How a Multiferroic Stopped Being Ferroic and Became Glassy

Multiferroic materials could make vastly better information storage devices than the ones we currently use. A hard drive made from a multiferroic could be written on using electricity, with less energy and a more stable structure that wouldn't degrade from random accidents or stray magnetic fields. Such a hard drive could use four-state logic; each bit could be a 0 or 1 in two different ways; up or down electric polarization and up or down magnetically. This would allow much more information to be written on much smaller devices. But multiferroic materials are not well understood, and the best ones work only at inconveniently low temperatures. Researchers used the APS to explain why one such multiferroic, erbium manganese oxide, undergoes a phase transition from ferroic (magnetic) to glassy, and what this might mean for other multiferroic materials.

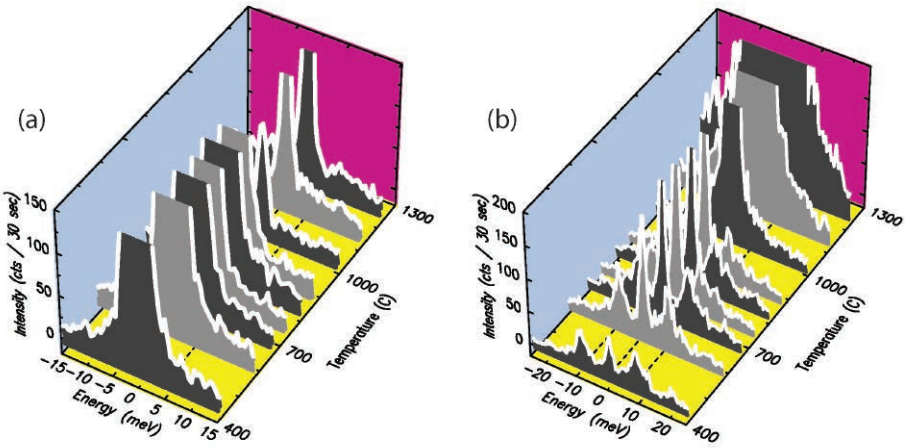

Fig. 1. Quasi-elastic scattered x-rays show a large peak in intensity at temperatures below about 880° C [middle peak in both (a) and (b)], suggesting the material is frozen in a glassy state.

Electricity and magnetism are linked; a stream of moving electrical charges—a current—creates a magnetic field. Conversely, a moving magnet can induce an electrical current. But some special materials such as iron, nickel and cobalt have their own permanent magnet moment, even without an electrical current running through them. We call them ferromagnets. Refrigerator magnets are ferromagnets, and they're also found in electrical generators, loudspeakers and transformers. There are also materials that have an intrinsic electrical field. These are called ferroelectrics. Then there are some materials, called multiferroics, that have both a magnetic moment and an intrinsic electrical field; most usefully, these two qualities are linked. If we learn how to reliably manipulate one, we can use it to change the other. And if we learn how and why these materials' unusual atomic structures lead to their multiferroic properties, we can potentially design better multiferroics that are more amenable to commercialization.

Erbium manganese oxide develops ferroelectricity at temperatures less than 1195° C. The ferroelectricity strengthens with a promising fast pace as temperature decreases. Then, the ferroelectricity suddenly degrades at ~800° and does not recover. Over decades, the exact reason for the degradation has been the subject of numerous studies. A team of researchers from Argonne, the Rochester Institute of Technology, and Rutgers University suspected a shift in the material's local symmetry—how the atoms are arranged—might be the reason for the change. The team used three different x-ray techniques to illuminate erbium manganese oxide's structural shifts between 20° and 1300° C. They found something very surprising: at lower temperatures, erbium manganese oxide behaved more like a glass than a crystalline solid (the vast majority of metals are crystalline). The manganese atoms each combined with three oxygen atoms to make little pyramid-like structures, and these pyramids were shifted around in a disordered way. When their positions were averaged the pyramids looked as if they were arranged in an orderly way, but this was an illusion. Each individual pyramid was a little off from where it should have been, as if a band of rampaging nano-children had run through and randomly kicked each pyramid out of place in a different direction. But at high temperatures, the material shaped right up.

"Ferroic" cont'd. on page 40

"Europium" cont'd. from page 38
needed to measure the magnetic properties of the element across a range of pressures. They used synchrotron Mössbauer spectroscopy and x-ray emission spectroscopy—and a diamond anvil cell to provide pressure in both cases—to watch the evolution of the magnetic properties of europium as the pressure increased high enough to induce superconductivity. The synchrotron Mössbauer spectroscopy was performed during five experimental runs at the XSD 3-ID-B,C,D beamline at the APS; the team used the high-brightness x-rays to probe the M1 nuclear transition 7/2 -> 5/2 in ^{151}Eu. The x-ray emission spectroscopy was performed at the HP-CAT 16-ID-D beamline at the APS; the team monitored the nonresonant Eu Lγ1 line for changes that would indicate the presence of *f-d* hybridization.

The team found that the onset of superconductivity occurred above 80 GPa and coincided with the disappearance of magnetic order. Figure 1 shows the change from the magnetic phase (below approximately 80 GPa) to the superconducting phase (above approximately 80 GPa). As the pressure increased, so did the magnetic hyperfine field, until approximately 80 GPa was reached. However, strong local magnetic moments persisted near the Eu cations after the onset of superconductivity. The team found no change in the $L\gamma_1$ spectral line of europium, meaning that the 4*f* magnetic state stayed intact with no measurable increase in *f-d* hybridized orbital shells.

The team concluded that magnetic fluctuations may play a role in europium's superconductivity because the effect of magnetic fluctuations on Cooper pairing has been shown to occur in other 4*f* heavy fermion materials where superconductivity occurs near a quantum critical phase transition, as was shown in these results for europium. *— Mary Alexandra Agner*

See: W. Bi[1,2,*], J. Lim[3,4], G. Fabbris[1,3,5], J. Zhao[1], D. Haskel[1], E.E. Alp[1], M.Y. Hu[1], P. Chow[6], Y. Xiao[6], W. Xu[7], and J.S. Schilling[3], "Magnetism of europium under extreme pressures," Phys. Rev. B **93**, 184424 (2016).
DOI: 10.1103/PhysRevB.93.184424
Author affiliations: [1]Argonne National Laboratory, [2]University of Illinois at Urbana-Champaign, [3]Washington University in St. Louis, [4]Washington State University, [5]National Laboratory, [6]Carnegie Institution of Washington, [7]Chinese Academy of Sciences,
Correspondence: * wbi@aps.anl.gov

Support by Consortium for Materials Properties Research in Earth Sciences (COMPRES), the National Science Foundation (NSF) through Grant No. DMR- 1104742, and by the Carnegie/Department of Energy (DOE) Alliance Center (CDAC) through the National Nuclear Security Administration(NNSA)/Department of Energy (DOE) Grant No. DEFC52- 08NA28554 is gratefully acknowledged. HP-CAT operations are supported by the DOE-NNSA under Award No. DE-NA0001974, with partial instrumentation funding by the NSF. This research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

3-ID-B,C,D • XSD • Physics, geoscience, life sciences, chemistry, materials science • Nuclear resonant scattering, inelastic x-ray scattering, high-pressure diamond anvil cell • 7-27 keV, 14.41-14.42 keV • On-site • Accepting general users •

16-ID-D • HP-CAT • Materials science, geoscience, chemistry, physics • Nuclear resonant scattering, inelastic x-ray scattering (1-eV resolution), x-ray emission spectroscopy, high-pressure diamond anvil cell • 5-37 keV, 14.41-14.42 keV • On-site Accepting general users •

"Ferroic" cont'd. from page 39

Because the structure was complicated and the difference subtle, the researchers used three different techniques at three different beam lines to figure it out. They used XSD beamline 11-ID-D to perform high-resolution x-ray diffraction to measure the lattice constants—the size of repeating units of atoms in the material—very precisely. At a separate XSD beamline, 3-ID-B,C,D, there is equipment that can resolve the energy of quasi-elastic scattered x-rays. These are x-rays scattered by atomic vibrations. This showed the team that the atoms in the erbium manganese oxide were shifted and frozen somewhat randomly in space, not in a perfectly ordered lattice (Fig. 1). At XSD beamline 8-ID-E, the team used x-ray speckles to measure the atoms' movement over time. They found the atomic shifts were frozen over time. APS is one of only three synchrotrons in the world that can do all three of these measurements. Its brilliance is especially valuable, making the x-ray speckle measurement possible.

Erbium manganese oxide's glassy behavior at low temperatures is undesirable. It disrupts the useful ferroelectricity and magnetism of the material. Now that they know the structure, materials scientists may be able to re-design the material to decrease the glassy behavior by adding in additional elements, or substituting the existing elements with something different that is less likely to shift in this disordered way. *— Kim Krieger*

See: A. Barbour[1*‡], A. Alatas[1], Y. Liu[1], C. Zhu[1], B.M. Leu[1], X. Zhang[1], A. Sandy[1], M. S. Pierce[2], X. Wang[3], S.-W. Cheong[3], and H. You[1*], "Partial glass isosymmetry transition in multiferroic hexagonal $ErMnO_3$," Phys. Rev. B **93** (5), 054113 (2016). DOI: 10.1103/PhysRevB.93.054113
Author affiliations: [1]Argonne National Laboratory, [2]Rochester Institute of Technology, [3]Rutgers University ‡Present address: Brookhaven National Laboratory
Correspondence: * hyou@anl.gov

The work of A.B., C.Z., and H.Y. at the Argonne Materials Science Division was supported by the U.S. Department of Energy (DOE)-Basic Energy Sciences (BES), Materials Sciences and Engineering Division (MSED), and the work of A.A., B.L., A.S., and X.Z. at the APS by the DOE-BES Scientific User Facilities Division under Contract No.DE-AC02-06CH11357. This research used resources of the Advanced Photon Source, a U.S. DOE Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357.

3-ID-B,C,D • XSD • Physics, geoscience, life sciences, chemistry, materials science • Nuclear resonant scattering, inelastic x-ray scattering, high-pressure diamond anvil cell • 7-27 keV, 14.41-14.42 keV • On-site • Accepting general users •

8-ID-E • XSD • Materials science, polymer science, physics • Grazing incidence small-angle scattering, x-ray photon correlation spectroscopy • 7.35-7.35 keV • On-site • Accepting general users •