Thesis title: **New High Entropy Alloys for Magnetocaloric Applications.**

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Research Lab: Institut Jean Lamour & IRP Materiomics

Scientific environment: The project will take place within the framework of the **new International Research Project "Materiomics of Complex Inorganic Materials - MATERIOMICS"** between the Jean Lamour Institute (IJL, Nancy, France) and the Jožef Stefan Institute (JSI, Ljubljana, Slovenia). It will involve more specifically researchers from the group Surfaces and Metallurgy (IJL) and from the Department for Nanostructured Materials (Prof. S. Šturm, JSI) as well as the High-Entropy Alloy group (Prof. J. Dolinsek, JSI). Both laboratories are part of the European consortium on complex metallic alloys (ECMetAC, https://ecmetac.eu/). The project will also benefit from the expertise of IMEM (CNR, Italy, Prof. F. Albertini; https://www.imem.cnr.it/en/AdR/4/Magnetic-and-Multiferroic-Materials/intro) on magnetocaloric materials.

Doctoral School: C2MP (Chemistry - Mechanics - Materials – Physics).

Keywords: High-entropy alloys, magnetocaloric materials, metallurgy of intermetallics, transmission electron microscopy, intermetallic compounds.

1. Introduction.

The magnetocaloric effect describes the reversible temperature change of a magnetic substance in response to the application or removal of a magnetic field. It is an intrinsic material's property. The magnetocaloric effect is maximum around the magnetic ordering temperature, and can be further enhanced if a first order structural transition is concomitant with the magnetic transition. It is linked to a strong variation in the magnetic entropy ΔSm, which, due to the magnetothermal coupling, induces a variation in the temperature of the material [1]. In some cases, this effect is giant and can be exploited in magnetic refrigeration systems around room temperature. In this case, the thermodynamic cycle of compression/expansion of the refrigerant gas used in conventional systems is replaced by a thermomagnetic cycle of magnetization/demagnetization of a material with a magnetocaloric effect which plays the role of refrigerant. In recent years, magnetic refrigeration has attracted growing interest because it represents a more efficient and less polluting alternative to traditional cold production technologies [2]. In particular, the solid-state magnetic refrigeration alternative does not use harmful gases and is a low noise solution that can also be made very compact. **Magnetocaloric research is extremely timely in the context of global warming, considering that 20% of total worldwide energy consumption involves the use of refrigeration and air conditioning, and that the global energy demand for air conditioning devices is expected to be multiplied by a factor of 3 in the next decade.**

Different classes of magnetocaloric materials are currently under scrutiny [2-4], each presenting advantages and disadvantages. It includes Laves phases, $La(FeSi)_{13}$ and related compounds, $RE_5(SiGe)_4$ intermetallics, Ln-manganites, MnFe(AsP), MnAs and FeRh compounds as well as Heusler intermetallics to name a few. Many different considerations have to be taken into account for an optimal magnetocaloric material, both of intrinsic and extrinsic origins. The ideal material should exhibit high isothermal entropy change ΔSm and large adiabatic temperature change ΔT_{ad} obtainable by permanent magnets (ideally less than 2T), tunable operating T and broad operating T range, low hysteresis, highly reversible effect, excellent mechanical stability, excellent heat exchanger capacity with fast dynamics, be stable on the long run (good resistance to corrosion) while relying on readily available, non-toxic, non-strategic chemical elements, and of low cost material for large scale production.

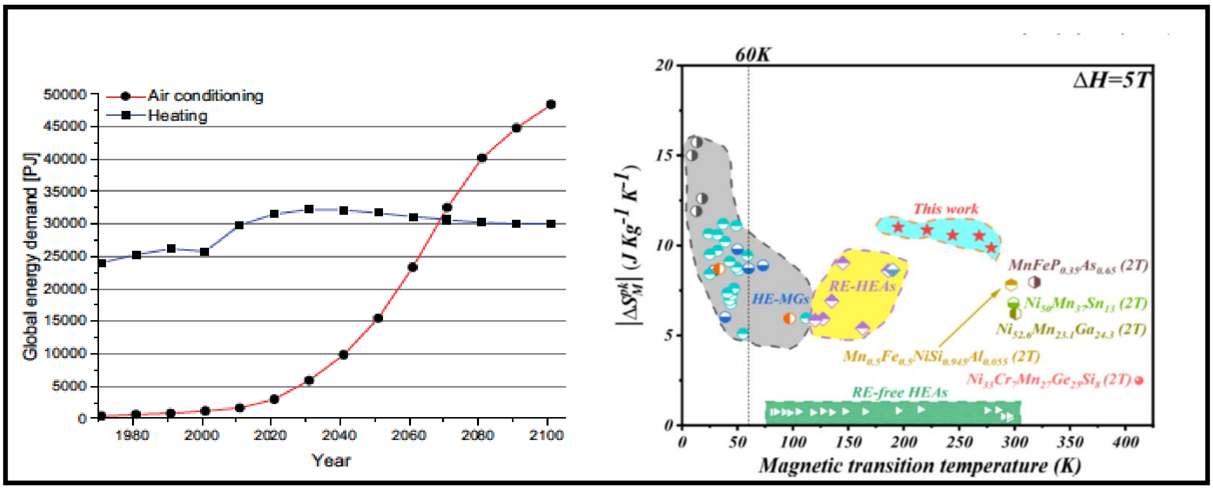

Figure: (Left) Projection of the global energy demand for heating and air conditioning systems. (Right) Isothermal magnetic entropy change versus magnetic transition temperature for different types of HEAs.

In this context, a new class of materials is being considered currently, potentially exhibiting mechanical properties superior to those of most conventional high-performance magnetocaloric materials, which could improve the reliability of devices in functional elements during cycling. These are high entropy alloys [5-7].

The term high entropy alloys (HEA) refers to a new concept of alloy design in which, unlike common alloys, there is no principal element [5-7]. In a HEA, at least five different elements are mixed at near equimolar concentrations and the atoms randomly occupy the crystallographic positions of a simple structure with a small unit cell, such as body-centered cubic (*bcc*), face-centered cubic (*fcc*) or hexagonal compact (*hcp*). Therefore, HEAs are structurally simple but chemically complex alloys, stabilized by a high entropy of mixing, which is a consequence of the chemical disorder. In the literature, the majority of studies on HEAs focus on the characterization of mechanical properties of interest for applications in the field of transportation and aeronautics (elevated hardness, high strength, high fracture toughness, combined with high melting points). They are also considered as hard coating materials with excellent surface properties, including resistance to oxidation, corrosion and wear. But these materials can also exhibit remarkable functional physical and chemical properties as demonstrated by recent reports, including thermoelectric properties, hydrogen storage, catalysis, superconductivity and magnetism. In particular, HEAs composed of rare-earth or ferromagnetic transition metal elements could have great advantages as candidates for magnetocaloric applications. The latest could exhibit good chemical stability, high ductility and should be easily processed in different shapes for applications. However, the ΔSm values reported so far in the literature for different types of HEAs remained relatively low and it is only very recently that some HEAs exhibiting a magnetocaloric effect comparable to conventional magnetocaloric materials have been discovered, both in rare-earth and rare-earth free HEAs [8-15].

2. Main objectives of the PhD program.

In this context, the objective of the thesis will focus on **the development of new HEA materials for magnetocaloric refrigeration**. The foreseen advantages of HEAs for magnetocaloric applications are an enhanced magnetocaloric effect (MCE) because of extreme disorder that could result in sluggish magnetic transitions. In addition, HEA may combine reasonable MCE and improved mechanical properties compared to other MCE materials. Also, 3d ferromagnetic transition metals (TM) based HEAs could feature good chemical stability and high ductility useful for processability.

For the moment, various works have been carried out on metallic high-entropy glasses, crystalline rare-earth HEAs as well as rare-earth free HEAs [13]. The performances of the different materials are compared by evaluating the isothermal magnetic entropy change ΔSm. This can be evaluated indirectly by measuring temperature- and field-dependent magnetization curves around a magnetic transition temperature, such as the Curie temperature (T_C) for ferromagnetic systems, and using the Maxwell relationship [2]:

$$\Delta S_m = \mu_0 \int_{Hi}^{Hf} \left(\frac{\partial M}{\partial T}\right)_H$$

High values of ΔSm can be obtained in materials exhibiting a first order phase transition, linked to the fact that the magnetic transition is coupled to a concomitant structural transition. This is not verified for most of the HEA cases reported in the literature, even if values of around 7 $J.Kg^{-1}.K^{-1}$ have been obtained for rare-earth based HEAs. The most promising results have been obtained in specific transition metal systems exhibiting a magnetostructural transition, such as the FeMnNiGeSi and FeMnCoNiGeSi systems [8-15]. **The strategy that will be adopted during the thesis to search for new HEA compositions will be based on isostructural chemical substitutions of elements starting from ternary intermetallic compounds presenting the desired magnetostructural transitions in order to bring them into the composition domain of high entropy alloys.** Other factors known to favor the formation of solid solutions, such as the configuration entropy, the pair enthalpies of mixing between the different elements, the size differences in atomic radii, the valence electron concentration, etc…, will also be taken into account. This alloy design strategy will be applied to both MnNiSi intermetallic and Ni_2MnGa Heusler compound, both exhibiting the desired magnetostructural transition.

3. Methods.

After an exhaustive analysis of the state-of-the-art on the magnetocaloric properties of HEAs, new alloy compositions will be proposed based on the above strategy. Samples will be produced by arc melting or/and by induction furnace, followed by long-term temperature annealing to improve homogeneity if necessary. The materials will be characterized by different techniques such as optical microscopy, scanning electron microscopy, transmission electron microscopy and x-ray diffraction techniques to obtain information on their atomic structure and microstructure. Diffraction and physical properties measurements will be carried out as a function of temperature to characterize possible structural transitions. The magnetocaloric properties will be evaluated by measuring the temperature and field dependence of the magnetization (4-400 K, 0 – 5T). All necessary equipment's are available at the Jean Lamour Institute, either within the host research group or within the IJL research platforms dedicated to x-ray diffraction, transmission electron microscopy and magnetometry. Additional measurements (Lorentz and 4D Scanning Transmission Electron Microscopy (4D-STEM), MFM, SPD, etc..) will be performed at partner's institution as described below (JSI in Slovenia as well as IMEM in Italy). The student will benefit from the state-of-the-art experimental environment offered by the Institute to carry out his/her research work.

4. International collaborations.

This PhD research program is embedded into **the newly created International Research Project "Materiomics" (IRP Materiomics)** between the Jean Lamour Institute (IJL-Nancy, France) and the Jožef Stefan Institute (JSI-Ljubljana, Slovenia) supported by the CNRS. Additional measurements on the HEAs synthesized in Nancy will be performed at IMEM-Parma, Italia, including Magnetic Force Microscopy (MFM), Singular Point Detection that is a unique technique developed at IMEM to measure the magnetic anisotropy of materials, direct adiabatic temperature change measurements, in-field DSC measurements as well as temperature dependent XRD in collaboration with the physics department of University of Parma. In addition, the most promising materials synthesized in Nancy could be further evaluated for thermomagnetic generation in a Curie wheel device prototype developed in Parma.

The student will thus benefit from an exceptional international environment to carry out his/her research work.

5. Doctoral school.

The PhD student will be affiliated to the C2MP doctoral school (Chemistry - Mechanics - Materials – Physics, https://doctorat.univ-lorraine.fr/en/doctoral-schools/c2mp/presentation).

The advisor and co-advisor of the PhD student will be:

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The PhD student will be hosted by the Research group: « Surface and Metallurgy » (203), Institut Jean Lamour, CNRS-Université de Lorraine, Campus Artem, Nancy.

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