EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Addendum to the ISOLDE and Neutron Time-of-Flight Committee

(Project IS487)

Study of Local Correlations of Magnetic and Multiferroic Compounds

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Abstract

In Project IS487, we propose to study magnetic and multiferroic strongly correlated electron materials using radioactive nuclear probe techniques at ISOLDE. Our aim is to provide local and element selective information on some of the mechanisms that rule structural, charge and orbital correlations, electronic and magnetic interactions and the coupling of the associated degrees of freedom. The main technique used is Perturbed Angular Correlations (PAC), which allows combined magnetic and electric hyperfine studies. This study is complemented by the use of conventional characterisation techniques, the investigation of relevant macroscopic properties and the theoretical modeling of the systems under study.

Two broad main topics are addressed:

1. Local environment in multiferroic (MF) compounds: a consistent and global study is enabled by the possibility of probing local electric ordering and magnetic hyperfine field. The sensitivity to static atomic displacements and its fluctuations allows a detailed study of the para/anti/ferroelectric phase transitions. Multiferroic compounds associated with distinct magneto-structural-electric coupling mechanisms will be studied:
   i) Charge-order induced or magnetically driven MF in $RMnO_3$ (R= trivalent lanthanides) manganites, $RNiO_3$ (R=Y,Lu) nickelates, $MCrO_2$ (M=Cu, Ag) chromites and chromium spinels DCr_2O_4, (D=Mg, Cd, Zn, Hg). New case studies of: RMn_2O_5 (R=Y,Lu) mixed valence manganites and $DMnO_3$divalent (D=Ca/Ba/Sr) perovskite manganites
   ii) MF where magnetism and ferroelectricity (FE) have distinct origins, the FE critical temperature being usually higher: $RMnO_3$ (R=Y,Lu) manganites, where lattice distortion provides the coupling to the spin

system through magnetostriction and drives the MF state and $BiFeO_3$ ferrite and variants, where FE is due to Bi lone pairs.

iii) A new case study is the recently addressed first-principle validation of relation between the electric polarization (P) and the electric field gradient (EFG), making this a direct local probe of polarization. Complementing previous studies the ionic displacement and electronic contributions to EFG/P will be studied in Sr/Ba/$CaMnO_3$ and rare-earth manganites.

2. Local distortions, polaron correlations and dynamics, magnetostructural effects near magnetic phase transitions: This study has three topics:
   i) an extension of a previous study in ferromagnetic insulator samples to ferromagnetic metallic (in the paramagnetic state) and to less distorted perovskites (rhombohedral). Systems to be studied include: $^{18}O/^{16}O$ isotopically modified $Sm_{1-x}Sr_xMnO_3$ and doped $SrTiO_3$ samples.
   ii) magnetostructural changes in first-order magnetic phase transition in Mn pnictides, Ni_2MnGa and related systems.
   iii) New case study of magnetic frustration reduction by local deformations in spin-ice systems, such as DCr_2O_4, (D=Mg, Cd, Zn, Hg) at low temperatures.

High quality pellets, single crystals and thin films samples will be used.

Requested shifts: 14 shifts, (split into 4 runs over 1 years)

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1 INTRODUCTION

The present addendum aims the completion of some of the studies initiated with IS487 whose main results are summarized. We also present a limited number of new/updated research topics on the physics of magnetic and multiferroic materials, whose relevance results from recent theoretical and experimental studies, for which we recognize that radioactive ion probe studies at ISOLDE are particularly useful and specific. For each main subject we present the motivation and discuss the experimental program to be followed, which involves new students thesis and post-doctoral programs. The annexed list accounts the publications and thesis that resulted from the previous work.

Motivation review – general (updated from IS487)

Oxide materials present a vast variety of physical behaviors. Magnetic, electronic and lattice interactions lead to cooperative phenomena like High-Tc superconductivity, colossal magnetoresistance or ferroelectricity, which are topics of advanced research in Physics and Materials Science. The coupling of magnetic and dielectric degrees of freedom has aroused a further interest on multiferroics oxides[1, 2, 3], on the quest to implement new device design architectures with magnetoelectric control of spintronic devices, such as new generation memory elements, high-frequency magnetic devices, and micro-electro-mechanical systems [4]. Independently of the prospect for new applications these modern functional materials have stimulated much scientific interest since the fascinating fundamental physics of colossal magnetoresistance and multiferroism challenge the scientific community understanding, particularly on phase separation and competition and also the combined role of ionic and electronic contributions to ferroelectric polarization [5].
Manganite and other transition metal-based oxides (chromites, nickelites, ferrites) with crystal structures derived from the cubic perovskite ABO_3, present a strong link of the magnetic coupling of transition metal spins with lattice and charge dynamics. As an example, in manganites, the mixed valence of Mn^{3+} and Mn^{4+} ions (due to doping by divalent ions as in $La_{1-x}Ca_xMnO_3$) controls the occurrence of coupled structural, magnetic or charge and orbital (C/O) ordering phase transitions, leading also to intrinsic and ubiquitous phase separation phenomena and nanoscale inhomogeneities [6]. In the undoped compounds, where only Mn^{+3} ions are present, the cubic structure is distorted by cation size mismatch and the Jahn-Teller (JT) effect. The distorted structures are frequently orthorhombic, rhombohedral or hexagonal and a large electron – Jahn-Teller phonon coupling drives an Mn ion 3d-orbital ordering (OO).

The competition of ferromagnetic and C/O orderings is the basis for the colossal resistive changes induced by magnetic field, pressure or radiation, and the magnetic or C/O ordering can break the spatial inversion symmetry driving ferroelectricity in manganites [7] and supporting very large magnetostructural effects [8]. The understanding of these phenomena requires the adequate description of the structural, magnetic and charge degrees of freedom down to local atomic length scales: structure of clusters, polaron dynamics, polar distortions and nanoscale ferroelectricity are outstanding issues. How far phase coexistence extends is another unsolved question.
PAC (perturbed angular correlations) uses radioactive ion probes and provides a sensitive method to detect hyperfine magnetic fields (MHF), local distortions through the electric field gradient (EFG) and their fluctuations. Such capabilities were illustrated by detailed studies from our group, using ^{111m}Cd PAC [9,10,11]: i) in the Ferromagnetic Insulator $LaMnO_{3.12}$ (Tc=145K) we showed a coexistence of local environments from 10 to 800K. For T>300K an almost axially symmetric EFG predominates while at low temperatures mainly a highly asymmetric EFG exists, associated to a Jahn-Teller (JT) distorted environment. The results

led to the picture that at high temperatures polarons are uncorrelated and highly JT distorted. On cooling, correlations start when the percolative limit is reached and distortion then decreases.

ii) in the $Pr_{1-x}Ca_xMnO_3$ manganite system, competing ferromagnetic ($x<1/3$) and C/O ordered phases [12] can coexist at nanoscopic scale [13]. The sensitivity of EFG to delocalized electrons and the charge asymmetry from the lattice ion cores led to large effects both as a function of x and temperature across the C/O ordering transition. We observed electrical polarization signatures at local scale, with critical behavior at the transition. This agrees with predictions of an intermediate situation of CO between the extreme limiting situations of charge localized at nodes or bonds breaking the inversion symmetry, settling a new paradigm for multiferroics [14].

iii) New results in the multiferroic $AgCrO_2$ with triangular spin lattice PAC revealed the coexistence of two distinct local environments (EFGu) and (EFGd) at temperatures below 100 K. The emerging second local environment (d) appears as a distortion of the Cr surrounding resulting in a local symmetry lowering concomitantly with the onset of short range magnetic correlations much above the magnetic transition. This is associated with a magnetoelastic instability, with distinct Cr-Cr exchange interaction pathways appear providing a channel for magnetic frustration release [11].

For multiferroics non-centrosymmetric manganites, $RMnO_3$ where R=Bi, Y and heavier rare-earths[15] several mechanisms have been proposed for the magnetoelectric coupling. The ferromagnetism of $BiMnO_3$ may be attributed to the orbital ordering that produces the 3D ferromagnetic super-exchange interaction of e_g electrons and an enhanced magnetoelectric coupling. Special situations occur in non collinear (spiral/helical) magnetic systems, like Tb/Dy manganites, where the polarization, associated with displacement of oxygen atoms, is explained by spin-orbit interactions and the spin current between Mn ions[16], while in Y manganites magnetoelastic distortions are proposed to dominate[8]. On the other hand, RMn_2O_5 (R=rare-earth) and other mixed valence manganites are an intriguing case, where competing ionic and electronic contributions to electric polarizations are found, and spin-dependent oxygen polarization plays a critical role [17]. The bismuth ferrite $BiFeO_3$ presents the highest combination of antiferromagnetic and ferroelectric transition temperatures, both well above room temperature. Spin-driven mechanisms are dominant in other systems: $ACrO_2$ chromites, $RNiO_3$ nickelites and spinels (DCr_2X_4, D=Cd, Hg, Co, Fe e X=O, S, Se). The study of the structural couplings and short-range order effects using PAC in manganites and other multiferroics is very timely and appropriate and was initiated by our team.

$CdCr_2S_4$ is one of the rare compounds presenting simultaneously colossal-magnetocapacitive, colossal-electrocapacitive, colossal-electroresistance and colossal magnetoresistance[18]. Our new experimental findings from complementary PDF (synchrotron), PAC, and magnetic measurements point to the presence of a dynamic state caused by the presence of simultaneous polar and magnetic clusters.

Magnetostructural phase transitions were studied in MnAs, a prototype Mn pnictide, where orthorrombic/tetragonal phase changes are coupled to magnetic phase transitions. We will extend the measurements for MnP and other allys, like the magnetic shape memory alloy Ni_2MnGa

2 WORK PROPOSITIONS

At ISOLDE, we perform local studies to understand some of the relevant structural and charge mechanisms of CMR oxides. γ–γ and e^--γ Perturbed Angular Correlation (PAC) probe local environments via the electric field gradients (EFGs) and magnetic hyperfine field (MHF). These experiments allow atomic scale insight to the contributions of point-like defects, dopants, as well as local structural deformations and charge/orbital distributions. Moreover, the dynamic or static character of the environment can be examined. The radioactive isotopes will be implanted into pellets, single crystals and thin films of these materials and the PAC studies will be performed after implantation and suitable annealing procedure. The measurements shall be done in a broad temperature range (10-1000K) to encompass the different magnetic and structural phase transitions.

The ISOLDE work is complemented by electric and magnetic measurements and characterisation by a large variety of crystallographic techniques offered by the home laboratories. In particular, complementary temperature dependent X-ray diffraction and high-resolution transmission electron microscopy with electron diffraction are performed in the same samples.

Moreover, the complementary ab-initio calculation of hyperfine parameters using appropriate Density Functional Theory codes (Wien 2k, VASP) provides a much more comprehensive approach to these studies, including the consideration of probe localization, phase competition and local/global deformations.

The availability of beams of radioactive isotopes of a large variety of elements with high purity and yields makes the ISOLDE laboratory the unique facility where this interdisciplinary experimental program is envisaged and executed.

2.1 Local environment in multiferroic compounds

A consistent and global study of multiferroic systems is enabled by the possibility of simultaneously probing local electric fields and charge distributions and also the magnetic hyperfine field using PAC. The complex physics of multiferroic materials with distinct magneto-structural-electric coupling mechanisms will be studied, with the purpose of examining the presence of inequivalent sites or bonds and associated mechanisms for MF behavior as well as associated short-range order effects. The sensitivity to static atomic displacements and its fluctuations allows a detailed study of the paraelectric to (anti)ferroelectric phase transitions.

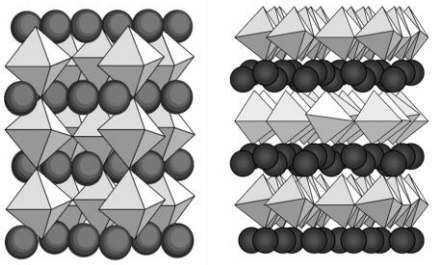

Fig.1.1: Perovskite (left) and hexagonal (right) phase structures of RMnO3 manganites, highliting the local octahedra. or trigonal bipyramid Mn-O environments.

An extensive study of the hyperfine interactions in a series of hexagonal and orthorhombic rare-earth manganites (RMnO3, R= Nd, Sm, Eu, Gd, Tb, Ho, Y, Er, Lu) was performed in IS487. These display an orthorhombic structure (distorted perovskite) for larger R (R=La to Dy) and hexagonal structure for smaller R (R=Ho to Lu, Y). The electric field gradients at the probe sites (^{111}Cd) have been measured and compared with the results obtained with first principle calculations via the augmented plane wave method of the charge densities in the compounds. All studied compounds present two distinct local environments, which only one can be directly attributed to the regular rare-earth crystallographic sites. The existence of a second local environment, which cannot be assigned to the regular rare-earth or manganese sites, suggests for the presence of distortions in the rare-earth local environment.

As an example we report in Fig 1.2 the study of the thermal dependence of the electric field gradient (EFG) in ErMnO3, which has the non centro-symmetric P63cm space group in the hexagonal crystalline structure at room temperature. A structural transition to the centro-symmetric P63/mmc space group occurs at ~1310K. Moreover, the electric dipole ordering,

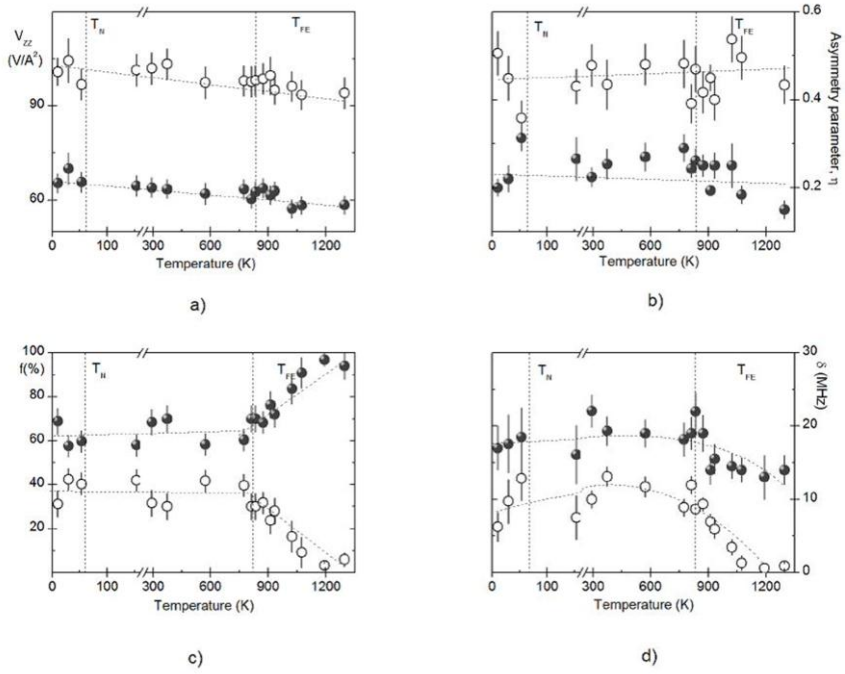

Fig.1.2: EFG parameters evolution with temperature for ErMnO3:a) EFG principal component, Vzz ;b) asymmetry parameter, η;c) fraction of probes interacting with each EFG distribution,d) and e) static attenuation parameter, δ.The vertical dashed lines indicate the ferroelectric (TFE) and magnetic (TN) transition temperatures. Dashed lines are guides for the eye.

i.e., the transition from the paraelectric to the ferroelectric phase is reported to be at lower temperatures, TFE~833K. The PAC data have been measured from 10K up to 1376K. The experimental data shows the coexistence of two distinct local environments in all temperature range. At high temperatures (above the ferroelectric transition), the major local environment (EFG1) is clearly dominant while the minor EFG distribution (EFG2) tends to vanish. This evolution is consistent with the fact that the high temperature crystalline structure allows only one nonequivalent rare-earth site. These results suggest that the minor EFG2 might be due to a distortion of the Er 4a site, whose contribution to the ferroelectric ordering of this compound shall be investigated.
There are several mechanisms proposed to underlie multiferroic behaviours, which require the simultaneous fulfilment of specific symmetry conditions [19]:. We intend to deepen the study of multiferroic materials, enlarging the range of compounds (oxide materials).
Following the work in IS487, the main lines considered are:

a) *Multiferroic materials where magnetism and ferroelectricity have distinct origins, the FE critical temperature being usually higher: RMnO3 hexagonal manganites, where lattice distortion provides the coupling to the spin system through magnetostriction and drives the MF state and $BiFeO_3$ ferrite and variants, where FE is due to Bi lone pairs.*

In this case (to which the described Er manganite belongs) we will complete some studies in the hexagonal manganites and focus on ferrites.

b) *Multiferroic materials with charge-order induced or magnetically driven MF in $RMnO_3$ (R= trivalent lanthanides) manganites, $RNiO_3$ (R=Y,Lu) nickelates, $MCrO_2$ (M=Cu, Ag) chromites and chromium spinels DCr_2O_4, (D=Mg, Cd, Zn, Hg).*
New case studies of: RMn_2O_5 (R=Y,Lu) mixed valence manganites and $DMnO_3$ divalent (D=Ca/Ba/Sr) perovskite manganites

In these materials there is a direct and intimate link between electric and magnetic cooperative phenomena, and the corresponding transition temperatures are closer. Ferroelectricity appears due to some magnetic related effect. For example, rare earth nickelates $RNiO_3$ (R=Y, Lu) are predicted [3] to present an electric polarization allowed by charge order disproportionation (not exactly Ni^{2+}/Ni^{4+}) triggered by a magnetostrictive effect on bonds. Preliminary experiments were performed and need to be continued. As referred in the introduction, detailed studies were performed in $AgCrO_2$ with triangular spin lattice finding a distortion of the Cr surrounding resulting in a local symmetry lowering concomitantly with the onset of short range magnetic correlations much above the magnetic transition [11].
Work on spinels (DCr_2X_4, D=Cd, Hg, and X=O, S, Se) was initiated by our team by $CdCr_2S_4$ Our new experimental findings from complementary PDF (synchrotron), PAC, and magnetic measurements point to the presence of a dynamic state caused by the presence of simultaneous polar and magnetic clusters, arising from the atomic off-center displacement of Cr^{3+} ions well above the ordering temperature These new insights directly prove the Cr^{3+} ion role on the onset of local polar distortions, activated by thermal mechanism.

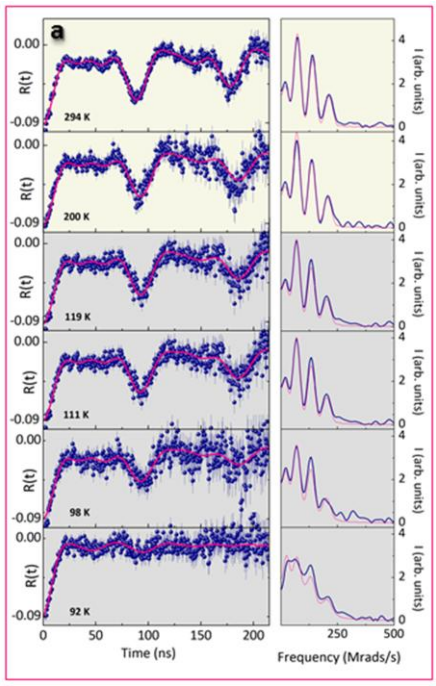

Fig.1.3: Representative R(T) functions (left), correspondent fits and respective Fourier transform (right) taken at different temperatures.in $CdCr_2S_4$

From the PAC measurements using the 111In→111Cd probe it can be inferred that the Cr site experiences a slow dynamics in the 119 K – 92 K temperature range. This dynamic off-centering leads to the formation of local dipoles responsible for the also observed magnetic correlations between Cr^{3+} neighbors. This correlation between electric and magnetic orders is modeled by the Landau theory of phase transitions with a bi-linear magnetoelectric coupling Finally, we highlight that the discovery of the present atomic displacement mechanism is related to the relaxor behavior in the PM regime.

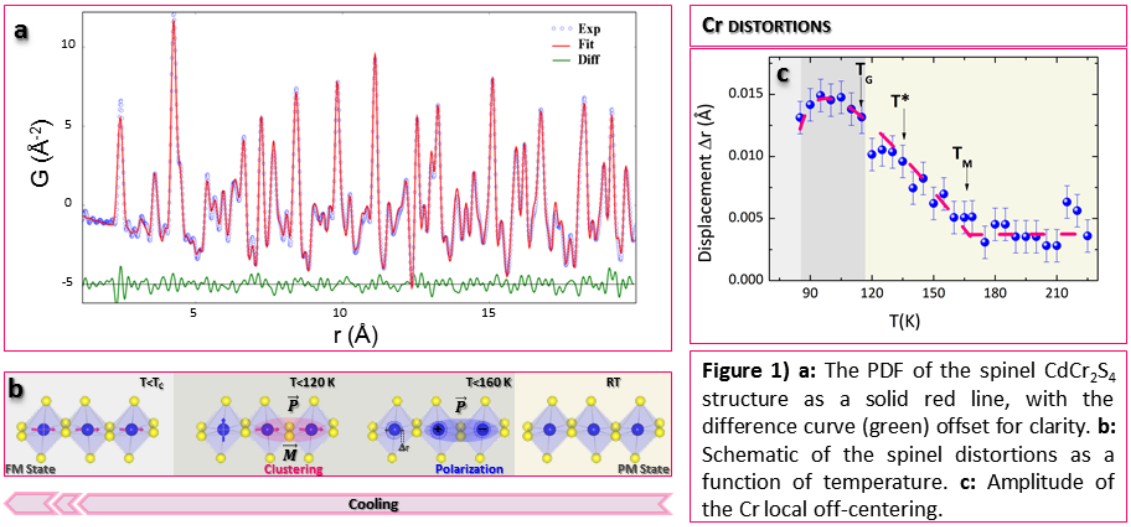

Figure 1) a: The PDF of the spinel $CdCr_2S_4$ structure as a solid red line, with the difference curve (green) offset for clarity. **b:** Schematic of the spinel distortions as a function of temperature. **c:** Amplitude of the Cr local off-centering.

Colossal magnetocapacitance and colossal magnetoresistance were also found in $HgCr_2S_4$ [20] with a short-range ferroelectric order assigned to it. and can be treated along the same theoretical basis as other spiral magnets. However, the suggested polar order in these compounds is a topic of great debate, together with its microscopic origin [21, 22, 23]. Previous studies by PAC [24] in some of these magnetic semiconductors did not address these issues, and so the investigation of multiferroicity here proposed using probes which belong and are chemically compatible to the system (Cd, Hg and Se) is very timely

In this line one refers the new cases of RMn_2O_5 (R=rare-earth) and other half mixed valence manganites ($La_{0.5}Ca_{0.5}MnO_3$) [17, 25], where competing ionic and electronic contributions to electric polarizations are found, and spin-dependent oxygen magnetic polarization plays a critical role.
In YMn_2O_5 Mn^{4+} ions occupy the center of oxygen octahedra and Mn^{3+} ions at pyramid dimers providing a challenging case for hyperfine studies, as the electric polarization appears in the magnetic commensurate order phase (20-40K), and is sustained by the oxygen magnetization, associated with a charge redistribution. The distinct roles of ionic and electronic contributions to EFG and electric polarization are now being studied by first principles theory, to sustain the analysis of the foreseen experiments.
The case of $DMnO_3$ divalent (D=Ca/Ba/Sr) manganites with strained perovskite structure follows the studies already performed in orthorrombic Ca and hexagonal Sr and Ba manganites which are the stable forms at room temperature. The metastable forms were recently shown to possess intrinsic polarizations comparable to prototypical BaTiO3 and having the largest magnetoelectric coefficient known [26]. Here the mechanism for ferroelectricity is the off-centering of the magnetic Mn4+ ions and is strongly dependent on lattice parameter, that can be tuned by average ion radius (maximum coupling at Sr0.6Ba0.4 ratio) and strain effects, in thin films.

c)Study of the relation between the electric polarization (P) and the electric field gradient (EFG) in ferroelectrics and multiferroics.

A new case study is the recently addressed first-principle validation of relation between the making this a direct local probe of polarization. Using ab-initio Density Functional calculations with codes Wien 2k and VASP, we found direct relation between the two quantities, encompassing a large range of values and situations. The experimental study of the global and ionic displacement and electronic contributions to EFG/P will be analysed in new and existing data, aiming to provide further contributions to the debates on the mechanisms for multiferroicity.

As in IS487, in the studies proposed so far we will use mainly the ^{111m}Cd (49 m) $\rightarrow$ ^{111}Cd, ^{199m}Hg (42 m) $\rightarrow$ ^{199}Hg, ^{117}Cd(2.4h) $\rightarrow$ ^{117}In and ^{111}Ag(7.45d) $\rightarrow$ ^{111}Cd PAC probes isotopes . Complementary test studies from the decays ^{48}Cr(21.6h) $\rightarrow$ ^{48}V are also requested.

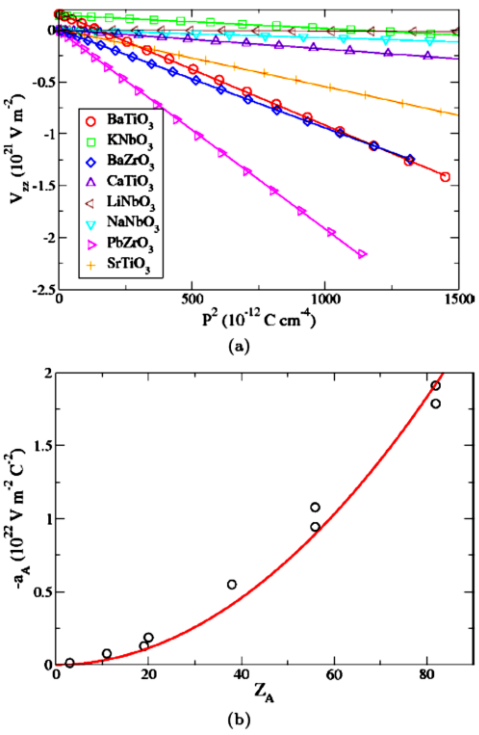

Fig.1.4 Vzz at the A site as a function of P^2, showing the different coefficients (slopes of straight lines). (b) Coefficients of quadratic term of Vzz(P), at the A site, for a series of materials with the perovskite structure, as a function of atomic number ZA. The line is a quadratic fit.

2.2 Local distortions, polaron correlations and dynamics, magnetostructural effects near magnetic phase transitions.

Strongly correlated electron materials often present structural phase transitions closely associated with magnetic ones, leading to the emergence of phase coexistence at the nanoscopic scale (nanoclusters). We propose to continue studies on spontaneously inhomogeneous systems (phase separated) and also on systems near a phase instability, where for instance the (oxygen) ionic dynamics change associated with the different isotope mass can trigger a new macroscopic behavior.

We propose to follow three relevant subjects, already started on the project, to different levels:

a) Magnetic and Ferroelectric instabilities:

i) a study of $^{18}O/^{16}O$ isotopically modified $Sm_{1-x}Sr_xMnO_3$ manganites (x~0.5), where the low-temperature state of ^{16}O samples is ferromagnetic metallic while the ^{18}O samples become CO/AF insulator.

ii) a complementary study of inhomogeneous ferroelectricity induced in insulator $SrTiO_3$ by analogous oxygen isotope exchange, promoting rhombohedral polar clusters that subsequently grow in concentration, freeze out, and percolate below Tc. [27].

An important point of these studies is the monitoring of the oxygen isotopic content at the surface by RBS, complementing bulk measurements that detect the properties change. A small chamber for isotope exchange is available.

b) Magnetostructural phase transitions were studied in MnAs, a prototype Mn pnictide, where orthorrombic/tetragonal phase changes are coupled to magnetic phase transitions. The PAC probe obtained from decay of $^{77}Br \rightarrow {}^{77}Se$ was successfully used for γ-γ PAC measurements in broad temperature ranges, taking advantage of the relatively generous half-life. A detailed description of phasechanges and phase coexistence in the first-order phase transition was achieved, complemented by structural and magnetic data [28]. We will extend the measurements for MnP and other allys, like the magnetic shape memory alloy Ni_2MnGa

c) Finally we mention the new case study of magnetic frustration reduction by local deformations in spin-ice systems, such as DCr_2O_4, (D=Mg, Cd, Zn, Hg) that requires low temperatures, below 10K.

For these studies, in general, we wish to use the $\underline{^{111m}Cd\ (49\ m)} \rightarrow {}^{111}Cd$, $\underline{^{199m}Hg\ (42\ m)} \rightarrow {}^{199}Hg$, $\underline{^{117}Cd(2.4h)} \rightarrow {}^{117}In$ and $\underline{^{111}Ag(7.45d)} \rightarrow {}^{111}Cd$ and $\underline{^{77}Br(57h)} \rightarrow {}^{77}Se$ isotopes for PAC studies. The radioactive isotopes will be implanted into pellets. The measurements shall be done in a broad temperature range, complemented by diffraction and TEM studies.

3 EXPERIMENTAL

3.1 SAMPLE PRODUCTION AND CHARACTERIZATION

Table I: Where and how the samples are produced

		Laboratory				
Family of samples	**Type of samples**	**Aveiro/Porto/ Vila Real**	**Moscow**	**Orsay**	**Stuttgart**	**Tokyo and Tsukuba**
$RMnO_3$ + RMn_2O_5 + $(Ca/Ba/Sr)MnO_3$	Pellets	Solid State Reaction		Solid State Reaction	-	Solid State Reaction
$BiFeO_3$	Pellets	Solid State Reaction				
$La_{1-x}(Ca/Sr)_xMnO_3$	Pellets	Solid State Reaction				
$La/Pr_{1-x}(Ca/Sr)_xMnO_3$	S. Crystals			Czochralski		Czochralski
above	Thin films	sputtering			Pulsed Laser Ablation	
DCr_2X_4	Pellets	Solid State Reaction				
$Sm_{1-x}Sr_xMnO_3$ ^{16}O and ^{18}O	Pellets		Solid State Reaction			
$RNiO_3$	Pellets	Solid State Reaction				
Mn pnictides +Ni_2MnGa	Pellets	arc melting				

All samples will be characterized using the techniques available at the home institutes before and after the experiments with radioactive isotopes. For structure, we mention X-ray powder, high resolution, single crystal diffraction (Aveiro, Porto), Scanning Electron Microscopy (SEM) with Energy Dispersive X-ray (EDX) analysis (Aveiro, Vila Real, Porto), Transmission Electron Microscopy (TEM) and High Resolution TEM (Aveiro, Vila Real) with temperature variation (20-300K), and Rutherford Backscattering/Channeling (RBS/C) (Sacavém), SPM, AFM and PFM probe microscopies (Aveiro, Porto).These techniques allow monitoring the sample's crystalline structure, orientation, composition, surface, as well as the characterization of the defects, implantation profile and residual damage from the ion implantation and annealing procedures. For comparison, in specific cases similar samples (particularly thin films) will be implanted with higher doses of stable ions at ITN-Sacavém, using the Danfysik-1090 high fluency ion implanter.
Magnetic (SQUID, VSM, ac susceptibility), dielectric and electric resistivity measurements (with magnetoresistance) are available at the home-institutes. These properties will be measured before and also after implantation.

3.2 TECHNIQUES USING RADIOACTIVE ISOTOPES

The γ-γ PAC technique is well established at ISOLDE. The PAC spectrometers actually working at ISOLDE, allow measurements to be performed from 10K up to 1100 K, in vacuum or under gas flow (Ar, N_2, O_2).

Table II: Radioactive isotopes and techniques

isotope	annealing	γ-γ PAC	β-γ PAC
^{111m}Cd (49 m)	✓		
↓		✓	
^{111}Cd			
^{199m}Hg (42 m)	✓		
↓		✓	
^{199}Hg			
^{117}Ag (73 s)	implant & wait for decay		
↓			
^{117}Cd (2.4 h)	✓		
↓		✓	
^{117}In (1.9 h)			
^{111}Ag (7.45 d)	✓		
↓		✓	✓
^{111}Cd			
^{77}Br (57 h)	✓		
↓		✓	
^{77}Se			
^{73}Se (7.2 h)	✓		
↓		✓	
^{73}As			
^{48}Cr(21.6 h)	✓		
↓		✓	
^{48}V			

3.3 EQUIPMENT AND LABORATORIES

All isotopes will be collected in the general-purpose implantation chambers at GLM and/or High Voltage Platform at the ISOLDE hall, building 170. All PAC measurements are done off-line, outside the ISOLDE hall, in the new Solid State Lab on building 115. Sample holders are transported on sealed containers inside the ISOLDE hall, up to building 115. The samples are of "solid form", consisting of crystals, thin films and self-sustaining pellets. For annealing treatments under vacuum or gas flow, several furnace systems exist at ISOLDE, which are equipped with traps for fixing volatile elements, like Hg. Closed glove boxes exist for handling samples and sample holders after implantation .

BEAM TIME REQUEST

We estimate a total of 14 (1 test) shifts of beam time within the available period distributed according the table below:

Table III: Beam time request

REQUIRED ISOTOPE	ISOLDE BEAM	INTENSITY [AT/μC]	TARGET	ION SOURCE	NUMBER OF SHIFTS
^{111m}Cd	^{111m}Cd	~ 5.0E8	Molten Sn	plasma	8
^{199m}Hg	^{199m}Hg	~ 2.0E8	Molten Pb	plasma	2
^{117}Cd (g.s.)	^{117}Ag (*)	~ 5.0E8	UC_2	laser (Ag)	2
^{111}Ag	^{111}Ag	~ 1.0E8			
^{77}Br	^{77}Br	> 1.0E8	ZrO_2	plasma	1
^{73}Se	^{73}Se	> 1.0E8			
^{48}Cr	^{48}Cr	~ 1.3E5(**)	ZrO_2	plasma	1-test
				total:	14

(*) The implantation of ^{117}Ag maximizes the ratio between ^{117}Cd/^{117m}Cd, what is needed to optimize the PAC measurements, which are performed onto the 89.73keV- 344.4keV cascade on ^{117}In obtained from decay of ^{117}Cd(g.s.).

Due to the nature of the sample preparation for PAC measurements, i.e., short time collections of 5… 15 min per sample for ^{111m}Cd and ^{199m}Hg each 4h, the beam time should be optimally used by sharing it with other users of the same type of target/ion-sources.

4 DELIVERABLES

An important part of the project concerns people formation and thesis.
The subject research of IS487 was addressed totally or partially by 4 Master and 4 PhD students. Students and young PhDs actively participate in beam times, sharing afterwards the sample preparation and crystallographic/transport properties characterization and the analysis of the PAC results.

List of former and present post-docs and students doing work within the subjects of the IS487 project and its addenda now proposed:

João Amaral: PhD in 2005-2009: Continued Pos-Doc 2010-2016
Tânia Manuela Mendonça: PhD in 2006-2012: Working at Isolde
João Nuno Gonçalves: PhD in 2008-2011: Continued Pos-Doc 2012-2018
Célia Sousa: PhD student 2008-2011: Continued Pos-Doc 2012-2018

Gonçalo Oliveira: MSc in 2009, PhD starting 2012
Marcelo Baptista Barbosa: MSc in 2010, PhD started 2011
João Horta Belo, MSc in 2010, PhD started 2011
Abel Fenta, MSc in 2011, PhD starting 2012
Carlos Amorim, BSc project 2011, MSc continuing 2011-2013
Luis Miguel Custódio, BSc project 2011
Narciso Soares: research grant 2008-2010

The financing of materials, equipments and some mobility is provided within national projects.

Annex: The following works resulted from the IS487 project (2009-2011)

PhD and MSc thesis associated totally or partially to work performed in IS487

Studies on magnetocaloric and magnetic coupling effects
João Cunha de Sequeira Amaral, PhD in Physics, at Universidade de Aveiro, December 2009

Measurements and modeling of hyperfine properties in ferroics
João Nuno dos Santos Gonçalves, PhD in Physics, at Universidade de Aveiro, December 2011

Advanced nanoscopic studies in magneto-electric manganites and High-Tc superconductors
Tânia Manuela de Melo Mendonça PhD in Physics, at Universidade do Porto, 2012

R5(SixGe1-x) Magnetocaloric Materials: Phase-Controlled Synthesis and Atomic Studies
João Filipe Horta Belo da Silva, MSc thesis on Physics at Universidade do Porto, November 2010

Synthesis, Macroscopic and Local Probe Characterization of $AgCrO_2$ and $CdCr_2S_4$
Gonçalo Nuno de Pinho Oliveira, MSc thesis on Chemistry at Universidade do Porto, December 2009

Implementation of ab initio Perturbed Angular Correlation Observables for Analysis of Fluctuating Quadrupole Interactions
Marcelo Baptista Barbosa: MSc thesis on Physics at Universidade do Porto, December 2010

Modelização e Estudo Experimental de Óxidos Multiferróicos
Abel Eduardo Silva Fenta, MSc thesis on Engineering Physics at Universidade de Aveiro, December 2011

Manuscripts in International Journals (5 published +1 submitted+ 4 in final preparation submission)

First principles calculations of hyperfine parameters on the Ca manganite with substitutional Cd - modeling of a PAC experiment
J. N. Gonçalves, H. Haas, A. M. L. Lopes, V. S. Amaral, J. G. Correia.
Journal of Magnetism and Magnetic Materials ,322, 1170-1173 (2010)

Perturbed Angular Correlations Investigations on $YMnO_3$ Multiferroic Manganite
T.M. Mendonça, A.M.L. Lopes, J.N. Gonçalves, J.G. Correia, P.B. Tavares, V.S. Amaral, C. Darie, J.P. Araújo
Hyperfine Interactions 197,83 (2010)

Magnetic hyperfine field at Cr site in AgCrO2 given by perturbed angular correlations
G.N.P. Oliveira, A.M.L. Lopes, J.P. Araújo, T.M. Mendonça, J. Agostinho Moreira, A. Almeida, V.S. Amaral, J.G. Correia
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J. N. Gonçalves, V. S. Amaral, J. G. Correia, A. M. L. Lopes
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A.M.L. Lopes, G.N.P. Oliveira, T.M. Mendonça, J. Agostinho Moreira, A. Almeida, J.P. Araújo, V.S. Amaral, J.G. Correia
Physical Review B, 84, 014434 (2011)

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G.N.P. Oliveira, A.M.L. Lopes, J.P. Araújo, T.M. Mendonça, J. Agostinho Moreira, A. Almeida, V.S. Amaral, J.G. Correia,
Physica Status Solidi C (submitted)

Ferroelectricity and Electric Field Gradients: an ab-initio study
J. N. Gonçalves, A. Stroppa, V. S. Amaral, J. G. Correia, T. Butz, and S. Picozzi
Physical Review (to be submitted)

Hyperfine local probe study of alkaline-earth manganites $BaMnO_3$ and $SrMnO_3$
J. N. Gonçalves, V. S. Amaral, J. G. Correia, H. Haas, A. M. L. Lopes, J. P. Araújo, P.B. Tavares.
Physical Review (to be submitted)

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J. N. Gonçalves, V. S. Amaral, J. G. Correia
Physical Review (to be submitted)

"Multiferroic" Cluster Systems in $CdCr_2S_4$ at the Paramagnetic Phase?
Gonçalo Oliveira, André Pereira, João Amaral, A. M. dos Santos, T.M. Mendonça, Yan Ren, Guilherme Correia, Armandina M. L. Lopes, João Pedro Araújo
(to be submitted)

Communications to International conferences:

Oral Communications (15)

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V.S. Amaral, F. Figueiras, I.K. Bdikin, A.L. Kholkin, A.M.L. Lopes, J.P. Araújo, J.G. Correia, Y. Tomioka, Y. Tokura
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Calculations and experimental values of hyperfine parameters in multiferroic manganites: electric field gradient and hyperfine magnetic field
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Appendix

Description of the proposed experiment

The experimental setup comprises: *(name the fixed-ISOLDE installations, as well as flexible elements of the experiment)*

Part of the Choose an item.	Availability	Design and manufacturing
SSP-GLM chamber	☒ Existing	☒ To be used without any modification
Existing equipment on the solid state labs in building 115 - 6 detector PAC standard setups - annealing furnaces - glove boxes	☒ 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

HAZARDS GENERATED BY THE EXPERIMENT

(if using fixed installation) Hazards named in the document relevant for the fixed SSP-GLM chamber and building 115 installations.

Additional hazards:

Hazards			
	SSP-GLM	*Building 115*	*[Part 3 of the experiment/equipment]*
Thermodynamic and fluidic			
Pressure	[pressure][Bar], [volume][l]		
Vacuum	10-6 mbar at SSP chamber 10 during collections		
Temperature			
Heat transfer	-		
Thermal properties of materials	-		
Cryogenic fluid		Liquid nitrogen, 1 Bar, few litres used during the PAC measurements on appropriate glass dewar.	
Electrical and electromagnetic			
Electricity	[voltage] [V], [current][A]		
Static electricity			
Magnetic field	[magnetic field] [T]		
Batteries	☐		
Capacitors	☐		
Ionizing radiation			
Target material	[material]		
Beam particle type (e, p, ions, etc)			
Beam intensity			
Beam energy			

Cooling liquids	[liquid]		
Gases	[gas]		
Calibration sources:	☐		
• Open source	☒ Produced at ISOLDE: 199mHg(42m) 111mCd (48m) 117Cd (2.4h)	Sources to be measured at 115	
• Sealed source	☒	22Na sources provided by RP services at CERN, used at 115	
• Isotope	199mHg(42m) 111mCd (48m) 117Cd (2.4h)		
• Activity	199mHg < 3e7 Bq 111mCd < 3e7 Bq		
Use of activated material:	none		
• Description	☐		
• Dose rate on contact and in 10 cm distance	[dose][mSV]		
• Isotope			
• Activity			
Non-ionizing radiation			
Laser	none		
UV light	none		
Microwaves (300MHz-30 GHz)	none		
Radiofrequency (1-300MHz)	none		
Chemical			
Toxic			
Harmful			
CMR (carcinogens, mutagens and substances toxic to reproduction)	[chemical agent], [quantity]		
Corrosive	[chemical agent], [quantity]		
Irritant	[chemical agent], [quantity]		
Flammable	[chemical agent], [quantity]		
Oxidizing	[chemical agent], [quantity]		
Explosiveness	[chemical agent], [quantity]		
Asphyxiant	[chemical agent], [quantity]		
Dangerous for the environment			
Mechanical			
Physical impact or mechanical energy (moving parts)	[none]		
Mechanical properties (Sharp, rough, slippery)	[none]		
Vibration	[none]		
Vehicles and Means of Transport	[none]		
Noise			
Frequency	[frequency],[Hz] Ambient noise at the ISOLDE Hall, building 170		
Intensity	Ambient noise at the ISOLDE Hall, building 170		
Physical			
Confined spaces	[none]		
High workplaces	[none]		
Access to high workplaces	[none]		

Obstructions in passageways	[none]		
Manual handling	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or fume houses on building 115 r-007	All samples and sample holders are manually handled either by long tweezers to insert and extract the sample holder into and out of the SSP implantation chamber at GLM, or when manipulating the samples and sample holders inside glove boxes or fume houses on building 115 r-007	
Poor ergonomics	[none]		

0.1 Hazard identification

3.2 Average electrical power requirements (excluding fixed ISOLDE-installation mentioned above): *(make a rough estimate of the total power consumption of the additional equipment used in the experiment)*

There is no additional equipment with relevant power consumption on these small-scale experiments.

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