PhD Subject : Development of Novel Synthesis and AI Optimization Methods for the Research of New Magnetocaloric Materials

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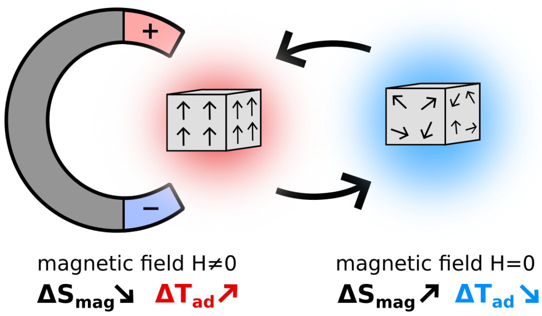
Context: Cooling systems are ubiquitous in modern society and are utilized across a broad spectrum of sectors—from household refrigeration and large-scale industrial temperature control to specialized fields such as biotechnology and quantum computing. Traditional cooling systems, primarily based on vapor-compression cycles, pose significant environmental and efficiency challenges. These systems frequently rely on harmful refrigerants such as hydrofluorocarbons and suffer from mechanical wear, leading to decreased efficiency and increased noise over time. In response to these challenges, magnetocaloric refrigeration emerges as a highly promising alternative. Leveraging the magnetocaloric effect (MCE), which is intrinsic to certain magnetic materials, this innovative technology offers a greener, more reliable, and theoretically more efficient solution [1]. The MCE involves a reversible adiabatic temperature change ΔT when magnetocaloric materials are exposed to changing magnetic fields. This effect results from an entropy change in the material (ΔS) due to the interaction between magnetic moments and the atomic lattice. The currently best-performing materials, such as $Gd_5Ge_2Si_2$ and $La(Fe,Si)_{13}$, exhibit giant MCE near room temperature, achieving $\Delta T \approx 8$ K when subjected to magnetic field changes from 0 to 2 T. Despite their potential, these magnetocaloric materials face limitations that restrict their widespread industrial application. Their mechanical durability under repetitive magnetization and demagnetization cycles, as well as the high cost, rarity, or toxicity of the constituent elements, remain significant hurdles [2]. There is a critical need for the discovery of new high-performance materials that meet industry requirements, enabling this technology to compete cost-effectively with conventional technologies and to be used on a larger scale.



Research topic: This PhD project seeks to tackle existing challenges by embarking on exploratory research into new magnetocaloric intermetallic materials. These materials will incorporate magnetic 3d transition metals and a mixed anionic framework composed of P with Si or Al. Phosphides, silicides, and aluminides are particularly promising for magnetocaloric applications due to their abundant constituent elements, substantial magnetocaloric effect (*e.g.* MnFe(P,As), $Fe_3Mn_2Si_3$), relatively low heat capacity, and high thermal conductivity. However, many ternary and most quaternary systems remain unexplored due to the challenging synthesis of compositions from elements with very different melting points. Additionally, the mixing of anionic atoms often results in complex crystal structures with exotic magnetic properties that have yet to be fully investigated.

The innovative research strategy of this project rests on two novel approaches that will be developed simultaneously:

- **Magnesioreduction Synthesis in Salt Flux:** This unconventional, yet efficient, method involves the co-reduction of metal oxides by highly reducing Mg to form intermetallic powders. This technique allows for the synthesis of materials from elements with very different physical properties and offers new reaction pathways via the formation of uncommon reaction intermediates [3, 4]. The adaptation of this method in a salt flux (alkaline or alkaline earth halides), still rarely used in literature, could lower synthesis temperatures and further facilitate the stabilization of new phases unattainable by conventional techniques.
- **Application of Artificial Intelligence:** Specifically, the use of Bayesian Optimization techniques to accelerate and optimize reaction conditions and chemical compositions of the materials. This active learning method is well-suited for chemical systems where the experimental training dataset is relatively small [5]. Despite its promise, it is still infrequently utilized in chemistry research.

The objective is to gain a fundamental understanding of the relationship between newly discovered crystal structures and chemical compositions and their magnetocaloric properties. This project not only aims to advance the field of magnetocaloric materials but also seeks to develop methodologies that could improve material synthesis and optimization processes.

Scientific skill: This project will engage the PhD candidate in the synthesis and the fundamental study of new magnetocaloric materials. The synthesis will predominantly involve the use of a glove box to handle air-sensitive materials, ball-milling and wet chemical methods to prepare oxide precursors and sealed Nb and silica tubes for magnesioreduction reaction. The characterization of these synthesized materials will be extensively carried out using powder and single-crystal X-ray diffraction (XRD) to assess product purity, resolve new structures, and investigate reaction mechanisms. Furthermore, the project will offer opportunities to engage in advanced diffraction experiments such as synchrotron or neutron diffraction, providing deeper insights into the crystal or magnetic structures of materials. The use of Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) will enable detailed examination of chemical compositions and structural analysis through electron diffraction. Additionally, the application of artificial intelligence in this research will involve using Python and open-source libraries such as GPyTorch and BoTorch. The PhD candidate will develop significant expertise in measuring magnetic and physical properties using tools such as a SQUID magnetometer and Physical Property Measurement System (PPMS). Furthermore, the candidate will enhance their scientific communication skills through the preparation and presentation of results in peer-reviewed scientific journals and at international conferences.

Keywords: Magnetocaloric Materials, Synthesis, Crystallography, Artificial Intelligence

Starting: September 2024

Application: Send a CV along with a motivation letter to Sylvain Le Tonquesse (CR CNRS, sylvain.letonquesse@cnrs.fr) and Wilfrid Prellier (CRISMAT director, wilfrid.prellier@ensicaen.fr)

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