$ thin film. The white dots indicate the columns of Bi atoms, which are spaced ~4 Å apart. Image courtesy of Marta Rossell, Swiss Federal Laboratories for Materials Testing and Research.

oriented along the [111] direction, which is therefore the direction of the ferroelectric polarization.

Ramesh grew the first thin films of bismuth ferrite, then measured its ferroelectric polarization and found that it was indeed ferroelectric with a polarization remarkably close to our calculated value.[9] Figure 2b shows the polarization as a function of electric field measured on that first sample, and we see a ferroelectric hysteresis loop with a saturation polarization of 60 $\mu C/cm^2$ along the out-of-plane cartesian axis. This corresponds to a large value of ~90 $\mu C/cm^2$ along the [111] direction, which at the time was the largest known ferroelectric polarization. There is a downside to bismuth ferrite though. The magnetic moments on the Fe ions actually align antiferromagnetically because of their strong superexchange interactions via the oxygen ions. Ideally, we would like to have made a ferromagnetic ferroelectric material. If one looks closely, however, the magnetic moments cant slightly, giving a very small net magnetization (known as weak ferromagnetism).

It should be noted that this progress was made possible not only by the developments in materials theory from which we understood where to start looking for new multiferroics, but also by massive improvements in materials synthesis methods. Perovskite-structured bismuth ferrite existed before our studies. **Figure 3**a shows a polycrystal grown from a $B_2O_3/Bi_2O_3/Fe_2O_3$ flux in the 1980s by the Schmid group.[11] It is an extraordinarily beautiful sample with its exquisite fern-like texture due to crystallographic twinning. However, it is not a good sample for measuring ferroelectric behavior because the twins clamp the ferroelectric domains, preventing them from switching, and the fern dendrites are conductive. In addition, $BiFeO_3$ is a wide-bandgap insulator, which should be colorless, so the black color indicates the presence of impurities. These could be Fe_3O_4, which is a decomposition product, or other competing phases.[11]

In contrast, Ramesh’s 21st century $BiFeO_3$ films are essentially perfect. Figure 3b shows a high-angle annular dark-field image of such a film, grown using pulsed laser deposition, with the large white spots indicating columns of Bi ions and the small white dots showing the Fe ions. Such improvements in growth methods were required in order for multiferroics to become a viable research field.

Electric-field control of magnetism in $BiFeO_3$

The holy grail of multiferroics research, at least from an applications point of view, is the ability to control—or even ultimately

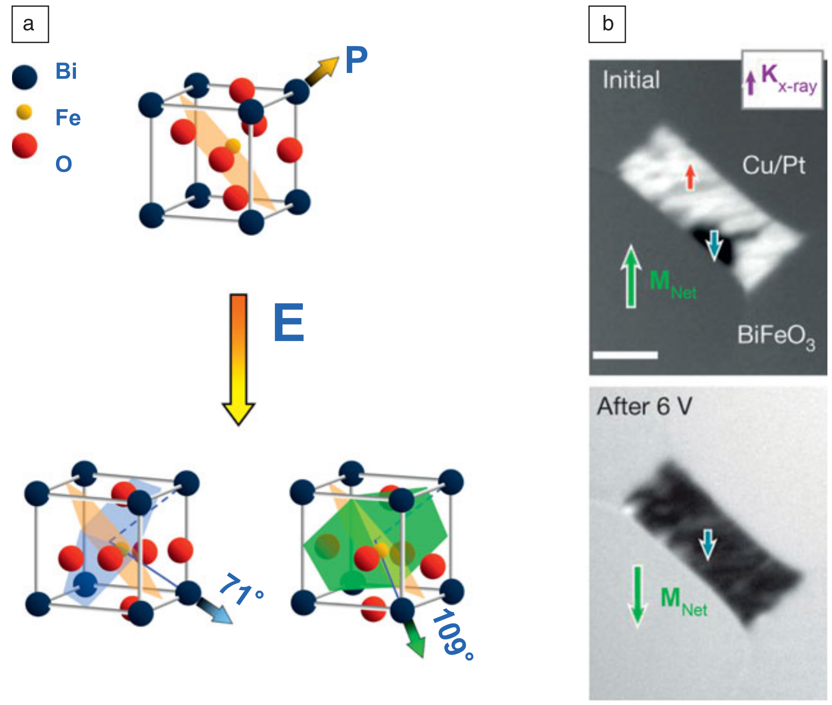

Figure 4. (a) Reorientation of the ferroelectric polarization, **P**, in $BiFeO_3$ by 71° or 109° from one [111] direction to another using an electric field, **E**, results in reorientation of the perpendicular antiferromagnetic easy plane (orange to blue or orange to green).[12] (b) A film of ferromagnetic CoFe deposited on top of $BiFeO_3$ reorients its magnetism when an electric field switches the ferroelectricity in the $BiFeO_3$. The orientation of the magnetism, $\mathbf{M}_{net}$, is measured using x-ray magnetic circular dichroism photoemission electron microscopy. $\mathbf{K}_{x\text{-ray}}$ indicates the direction of the in-plane component of the incident x-ray beam, and the red and blue arrows indicate magnetization parallel or antiparallel to $\mathbf{K}_{x\text{-ray}}$. Scale bar = 2 µm. Reprinted with permission from Reference 14. © 2014 Macmillan Publishers Ltd.

switch—the magnetism with an electric field. In spite of the fact that $BiFeO_3$ is overall antiferromagnetic, such control has been demonstrated, first through reorientation of the magnetic easy axis by reorienting the ferroelectric polarization,[12] and second by exchange-bias coupling the antiferromagnetism in $BiFeO_3$ to an additional ferromagnetic layer.[13,14] The first demonstration relied on the elastic coupling of both properties to the crystallographic structure (see **Figure 4**a).[12] Rotating the ferroelectric polarization by 180° had no effect on the elastic distortion or the orientation of the magnetization. However, polarization rotations of 71° and 109° reoriented the magnetic easy plane and hence switched the antiferromagnetic domains. The Ramesh group subsequently demonstrated electric-field switching of an exchange-bias coupled CoFe layer, illustrated in Figure 4b.[14]

Tabletop cosmology and high-energy physics

In addition to the obvious potential applications in information technology and devices, multiferroics are also useful in areas that we had not even dreamed about in the beginning. One area that has been particularly exciting is an application in cosmology. We used multiferroic yttrium manganite, $YMnO_3$, to test theories of early universe behavior. **Figure 5**a shows a schematic of the high- and low-symmetry crystal structures of $YMnO_3$, and a piezoforce microscope image of the highly unusual ferroelectric domain structure that forms during the phase transition between them (Figure 5b). The black and white regions correspond to opposite directions of ferroelectric polarization, which always intersect at meeting points with six alternating domains. Since this is a cross section, the intersection is actually a one-dimensional line or "string." This unusual domain structure is a consequence of the so-called improper geometric ferroelectricity of $YMnO_3$,[15] which is compatible with the coexistence of magnetism, and therefore allows the multiferroic behavior.

Detailed analysis of the ferroelectric phase transition[16] shows that it is described by the same "Mexican-hat" potential energy surface (Figure 5a) as that proposed for the formation of cosmic strings in the early universe. As a result, we were able to use quenching experiments across the ferroelectric phase transition to answer questions about the nature of cosmic string formation that are, of course, not directly answerable in the laboratory.[17]

A second "crossover" application is the use of multiferroic materials in the search for the electric-dipole moment of the electron, which is an indicator of time-reversal, and therefore, of charge-parity (CP) symmetry violation. Fundamental theories, such as supersymmetry, incorporate CP violation in different ways. Each predicts different values for the electron-electric-dipole moment, which can be used to test the models. In the standard model, the predicted value of the electron-electric-dipole moment is tiny and many orders of magnitude below the present experimental limits. Since an electron's electric-dipole moment would, by symmetry, lie parallel or antiparallel to its spin axis, the electron is an ideal multiferroic, with its magnetic and electric dipoles intimately coupled. This property allows one to search for the electric-dipole moment by measuring the magnetization imbalance induced in an ensemble of electrons by an electric field. Multiferroic (Eu, Ba)TiO_3, designed especially for such a search,[18] has enabled the highest precision solid-state search to date.[19]

What next?

With the specter of information technology consuming a majority of the world's energy supply within a few decades, the search for new materials that enable entirely new device paradigms is becoming urgent. Here, multiferroics, with their multiple competing and cooperating functionalities, are of tremendous interest. Exotic behaviors such as the angstrom-scale conducting channels that have been discovered at multiferroic domain walls[20] could form the basis for new storage or processing

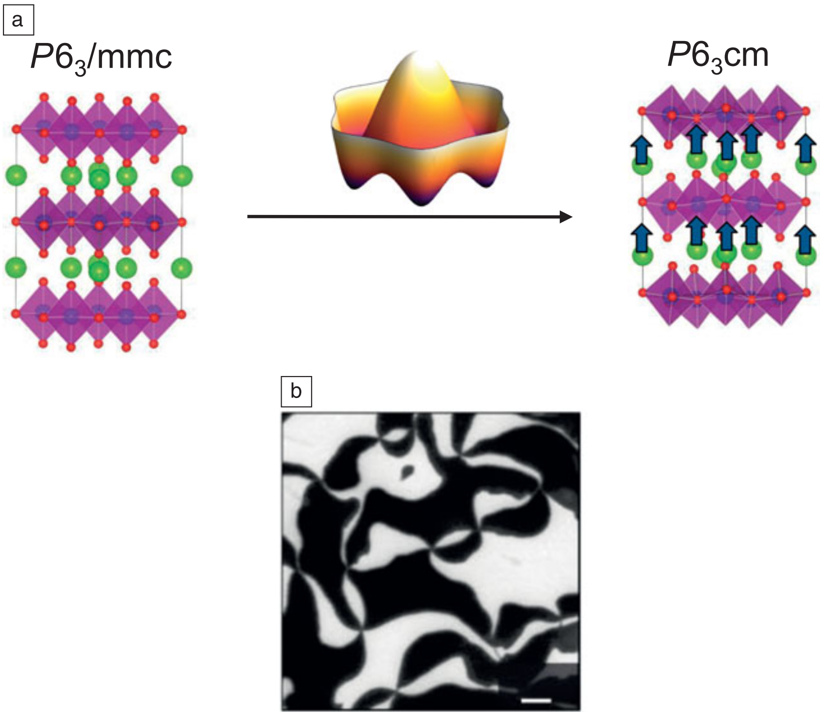

Figure 5. (a) Crystal structure of multiferroic $YMnO_3$ in its (left) high-temperature paraelectric and (right) low-temperature ferroelectric phases. The Y, Mn, and O atoms are shown in green, purple, and red, respectively, with the trigonal bipyramids shaded in purple. The blue arrows show the net displacements of the Y ions that lead to the ferroelectric polarization. The transition between the para- and ferroelectric phases is described by a similar Mexican-hat potential (inset) to that proposed for early universe phase transitions. (b) Ferroelectric domain structure of $YMnO_3$ measured using piezoforce microscopy.[17] The lines of intersection between the six alternating domains provide laboratory analogues to cosmic strings. Scale marker = 4 μm.

architectures. Likewise, related magnetic textures such as skyrmions[21] and magnetic monopoles[22] might provide new paradigms for storing or manipulating information that are far more energy efficient than existing technologies. The multiple hierarchical ground states of multiferroics capture some of the complexity of the human brain, suggesting promise in neuromorphic computing. In a different direction, the possibility of magnetic-field control of electrical properties is being explored for *in vivo* medical applications, since it offers the possibility of remote actuation via external magnetic fields, thereby circumventing the need for *in vivo* electrodes.

At the fundamental level, research on multiferroics sometimes feels like peeling an onion, with each new layer of understanding generating a host of new interesting questions. Among the many new directions are the description of multiferroic ordering in terms of magnetoelectric multipoles, such as the toroidal moment,[23] and the addition of a fourth axis to expand the "multiferroic triangle" of Figure 1 to a tetrahedron with the chemical potential as an additional conjugate field.[24] In the latter context, as the size of devices approaches the diffusion length of point defects, such as oxygen vacancies, at ambient temperatures, the interplay between the defect chemistry and the conventional ferroic orders becomes increasingly relevant. Exploration of the relevance of multiferroicity for exotic superconductivity[25,26] is also intriguing.

Summary

It is hoped that this article conveys some of the excitement from being involved in this vast playground of multiferroics from the very beginning. This article is based on a conference talk, and it necessarily overemphasizes my own contributions and is far from being a comprehensive review; for a broader overview, the reader is directed to References 27–31.

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Nicola A. Spaldin is the Professor of Materials Theory at ETH Zürich, Switzerland. She obtained her PhD degree in chemistry at the University of California, Berkeley. She was a postdoctoral researcher in applied physics at Yale University. She then joined the Materials Department at the University of California, Santa Barbara. Her research focuses on the development of magnetoelectric multiferroics, and exploring their applications in areas ranging from device physics to cosmology. Spaldin can be reached by phone at +41 (0)44 633 37 55 or by email at nicola.spaldin@mat.ethz.ch.


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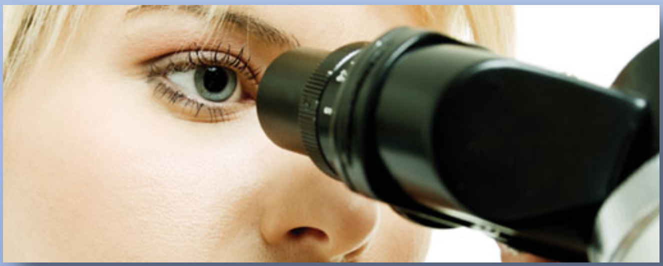

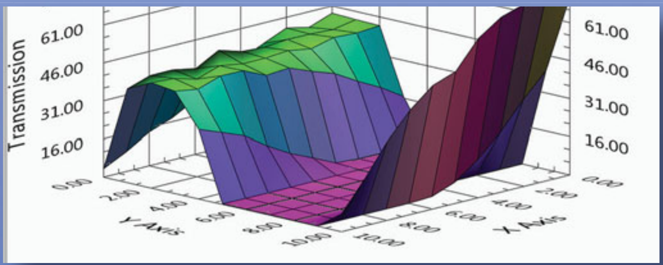
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