Structure and Magnetocaloric Effect in MM'X Ferromagnets

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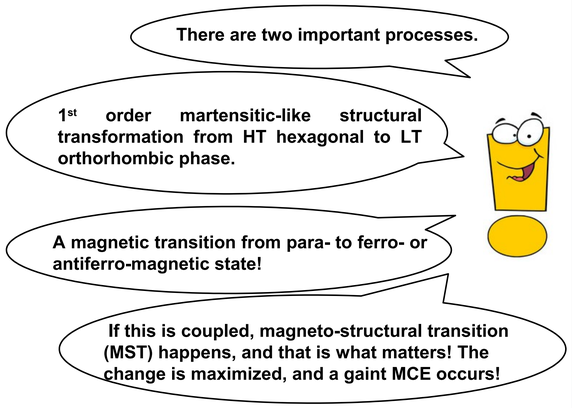
Introduction

A family of isostructural *MM'X*-type intermetallic alloys (where *M* and *M'* are first period transition metals and *X* is a half-metal) experience exceptional structural and magnetic behavior, resulting in appearance of so-called magnetocaloric effect (MCE): material exposed to a magnetic field heats up or cools down due to the changes in its inert structure.

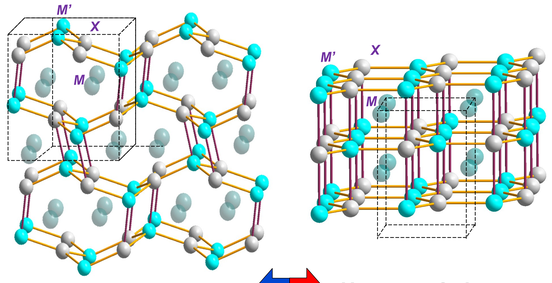


Unfortunately, no MST occurs for ideal compositions of ternary phases of *MM'X* systems. However, introducing of a suitable change could provide the tool how to approach them together – by substitution of an element, deficiency, or additional doping [1]. Via these processes, one could tune the phase transitions temperatures and the magnetostructural coupling could be eventually achieved.

Here we focus on the Mn-Ni-Si system, with partial Fe substitution on the Mn site as well as Si substitution by Ge and their isostructural alloying.

Structure and Bonding in MM'X

Figure 1: Structure of *MM'X*

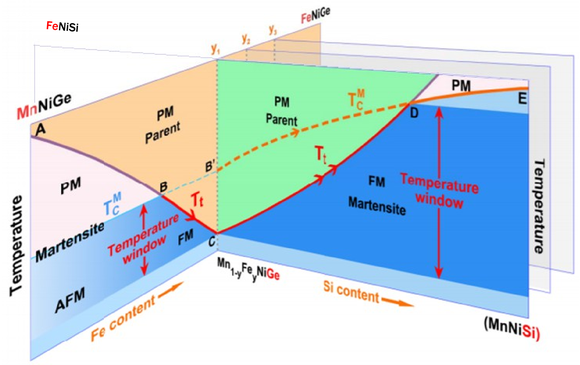


The simple Zintl picture of complete electron transfer from the more electropositive metal *M* to the network of electronegative elements is not followed in *MMX'*, instead the cation *M* keeps a portion of its electron density. This results in two scenarios: a) *M* bonds to the *M'X* network via *M-X* or *M-M'* bonds or b) it bonds along/across the cavity via *M-M* bonds [2].

In our case of MnNiSi, the Mn-Mn distances are fairly large, the interaction is rather weak; this promotes formation of the orthorhombic phase and the ferromagnetic ordering. In the case of MnNiGe, the opposite trend applies: the Mn-Mn distances are rather short, promoting formation of hexagonal phase and its magnetic moments to order antiferomagnetically. Useful tool is the Fe substitution for Mn atoms. Fe-Fe bonds are expected to form, and the structure should straighten up, promoting further formation of hexagonal phase in its ferromagnetic state [2].

Alloy Design

Figure 2: Strategy of Tuning Transition Temperatures in *MM'X*



As a starting material, MnNiSi is selected, with relatively high structural transformation temperature T_t = 1206 K; and magnetic transition temperature from paramagnetic to ferromagnetic state T_c = 622 K. Consequently, the Mn atoms are substituted by Fe atoms and $Mn_{1-x}Fe_xNiSi$ system is investigated for a wide range of compositions ($0 < x < 1$). This is expected to lower the T_t into the magnetic transition temperature range, likewise for $Mn_{1-y}Fe_yNiGe$ system [3], highlighted in Figure 2. Also the Si substitution is performed, using an alloying counter part MnNiGe (transition temperatures as low as T_t = 493 K; and T_N = 346 K (paramagnetic to antiferromagnetic)): final $Mn_{1-x}Fe_xNiSi_{1-z}Ge_z$ system is created; and investigated.

Results

Figure 5: X-ray Diffraction Patterns for $Mn_{1-x}Fe_xNiSi$ (x= 0.6, 0.5, 0.4, 0.3, 0.2, 0.1 and 0)

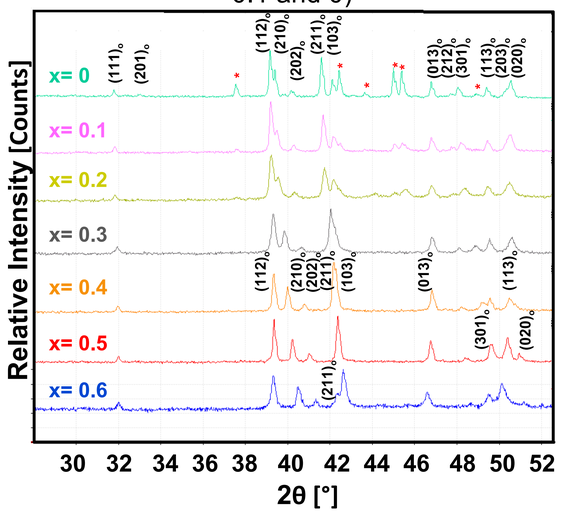
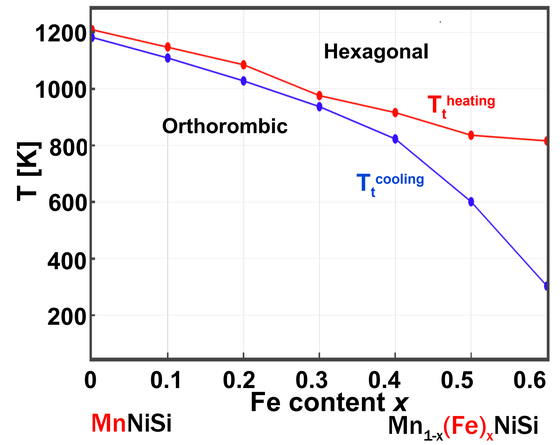


Figure 6: Structural Phase Diagram of $Mn_{1-x}Fe_xNiSi$ system



Solid State Refrigeration

- *no harmfull gasses*
- *compact refrigeration unit*
- *less noisy*
- *environmentally friendly materials*

- *MST coupling required to maximize the entropy change*
- *magnetic fields up to 5 T for sufficient cooling power*
- *cracking of materials under MST brings some inconveniences*

Figure 3: Principle of Solid State Refrigeration

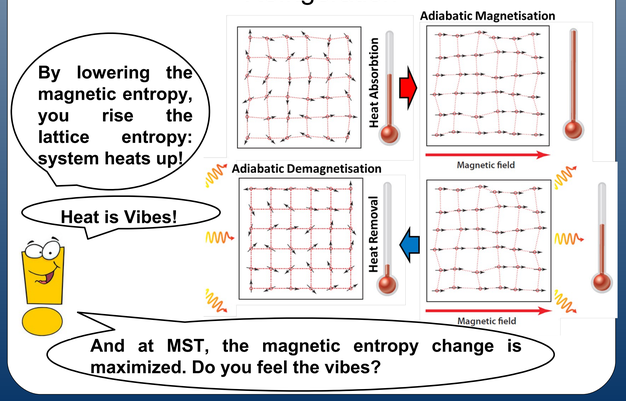
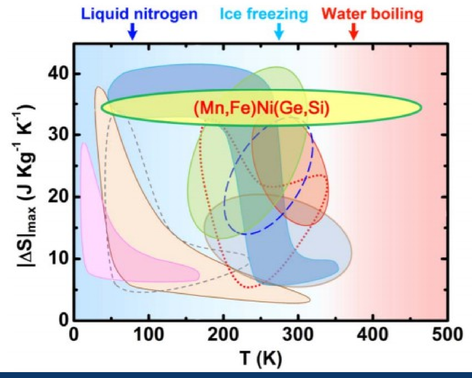


Figure 4: Potential Magnetostructural Coupling in (Mn,Fe)Ni(Ge,Si) [3]



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