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EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Study of Local Correlations of Magnetic and Multiferroic Compounds

PROPOSAL TO THE ISOLDE COMMITTEE

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ABSTRACT

We propose to study magnetic and multiferroic strongly correlated electron materials using radioactive nuclear probe techniques, at ISOLDE. Following the strategy of a previous project, IS390, 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, and the investigation of relevant macroscopic properties.

Three broad main topics are addressed:

1. <u>Local environment in multiferroic (MF) compounds</u>: 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 paraelectric to (anti)ferroelectric phase transitions. Multiferroic compounds associated with distinct magneto-structural-electric coupling mechanisms will be studied:
   i) Charge-order induced MF in $RMnO_3$ (R=Tb,Dy) Manganites, $RNiO_3$ (R=Y,Lu) nickelates; Spin-driven ferroelectricity (FE) in $MCrO_2$ (M=Cu, Ag) chromites and chromium spinels DCr_2X_4, (D=Cd, Hg, Co, Fe and X=O, S, Se)
   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.

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[1] Institute addresses are shown on page 2.

2. Concurrence or competition between charge (CO) and orbital (OO) order-related effects. The study of local distortions and charge distributions modifications associated with each process is proposed. In some cases, the competition of CO/OO and magnetic phases is observed and phase separation, formation of nanoclusters of charge and spin order occurs. Systems to be studied include: Lightly doped manganites $La_{1-x}Ca_xMnO_3$, triangular lattice antiferromagnets $AgNiO_2$ and Ag_2NiO_2.

3. Local distortions, polaron correlations and dynamics, magnetostructural effects near magnetic phase transitions: This study has two parts:

   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: doped manganites $La_{1-x}(Ca/Sr)_xMnO_3$; $^{18}O/^{16}O$ isotopically modified $Sm_{1-x}Sr_xMnO_3$ and doped $SrTiO_3$ samples.
   ii) magnetostructural changes in first-order magnetic phase transition in MnAs, Ni_2MnGa and related systems.

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

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1 INTRODUCTION

The present proposal follows the experienced research methodology on new materials and subjects of the previous project IS390 whose main related results are summarized. We define a new working program based on the recognition of the possibilities that are offered by radioactive ion probe studies at ISOLDE to study specific aspects of the physics of magnetic and multiferroic compounds. For each main subject we present the motivation and discuss the experimental program to be followed. The reference list also accounts the publications and thesis that resulted from the previous related work.

Motivation review - general

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 [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 recent detailed studies from our group, using ^{111m}Cd PAC [9,10]: 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, like pure $LaMnO_3$. The temperature dependence of the environment fractions follows a 3D free percolation law, leading 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. The high temperature behavior of the distorted octahedra near the JT transition remains a subject of great interest and some controversy [11].

ii) in the $Pr_{1-x}Ca_xMnO_3$ manganite system, where competing ferromagnetic ($x<1/3$) and C/O ordered phases [12] can coexist at nanoscopic scale [13], the theoretical situation is still unclear at a microscopic level and alternative interpretations are given as polaronic charge trapping [14]. 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. The surprising result was the observation of electrical polarization at local scale, with critical behavior at the transition. This agrees with Efremov and collaborators [15] who predicted that an intermediate situation of CO between the extreme limiting situations of charge localized at nodes or bonds [16] breaks the inversion symmetry, leading to multiferroic materials, settling a new paradigm for ferroelectricity.

For multiferroics non-centrosymmetric manganites, $RMnO_3$ where R=Bi, Y, Tb, Dy, Ho[17] 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[18], while in Y manganites magnetoelastic distortions are proposed to dominate[8]. The bismuth ferrite $BiFeO_3$ presents the highest combination of antiferromagnetic and ferroelectric transition temperatures, both well above room temperature. The incorporation of divalent ions as dopants (Bi site) has resulted in an increase of magnetization whose mechanism has been proposed to depend on local vacancy structures[19]. 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). Outstanding cases are: $CoCr_2O_4$ with a strong clamping of ferroelectric and ferrimagnetic domains, and $CdCr_2S_4$ with colossal magnetocapacitive effects.

The study of the structural couplings and short-range order effects using PAC in manganites and other multiferroics is very timely and appropriate and has been initiated by our team.

Dramatic demonstrations of the delicate balance of interactions in manganites and oxides are associated with the oxygen isotope effect. In La-Pr-Ca and Sm-Sr manganites the isotope exchange of ^{18}O for ^{16}O induces a crossover between FM metallic behaviors and CO/AF insulator [20]. The detailed mechanism is not yet clear, but is probably connected with the decrease in the electron bandwidth for heavier isotopes, due to zero-point oscillations or to polaronic effects. Additionally, inhomogeneous ferroelectricity can be induced in $SrTiO_3$ by such isotope exchange, promoting rhombohedral polar clusters that subsequently grow in concentration and freeze out, and percolate below Tc [21].

2 WORK PROPOSITIONS

At ISOLDE, we perform local studies to understand some of the relevant structural and charge mechanisms of CMR oxides. $\gamma-\gamma$ 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.

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.

In the IS390 project we made an investigative study of the rare-earth manganites $RMnO_3$ encompassing a large range of ionic radius (R=Eu, Gd, Ho, Y, Er, Yb, La, Pr, Lu) and two structural phases: orthorhombic structure (distorted perovskite) for larger R (R=La-Dy) and hexagonal structure for smaller R (R=Ho-Lu, Y, In, Sc) (Fig. 1.1). Magnetic ordering occurs in both structural types but ferroelectric order occurs in the hexagonal manganites and only in part of the orthorhombic ones. The hyperfine studies up to date consisted of an analysis of characteristic parameters across the series (systematized in terms of ionic radius) and also the temperature dependence in selected samples: Eu, Gd, Y and Er manganite in order to establish a correlation with crystallographic, electric and magnetic data. Figure 1.2 shows representative R(t) experimental functions (left) and corresponding fits and Fourier transforms (right) measured at room temperature. The Cd probes interact with two electric field gradient (EFG) distributions, assumed as Lorentzian-like. In hexagonal manganites (R=Ho-Lu) the main EFG distribution has a frequency of ~120Mrad/s and an average asymmetry parameter (η) of 0.2. Orthorhombic $EuMnO_3$ and $GdMnO_3$ show also two EFG distributions. The main distribution is characterized by a higher frequency (~180Mrad/s) and also a higher η, showing a highly distorted local environment. The evolution of the asymmetry parameter and V_{ZZ} as function of the R ionic radius is presented in figure 1.3. On the hexagonal samples there is a decrease of the asymmetry parameter with the increase of the ionic radius; the higher distorted orthorhombic ones present an increase of η with the ionic radius. The inversion on the evolution trend seems to be in the border between the two crystalline structures.

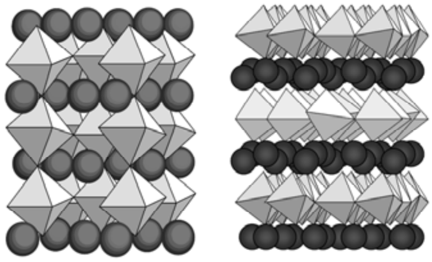

Fig.1.1: Perovskite (left) and hexagonal (right) phase structures of RMnO3 manganites, highliting the local octahedra. or trigonal bipyramid Mn-O environments.

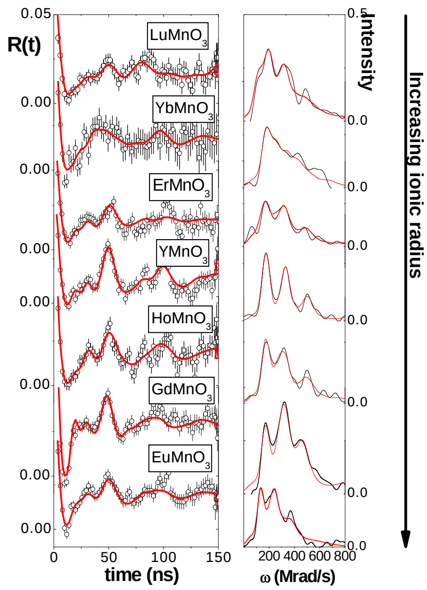

Fig.1.2: Representative R(t) experimental functions and correspondent fits for $RMnO_3$ measured at room temperature. (right) Corresponding Fourier transforms..

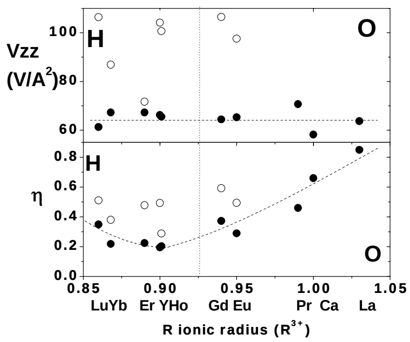

Fig.1.3: EFG principal component V_{zz} (top)., and asymmetry parameter η for the two EFG distributions as function of the rare earth ionic radius. Lines are guides for the eye.

One of the main findings of the IS390 project was the observation in $Pr_{1-x}Ca_xMnO_3$ manganite of particular features in the EFG that are signature of the presence of an electrical polarization at local scale, with critical behavior at the transition [10]. Figure 1.4 shows the component Vzz of the EFG tensor for sample x=0,35 across the C/O transition (at T_{CO}=235 K as confirmed by magnetic measurements) and the thick line an analysis including the contribution of local electric polarization. Fluctuations of EFG develop below T_{CO} and using the Landau theory of phase transitions, the critical temperature for the electric order was obtained (T_{EO}=206 K), signaled by the discontinuity in Vzz. Below T_{EO} the contribution of the spontaneous polarization gives a mild temperature dependence. This polarization, predicted recently [15] had until now, been undisclosed in this or similar systems. It is particularly relevant since it results from a new mechanism, where Charge and Orbital order sets an intermediate situation between the extreme limiting situations of charge localized at nodes or bonds breaking the inversion symmetry and leading to multiferroic behavior.

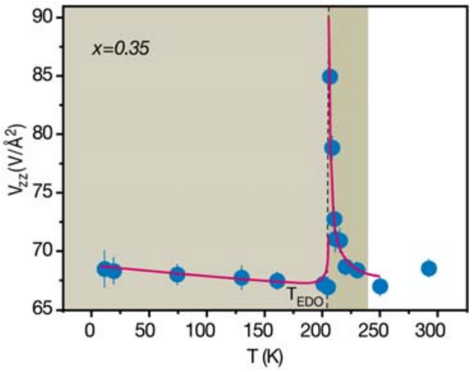

Fig.1.4: EFG V_{zz} thermal dependence and fits below the CO transition using the Landau theory of phase transitions for *x*= 0*:*35.

There are several mechanisms proposed to underlie the multiferroic behaviour, which requires the simultaneous fulfilment of specific symmetry conditions. In this new proposal we intend to deepen the study of multiferroic materials, enlarging the range of compounds (oxide materials). Two main lines are considered [22]:

a) *Multiferroic materials where magnetism and ferroelectricity have distinct origins, the FE critical temperature being usually higher: RMnO3 (R=Y, Lu, Ho) 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 line one highlights the case of $YMnO_3$ where large atomic displacements (0.05–0.09Å) comparable to those reported for archetypal ferroelectric materials are found. However this is not associated to orbital degrees of freedom (which could induce a Jahn–Teller mechanism, as in orthorhombic manganites). But these displacements are found well below the ferroelectric transition point (~900K), providing on the other hand a change in magnetic interactions (T_N~75K).

b) Charge-order induced MF in $RMnO_3$ (R=Tb, Dy) orthorhombic manganites, $RNiO_3$ (R=Y, Lu) nickelates; Spin-driven ferroelectricity (FE) in $MCrO_2$ (M=Cu, Ag) chromites and chromium spinels DCr_2X_4, (D=Cd, Hg, Co, Fe and X=O, S, Se)

In these materials there is a direct and intimate link between electric and magnetic cooperative phenomena, and the corresponding transition temperatures are closer. Ferroelectricity only appears due to some magnetic related effect, sometimes a change in the magnetic type of arrangement, as in some manganites.

Another interesting case that we will consider are chromium-based oxides is the $ACrO_2$ (A=Ag, Cu,..) (figure 1.5) delafossite system which has a triangular-lattice antiferromagnetic structure. Recent reports confirm that the geometrical frustration of the antiferromagnetic interaction favours a 120-degree spiral spin structure and

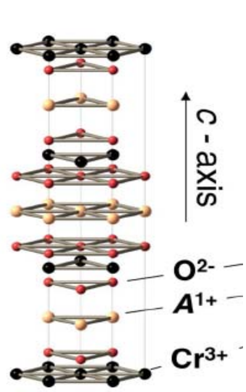

Fig.1.5: Crystal structure of *A*CrO_2 :delafossite structure (*A* =Cu or Ag)

antiferroelectricity emerges upon that spin order [23]. Preliminary results using ^{111}In are shown in figure 1.6.

Rare earth nickelates $RNiO_3$ (R=Y, Lu) are also predicted [3] to present an electric polarization allowed by charge order disproportionation (not exactly Ni^{2+}/Ni^{4+})and triggered by a magnetostrictive effect on bonds.

Finally, magnetically-driven multiferroism was also observed in some magnetic spinels (DCr_2X_4, D=Cd, Hg, Co, Fe e X=O, S, Se). Outstanding cases are: $CoCr_2O_4$, [24] which is ferrimagnetic and therefore has a net magnetic moment and is an example of the multiferroic compounds with both spontaneous magnetization and polarization of spin origin, in which there is strong clamping between the ferromagnetic and ferroelectric domains, namely leading to the magnetic reversal of the ferroelectric polarization. (Fig. 1.7). The other is $CdCr_2S_4$, [25] which presents ferromagnetic and relaxor ferroelectric order and a huge magnetocapacitive effect. Similar, but weaker, effects were also reported in $CdCr_2Se_4$. Colossal magnetocapacitance and colossal magnetoresistance were found in $HgCr_2S_4$ also [26] with also a short-range ferroelectric order assigned to it. This system exhibits complex spiral spin arrangement at low temperatures and thus $HgCr_2S_4$ 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 [27, 28, 29]. Previous studies by PAC [30] in some of these magnetic semiconductors did not address these issues, and so the investigation of multiferroicity here proposed using probes which belong to the system (Cd and Hg) is very timely.

We will use mainly the ^{111m}Cd (49 m) → ^{111}Cd, ^{199m}Hg (42 m) → ^{199}Hg, ^{117}Cd(2.4h) → ^{117}In and ^{111}Ag(7.45d) → ^{111}Cd PAC probes isotopes . Complementary test studies from the decays ^{204m}Pb(67m) → ^{204}Pb and ^{204}Bi(11h) → ^{204}Pb are also envisaged, to compare the hyperfine fields measured with different probe elements, thus inferring some element-specific local behaviour. Preliminary test studies from the decays ^{48}Cr(21.6h) → ^{48}V are also requested.

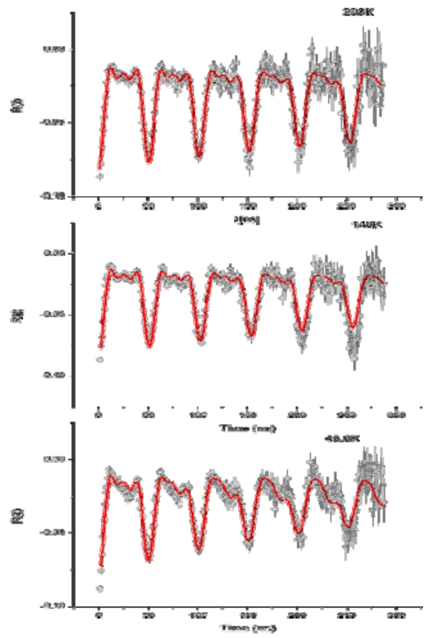

Fig.1.6: Perturbation function R(t) of ^{111}In on $AgCrO_2$ at different measuring temperatures.

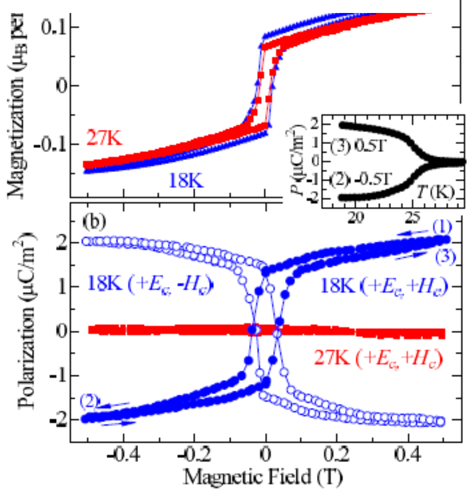

Fig. 1.7 Magnetic-field dependence of (a) magnetization and (b) electric polarization at temperatures above (27 K) and below (18 K) the ferroelectric transition temperature (25 K) of the spinel spinel $CoCr_2O_4$. The inset shows the temperature dependence of the polarization with two magnetic-field.

2.2 Concurrence or competition between charge- and orbital-order related effects

The study of local distortions and charge distributions modifications associated with charge (CO) and orbital (OO) orders is envisaged. Besides being most relevant to multiferroic mechanisms, the competition of CO/OO and magnetic phases is one of the cornerstones of the understanding of the colossal magnetoresistance phenomena, as it underlies the observed phase separation, formation of nanoclusters of charge and spin order. In undoped stoichiometric manganites ($AMnO_3$), where A can be a trivalent ion (La, or rare-earth) or a divalent (Ca, Sr, Ba) Mn has a single valence, Mn^{3+} or Mn^{4+} respectively. With a single electron in the degenerate eg Mn levels, Mn^{3+} is likely to promote the well known Jahn-Teller distortion of the MnO_6 octahedra (Fig 2.1), leading to orbital ordered structures. In IS390 the full $Pr_{1-x}Ca_xMnO_3$ orthorhombic series was studied presenting a change of EFG asymmetry parameter with Ca content x consistent with the Mn^{3+} /Mn^{4+} valence proportion and the macroscopic observation of charge and orbital ordering.

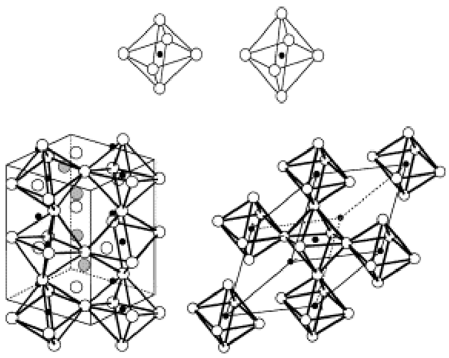

Fig.2.1: Jahn-Teller distortion of MnO_6 octahedra. and schematic orthorhombic and rhombohedral structures.

In parallel with the studies in multiferroics, which usually have a more complex phenomenology, we propose to study the following related cases:

a) To complement the study of orthorhombic $CaMnO_3$, a study of the divalent ion manganites $SrMnO_3$ and $BaMnO_3$ which lead to other crystallographic structures, rhombohedral and hexagonal is of importance to understand the local environments in these different structures, without the complexity magnetic/electric effects of multiferroic related compounds. Preliminary test results were of good quality and also enabled a consistent comparison with ab-initio calculations.

b) Recent theoretical analysis [31] presented the suggestion that charge-ordering (whether full disproportionation or charge density wave-like), may be a competing mechanism to the Jahn-Teller deformation to eliminate the degeneracy of d-electron levels. This alternative is theoretically more plausible and relevant the broader will be the degenerate band in the crystal (higher the conductivity). We propose to study this issue in lightly doped manganites $La_{1-x}Ca_xMnO_3$ (Fig 2.1). Increasing x, the conductivity increases dramatically (double-exchange). Preliminary results in x=0.05 Ca with ^{111}Cd are complex and controversial: while the macroscopic magnetic measurements point to the existence of a transition at ~500K, in agreement with the phase diagram, the EFG measurements only reveal the presence of anomalies at ~900K (rhombohedral- orthorhombic transition) and at ~750K (with a strong change of distorted fraction). No anomalous change was observed at or near 500K. To

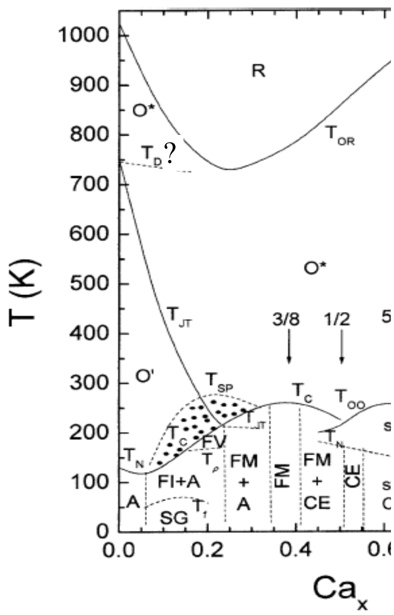

Fig 2.1: structural and magnetic phase diagram of the $LaCaMnO_3$ manganite

understand this situation and analyze it in view of the proposed mechanism, we need more data collection, with temperature detail and with one more composition (x~0.10).

Triangular lattice antiferromagnets $AgNiO_2$ and Ag_2NiO_2 were recently reported [32] to be another example of the charge-ordering competition with Jahn-Teller deformation, leading to novel magnetic ground state is observed at low temperatures with the electron-rich Ni^{2+} sites arranged in alternating ferromagnetic rows on a triangular lattice, surrounded by a honeycomb network of nonmagnetic and metallic Ni ions. This charge ordering occurs at some temperature above room temperature, which has not yet been reported, since neutron scattering studies are not sensitive enough. In Ag_2NiO_2 the situation is analogous and there is a valence change of the two Ag, with average valence 0.5 per ion (Fig 2.3), keeping Ni^{3+} ions undistorted.

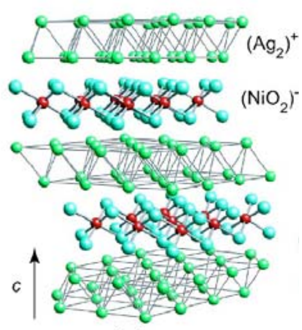

Fig.2.3: Ionic charge picture of Ag_2NiO_2 .

This study shall be performed with the PAC technique using the ^{111m}Cd (49 m) → ^{111}Cd isotope. Complementary studies onto decay from ^{117}Cd(2.4h) → ^{117}In and ^{111}Ag(7.45d) → ^{111}Cd PAC probes shall be done. Preliminary test studies from the decays ^{204m}Pb(67m) → ^{204}Pb and ^{204}Bi(11h) → ^{204}Pb are also envisaged. The aim is to compare the hyperfine fields, which are measured with different probe elements, thus inferring/probing some element-specific local behaviours.

2.3 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). Whether structural such phase transitions can in some cases be related to polaron formation is still an open issue. Structure of clusters, polaron dynamics and how far does phase coexistence extend are other important unsolved questions at the nanoscale level. As presented in the introduction, in our previous project we have shown that PAC provides a sensitive method to detect local distortions and their fluctuations occurring during PAC time scale allowing the investigation of local distortion, polaron correlations and dynamics. We propose to continue such studies on spontaneously inhomogeneous systems (phase separated) and also on systems near a phase instability, where the (oxygen) ionic dynamics change associated with the different isotope mass can trigger a new macroscopic behavior.

We propose the following three relevant subjects, already started on the previous project:

a) Polaron dynamics: an extension of a previous study of polaron dynamics in ferromagnetic insulator samples to ferromagnetic metallic (in the paramagnetic state) and to less distorted perovskites (rhombohedral). The system to be studied is the doped manganites $La_{1-x}(Ca/Sr)_xMnO_3$, with the possibility of tuning a orthorhombic-rombohedric structural transition by the doping x and Ca/Sr ratio.

b) 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 [21]
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 was built.

c) magneto-structural changes in first-order magnetic phase transition in MnAs, Ni_2MnGa and related systems.
The PAC probe obtained from decay of $^{77}Br \rightarrow {}^{77}Se$ was recently tested for γ-γ PAC measurements. The sample studied was MnAs with a magnetic and structural transition just above room temperature that has aroused particular attention in recent years in relation to the magnetic entropy change (latent heat) associated with the first-order transition due to the coupling of the magnetic and structural order parameters. Near 45ºC a transition occurs from a low temperature magnetic hexagonal phase to a paramagnetic orthorhombic phase. Strong thermal irreversibility effects are observed in magnetic measurements, as shown in fig. 3.1.

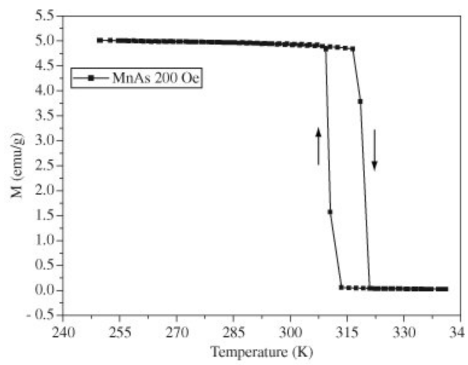

Fig. 3.1: Magnetization thermal cycle measured in MnAs near the magneto-structural transition.

The quite long half-life of ^{77}Br (57 h) allowed the data collection lasting for a few days, with several temperatures measured after one single implantation. Figure 3.2 show the PAC results measured on heating from room temperature to 100ºC (and down again, not shown), showing the dramatic change at the transition: disappearance of the hyperfine magnetic field and a very low remaining electric field gradient. Figure 3.3 shows the hyperfine parameters from the main local environment, fitted from the spectra measured at various temperatures. Second fractions not shown normally correspond to defects of undetermined origin, but for two cases when lowering the temperature at the hexagonal phase (shown in the figure at the dashed lines), the results suggest a coexistence of the two phases at those temperatures.
A hyperfine field of about 600 Mrad/s or 30 T represents the hexagonal phase. The orthorhombic phase is characterized by a very small electric field gradient and no magnetic field. The second fraction of a small E is represented at two temperatures suggesting phase co-existence of the two phases in that region.
The temperature irreversibility of the 1st order phase transition is seen locally by the hysteresis of the hyperfine field, similar to the hysteresis already found in the magnetization.
We propose to pursue these preliminary studies to analyse in more detail the magnetostructural phase transition in MnAs (another transition occurs at higher temperatures, ~120 ºC) and to extend the use of these isotopes to study other magneto-structural effects, such as in the magnetic shape-memory alloy Ni_2MnGa.

For these studies, we wish to use the ^{111m}Cd (49 m) $\rightarrow$ ^{111}Cd, ^{73}Se (7.2h) $\rightarrow$ ^{73}As and ^{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.

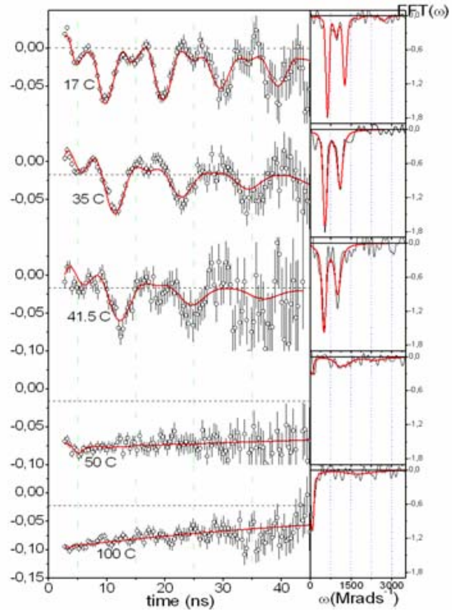

Fig.3.1: PAC spectra and Fast Fourier transforms for MnAs on heating. The top three spectra on the left correspond to the ferromagnetic hexagonal phase. Above the first-order transition at 45C, the orthorhombic paramagnetic phase is obtained.

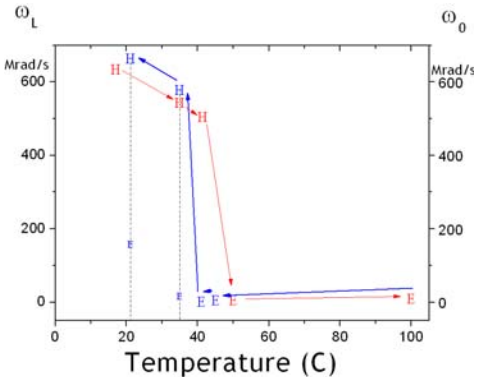

Fig.3.3: Hyperfine parameters :
Red/Blue :Raising/Lowering temperature
H – HMF; E -. V_{zz}.

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**
$RMnO_3$ +	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	
$Sr/BaMnO_3$	Pellets	Solid State Reaction				
$MCrO_2$ $+DCr_2X_4$	Pellets	Solid State Reaction				
$Sm_{1-x}Sr_xMnO_3$ ^{16}O and ^{18}O	Pellets		Solid State Reaction			
RNiO3 $+AgNiO_2$	Pellets	Solid State Reaction				
$MnAs+Ni_2MnGa$	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			
^{204m}Pb(67 m)	✓		
↓		✓	
^{204}Pb			
^{204}Bi(11.2h)	✓		
↓		✓	
^{204}Pb			
^{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 of ^{204m}Pb and ^{204m}Bi, since the beam is known to be contaminated with short lived alpha emitters.

BEAM TIME REQUEST

We estimate a total of 32 shifts of beam time plus 2 shifts of tests within two years 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	18
^{199m}Hg	^{199m}Hg	~ 2.0E8	Molten Pb	plasma	4
^{117}Cd (g.s.)	^{117}Ag (*)	~ 5.0E8	UC_2	laser (Ag)	4
^{111}Ag	^{111}Ag	~ 1.0E8			
^{204m}Pb	^{204m}Pb(*)	~ 3.0E7	UC_2	laser (Pb)	2
^{204}Bi	^{204}Bi	~ 6.6E6	UC_2	laser (Bi)	1-test
^{77}Br	^{77}Br	> 1.0E8	ZrO_2	plasma	4
^{73}Se	^{73}Se	> 1.0E8			
^{48}Cr	^{48}Cr	~ 1.3E5(**)	ZrO_2	plasma	1-test
				total:	32+2-test

(*) 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.).

(**) Actual developments performed at the plasma ion sources and the possible replacement of ZrO_2 fibbers by Y_2O_3 powder are expected of producing a significant increase of yields.

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 is now addressed by one Master and four PhD students They actively participate in beam times, sharing afterwards the sample preparation and crystallographic/transport properties characterization and the analysis of the PAC results.

Present post-docs and students doing work with the subjects of the project:

Pradip Kumar Jana: Post doctoral to start 2009
João Amaral: Started PhD in 2005
Tânia Manuela Mendonça: Started PhD in 2006
João Nuno Gonçalves: Started PhD in 2008
Narciso Soares: research grant; PhD to start 2009
Mariana Proênça, Started PhD in 2008
Gonçalo Oliveira: MSc Student
Marcelo Baptista: MSc Student

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

Annex: The following works resulted from the IS390 project (2001-2008)

PhD and MSc thesis associated totally or partially to work performed in IS390

Local Probe and Bulk Property Studies on Highly Correlated Electron Systems
João Pedro Araújo, PhD in Physics, at Universidade do Porto, January 2002

Local Probe Studies on Lattice Distortions and Electronic Correlations in Colossal Magnetoresistive Manganites
Armandina Maria Lima Lopes, PhD in Physics, at Universidade de Aveiro, December 2006

Cálculos de estrutura electrónica e parâmetros hiperfinos em óxidos
João Nuno Santos Gonçalves MSc thesis on Engineering Physics at Universidade de Aveiro, September 2007

Manuscripts in International Journals (10+2 submitted)

New phase transition in $Pr_{1-x}Ca_xMnO_3$ system: evidence for electrical polarization in charge ordered manganites
A.M.L. Lopes, J.P. Araujo, V.S. Amaral, J.G. Correia, Y.Tomioka and Y. Tokura
Physical Review Letters, 100, 155702 (2008)

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A.M.L. Lopes, J.P. Araujo, T.M. Mendonca, J.S. Amaral, A.M. Pereira, P.B.Tavares, V.S. Amaral, J.G. Correia.
Journal of non-crystalline solids 354 (2008) 5315–5317

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Cadmium Doping at Mn Site in $Pr_{0.5}Ca_{0.5}MnO_3$
A.M.L Lopes, J.P. Araújo, A.M. Gomes, M.S. Reis, V.S. Amaral, P.B. Tavares
Journal of Magnetism and Magnetic Materials, 272-276,1767 (2004)

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J.P. Araújo, J.G. Correia, V.S. Amaral, P.B. Tavares, F. Lencart-Silva, A.A.C.S. Lourenço, J.B. Sousa, J.M. Vieira, J.C. Soares
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J. N. Gonçalves, H. Haas, A. M. L. Lopes, V. S. Amaral, J. G. Correia.
Journal of Magnetism and Magnetic Materials (Submitted)

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Physica B (submitted)

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J.P. Araújo, A.M.L. Lopes, V.S. Amaral, J.G. Correia
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Nanoscopic scale studies: a key role to understand manganites
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New phase transition in $Pr_{1-x}Ca_xMnO_3$ Charge Ordered manganites
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Jahn-Teller polaron clusters in ferromagnetic insulator manganites
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