EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Letter of Intent to the ISOLDE and Neutron Time-of-Flight Committee

MULTIPAC-Setup for γ–γ Perturbed Angular Correlation Experiments in Multiferroic (and Magnetic) Materials

January 8th 2020

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CERN-INTC-2020-011 / INTC-I-212
08/01/2020

Abstract

Multiferroics are solid state materials that exhibit multiple ordering phenomena, which may be magnetic, ferroelectric, mechanical, torsional or coupled forms thereof. Among the strain driven phase transitions, not all will lead to a polar (potentially ferroelectric) state. But grossly all ferroelectrics show some mechanical ordering. These materials are multiferroics as mechanical and electric ordering can be decoupled or not. A more challenging type of multiferroics are those materials that exhibit magnetic as well as ferroelectric ordering in the same crystal. These are often referred to as the (real) multiferroic materials. Many times and in particular at moderate temperatures, both ordering phenomena are de-coupled. At certain lower temperatures a mutual coupling arises due to further ordering phenomena at the atomic scale. Often these ordering phenomena can be detected in structural synchrotron XRD or neutron diffraction. But certain transitions are not well reflected in experiments bound to periodic structures and are of second order, so not detectable in a thermal test. Thus, a local assessment like Mössbauer spectroscopy [0] or perturbed angular correlation (PAC) spectroscopy becomes essential. Furthermore, in most multiferroics the interaction of the relevant ordering parameter with point defects is practically unknown.

This letter asks for space in the ISOLDE hall to install a cryogenic magnetic system that simultaneously allows to measure magnetic as well as ferroelectric properties concurrent with local probe experiments using PAC-isotopes. On the long run (or in certain shifts), the very same set-up can serve for the investigation of purely magnetic materials of all types. A multitude of questions regarding defects and local order parameter coupling are open and become accessible through this set-up singular in the world. It permits to expand the constraint of Mössbauer-experiments (essentially two possible isotopes) to the broader range of suitable PAC probes.

Requested shifts: No shifts required this time

Introduction

Polar order in a crystal relies on the displacement of atoms in a crystal or on the directional ordering of existing electric dipoles. It is thus a structural phase transition that is typically also visible in structural experiments like X-ray diffraction (XRD), in particular in the case of synchrotron experiments where sufficiently high resolution is available. In order for the atoms to be locally mobile and thus providing potential polar order in an ionic solid, their effective radius must be small enough to permit their shift in a crystallographic unit cell. Other mechanisms may also involve the ordering of lone pair electrons for the heavier elements like lead or bismuth. In all cases more or less spherical ions are involved and their mutual attractive forces are of purely coulombic character.

Magnetic ordering, on the other hand, relies on the coupling of outreaching only partly filled electronic shells like d- or f-orbitals. At the onset of magnetic ordering, these outreaching orbitals couple via their spins generating geometrically well-defined doubly occupied orbitals. Concurrently, the mechanical coupling within the sub-lattice also increases, typically interfering with polar order. Most magnetic systems do not permit their magnetically ordered atoms to displace within the unit cell and ferroelectricity is suppressed. For a while people even considered them to be mutually exclusive.

Two options exist for these systems to develop both ordering parameters. Either they reside on different sub-lattices, like it is the case in e.g. $BiFeO_3$, or more complex ordering sets in, which is the case in e.g. rare earth manganates.

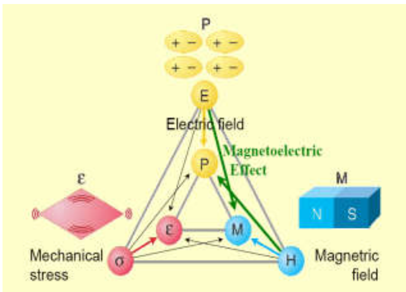

Figure 1: Ferroic ordering phenomena and their coupling scheme (N.A. Spaldin & M. Fiebig, Science 2005).

The long term goal of research that is aimed at at ISOLDE is to use the nuclear γγ-PAC-probes to unravel the influence of point defects on the magnetic as well as polar orders in multiferroic systems. The local ordering phenomena are magnificently manifold. Spin cycloids ($BiFeO_3$ [0,7]), toroidal ordering ($LiCoPO_4$ [8]), local spin loops (Rare earth manganates [9]), skyrmions (Cu_2OSeO_3 [10] and others) exist. Most systems show or are expected to show (with still open experimental proof) coupling between electric and magnetic ordering phenomena. Unraveling only some of these coupling phenomena locally offers an enormous wealth in physics to be dealt with.

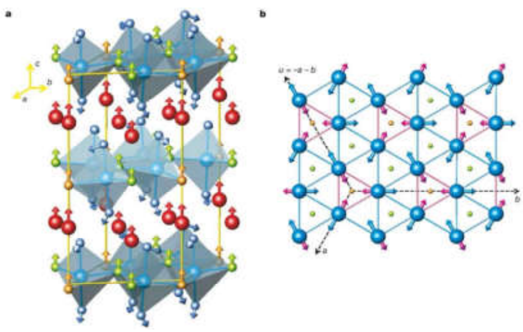

Figure 2: Example of the complexity of local spin ordering
("Model showing how Mn atoms (large blue circles) move below TN with respect to O3 (small orange circles) for YMnO3 (blue arrows) and LuMnO3 (purple arrows). The small green circles represent O_4." [9]).

MULTIPAC-Setup at ISOLDE-CERN

As the measurement challenges are higher for multiferroics, this setup is designed to serve both solid state systems in one setup rendering it more versatile for a single invest. In multiferroics combined electrical and magnetic ordering occurs and magnetoelectric coupling is possible. One of the technological drawbacks is the fact that this ordering typically occurs at low temperatures (between 10 K and ca. 150 K). A few systems show two ferroic orders also at room temperature, but magnetic ordering is antiferromagnetic, so magnetoelectric coupling vanishes. One of the ways to alter these structures is doping or alloying.

We offer a cryo-setup (as shown in figure 2) to the ISOLDE Solid State Physics community permitting to go to 10 Tesla magnetic fields and measure perturbed γ–γ angular correlations [4,5]. Alongside, high voltage wiring to the sample will permit to apply electric fields and tune the multiferroic structures electrically. Local structures on the scale of the unit cell and doping of intrinsic multiferroics will subsequently be accessible. The general goal is to offer the solid-state physics community the opportunity to use a unique setup for understanding how multiferroic ordering will be reflected in γ–γ perturbed angular correlation spectra and how doping (among others by the probe isotope itself and its same chemical species or other species added intentionally) will alter the magnetic and electric structures of the materials as well as the defect structures.

The proposal is part of the Consortial Project "Ecomarl" comprising the groups of Prof. Hans Hofsäss from University Göttingen, Prof. Peter Schaaf from TU-Ilmenau and Prof. Doru Lupascu from University of Duisburg-Essen. It has proven that these three teams form a very powerful team to foster German and international solid state activity at ISOLDE [6].

The community of users can profit from the use of MULTIPAC device at ISOLDE-CERN due to the high quality and availability of the beams presented in table 1. Additional isotopes of interest are ^{120}Sb(^{120}Sn), ^{181}Hf(^{181}Ta), ^{100}Pd(^{100}Rh), ^{99}Mo(^{99}Tc) and ^{140}La(^{140}Ce). MULTIPAC will thus serve much on purely magnetic material system to be investigated at ISOLDE in the future, keeping the material science program at the highest level. It will thus serve many groups at very long term.

Table 1: List of ISOLDE beams, which can be used with MULTIPAC. The μ and Q values were collected from [Stone N J 2016 At. Data Nucl. Data Tables 111 1–28] and [Stone N J 2005 At. Data Nucl. Data Tables 90 75–176]. (a) H. Haas et al, Accurate nuclear quadrupole moments determined by gas phase PAC spectroscopy and first principles calculations, writing in progress.

Probe	$t_{1/2}$	Q (b)	μ (μ_N)
^{111}Ag(^{111}Cd)	7.45 days	+0.662(x) ^{a}	−0.7656(25)
^{111}In(^{111}Cd)	2.8 days	+0.662(x) ^{a}	−0.7656(25)
^{172}Lu(^{172}Yb)	6.7 days	**−2.9(3)**	+0.65(4)
^{117}Cd(^{117}In)	2.5 hours	(-)0.59(1)	**+0.938(10)**
^{77}Br(^{77}Se)	57 hours	+0.76(5)	**0.9731(6)**
^{80m}Br(^{80}Br)	4.42 hours	0.159(7)	**-1.67(12)**
^{204m}Pb(^{204}Pb)	67 min (its generator ^{204}Bi(^{204m}Pb) has 11.2 hours)	**0.44(2)**	+0.225(4)

The MULTIPAC challenges lie in the combination of the different measurement modes. In order to understand magnetic ordering, a good value of magnetization must be known. For this purpose, the VSM-insert is available. It is the very same unit that will serve as sample stage for the PAC-measurements. So complete in situ information is available. Concurrently, the magnetoelectric coupling can be tested using the magnetic coil of the VSM (vibrating sample magnetometer) in conjunction with the electrical sample wiring. The latter has to provide DC high voltage and simultaneously permit to use a Lock-In amplifier for extracting low level signals for determining the magnetoelectric coupling coefficient in situ, so in the sample state under magnetic and electric load. The testing of the local probe ion environment is then provided at the same site and in the same sample. This is a crucial asset of the device.

Provided by the goniometer also orientational dependencies that arise in single crystals or due to an angle between electric and magnetic fields can be monitored. All information will be mapped onto the magnetic state of the sample by the information from the VSM. Linking all these functionalities and building the signal-splitting electronics is the major task for the experimental PhD student. After a build-up time in Essen, the student will then test-run the device at ISOLDE in the next beam time available in 2021 together with the solid state physics coordinator and the interested user community.

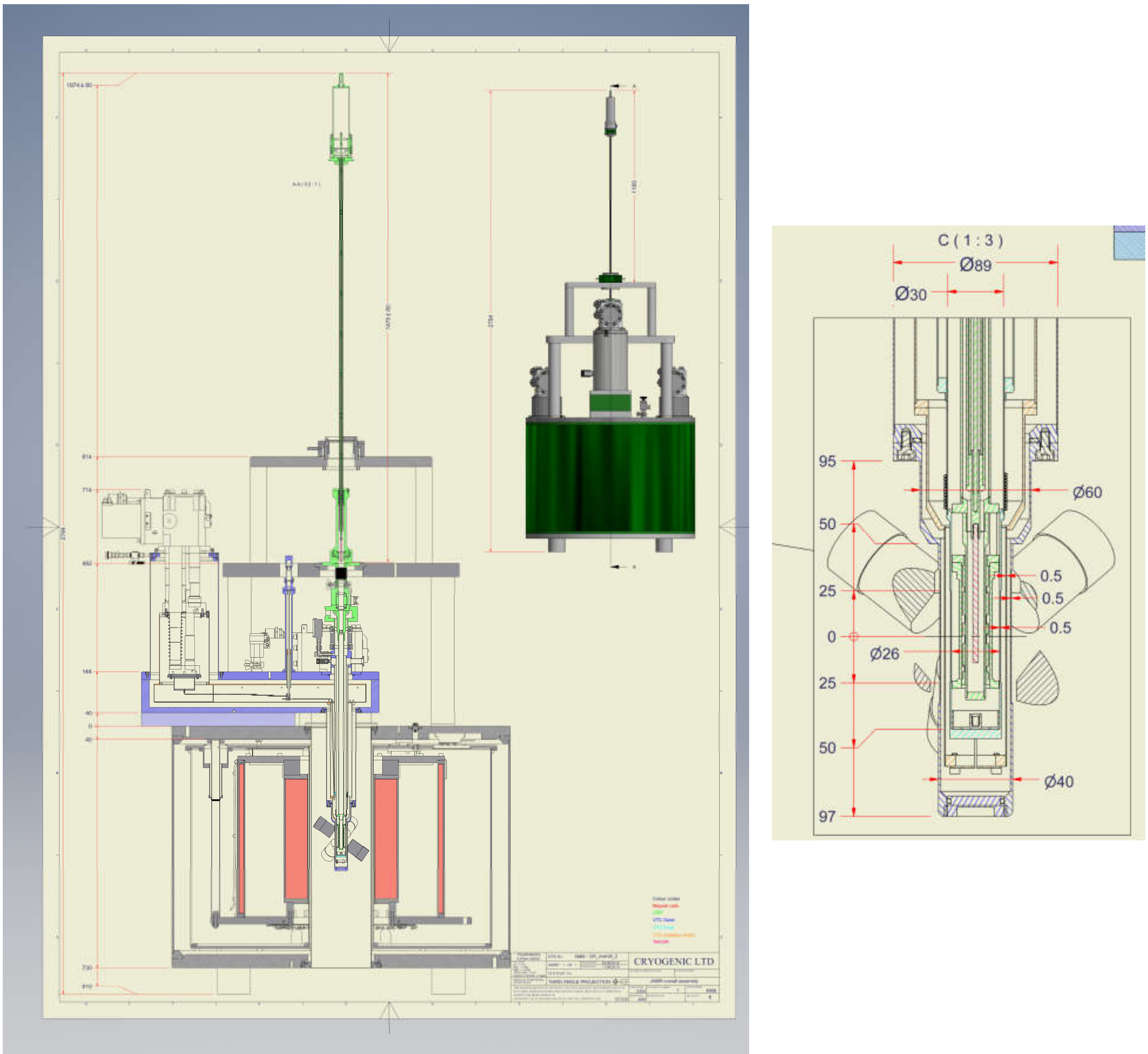

Figure 3: Drawing of the set-up in construction. Sample holder centred in the 6-detector PAC-set-up. A second configuration allows for 4-detector geometry (each perpendicular to the magnetic field axis).

Modelling

Combined hyperfine interactions are not easy to interpret. In PAC the combined interaction yields a superposition of the nuclear transition lines (level splitting) in the probe nucleus. This superposition may yield spectra which are very hard to understand or will not yield an interpretable data set at all. *Ab initio* calculations are required for the simulations of the hyperfine parameters and are incorporated into the build-up project in order to provide the necessary device settings for successful experiments. Theory data will be available beforehand, so that the measurement settings are suitable for successfully interpretable data.

Examples of materials to be investigated

Initial tests will deal with $BiFeO_3$, which is the drosophily of multiferroics, then manganates for their cyclic spin structure, then phosphates or selenates with toroidal and skyrmion structures. Lead iron niobate is interesting because of its coupling to optical irradiation etc. The list will fill 10 PhD.

The beauty of the present set-up is that the local magnetic structure can be changed or broken up under high field and the corresponding changes in local environment can be directly measured.

Summary of requested shifts

No shifts required this time

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Appendix

DESCRIPTION OF THE PROPOSED EXPERIMENT

The experimental setup comprises a high field magnet (9 Tesla) that is fully screened by counter-coils to yield a 5 Gauss line at 1 m from the magnet core.

The set-up must be place in a hall that offers sufficient ceiling height for manipulating the sample holder (350 cm from ground). It needs sufficient cooling water for the three standard closed cycle coolers that run the experiment. 3 x 3 phase 16 A power supply must be available. The set-up is not bound to any of the beamlines so can fill space in between other experiments. Total ground floor needed: 2,20 m x 3,20 m which includes all computer racks etc.

Part of the Choose an item.	Availability	Design and manufacturing
Space, water cooling and power are required at the SAS, where the MULTIPAC should be installed	☐ Existing	☒ To be used without any modification
MULTIPAC	☐ Existing	☐ To be used without any modification ☐ To be modified
	☒ New	☐ Standard equipment supplied by a manufacturer ☒ CERN/collaboration responsible for the design and/or manufacturing
Annealing furnaces at 508/R-004	☒ Existing	☒ To be used without any modification ☐ To be modified
	☐ New	☐ Standard equipment supplied by a manufacturer ☐ CERN/collaboration responsible for the design and/or manufacturing
[insert lines if needed]		

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed [COLLAPS, CRIS, ISOLTRAP, MINIBALL + only CD, MINIBALL + T-REX, NICOLE, SSP-GLM chamber, SSP-GHM chamber, or WITCH] installation.

Additional hazards:

Hazards	*[MULTIPAC]*	*[Part 2 of the experiment/equipment]*	*[Part 3 of the experiment/equipment]*
Thermodynamic and fluidic			
Pressure	10 Bar, 20 l (closed cycle He-cooler)		
Vacuum	10^{-6} - 10^{-7} mbar		
Temperature	4-400 K		
Heat transfer	-		
Thermal properties of materials	-		
Cryogenic fluid	Helium		
Electrical and electromagnetic			
Electricity	3 x 3 phase 400 V, 16 A		
Static electricity	-		

Magnetic field	0-10 T		
Batteries	☐		
Capacitors	☐		
Ionizing radiation			
Target material	[material]		
Beam particle type (e, p, ions, etc)	Ions		
Beam intensity	Up to 60 keV implanted into materials at GLM or GHM beam line. The materials are transported to annealing room (508/R-004) and to MULTIPAC (at HIE-ISOLDE)		
Beam energy			
Cooling liquids	Water		
Gases	He (closed cycle)		
Calibration sources:	☐		
• Open source	☐		
• Sealed source	☐ [ISO standard]		
• Isotope			
• Activity			
Use of activated material:			
• Description	☐		
• Dose rate on contact and in 10 cm distance	Not relevant		
• Isotope	Mentioned in Table 1		
• Activity			
Non-ionizing radiation			
Laser	-		
UV light	-		
Microwaves (300MHz-30 GHz)	-		
Radiofrequency (1-300MHz)	-		
Chemical			
Toxic	-		
Harmful	-		
CMR (carcinogens, mutagens and substances toxic to reproduction)	-		
Corrosive	-		
Irritant	-		
Flammable	-		
Oxidizing	-		
Explosiveness	-		
Asphyxiant	-		
Dangerous for the environment	-		
Mechanical			
Physical impact or mechanical energy (moving parts)	None		
Mechanical properties (Sharp, rough, slippery)	None		
Vibration	Only from cryo-coolers		
Vehicles and Means of Transport	Fixed location for MULTIPAC is required. Samples are transported inside lead containers.		

Noise			
Frequency	[frequency],[Hz]		
Intensity			
Physical			
Confined spaces	[location]		
High workplaces	[location]		
Access to high workplaces	[location]		
Obstructions in passageways	[location]		
Manual handling	[location]		
Poor ergonomics	[location]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): The rough overall powers are:

- 25 kW electrical (peak)

- 30 kW cooling power from water cooling system