LOCAL PROBING OF FERROIC AND MULTIFERROIC COMPOUNDS

INTC MEETING, CERN, CH, 2017
The collaboration


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Institute for Materials Science and Center for Nanointegration, Essen, Germany

Department of Physics and CICECO, Univ. Aveiro, Portugal

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CNR-SPIN L’Aquila, Italy

Department Chemistry, Vila Real, Portugal

Institute of Solid State Physics and Chemistry, Uzhgorod Univ, Ukraine
The collaboration

Ferroic & Multiferroic systems
Multiferroic system

Systems exhibiting simultaneously ferroelastic, ferroelectric and ferromagnetic orders

Possibility to manipulate the magnetic degrees of freedom electrically or vice-versa.

Path to faster, smaller, and more energy-efficient spintronic devices (e.g. memory elements, high-frequency magnetic devices, and systems for data-storage technologies)

But only a few multiferroic materials exist as a concomitant breaking of space-and time-inversion symmetries is necessary.
Proper Ferroelectrics:

\[ \text{BiFeO}_3 \text{ and BiMnO}_3 - \text{Ordering of the 6s}^2 \text{ lone pairs of Bi}^{3+} \]
\[ \text{(TFE} \sim 1100\text{K, TN} = 643\text{ K, P} \sim 90\mu\text{C/cm}^2) \]

Ferroelectricity and magnetism have different sources.
High FE order temperature and polarization / Low ME coupling

Improper Ferroelectrics:

\[ \text{TbMnO}_3 \text{ and LuMnO}_3 - \text{Mn magnetic order} \]
\[ \text{(TFE} = \text{TN} \sim 28\text{ K, P} \sim 0.06\mu\text{C/cm}^2) \]

Ferroelectricity and magnetism have the same source.
Low FM and FE order temperature and polarization/ High ME coupling

Hybrid improper Ferroelectrics

\[ \text{Ca}_3\text{Ti}_2\text{O}_7 \text{ and Ca}_3\text{Mn}_2\text{O}_7 \]
\[ \text{(TFE} \sim 1100^\circ\text{K and 280 K, P} \sim 1\mu\text{C/cm}2) \]

Ferroelectricity is drive by a the coupling of two non polar modes.
High FE order temperature/High ME coupling
1 - In most cases the **Microscopic Mechanisms** controlling the magnetoelectric coupling are unknown

2 - The strong coupling among degrees of freedom offers a fertile playground of fundamental physics to be searched

3 - In many cases the systems are claimed to be multiferroic but experimental proof are inexistent since:

   - high electric leakage currents might lead to unrepresentative features of the intrinsic material properties
   - properties arising from local structural features that are not well described by a crystallographic approach based on long-range average models

4 - The correct symmetries of the ferroelectric phases are sometimes unknown

Thus, **complementary local scale information is necessary** to: Provide local and element selective information on the mechanisms that rule structural, charge, and orbital correlations, electronic and magnetic interactions.
Our previous achievements in multiferroic using PAC
EFG sensitive to atomic vibrations and critical fluctuations.
Expanding $V_{zz}$ in powers of ionic charge displacements

$$V_{zz} = V_{zz}^0 + \alpha P_s^2 + \beta T \chi_{el}$$

A M L Lopes et al. PRL 100, 155702 (2008)
The sensitivity of the EFG to the polarization and the atomic number of the A site in the perovskite structure is seen.

Proposed multiferroics to be studied using PAC
For a consolidated overview we will target:

Proper Ferroelectrics

BiFeO$_3$ and AgNbO$_3$

Improper Ferroelectrics

Lu-Fe-O and LuMnO$_3$

Hybrid Improper Ferroelectrics

Ca$_3$(Mn/Ti)$_2$O$_7$
Proper ferroelectricity: BiFeO$_3$

Ferroelectricity and antiferromagnetism at room temperature

$T_N \sim 370 \degree C$ and $T_C \sim 830 \degree C$

Varying as a function of the particle size

Magnetic properties change considerably when approaching the cycloidal period length

Mössbauer Study of Temperature-Dependent Cycloidal Ordering in BiFeO$_3$ Nanoparticles

J. Landers,$^1$ S. Salamon,$^{*2}$ M. Escobar Castillo,$^3$ D. C. Lupascu,$^2$ and H. Wende$^3$

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$^2$Institute for Materials Science and Center for Nanointegration Duisburg-Essen (CENIDE), University of Duisburg-Essen, 47047 Essen, Germany
Proper ferroelectricity: BiFeO$_3$

Local magnetic structure and its evolution with nanoparticles size

Aim: Bi site probing of local magnetic structure and magneto-electric coupling

Combination of $^{204}$Bi/Pb, $^{111}$In/Cd, $^{111}$mCd/Cd and $^{181}$Hf/Ta

Information source: EFG(T) + B(T)

PAC measurements above and below the magnetic phase transition at ISOLDE using $^{181}$Ta $\gamma-\gamma$ decay from $^{181}$Hf

Critical temperatures of BiFeO$_3$

- 830 °C: Paraelectric to Ferroelectric
- 370 °C: Paramagnetic to Antiferromagnetic
Proper ferroelectricity: AgNbO$_3$

Large polarization at room temperature

Clarification of the anti/ferroelectric phases symmetries

Aim: Ag site probing of structural paraelectric, antiferroelectric and ferroelectric transitions $^{111}$Ag/Cd, crosscheck for electronic relaxation effects upon parent decay $^{111m}$Cd/Cd and $^{111}$In/Cd. Information source: EFG (T) + B (T)
Improper ferroelectricity: Lu-Fe-O systems and LuMnO₃

Ferroelectricity at room temperature

**LuFeO₃** – hexagonal multiferroic with large Lu plane rumpling, with net ferromagnetic moment, and orthorrombic non-polar phases

**LuFe₂O₄** – spin and charge frustration in the Fe lattice due to frustration geometry

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**LETTER**

J. A. Mundy et al., Nature 537, 523 (2016)

doi:10.1038/nature19743

Atomically engineered ferroic layers yield a room-temperature magnetoelectric multiferroic

Julia A. Mundy⁵⁶, Charles M. Brooks⁵⁶, Megan E. Holzer⁶, Jarrett A. Moyer⁵⁶, Hema Das⁵⁶, Alejandro F. Robles⁵⁶, John T. Heron⁵⁶,⁴⁴, James O. Chalker⁵⁶, Steven M. Daines⁵⁶, Ziqing Liu⁵⁶, Alan Farhan⁵⁶, Rainer Hoffmann⁵⁶, Robert Howeder⁵⁶, Elliot Dwight⁵⁶, Gregory Macionalis⁵⁶, Hanjeng Pak⁵⁶, Rajiv Mitra⁵⁶, Lena E. Kourkoutis⁵⁶, Elke Arechigoz⁵⁶, Andreas Schlöter⁵⁶, Julie A. Borchers⁵⁶, William D. Ratcliff⁵⁶, Ramanoothi Ramasubramaniam⁵⁶, Craig J. Fernie⁵⁶, Peter Schiffer⁵⁶, David A. Muller⁵⁶, and Darnell G. Schlom⁵⁶

RT magnetoelectric multiferroic in \((\text{LuFeO}_3)_m/(\text{LuFe}_2\text{O}_4)_n\)

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Giant magneto-elastic coupling results in large atomic displacements as f(T)

**Exploration of self-doped LuMnₓO₃₋₅ with weak ferromagnetic moments.**

**Lu₃Fe₅O₁₂** – magnetodielectric response and **Lu₂Fe₃O₇** – 2D antiferromagnet, charge order
Improper ferroelectricity

Magnetoelectric coupling through the hyperfine parameters

PAC measurement with implanted $^{111m}$Cd

One local environment by the preliminary fit, which corresponds to a $V_{zz}=5.4 \times 10^{-21} \text{ V m}^{-2}$, and $\eta=0.4$.

Aim: Lu site probing of the phase transitions using $^{172}$Lu, $^{111m}$Cd and $^{149}$Gd. Information source: EFG(T) + B(T)

Critical temperatures of LuMnO$_3$

- $727 \degree \text{C}$: Paraelectric to Ferroelectric
- $-183 \degree \text{C}$: Antiferromagnetic
Hybrid improper ferroelectricity

Tri-linear coupling of two non-polar lattice distortion modes
Octahedral rotation/tilting modes with a polar displacement mode

R.P. phase series:
$\text{AO(ABO}_3)_n \ n = \infty, 1, 2$

Breaking of inversion center at the B-site by the AO layers
Hybrid improper ferroelectricity

No direct evidence for spontaneous polarization in Ca$_3$Mn$_2$O$_7$
Symmetry details unknown

PAC measurements at ISOLDE using $^{111m}$Cd

Critical temperatures of Ca$_3$Mn$_2$O$_7$
- $T_m = 386.9^\circ C$, Tetragonal to orthorhombic
- $T_m = 6.9^\circ C$, Structural & HIF
- $T_m = -148.2^\circ C$, Paramagnetic to Antiferromagnetic

Aim: Ca site probing of the phase transition using $^{111m}$Cd and $^{149}$Gd. Information source: EFG(T) + B(T)
Other systems to be studied by PAC:

**CuInP\(_2\)S\(_6\)**

In site probing of paraelectric to ferrielectric phase transition with \(^{111}\text{m} \text{Cd}(48\text{m})/\text{Cd}\) (crosscheck for electronic relaxation effects upon parent decay of \(^{111}\text{In}/\text{Cd} @ \text{In site}\)

Information source: EFG(T)

**ATiO\(_3\), AZrO\(_3\) A = Ba, Pb**

Sensitive probing of spontaneous polarization variations at A site with \(^{111}\text{m} \text{Cd}(48\text{m})/\text{Cd}\) and \(^{204}\text{m} \text{Pb}(67\text{m})/\text{Pb}\).

Information source: EFG(A, T) + B(A, T)

**ANiMnO\(_6\), A = In, Y, Bi, Gd**

Probing A site role on polarization values/switching and short-range magnetic correlations with \(^{111}\text{m} \text{Cd}(48\text{m})\text{Cd}\) and \(^{204}\text{m} \text{Pb}(67\text{m})/\text{Pb}\) (crosscheck for electronic relaxation effects upon parent decay of \(^{111}\text{In}/\text{Cd}\) and \(^{204}\text{Bi}/\text{Pb} @ \text{A site}\) and \(^{149}\text{Gd}(9.3\text{d})/\text{Eu}\)

Information source: EFG(A,T) + B(A,T)
<table>
<thead>
<tr>
<th>ISOLDE Beam</th>
<th>Approximate intensity (ion/μC of p-beam)</th>
<th>Target</th>
<th>Ion source</th>
<th>SHIFTS 1 + 1 years</th>
<th>Machine days per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{111m}$Cd (49m)</td>
<td>$1.10^8$</td>
<td>Molten Sn</td>
<td>Vadis MK5</td>
<td>12+12</td>
<td>4</td>
</tr>
<tr>
<td>$^{111}$Ag (7.45d)</td>
<td>$10^9$</td>
<td>UC2</td>
<td>RILIS</td>
<td>2 + 2</td>
<td>2/3</td>
</tr>
<tr>
<td>$^{149}$Gd (9.3d)</td>
<td>$3.10^9$</td>
<td>Ta foil</td>
<td>Surface ioniser</td>
<td>1 + 1</td>
<td>1/3</td>
</tr>
<tr>
<td>$^{172}$Lu (6.7d)</td>
<td>$2.10^7$</td>
<td>Ta foil</td>
<td>Surface ioniser</td>
<td>2 + 2</td>
<td>2/3</td>
</tr>
<tr>
<td>$^{204m}$Pb (67m)</td>
<td>$5.10^7$</td>
<td>UC2</td>
<td>RILIS</td>
<td>6 + 6</td>
<td>2</td>
</tr>
<tr>
<td>$^{204}$Bi (11.2h)</td>
<td>$1.10^7$</td>
<td>UC2</td>
<td>RILIS</td>
<td>2 + 2</td>
<td>2/3</td>
</tr>
<tr>
<td>TOTAL (two years)=</td>
<td>25 + 25</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>
Deliverables with radioactive nuclear methods (2012-2016)

IS487 - Study of Local Correlations of Magnetic and Multiferroic Compounds

2 Ph. D. in Physics concluded

4 Ph. D. in Physics ongoing

11 Publications (3 Proceedings)

11 Oral Communications in international meetings

13 Posters in international meetings

Collaboration publications with NON - radioactive nuclear methods

+ 60 publications in international scientific journals with referee
THANK YOU!
### Sample production

#### Laboratory

<table>
<thead>
<tr>
<th>Family of samples</th>
<th>Type of samples</th>
<th>CENIDE UDEMAT Essen</th>
<th>CICECO Aveiro</th>
<th>IFIMUP Porto</th>
<th>Uzhgorod Univ.; Vilnius University</th>
<th>Acad. Sciences Czech Republic; Commercial</th>
</tr>
</thead>
<tbody>
<tr>
<td>BiFeO3</td>
<td>Pellets</td>
<td>Solid State Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgNbO3, AgTaO3</td>
<td>Pellets</td>
<td>Czochralski</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuInP2S6</td>
<td>Pellets</td>
<td>Czochralski</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lu(Mn/Fe)O3, LuFe2O4, Lu3Fe5O12</td>
<td>Pellets</td>
<td>Solid State Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ATiO3, AZrO3 A = Ba, Pb</td>
<td>Pellets</td>
<td>Czochralski</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca3(Mn/Ti)2O7, Ca2-xGdx(Mn/Ti)2O7</td>
<td>Pellets</td>
<td>Solid State Reaction</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A NiMnO6 A = In, Y, Bi, Gd</td>
<td>Pellets</td>
<td>Hydrothermal synthesis</td>
<td></td>
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</tr>
</tbody>
</table>
Samples are methodically characterized before and after PAC experiments.

At our home institutes we have at our dispose:

- X-ray powder, high resolution and single crystal diffraction: Aveiro, Essen, Porto
- Scanning Electron Microscopy (SEM) with (EDX): Aveiro, Essen, Porto
- Magneto-electro characterization Magnetic (SQUID, VSM, ac Susceptibility), Dielectric and Electric resistivity measurements (with magnetoresistance): Aveiro, Essen, Porto
- Scanning Probe Microscope (SPM), Atomic-force microscopy (AFM) and Piezoresponse Force Microscopy (PFM) techniques.
- Transmission Electron Microscopy (HRTEM) with temperature variation: Aveiro and Essen
- Rutherford Back Scattering/Channeling (RBS/C) ion beam analysis characterizing surface composition and defects on implanted regions: Lisboa/Sacavém
- Mossbauer spectroscopy: Essen and Porto
Practical information

CPM diagram

170-ISOLDE

- Mounting samples at the sample holder: 15 min
- Pumping the GLM Implantation Chamber: 20 min
- Implantation: 20...40 min
- 2 hours shifted
- Tubular Furnace Annealing Two samples: 10...20 min

508 R-004

508 R-008 3 hours measurement and CPM restart

- TYPE A Sample
- 10K...300K T1
- 300K...1173K T2
- TYPE A Sample
- 6Det PAC 1
- 6Det PAC 4

- TYPE B Sample
- 300K...1173K T2
- 6Det PAC 2
- 6Det PAC 3
- LN2 or 300K
- TYPE C Sample
Images taken From:
S. Lee et al, Nature 451, 805, 2008
J. Hemberger et al, Nature 434, 364, 2005
http://www.lpem.espci.fr/ocg/
<table>
<thead>
<tr>
<th>Isotope</th>
<th>Samples prepared at</th>
<th>Experiments at ISOLDE</th>
<th>Atoms per collection, per sample (10^{11})</th>
<th>Activity (MBq)</th>
<th>Nº of spectra per collection, per sample</th>
<th>Acq. time per spectrum</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{113m}$Cd (49 m)</td>
<td>ISOLDE</td>
<td>$1^{st}$ annealing</td>
<td>$0.3$</td>
<td>$8$</td>
<td>$1$</td>
<td>$3h$</td>
</tr>
<tr>
<td>$^{111}$Cd(stable)</td>
<td></td>
<td>$\gamma-\gamma$ PAC</td>
<td>$T_{1/2} = 85ns, I= 5/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{113}$In (2.8d)</td>
<td>BONIS RUBION</td>
<td>$1^{st}$ annealing</td>
<td>$1$</td>
<td>$0.28$</td>
<td>$15 - 25$</td>
<td>$3h$ $12h^{(*)}$</td>
</tr>
<tr>
<td>$^{111}$Cd(stable)</td>
<td></td>
<td>$\gamma-\gamma$ PAC</td>
<td>$T_{1/2} = 85ns, I= 5/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{111}$Ag (7.45 d)</td>
<td>ISOLDE</td>
<td>$1^{st}$ annealing</td>
<td>$3 - 5$</td>
<td>$0.2 - 0.5$</td>
<td>$5 - 10$</td>
<td>$1d$ $1w^{(*)}$</td>
</tr>
<tr>
<td>$^{111}$Cd(stable)</td>
<td></td>
<td>$\gamma-\gamma$ PAC</td>
<td>$T_{1/2} = 85ns, I= 5/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{140}$Gd (9.3d)</td>
<td>ISOLDE</td>
<td>$1^{st}$ annealing</td>
<td>$1.5 - 2.5^{(***)}$</td>
<td>$0.1 - 0.2$</td>
<td>$\sim 5$</td>
<td>$2d$ $1w^{(\star \star \star)}$</td>
</tr>
<tr>
<td>$^{149}$Eu(93.1d)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$^{172}$Lu (6.7d)</td>
<td>ISOLDE</td>
<td>$1^{st}$ annealing</td>
<td>$2 - 5$</td>
<td>$0.2 - 0.6$</td>
<td>$5 - 10$</td>
<td>$1d$ $1w^{(*)}$</td>
</tr>
<tr>
<td>$^{172}$Yb(stable)</td>
<td></td>
<td>$\gamma-\gamma$ PAC</td>
<td>$T_{1/2} = 2450ns, I= 11/2$</td>
<td></td>
<td></td>
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<tr>
<td>$^{180}$Hf (42d)</td>
<td>BONIS RUBION</td>
<td>$1^{st}$ annealing</td>
<td>$5$</td>
<td>$0.1$</td>
<td>$20 - 30$</td>
<td>$12h - 5d^{(*)}$</td>
</tr>
<tr>
<td>$^{181}$Ta(stable)</td>
<td></td>
<td>$\gamma-\gamma$ PAC</td>
<td>$T_{1/2} = 10.8ns, I= 5/2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^{204m}$Pb (67m)</td>
<td>ISOLDE</td>
<td>$1^{st}$ annealing</td>
<td>$0.15^{(***)}$</td>
<td>$2.6$</td>
<td>$1$</td>
<td>$4h$</td>
</tr>
<tr>
<td>$^{204}$Pb(stable)</td>
<td></td>
<td>$\gamma-\gamma$ PAC</td>
<td>$T_{1/2} = 265ns, I= 4$</td>
<td></td>
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<td></td>
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<tr>
<td>$^{208}$Bi (11.2h)</td>
<td>ISOLDE</td>
<td>$1^{st}$ annealing</td>
<td>$1^{(***)}$</td>
<td>$1.7$</td>
<td>$2 - 5$</td>
<td>$3-6$</td>
</tr>
<tr>
<td>$^{204}$Pb(stable)</td>
<td></td>
<td>$\gamma-\gamma$ PAC</td>
<td>$T_{1/2} = 265ns, I= 4$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Magneto-Electric Clusters

Cr$^{3+}$ dynamic off-centering leading to Magneto-electric Clusters

Combined PAC, PDF and M(T) analysis → dynamic state caused by the presence of simultaneous polar and magnetic nanoclusters

G. N. P. Oliveira et al. PRB 86, 224418 (2012)
Local distortions in multiferroic AgCrO$_2$ triangular spin lattice

Still above TN, part of the system loses the local rhombohedral symmetry

Coupling between the elastic and magnetic degrees of freedom provides a channel for magnetic frustration release through a lattice distortion

A M L Lopes et al. PRB 84, 014434 (2011)