

## Proposal 20130191 (Standard)

| Scientific general part |                                                                                                            |
|-------------------------|------------------------------------------------------------------------------------------------------------|
| <b>Title</b>            | Mechanism of the magnetostructural transition in p-electron enriched Mn-based antiperovskites: EXAFS study |
| <b>Keywords</b>         | EXAFS, antiperovskite, magnetostructural transition                                                        |
| <b>Research Area</b>    | Condensed matter physics                                                                                   |

| Proposers description |                       |                        |          |
|-----------------------|-----------------------|------------------------|----------|
|                       | Name                  | Institute              | City     |
| MP                    | Prof. Dr. Mehmet ACET | Univ. Duisburg-Essen   | Duisburg |
|                       | Dr. Kaustubh PRIOLKAR | Goa Univ.              | Goa      |
|                       | Dr. Öznur ÇAKIR       | Yildiz Technical Univ. | Istanbul |
|                       | Mrs. Elaine DIAS      | Goa Univ.              | Goa      |

| Beamlines/Branches Requirements Choice 1          |                                |
|---------------------------------------------------|--------------------------------|
| <b>Requested Beamline/Branch</b>                  | ODE                            |
| <b>Beamline/Branch responsible contacted</b>      | Dr. François BAUDELET          |
| <b>Experimental station or type of techniques</b> | A.1-EXAFS                      |
| <b>Experimental station responsible contacted</b> | Dr. François BAUDELET          |
| <b>Samples environment</b>                        | Low temperature : down to 10 K |
| <b>Electron beam requirements</b>                 | No requirement                 |
| <b>Photons energy range requested</b>             | keV                            |
| <b>Number of Shifts (8h) Required</b>             | 12                             |

| Other Experiment Requirements                             |                                                                            |
|-----------------------------------------------------------|----------------------------------------------------------------------------|
| <b>Unacceptable dates</b>                                 | July, August 2013                                                          |
| <b>Prefering starting time</b>                            | October-December 2013                                                      |
| <b>Peer Review Committee</b>                              | PRC2: Electronic and magnetic property of matter / Surfaces and Interfaces |
| <b>Second Peer Review Committee required</b>              | No                                                                         |
| <b>Chemistry lab. 1 required</b>                          | No                                                                         |
| <b>Chemistry lab. 2 (with restricted access) required</b> | No                                                                         |
| <b>Surfaces lab. required</b>                             | No                                                                         |
| <b>Biology lab. 1 required</b>                            | No                                                                         |
| <b>Biology lab. 2 (with restricted access) required</b>   | No                                                                         |
| <b>High pressure lab. required</b>                        | No                                                                         |

| Experiment Context                                      |                   |
|---------------------------------------------------------|-------------------|
| <b>Reasons of the need of the Synchrotron Radiation</b> |                   |
| Synchrotron radiation is required for EXAFS studies     |                   |
| <b>Previous Synchrotron Radiation experiment</b>        | Yes               |
| <b>... where?</b>                                       | LURE, ESRF, BESSY |
| <b>Synchrotron Radiation already used project</b>       | No                |
| <b>Already submitted proposal</b>                       | No                |

| Proposal framework                                                |     |
|-------------------------------------------------------------------|-----|
| <b>Is the proposal supported by any contract?</b>                 | No  |
| <b>Is the proposal in collaboration with an industrial group?</b> | No  |
| <b>Is the proposal a significant part of PhD thesis?</b>          | Yes |
| <b>Do you request European support (TNA program)?</b>             | No  |

**Abstract**

The magnetostructural transformation in Mn<sub>3</sub>GaC is a cubic ferromagnetic to cubic antiferromagnetic transition wherein the unit cell volume exhibits a pronounced discontinuity. Anomalously, the high temperature ferromagnetic phase has a smaller cell volume than the low temperature antiferromagnetic phase. This is thought to be related to an increased Mn3d  $\zeta$  C2p hybridization in the antiferromagnetic state which strengthens the Mn-C-Mn antiferromagnetic interactions over the Mn-Mn ferromagnetic interactions causing the sample to contract on cooling to the antiferromagnetic state. However, there is no direct evidence available for this hypothesis yet. By using p-electron enriched Mn<sub>3</sub>GaC samples, i.e., by adding excess C (Mn<sub>3</sub>GaC<sub>1.05</sub>), replacing partially C by N (Mn<sub>3</sub>GaC<sub>0.85</sub>N<sub>0.15</sub>), and replacing Ga by Sn (Mn<sub>3</sub>Ga<sub>1-x</sub>Sn<sub>x</sub>C), we aim in this proposal to shed a light on the change in the hybridization between Mn3d and C2p bands by Mn K edge EXAFS and XANES studies.

**1/ Background:**

The antiperovskite  $\text{Mn}_3\text{GaC}$  has a cubic structure and belongs to a class of materials that are gaining interest due to their magnetocaloric properties [1,2]. The nominally stoichiometric composition of  $\text{Mn}_3\text{GaC}$  has an antiferromagnetic (AFM) ground state. It undergoes a second order magnetic transition from paramagnetic to ferromagnetic state at  $T_C = 249\text{K}$  followed by a first order magnetic transformation to antiferromagnetic state at  $T = 160\text{K}$  [3,4].

Concentration of carbon plays a vital role in inducing the first order magnetic transformation. While the composition deficient in carbon exhibits only a paramagnetic to ferromagnetic transition at  $T_C = 318\text{K}$ , the composition with excess carbon undergoes a first order magnetic transition from a “strongly paramagnetic” state to antiferromagnetic state [5]. Such a transition can also be induced by nitrogen substitution resulting in  $\text{Mn}_3\text{GaC}_{1-x}\text{N}_x$  ( $x \leq 0.15$ ) for which  $M$  v/s  $T$  is recorded under various fields for  $x=0.15$  is shown in Fig. 1.

The magnetostructural transformation is a cubic-cubic phase transition wherein the cell volume exhibits a pronounced discontinuity. The high temperature cubic phase has a lattice constant of  $3.89 \text{ \AA}$  while the low temperature phase has a lower value of lattice constant  $a = 3.878 \text{ \AA}$ . Although the role of carbon in inducing the magnetic phase transformation has been contemplated in literature, the exact nature of the driving force in inducing magnetostructural transformation is not yet understood. Neutron and X-ray diffraction studies have shown that increase in C concentration results in a lattice expansion increasing the Mn-Mn next nearest neighbour distance. This is implied to result in an increased  $\text{Mn}3d - \text{C}2p$  hybridization which strengthens Mn-C-Mn antiferromagnetic interactions over the Mn-Mn ferromagnetic interactions causing the sample to transform via a discontinuous volume contraction [1]. There is no direct evidence hitherto available for this hypothesis.

Furthermore, by using magnetic field of the order of 1T, the antiferromagnetic ground state can be transformed to ferromagnetic one without any kinetic arrest. This makes it a very important candidate for studying the effect of field induced magnetic transformations. This is shown in Fig. 2(a) where  $M$  v/s  $H$  is shown across the transformation region showing conversion of AFM state to FM state and in Fig. 2(b) where  $M$  v/s  $T$  is recorded in 100 Oe for a sample cooled in 6 T applied field during warming, cooling and re-warming cycles.

**2/ Objective:**

Our main aim is to study Mn K edge EXAFS as a function of temperature and magnetic field in order to understand the mechanism of magnetostructural transformation. We propose to study Mn K EXAFS in the paramagnetic, ferromagnetic and antiferromagnetic phases of  $\text{Mn}_3\text{GaC}$  in presence and in absence of magnetic field. Studies in absence of magnetic field will allow us to determine Mn-C nearest neighbour and Mn-Mn next nearest neighbour bond distances and map any kind of local structural disorder that takes place as a result of first order magnetic transition. The proposed EXAFS experiments in presence of magnetic field will allow us to study the changes in Mn-C and Mn-Mn bond distances due to the transformation from antiferromagnetic state to ferromagnetic state as observed in magnetization and neutron diffraction studies.

**3/ Experimental method:**

It is planned to record Mn K edge XAFS in transmission as a function of temperature and magnetic field. XAFS data will be recorded from -200 eV to about 1200 eV with respect to the absorption edge. Each XAFS spectrum will be repeated at least 3 times to average out statistical noise.

The following compounds belonging to  $\text{Mn}_3\text{GaC}$  type antiperovskites prepared by solid state reaction will be taken up for EXAFS study:

Mn<sub>3</sub>GaC, Mn<sub>3</sub>GaC<sub>1.05</sub>, Mn<sub>3</sub>GaC<sub>0.85</sub>N<sub>0.15</sub>, and Mn<sub>3</sub>Ga<sub>1-x</sub>Sn<sub>x</sub>C (x = 0.2, 0.4, 0.5, 0.6, 0.8 and 1). XAFS at Mn K edge will be recorded at about 3-4 temperatures, carefully chosen in different magnetic states of each compound. In case of first three samples and Mn<sub>3</sub>SnC, XAFS will also be recorded in magnetic field of 1T. Unlike Mn<sub>3</sub>GaC, Mn<sub>3</sub>SnC is reported to exhibit a para to ferromagnetic transformation with very small hysteresis. It also exhibits kinetic arrest which is absent in Mn<sub>3</sub>GaC. Therefore a contrast will be available to understand magnetic field induced effects in these antiperovskites.

In all there will be 36 XAFS scans at Mn K edge at various temperatures in zero applied fields and 16 XAFS scans in a magnetic field of 1T. Mn K edge energy is 6539 eV which is suitable for ODE beamline at Soleil. This beamline has the facility of variation of temperature and magnetic field and therefore is ideally suited for our experiments.

#### 4/ Describe the results expected:

Variation of carbon content and nitrogen doping critically affects the magnetic and transport properties of Mn<sub>3</sub>GaC type antiperovskites. The carbon excess and nitrogen doped samples do not undergo a transition to ferromagnetic state, instead they transform to an antiferromagnetic ground state even before the para to ferromagnetic transition is complete. Resistivity measurements on carbon excess compound show a semiconductor like behaviour, hinting at localization of conduction electrons in the hybrid Mn 3d – C 2p band. This localization is expected in spite of increase in unit cell volume of carbon excess compound. EXAFS and XANES at Mn K edge will shed a light on this increased hybridization between Mn3d and C2p bands.

A change from first order magnetic transition from antiferromagnetic state to a ferromagnetic state can also be achieved by substitution of Ga by Sn resulting in Mn<sub>3</sub>Ga<sub>1-x</sub>Sn<sub>x</sub>C (0 ≤ x ≤ 1) series of compounds. Local structural study around the Mn K edge in these set of compounds wherein x is carefully varied will enable to develop an understanding of the factors responsible for the above magnetic transition. We also propose to conduct EXAFS study at several temperatures across magnetic transitions in Mn<sub>3</sub>Ga<sub>1-x</sub>Sn<sub>x</sub>C (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8 and 1). With these proposed experiments we intend to unravel all factors responsible for magnetostructural transformation in Mn<sub>3</sub>GaC type antiperovskites.

#### 5/ Beam time requested justification:

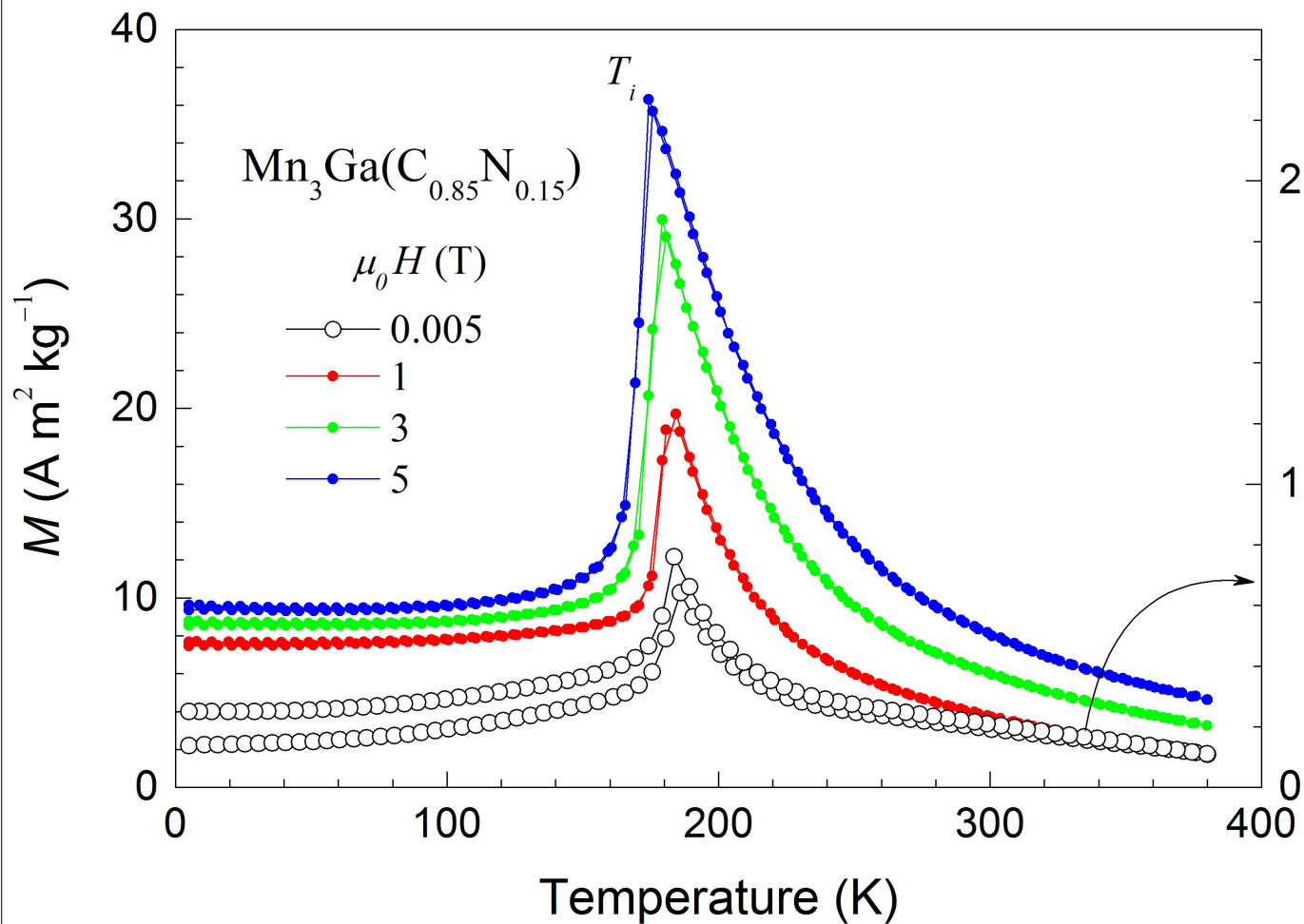
Total time proposed is as follows:

- Total no. of scans in no magnetic field at 4 different temperatures (9 samples) – 36
  - Total no. of scans in 1T magnetic field at 4 different temperatures (4 samples) – 16
  - Time for one XAFS (along with repeats) scan in transmission mode – 1.5 h each
  - Total time for XAFS in no magnetic field – 54 hours
  - Total time for XAFS in 1T magnetic field – 24 hours
  - Time for beamline alignment and cooling and warming of cryostat = 15 h
- Total beamtime requested at the XAFS beamline 93 h (~12 shifts)

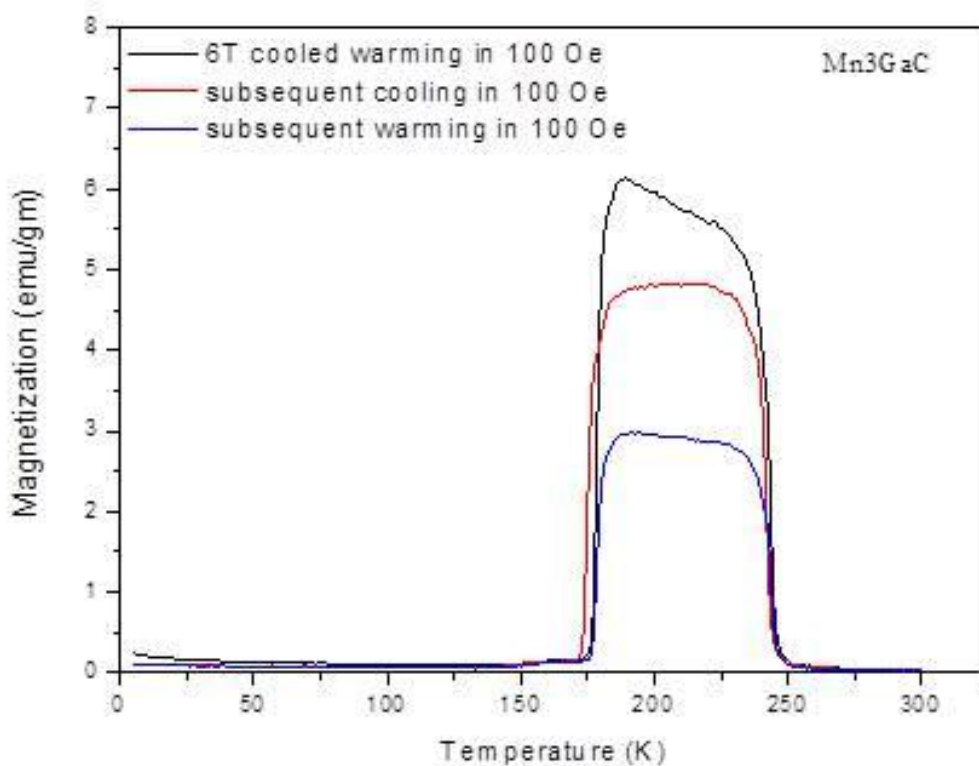
#### 6/ References:

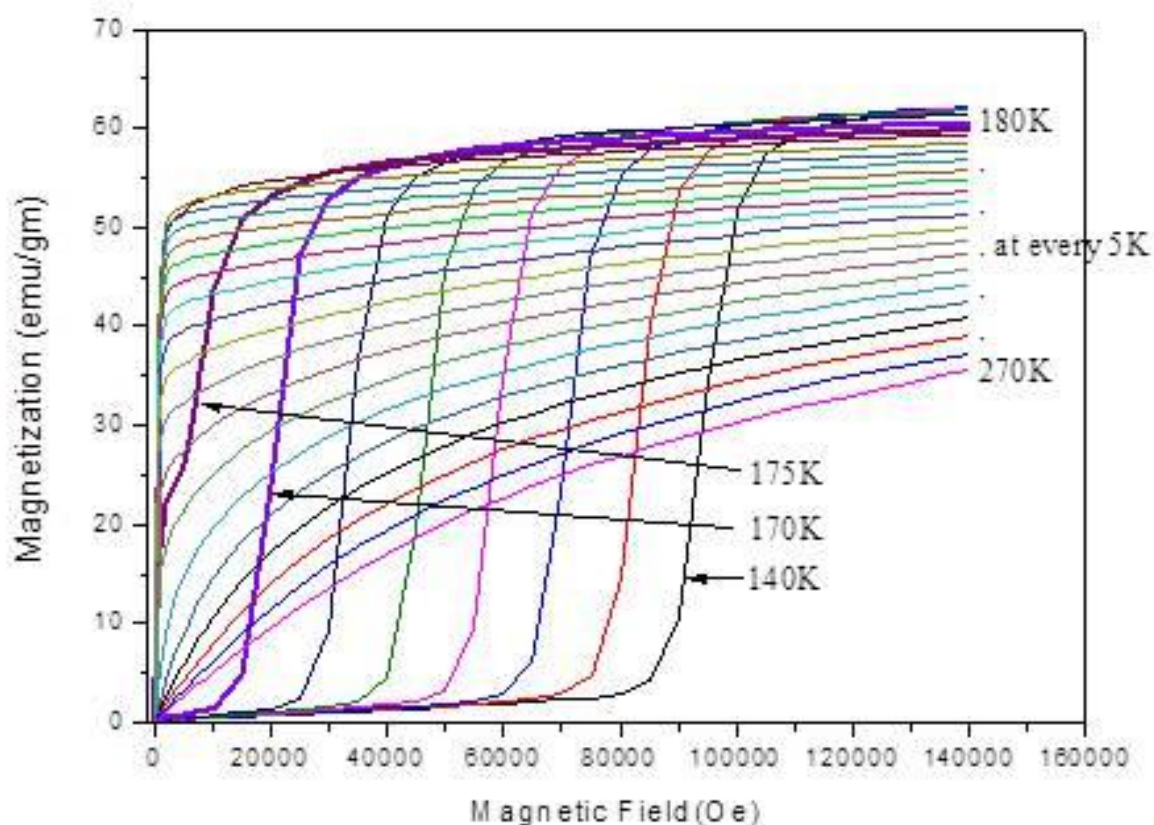
1. **c/** Fruchart, D and Bertaut E, J. Phys. Soc. Jpn. 44, 781 (1978)
2. **b/** Çakir, Ö and Acet, M Appl. Phys. Lett. 100, 202404 (2012)
3. **c/** Kamishima, K, Bartashevich M, Goto, T, Kikuchi, M and Kanomata, T J. Phys. Soc. Jpn. 67, 1748 (1998)
4. **c/** Kamishima, K, Goto, T, Sasaki, T, Kanomata, T and Inami, T J. Phys. Soc. Jpn. 71, 922 (2002)
5. **b/** Dias E, Priolkar K and Nigam A K, J. Phys D: Appl. Phys. (2013).

Attachment: Fig. 1. M v/s t of Mn<sub>3</sub>Ga(C<sub>0.85</sub>N<sub>0.15</sub>) recorded under various fields



Attachment: Fig 2a. M v/s H across the AF-FM transformation region



Attachment: Fig. 2b. M v/s T in 100 Oe for Mn<sub>3</sub>GaC

## Other sample (gas, chemical, solids) : Antiperovskite

If no data sheet is available give detailed information about samples and chemical substances to be used in the experiment

|                              |                |
|------------------------------|----------------|
| Name                         | Antiperovskite |
| Is the sample                | a bulk         |
| Mass (in g)                  | 3              |
| Volume (in cm <sup>3</sup> ) | 1              |
| Mole [ mole ]                | n/a            |
| Concentration                | n/a            |
| Packaging temperature [°C]   | 20             |
| Packaging pressure [bar]     | 1              |

## Safety aspects

|                                                                                         |     |
|-----------------------------------------------------------------------------------------|-----|
| Is the sample toxic?                                                                    | No  |
| Is the sample explosive?                                                                | No  |
| Is the sample inflammable?                                                              | No  |
| Is the sample carcinogenic?                                                             | No  |
| Is the sample harmful (noxious)?                                                        | No  |
| Is the sample irritant?                                                                 | No  |
| Is the sample pollutant?                                                                | No  |
| Is the product corrosive?                                                               | No  |
| Does the sample present any risk to human health?                                       | No  |
| Does the sample present any risk to environment?                                        | No  |
| Is there any danger associated with the reception, the use or the disposal of a sample? | No  |
| Is the sample prepared outside SOLEIL?                                                  | Yes |
| Is the sample manipulated at SOLEIL?                                                    | No  |

| Other sample (gas, chemical, solids) : Antiperovskite |                     |
|-------------------------------------------------------|---------------------|
| After the experiment the sample will be?              | Removed by the user |