Institut Farman FR 3311 : appel à projets AAP 2016

Proposition de projet Farman – Volet scientifique

MaTher – Materials for Thermo-magnetic Energy Harvesting
SATIE – LMT - GeePs

Intitulé du projet (acronyme ou autre) : MaTher

Titre explicite : Materials for Thermo-magnetic Energy Harvesting

Version : Paris-Saclay

Responsables scientifiques :

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Durée du projet : 24 mois

Membres pressentis de l'équipe-projet :

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Abstract:

The goal of this project is to foster the research on magnetocaloric materials (MCM) as working substances in thermo-magnetic power generation (TMG) devices designed to use low grade waste heat as their input, through an improved and multi-scale tailoring of magnetic properties and phase transitions of novel materials. Focusing on one of the most promising family of MCM, the Mn-Fe-P-Z (where Z=Si, B, As) our primary scientific aim is to demonstrate that a breakthrough advance in our understanding and control of the strong magneto-elastic nature of the phase transition in these materials is the key to tailor material performances towards the achievement of the researched properties. The project relies on the combination of advanced characterization and multiscale modelling expertises of the partners

1. Scientific and Technological Objectives

Nowadays much of the industrial energy consumption consists in thermal processes such as cement and steel production, where about one third of the used energy is discarded as low grade heat. Therefore the supply of waste heat is sufficiently abundant as to make it a key target for technology development. A thermal energy harvesting system with high power density and/or efficiency does not currently exist. Many efforts have been done on thermoelectric systems (TE). However TE efficiency and power density are still too small for application purposes. Energy harvesting systems from waste heat based on thermomagnetic generation (TMG) have been studied since the Patents by Edison and Tesla in 1890, and the 1948 paper by Brillouin and Iskenderian[1]. The advent of giant magnetocaloric material (MCM)[2] imposes a fresh assessment of the potential of TMG in terms of efficiency and power, and an increasing interest towards this opportunity is apparent from recent publications[3]. TMG from waste heat involves harnessing the pyromagnetic effect (PE), namely the induction of a magnetization by the action of a temperature change. **The goal of this project is to foster the research on MCM systems as working substances in thermo-magnetic power generation (TMG) devices designed to use low grade waste heat as their input, through an improved and multi-scale tailoring of magnetic properties and phase transitions of novel materials.**

To achieve this objective we propose to raise the transition temperature of some of the most promising MCE materials (the ΔT defining low grade heat is still not universally accepted, however the interval of interest lay between room temperature and 500 K) preserving the relevant properties (i.e. a sharp transition with relevant values of entropy and magnetization changes).

Focusing on one of the most promising family of MCM, the Mn-Fe-P-Z (where Z=Si, B, As) **our primary scientific aim is to demonstrate that a breakthrough advance in our understanding and control of the strong magneto-elastic nature of the phase transition in these materials is the key to tailor material performances towards the achievement of the researched properties**. More precisely, connecting material design at several length-scales to advanced characterization and to the simulation of key technological

1 L. Brillouin et H. P. Iskenderian, « Thermomagnetic generator », *Fed. Telecommun. Lab.*, 1948.
2 E. H. Brück, *J. Phys. D* **38**, R381 (2008).
3 D. Vuarnoz, A. Kitanovski, C. Gonin, Y. Borgeaud, M. Delessert, M. Meinen, et P. W. Egolf, *Appl. Energy*, vol. 100, p. 229-237 (2012) ; T. Christiaanse et E. Brück, *Metall. Mater. Trans. E*, vol. 1, nº 1, p. 36-40, (2014).

properties of a device, we shall show that the use of giant magnetocaloric materials into TMG devices can push the current TMG's technology readiness level (TRL) from 3 to 4[4].

In synthesis our objectives are:

a) to tailor relevant magnetic properties above room temperature (e.g. magnetization change, latent heat, magnetic anisotropy) of Mn-Fe-P-Z (Z= Si, B, As) alloys using magneto-elastic coupling at different scales;

b) to explore high temperature magnetic phase transitions for deployment in TMG in low grade waste heat scenarios (between room temperature and 200 C).

2. Context

The alloys that make the object of our proposal show an itinerant electron metamagnetic transition (IEM) with a strong magneto-elastic coupling. IEM are extremely sensitive to intrinsic properties (the metamagnetic transition is lead by the electronic density of states at the Fermi level with a key role of spin fluctuations[5]) and notably to composition. In the same time the strong magneto-elastic coupling makes the role of microstructural features (local strains, coupling with surface and linear defects) as relevant as the intrinsic ones[6]. However, while Mn-Fe-P-Z alloys have been often pointed out as a suitable and cheap (i.e. critical raw materials free) material for TMG[7], no systematic studies of their high temperature properties have been published. Moreover, the modelling of the transition is far more difficult than in the case of the La-Fe-Si IEM due to the highly anisotropic magneto-elastic effect.

3. Concept and approach

In two recent publications by the SATIE MME[8] [9] group the interplay between magneto-elastic nature of the transition and the extrinsic properties of the materials (i.e. microstructure, porosity, nature and density of the defects) has been studied form a global point of view (magnetometry, XRD as a function of temperature) as well as from the local point of view (Hall probe imaging performed in collaboration with Imperial College Solid State Physics group).

Here the global XRD measurement of the lattice parameters allows to follow the evolution of phase coexistence all along the first order transition (see Fig. 1).

The in-situ XRD equipment recently developed at LMT laboratory in the frame of the 2013 Farman project IDEFIX[10] offers a unique opportunity to achieve a relevant advancement in this direction by studying the interplay between strain distributions at different scales and the properties of the magnetic phase transition

4 Namely from “Analytical and experimental critical function and/or characteristic proof of concept”, correspondting to TLR 3, to “Component and/or breadboard validation in laboratory environment” correspondting to TLR 4.
5 E. Wohlfarth, and P. Rhodes, *Philos. Mag.* **7**, 1817-1824 (1962); A. Fujita, S. Fujieda, K. Fukamichi, H. Mitamura, and T. Goto, *Phys. Rev. B* **65**, 014410 (2001)
6 A. Fujita, D. Matsunami, and H. Yako, *Appl. Phys. Lett.* **104**, 122410 (2014).
7 O. Tegus, B. Li-Hong, and S. Lin, *Chinese Phys. B* **22**,037506 (2013); N. H. Dung, et al.,Adv. Energy Mater. 1,1215-1219 (2011)
8 A. Pasko, A. Bartok, K. Zehani, L. Bessais, F. Mazaleyrat et M. LoBue, *AIP Advances*, accepted (2015) – in press
9 A. Bartok, M. Kustov, L.F. Cohen, A. Pasko, K. Zehani, L. Bessais, F. Mazaleyrat et M. LoBue, *J. Magn. Magn. Mater.*, (2015), doi:10.1016/j.jmmm.2015.08.045.
10 M.D. Fall, O. Hubert, K. Lavernhe-Taillard et A. Maynadier, *SEM 2014 Annual conference proceeding* (2014)

(see Fig. 2). Besides, the long term experience of the GeePs PIEM group where an original multi-scale model of the reversible magneto-elastic[11] behaviour of ferromagnetic materials has been developed and validated, shall make possible to reach an unprecedented control on material properties through the microstructure/defect engineering.

In summary we propose to:

1. Produce structurally controlled samples of Mn-Fe-P-Si high temperature phases using SATIE experience in this field (trough its long term collaboration with ICMPE and its participation to the Ile de France SPS platform) and perform standard magnetometric and thermo-magnetic characterization (SATIE) and global XRD measurements.

2. Use the in-situ XRD equipment at LMT to study the relationship between local microstructural features and global behaviour of the samples performing diffraction measurements during tensile tests and heating-cooling cycles in applied magnetic field.

3. Modelling the interplay between local and average magnetic properties of the samples using the multi-scale approach developed in collaboration between LMT and GeePs.

Expected results and impact

The project approach is based on a wise balance between novel high risk concepts (thermomagnetic generation is a low TRL technology and the use MCM as active substance is an emerging concept) and well established knowledges and know-hows (MCMs for magnetic cooling have been studied and modelled since many years at SATIE, the study of shape memory alloys and magneto-elastic coupling is one of the key skills at LMT and multi-scale multi-physical modelling are well established techniques at GeePs). The main scientific output shall be an enhanced capability to control and understand properties of first order magnetic transitions for applications in a thermomagnetic technology. Waste heat scavenging will be one of the key energy technologies able to improve the sustainability of our electricity base.

This project has been conceived in full synergy with the LASIPS Labex project MaTEC where a 12 moths post doctoral position shall be founded on the very same topic. The two projects together will contribute to create a robust cooperation between two ENS de Cachan laboratories (SATIE and LMT) and a Paris Saclay University one (GeePs) on an emergent topic. This collaboration will be the starting point for further actions at the national (ANR) and international (H2020) scale. Moreover at least two of the partners (SATIE and GeePs) could share, in the frame of larger scale forthcoming projects, their skill in energy-system prototyping and modelling making this project, a material science one at this stage, a promising starting point for more advanced technological actions.

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11 L. Daniel, O. Hubert, N. Buiron et R. Billardon, *J. Mech. Phys. Sol.*, **56**, 1018-158 (2008).

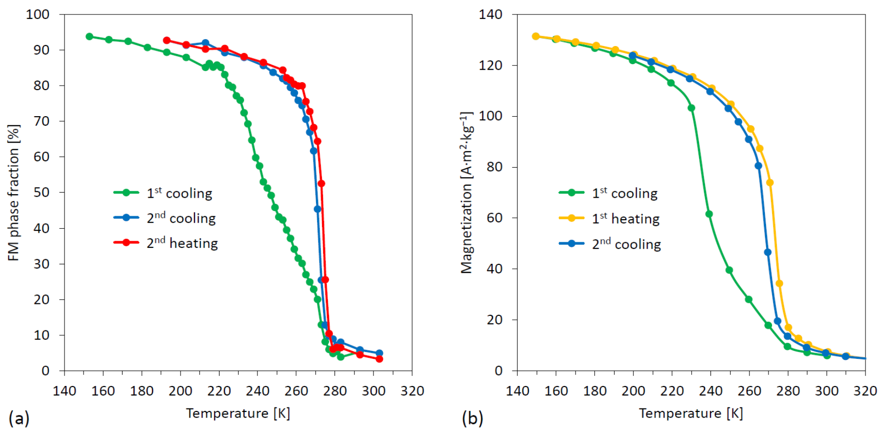

FIG. 1. Structural and magnetic characterization of the temperature-induced phase transition ($Mn_{1.30}Fe_{0.65}P_{0.5}Si_{0.5}$ powder sample): (a) volume fraction of the ferromagnetic phase calculated from the XRD data; (b) specific magnetic moment in an applied field of 1 T obtained from the VSM measurements.

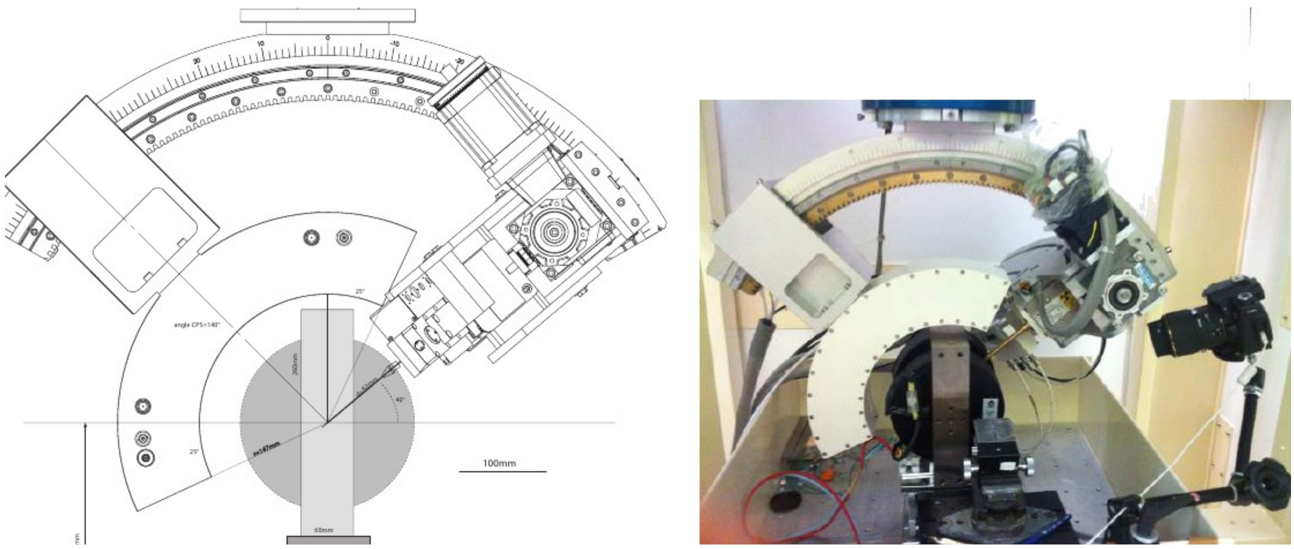

FIG. 2. The XRD equipment developed in the frame of the IDEFIX Farman project has been designed to study the phase fraction of different variants in shape memory alloys. The equipment will be optimised to the study of magnetocaloric systems by improving the temperature control system to perform thermal cycling under different field and load conditions.

Originalité du projet (1/2p)

The use of magnetocaloric alloys as working substance in thermo-magnetic power generation is nowadays an emergent technology. The interest towards the opportunity for energy harvesting at different scales using pyromagnetic effect is growing in different countries (US, Switzerland, Netherlands and Denmark). In spite of the presence, in France, of a major industrial producer of magnetocaloric materials (Erasteel) there is no, at present, relevant research commitments on this topic. Our project represent, from this point of view, a pioneering contribution whose success can contribute to the creation of a larger, national scale, consortium of labs and industrial partners focused on novel high impact energy harvesting technology.

Besides, the study of the interplay between intrinsic and extrinsic properties in functional materials represents one of the mayor challenges of modern material science. The advancements expected from our project represent a real breakthrough in our control and understanding of multi-scale behaviour of functional magneto-elastic materials beyond the frame of the aimed technology.

Valeur ajoutée des différents partenaires à la réalisation du projet (1/2p)

The MME (Magnetic Materials for Energy) group at SATIE has a long term experience in modelling and characterizing functional magnetic materials. Since 2008 MME-SATIE group has been involved, as a partner, in two mayor European Union founded FP7 projects on magnetocaloric materials for magnetic refrigeration (SSEEC, DRREAM). Magnetic characterisation (VSM), synthesis (high energy ball milling and alloying) and sintering (using the Ilde de France SPS platform) and modelling of hysteresis in first order transitions will be performed at SATIE.

The M&Ms (Mechanics and materials) department is one of the three parts of LMT lab. Inside this department, the multi physic couplings team aims at answering the scientific needs of industry in terms of use of materials and conception especially when several physics are involved. A special attention is paid in the study of global and local, state and/or dissipative couplings, leading or not to microstructure transformations. Typical tools are: observations and experiments at different scales (thermo-magneto-mechanical loadings), modelling using multiscale approaches, thermodynamics and finite elements. Addressed problems are : Magneto-elastic couplings (magnetostriction, piezomagnetism) under multiaxial stress, (magnetic) shape memory alloys under multiaxial thermo-mechanical loading, coupling between plasticity, phase transformation or recrystallization, and magnetics.

The PIEM (Physics and Engineering of Electromagnetism) department at GeePs is dedicated to the modelling of electromagnetic systems. Within this department, the “Multiphysics group” develops advanced modelling tools for the description of the constitutive behaviour of materials under coupled loadings. It has notably a long tradition in multiscale approaches to establish the relationship between microstructure and macroscopic behaviour.

Publication du projet scientifique sur site web Farman

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