Ni-Mn-Z Heusler compounds for magnetocalorics

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The magnetocaloric effect (MCE), which was originally used to attain very low cryogenic temperatures emerged as an alternative to the conventional gas-compression based cooling, which contains fluorocarbons and therefore detrimental for environment. Heusler alloys have generated a vast interest for applications based on the MCE due to the possibility of large magnetization and combine magnetic and structural (martensitic) phase transitions to obtain large MCE. Our aim to study the Ni-Mn based magnetocaloric Heusler alloys form both fundamental physics and practical aspects. Since the transition temperature and magnetocaloric properties in Heusler alloys are highly compositional dependent, the effect can be easily tuned by varying the composition for room temperature applications. We are dedicated to design the Heusler alloys compositions with large magnetization difference and volume conserving magneto-structural transition, which is a necessary criteria for the reversibility of phase transformation and thus for the MCE. To take the advantage of complete reversible behavior of 2nd order transition, we also design non-phase transforming Heusler alloys, which show large magnetic moment and ferromagnetic transition close to room temperature. To check the practical applicability of the materials we do the cyclic direct adiabatic temperature change measurement using pulsed magnetic fields, which provide conditions for real magnetic cooling devices.

In Ni-Mn-Z Heusler alloys the stoichiometric Ni_2MnGa is the most studied system, undergoes martensite, premartensite and ferromagnetic transition at 210 K, 260 K and 373 K, respectively. This alloy does not only shows MCE but also exhibits large magnetic field induced strain (10%). The Ni_2MnGa Heusler alloy exhibit perfect shape memory and superplastic behavior, which is closely related to its volume conserving martensite transition and the existence of modulated structure in the low temperature martensite phase. The modulation is an important parameter provides low twining stress, which influences the magnetic field induced shape recovery in Ni-Mn-Z MCE Heusler alloys. However a long going controversy exist about the nature and origin of modulation in Ni_2MnGa. Therefore, it is necessary to understand the nature and mechanism of modulation in these system, which might help to design new MCE Ni-Mn-Z Heusler alloys with improved properties especially reversibility of phase transition as a function of magnetic field, stress and temperature etc.

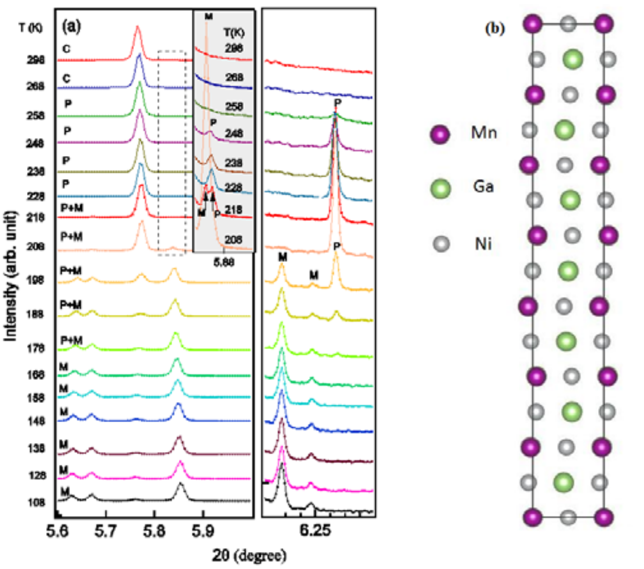

Fig.1: (a) Evolution of XRD patterns of Ni_2MnGa as a function of temperature during cooling cycle . "C", "P" and "M" represent the cubic, premartensite and martensite phases, respectively. (b) The 7M- modulated (along c direction) orthorhombic unit cell of Ni_2MnGa martensite phase .

We investigated the phase transformation behavior of Ni_2MnGa as a function of temperature using (3+1) D Superspace group Rietveld analysis of very high resolution synchrotron x-ray diffraction data (at PETRA III, Hamburg). The results of Superspace group Rietveld analysis show that the modulation in the premartensite and martensite phases are incommensurate 3M and 7M, respectively. We further show that the incommensurate 7M like modulation is the ground state of Ni_2MnGa and not the Bain distorted tetragonal $L1_0$ phase or any other lock-in phase with a commensurate modulation. This established that the modulation in Ni_2MnGa can be explained within the framework of the soft phonon model. [1]

One of the biggest challenge to use Heusler alloys for magnetocaloric cooling applications is the irreversibility of the first order magneto-structural transition w.r.t. the application of magnetic field cycles. The magneto-structural transition accompanied with a steep drop in magnetization (i.e., ΔM) around the martensite start temperature (Ms) due to the lower Magnetization of the martensite phase.

We show that ΔM around Ms in these (Ni-Mn-Z) alloys is highly sensitive to the residual stress and gets suppressed by more than an orders of magnitude due to the stabilization of the martensite phase at temperatures well above Ms (fig.2). Even after annealing at temperature lower that the initial annealing temperature, the residual stress stabilized martensite phase does not fully revert to the equilibrium cubic austenite phase as the magneto-structural transition is only partially restored with a reduced value of ΔM. Therefore, our work show that the sample preparation procedure is crucial to improve the reversibility in the MCE Heusler material. [2]

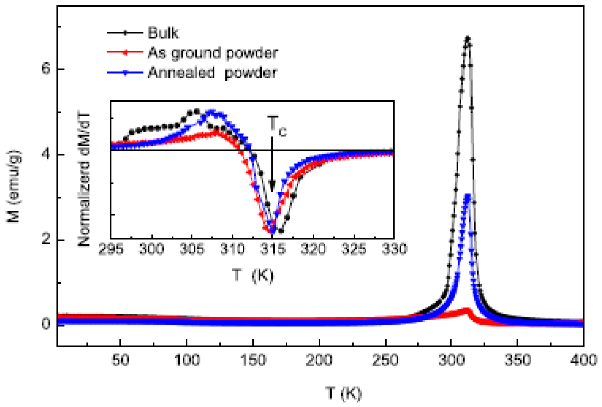

Fig.2: Effect of residual stress on ΔM at magneto-structural phase transition in $Mn_{1.8}Ni_{1.8}In_{0.4}$. [2]

In order to determine the usefulness of a material as an active magnetocaloric cooling device the direct temperature change of the sample responding to the magnetic field on a time scale of ~10 to 100 ms, which is on the order of typical operation frequencies (10–100 Hz) of magnetocaloric cooling devices, must be characterized. We have studied the MCE in the shape-memory Heusler alloy $Ni_{50}Mn_{35}In_{15}$ by direct measurements in pulsed magnetic fields (with Dr. Y. Skourski, High magnetic field, Dresden) at 20 T (fig.3).

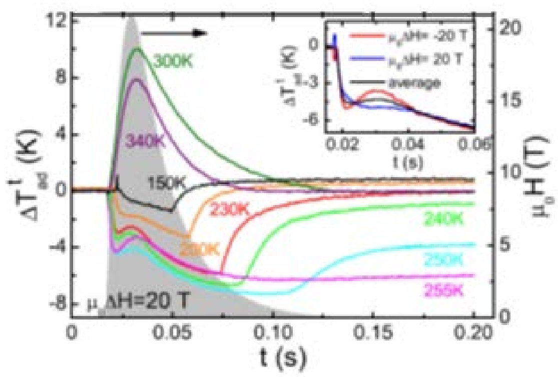

Fig.3: Time dependences of the adiabatic temperature change at 20 T measured for $Ni_{50}Mn_{35}In_{15}$ in pulsed magnetic fields.[3]

Our results reveal that in shape-memory alloys, the different contributions to the MCE and hysteresis effects around the martensitic transition have to be carefully considered for the use in future cooling applications. [3]

As second order transition are fully reversible and can be use in magnetic cooling for which the Gd is a best example. So, we also focus in cubic Heusler alloys, which does not undergoes to a structural phase transformation but own a large magnetic moment in cubic phase and having ferromagnetic transition (Tc) close to room temperature. As an example we studied the cubic $Ni_2Mn_{1.4}In_{0.6}$ Heusler alloy,[4] which have large ground state moment ~6.17 μB/f.u and Tc~316 K (Fig.4).

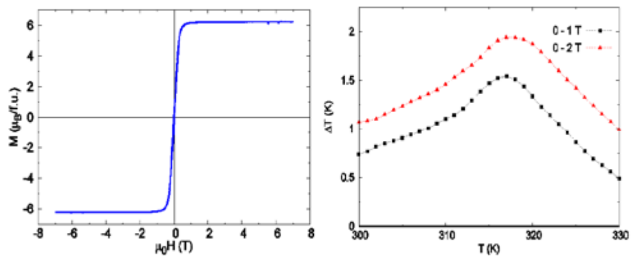

Figure 4: Magnetization and MCE results for cubic $Ni_2Mn_{1.4}In_{0.6}$ Heusler alloy (a) Magnetization loop at 2K. (b) Isothermal magnetization at 2K (c) comparison of entropy change with Gd and (d) direct adiabatic temperature change. [4]

We measured the direct adiabatic temperature change and it turns out to be ~2 K for applied magnetic field of 2 Tesla, which is comparable to the value reported for some of the Heusler alloys at their first order magneto-structural transition. This shows that the cubic Heusler alloys, which does not show magneto-structural transition can also be a good candidate for MCE applications.

References

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