

Final report for the ÅForsk project 16-415 titled “Solid-state refrigeration via thin film magnetocalorics”

Principal Investigator: Kostas Sarakinos, Nanoscale Engineering Division, Department of Physics, Chemistry and Biology, Linköping University, 58183 Linköping, Sweden

Project period: September 2016 – February 2019

Abstract

Funding has been provided by ÅForsk to research and develop next generation new magnetocaloric materials in the form of thin films. Stringent environmental goals¹ are beginning to render vapor compression technologies insufficient; these technologies are the basis for cooling applications ranging from refrigerators to ultra-large cloud server farms used by, e.g., Google, Amazon, Facebook and Spotify. Magnetic (solid-state) refrigeration, based on the magnetocaloric effect (MCE), is receiving increased attention as an alternative to vapor compression cooling. However, efficiencies achieved by state-of-the-art magnetocaloric materials are far from the theoretical Carnot maximum efficiency of 50-60%.² It is believed that the true potential of this technology can be unlocked when the magnetocaloric material is fabricated as a thin film, where nanoscale size effects can amplify the MCE. This would be transformational, opening up a diverse set of new energy saving applications, e.g., solid-state cooling of microelectronic devices.³

We have recently developed a unique technology called MIMSI⁴ (Modulated Impulse Magnetron Sputtering Interplay), which is an industrially relevant thin film synthesis process that enables control of atomic arrangement at levels of precision inaccessible by state-of-the-art methods. In this project, we investigated the way by which the atomic arrangement, as determined by the MIMSI process parameters, affects the magnetocaloric performance of Fe-Cr alloys. We performed deterministic molecular dynamics (MD) simulations of MIMSI-based Fe-Cr film growth which showed that by changing the temporal profile of the Fe and Cr vapor deposition flux alloy films with different atomic arrangements, ranging from ordered to clustered arrangement, can be synthesized. We then developed a computational interface which enabled to use data from MD simulations as input for Monte-Carlo simulations of the magnetocaloric response of Fe-Cr alloys. The results of the magnetic simulations showed that film growth conditions at which favor the formation of ordered Fe-Cr alloys lead to enhancement of the alloy magnetocaloric performance.

The results generated in the framework of this project, thanks to the generous support from the ÅForsk foundation, triggered the interest of *Vetenskapsrådet* (VR), which funded the amount of 3,800,000 SEK for a joint project between our group at Linköping University and the group of Prof. Gabriella Andersson at Uppsala University. The objective of the new VR-funded project is to explore *experimentally* the viability of the concepts and knowledge generated in the framework of the ÅForsk project 16-415 in technologically relevant magnetic materials, including amorphous magnetic alloys. In addition, a new funding application is in preparation from our group for an upcoming call from *Energimyndigheten* that aims at developing a new generation of magnetocaloric thin films based on perovskite-type materials leveraging the atomic configurational degree of freedom (i.e., the MIMSI

¹www.miljomal.se

²U.S. Department of Energy, “*Energy Savings Potential and RD&D Opportunities for Non-Vapor-Compression HVAC Technologies*”, March 2014.

³Casey W. Miller, D. D. Belyea, and D. J. Kirby, “*Magnetocaloric effect in nanoscale thin films and heterostructures*”, *J Vac. Sci. Technol. A* 32, 04082 (2014).

⁴“*METHOD OF COATING A SUBSTRATE SO AS TO PROVIDE A CONTROLLED IN-PLANE COMPOSITIONAL MODULATION*”, Patent Pending Application, PCT/EP2014/052831.

process) as design route. The overall outcome of the project has been successful; the Åforsk support has served as the seed funding for establishing a technologically-relevant research activity.

1. Background and state-of-the art

Modern society relies heavily upon refrigeration based on vapor compression technology (e.g., HVAC) for commercial and residential use, with energy requirements being a substantial fraction of the total energy consumed by households.⁵ Vapor compression technology exhibits an efficiency of ~40%, with reference to the maximum theoretical efficiency limit of the compression-evaporation cycle.⁶ Moreover, this technology is associated with ozone depleting gases (CFCs) hazardous chemicals (NH₃) and gases that are responsible for the greenhouse effect (HCFCs and CFCs).⁵ Non-vapor compression technologies can offer significant energy and cost savings, and can have a widespread positive environmental impact. Magnetic refrigeration, based on the MCE, is receiving increased attention as an alternative route for near-room-temperature refrigeration applications.^{2,6} The MCE is a phenomenon that enables the temperature of a material to be altered when subjected to external magnetic fields.⁷ The physical origin of the MCE is found in the coupling between atom and spin vibrations in solids when an external magnetic field is applied.⁶ A magnetic refrigeration cycle is depicted in Fig. 1. Initially, randomly oriented magnetic moments in a material are aligned by a magnetic field, resulting in heating of the magnetic material. This heat is removed from the material to the ambient using a suitable transfer medium (e.g., water or air).⁶

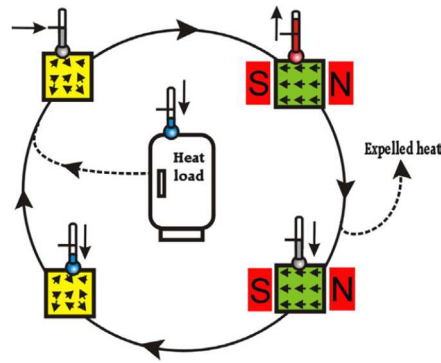


Fig. 1. Schematic representation of a magnetic refrigeration cycle. Thermal energy is transported from the heat load by changing the magnetic state of the MCE material to the ambient (adopted from Ref. 6).

While the MCE has been known since the 1910s,⁷ it has become an important research area during the last two decades after the discovery of the near-room-temperature giant MCE,^{8,9} which opened up the prospect of developing environmentally friendly solid-state refrigeration for residential purposes. Within this framework, significant research effort has been directed toward understanding the MCE on a fundamental level, as well as to the design and synthesis of new *bulk* magnetocaloric materials.¹⁰ Despite research efforts, bulk magnetocaloric materials are far from being widely implemented in commercial refrigeration applications. This is due to the high cost of materials that exhibit MCE

⁵The US Energy Department (DOE) estimates that this fraction is ~20%; see e.g., Ch. Binek and V. Burobina, “Near-room-temperature refrigeration through voltage-controlled entropy change”, *Appl. Phys. Lett.* 102, 031915 (2013).

⁶E. Brück, “Developments in magnetocaloric refrigeration”, *J. Phys. D: Appl. Phys.* 38, R381 (2005).

⁷F. Pobell, *Matter and Methods at Low Temperatures* (Springer-Verlag, Berlin, 1992).

⁸V. K. Pecharsky and K. A. Gschneidner, Jr., “Giant magnetocaloric effect in $Gd_5(Si_2Ge_2)$ ”, *Phys. Rev. Lett.* 78, 4494 (1997).

⁹V. K. Pecharsky and K. A. Gschneidner, Jr., “Tunable magnetic regenerator alloys with giant magnetocaloric effect for magnetic refrigeration from ~20 to ~290 K”, *Appl. Phys. Lett.* 70, 3299 (1997)

¹⁰The latter entails both discovery of new magnetocaloric phases and alloys as well as control of the microstructure of existing materials to tune and optimize the way that they respond to external magnetic fields.

figures-of-merit that are relevant to applications,^{6,11,12} combined with performance deficiencies, e.g., magnetic hysteresis and magneto-structural transitions that compromise the mechanical integrity of the material.⁶ Magnetocalorics in the form of *thin films* grown by vapor condensation on solid surfaces exhibit great potential for circumventing the drawbacks of bulk magnetocaloric materials.³ The non-equilibrium character of thin film deposition methods facilitate the synthesis of nanostructured metastable phases which provide the ability to tune the response to external magnetic fields beyond what is possible in bulk materials.³ However, this route is largely unexplored as state-of-the-art thin film synthesis methods (e.g., magnetron sputtering) do not allow for a precise control of nanoscale atomic structure—the latter being a prerequisite for performing in-depth studies and developing solid understanding of the effect of atomic arrangement on the MCE of thin films. Bridging this gap in knowledge is critical for the development of new thin film magnetocaloric materials.

2. Goal and objectives

The goal of the proposed research has been to explore the potential of thin films to achieve highly efficient near-room-temperature solid state refrigeration by elucidating the complex correlation between atomic arrangement and the MCE. The MIMSI technique (developed by us) has been a key component of this project, since it is a non-equilibrium vapor-based deposition process that can control atomic arrangement in multicomponent materials from the mesoscale down to sub-nanometer level. The focus of this project has been the model magnetic system Fe-Cr with specific objectives to:

- (i) Establish the relationship between the MIMSI parameter space and atomic arrangement of Fe-Cr thin films.
- (ii) Understand the effect of Fe-Cr atomic arrangement at different length-scales on magnetic exchange interactions. The project objectives were achieved by a combination of advanced computational tools which allowed for maximum flexibility and optimum usage of resources during the project execution.

3. Project results

3.1. Thin film growth simulations

We employed molecular dynamics (MD) to simulate growth of our model Fe-Cr system and establish and predict theoretically the relationship between the MIMSI parameter space and the atomic arrangement in our films (**Objective (i)**). All simulations were performed with the LAMMPS software¹³ and the Fe-Cr interactions were described by a MEAM interatomic potential developed by B.J. Lee *et al.*¹⁴. A BCC-Fe lattice of 19200 atoms (11.456 x 11.456 x 17.184 nm³) has been used as substrate equilibrated at ambient pressure and temperature of 500 K. The periodic boundary conditions at the z-axis were then revoked simulating an open (001) BCC-Fe surface. Film growth was simulated by sequential deposition of 100 atoms of either Fe or Cr (6.25% of a monolayer (ML)) on the surface every 150 picoseconds. The depositions were applied until a total number of 24 ML have been deposited. The sequence of the deposited species was decided based on a deposition pattern. The pattern was representing a pulse train (PT) containing to 0.5 to 6 ML of Fe or Cr in order to resemble the growth conditions encountered during the MIMSI process. Depositions where Fe and Cr were deposited simultaneously were also simulated for reference.

Snapshots of MD growth simulations after deposition of 12 ML of atoms (both Fe and Cr) and for various amounts of atoms deposited per pulse train (Fe or Cr) are presented in Fig. 2. In the limit of long pulse trains of 4 ML, a well-defined multilayer structure with alternating Fe- and Cr-rich layers is obtained, while some intermixing is observed in the layers immediate to the Fe/Cr interfaces. On the

¹¹Casey W. Miller, D. D. Belyea, and D. J. Kirby, “*Magnetocaloric effect in nanoscale thin films and heterostructures*”, J Vac. Sci. Technol. A 32, 04082 (2014).

¹²The best available bulk magnetocaloric materials are based on scarce and costly rare-earth compounds.

¹³S. Plimpton, J Comp Phys, 117, 1-19 (1995), <http://lammps.sandia.gov>

¹⁴B.J. Lee et al., Calphad, 25, 527 (2001).

configurational level, such structure approaches clustering as it is only the interface atoms that have dominating opposite-type neighbors, and that only in one direction. This is reflected in the evolution of the short-range order (SRO) parameter for the nearest neighbor shell in Fig. 3, which exhibits increasingly positive values with increasing the pulse train length. For 4 ML per pulse train and element we obtain a SRO value of 0.5 that correspond to an average of 75% of the nearest-neighbor pairs are Fe-Fe or Cr-Cr bonds, and only 25% are Fe-Cr bonds. In the opposite limit of co-deposition, MD simulations yield a seemingly random Fe-Cr bcc structure, as seen in Fig. 2. Figure 3 shows that, in the case of co-deposition (represented by 0 ML of pulse train length), we obtain a slightly positive value SRO values of ~ 0.01 . This value reflects the existing thermodynamic driving force for clustering in Fe-Cr system, which is suppressed by the low interlayer diffusion during our growth simulations resulting in an almost random alloy configuration.

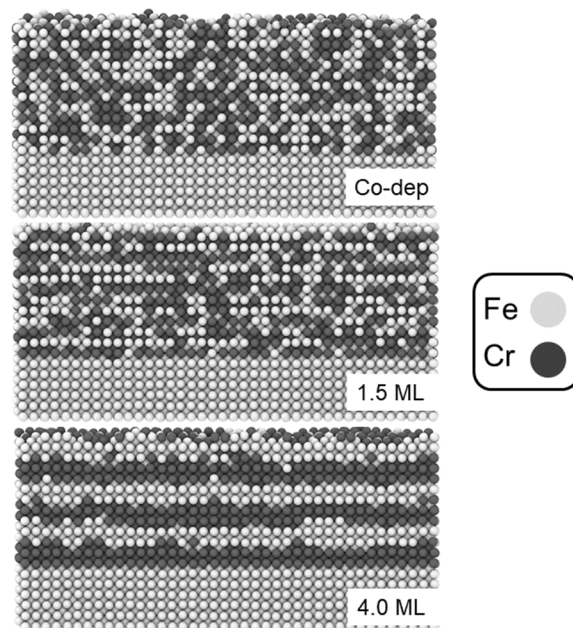


Fig.2. Snapshots from growth simulations after deposition of xx ML of atoms for co-deposition, 1.5 and 4.0 ML per pulse train and elements.

For intermediate pulse train lengths, e.g., 1.5 ML in Fig. 2, a structure that resembles broken multilayers with intermixing between layers is observed. Concurrently, an SRO value of approximately -0.1 is obtained (see Fig. 3), which indicates a tendency for ordering, i.e. more Fe-Cr nearest neighbor bonds, as compared to their Fe-Fe and Cr-Cr counterparts. One can understand this as if we managed to obtain a perfect growth of alternating one (001) monolayers in the bcc structure we would end up with a CsCl-type structure where every atom only has opposite type nearest neighbors below and above. In practice there is a degree of intermixing on the level of individual atomic planes resulting that the minimum SRO parameters obtained is close to -0.1 corresponding to 55% of the nearest neighbors being of opposite kind while 45% are of same kind in the cases of 1 and 1.5 ML per pulse train, as seen in Fig 2.

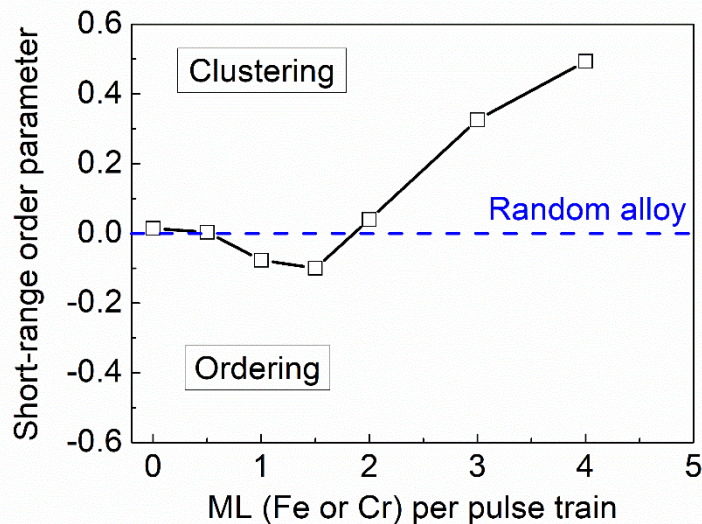


Fig. 3. Calculated atomic short-range-order parameter on the nearest-neighbor shell for Fe_{0.5}Cr_{0.5} alloys as a function of the number of monolayers per pulse train during growth. Co-deposition is represented by 0 ML per pulse train.

3.2. Magnetic simulations

We have programmed an interface between the large-scale molecular dynamics program LAMMPS (used for simulating film growth as explained in Section 3.1) and our in-house Magnetic alloy Monte Carlo code IPH in order to simulate the magnetic response of the exact atomic configurations obtained from our thin film growth simulations (**Objective (ii)**). The Monte Carlo simulation is a probabilistic and highly computationally efficient way to obtain equilibrium properties as a function of temperature. Our Magnetic Monte Carlo simulation uses magnetic exchange interactions obtained from first principles Green's function methods of Quantum Mechanics and describe how strongly the direction of the magnetic moments of particular magnetic atoms are coupled to each other. Given the input from thin film growth simulations, we are thus able to simulate how the different configurations of Fe and Cr atoms in our case give rise to particular behavior of net magnetization and magnetic specific heat as a function of temperature and external magnetic field. These are the quantities needed to calculate the magneto-caloric figure of merits for a particular film and temperature and thereby understand the effect of atomic arrangement at various length scales on the magnetocaloric response of the model system we investigate here.

Figure 4 shows the calculated magnetization at zero magnetic field, in μ_B per Fe atom, as a function of temperature for the five cases of: co-sputtering, pulse train length of 0.5 ML, 1.0 ML, 1.5 ML, and 2.0 ML. The critical temperature T_c , when the magnetization goes to zero is the highest for the co-sputtered film corresponding to a random alloy. T_c in this case is ~ 475 K which is just below existing literature calculations for Fe_{0.5}Cr_{0.5} alloys and also to bulk experiments. With increasing pulse train length, which leads to a development of a short-range-order tendency, the calculated critical temperature decrease to 450 K (0.5 ML), 425 K (1.0 ML), and 400 K (1.5 ML) respectively. For films with pulse train lengths above 1.5 ML, i.e., with thicker Fe-rich and Cr-rich layers, we start to see an absence of full ferromagnetic saturation, owing to competing ferromagnetic and anti-ferromagnetic interactions on the typical distances between the Fe-rich layers.

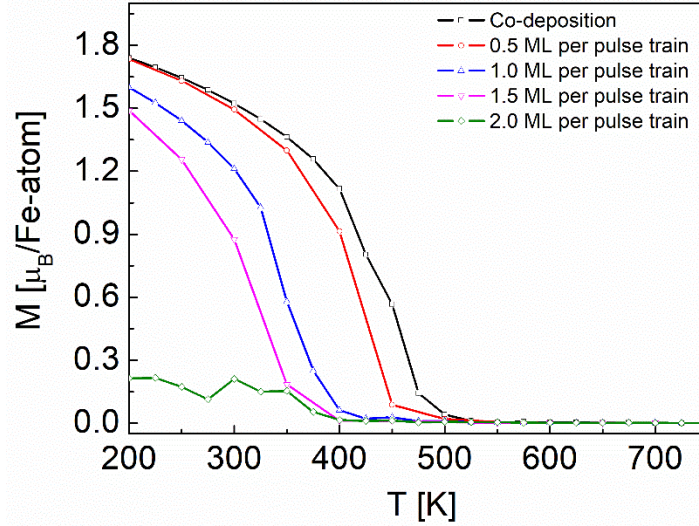


Fig. 4. Temperature-dependent magnetization at zero field for atomic configuration obtained from growth simulations for co-deposition, 0.5, 1.0, 1.5, and 2.0 ML per pulse train and element.

Figure 5 presents the calculated magnetic entropy change ΔS_M , which is the MCE figure-of-merit, for the various atomic configurations. There it is seen that the maximum values of ΔS_M and hence the potentially largest MCE is obtained for pulse trains delivering 0.5 to 1.0 ML of Fe and Cr atoms. According to Fig. 3, this deposition conditions lead to the formation of ordered Fe-Cr alloys, which underscores the complex interplay among nanoscale atomic arrangement, spin vibrations, and atomic vibrations in the crystal. It is also highlights a potential route for synthesizing alloy films with enhanced magnetocaloric performance by increasing the degree of short range atomic ordering.

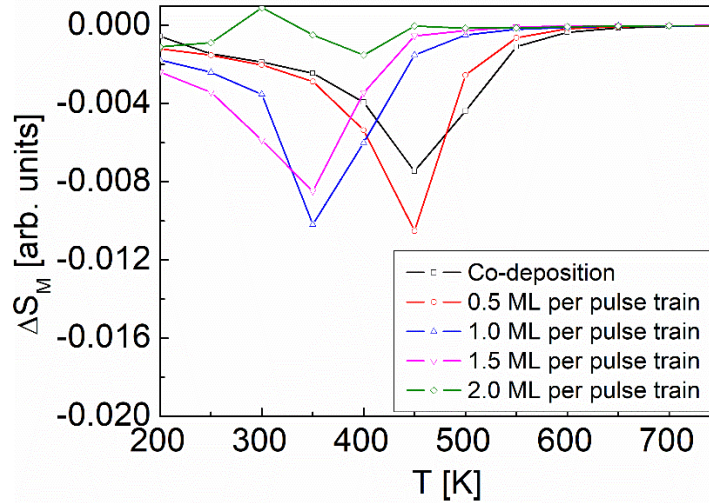


Fig. 5. Calculated magnetic entropy change ΔS_M for atomic configurations obtained from growth simulations for co-deposition, 0.5, 1.0, 1.5, and 2.0 ML per pulse train and element.

4. Summary

We investigated the way by which the atomic arrangement, as determined by the MIMSI process parameters, affects the magnetocaloric performance of Fe-Cr alloys. We performed deterministic

molecular dynamics (MD) simulations of MIMSI-based Fe-Cr film growth which showed that by changing the temporal profile of the Fe and Cr vapor deposition flux alloy films with different atomic arrangements, ranging from ordered to clustered arrangement, can be synthesized. We then developed a computational interface which enabled to use data from MD simulations as input for Monte-Carlo simulations of the magnetocaloric response of Fe-Cr alloys. The results of the magnetic simulations showed that film growth conditions at which favor the formation of ordered Fe-Cr alloys lead to enhancement of the alloy magnetocaloric performance. The overall findings of the project unlock a new dimension in the design of new magnetocaloric alloy materials by controlling the atomic configuration degree of freedom.