Magnetocalorics and magnetism in MnFe(P,Si,Ge) materials
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Summary

This thesis presents a study of the phase formation, crystal structure, magnetism and MCE of MnFe(P,Si,Ge) compounds. These materials are relatively low cost and nontoxic for room-temperature magnetic-refrigeration applications.

Chapter 1 addresses recent developments in magnetocaloric studies, and the motivation of this thesis.

Chapter 2 presents the relevant formulas to determine the MCE from experiments. The last part of this chapter presents an overview of Density Functional Theory and some methods used to calculate magnetic moments and density of state for the MnFeP\(_{1-x}\)Si\(_x\) compounds.

All samples studied in this thesis were synthesized by high-energy ball milling in vacuum up to 10\(^{-7}\) mbar for about one week until the milled powder is close to an amorphous state. After ball milling, the powder is sintered at 1000-1200 °C for 5-10 hours, followed by annealing at 550-850 °C for 50 hours. The heat treatment is performed in quartz ampoules under 100-200 mbar argon atmosphere. Additional information about sample preparation and experimental setups used in this work is given in chapter 3.

In the first part of chapter 4, we describe the successful replacement of As by Si and Ge in the magneto-refrigerant MnFe(P,As) without losing the favourable magnetic properties. However, the thermal hysteresis of the new compounds is quite broad; therefore a new method to perform magnetization measurements was introduced. It is possible to reliably obtain the isothermal magnetic-entropy changes in first-order magnetic-phase transition compounds using the Maxwell relation, if the magnetization
measurements are carried out in the appropriate way. Because the magnetization is proportional to B/T, in the measurement process we need to combine increasing temperature with decreasing field or decreasing temperature with increasing field. The magnetic-entropy change recorded for the new alloys are comparable to the ones in MnFe(P,As) compounds. The new compounds do not contain any hazardous components; therefore they are promising for magnetic-cooling applications.

In the second part of chapter 4, we have prepared several MnFe(P,Si,Ge) compounds, where the influence of the Si, Ge ratio on the structure, magnetic and magnetocaloric properties are investigated. Si and Ge substitutions affect very differently the magnetic and magnetocaloric properties of the MnFe(P,Si,Ge) compounds, for instance, T_C is proportional to the Ge concentration in MnFeP_{0.59}Si_{0.41-x}Ge_x and MnFeP_{0.67}Si_{0.33-x}Ge_x compounds. On the other hand, in MnFeP_{0.85-y}Si_yGe_{0.15} compounds, the dependence of T_C on the Si concentration is found to be extremely strong but nonlinear. Generally, the T_C dependence of all samples is correlated with the change in a and c parameters. T_C is higher in samples with larger a parameter and smaller c parameter. The thermal hysteresis is reduced with increasing Ge concentration. We achieved large MCE, spanning a range of working temperatures from about 235 up to 372 K. This temperature range is of great importance for magnetic cooling applications near room temperature.

Particularly interesting is the successful replacement of As by the abundant, cheap and non-toxic Si in MnFe(P,As). Chapter 5 presents the structure, magnetism, and magnetocaloric effect of MnFeP_{1-x}Si_x compounds. Samples in the range from x = 0.28 to 0.64 crystallize in the hexagonal Fe2P-type structure with a small amount of a second phase which increases with increasing Si content. Samples with lower Si content show the orthorhombic Co2P-type structure. We have obtained large magnetocaloric effects in the MnFeP_{1-x}Si_x compounds, especially for x = 0.50 and x = 0.52. However, better homogeneity must be achieved. Another concern for applications is the large thermal hysteresis that calls for improved processing. The large MCEs, persistent up to high working temperatures may be useful for heat-pumping applications.

In chapter 6, the MnFeP_{1-x}Si_x compounds are investigated theoretically. The electronic structure and magnetism of the compounds are studied by the virtual-crystal
approximation in the framework of density functional theory, and by the Localized Spherical Wave method with a supercell approach. We discuss the spin-polarized LSDA-calculated DOS for both spin up and down. The result show that there is a visible exchange splitting in the main valence band that originates mainly from the Mn-3d and Fe-3d states. We have investigated the total magnetic moments of the MnFeP\(_{1-x}\)Si\(_x\) compounds with composition range of 0.44 \(\leq\) x \(\leq\) 0.60. The calculated magnetic moments are in good qualitative agreement with the experimental values. The total and local magnetic moments, the atom-projected and the total DOS are better described by the super-cell approach since in the super-cell approach the difference in chemical properties of Si and P is taken into account.