Structure and enhanced magnetocaloric effect in rare-earth free high-entropy alloys.

V. Fournée[1*], G. Lengaigne[1], D. Sihom Kwekam[1], P. Boulet[1], S. Migot[1], J. Ghanbaja[1], J. Ledieu[1], S. Semsari Parapari[2], S. Šturm[2], R. Cabassi[3], S. Fabbrici[3], F. Cugini[3,4], M. Solzi[3,4], F. Albertini[3].

[1] Institut Jean Lamour, Université de Lorraine – CNRS, Nancy, France, [2]J. Stefan Institute, Ljubljana, Slovenia, [3]J. Institute of Materials for Electronics and Magnetism, IMEM-CNR, Parma, Italy, [4]Department of Physics, University of Parma, Parma, Italy.
*vincent.fournee@univ-lorraine.fr

High-entropy alloys (HEAs), in contrast to conventional alloys and intermetallics, mix five or more elements at equal or near-equal compositions in a single crystalline phase. In principle, they form an ideal solid solution stabilized through a high configurational entropy of mixing [1,2]. This huge compositional space of HEAs offers opportunities to discover new functional materials with improved properties. Yet this ideal scenario occurs only rarely, and rational approaches are needed to design HEAs with the desired properties. Inspired by recent reports on rare-earth free HEAs with promising magnetocaloric performances [3,4], we present new results on the structure and magnetic properties of some ultra-pure single phase HEAs in different systems.

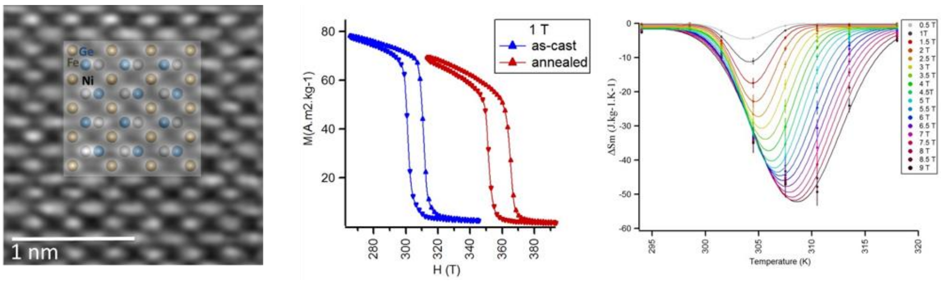

Figure 1. (Left) HR-TEM showing a perfect solid solution in $(Fe,Mn,Ni)_{66.6}(Ge,Si)_{33.3}$.(Center) Thermomagnetic curves and (right) isothermal entropy change at various field in $(Fe,Mn,Ni,Co)_{66.6}(Ge,Si)_{33.3}$.

Samples have been prepared by arc-melting or induction furnace followed by post-annealing treatments in the quinary $(Fe,Mn,Ni)_{66.6}(Ge,Si)_{33.3}$ or the senary $(Fe,Mn,Ni,Co)_{66.6}(Ge,Si)_{33.3}$ systems. Both are derived from the MnNiSi ternary system exhibiting the desired magnetostructural phase transition in order to enhance the magnetocaloric effect. High-resolution transmission electron microscopy indicates that a perfect solid solution is realized in the post-annealed samples, meaning that all atomic species are indeed randomly occupying all the crystallographic sites. These HEAs undergo a structural transformation from hexagonal at high T into orthorhombic upon cooling, as evidenced by temperature dependent powder and single crystal XRD as well as HRTEM. Our recent results investigate the effect of Mn- and Co-doping, showing that the temperature of the transition can be tuned close to room temperature in $(Fe,Mn,Ni)_{66.6}(Ge,Si)_{33.3}$ and even above in $(Fe,Mn,Ni,Co)_{66.6}(Ge,Si)_{33.3}$. The magnetization versus field M(H) curves reveal magnetic hysteresis at temperatures close to the transition reflecting a field induced first-order transition. The magnetocaloric effect has been evaluated from magnetic measurements using the Maxwell relation and from the direct adiabatic temperature change measurements. An isothermal entropy change as large as about 40 $J.kg^{-1}.K^{-1}$ is attained at 5 T. Other Heusler-based HEA are being investigated, derived from the ternary Ni_2MnGa. In this case, a high entropy compound forms instead of a random solid solution. We found that the paramagnetic to ferromagnetic transition occurs at 550 K but can be tuned to lower T through Cu doping.

References

[1] E.P. George *et al.*, Nat. Review, **2019**, *4*, 515.
[2] L. Han *et al.*, Nature Reviews Materials, **2024**, *9*, 846–865.
[3] J.Y. Law *et al.*, J. Alloys. Comp., **2021**, *855*, 157424.
[4] Y. Guo *et al.*, APL Mater., **2022**, *10*, 091107.