The crystal and magnetic structure of the magnetocaloric compound $FeMnP_{0.5}Si_{0.5}$

Delft Days on Magnetocalorics
24 - 25 Oct 2011

UPPSALA UNIVERSITET

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Conclusions

- Samples of stoichiometric $FeMnP_{0.5}Si_{0.5}$ have been synthesized by the drop synthesis method with losses <0.5%.

- $FeMnP_{0.5}Si_{0.5}$ was confirmed to cristallize in the hexagonal Fe_2P-structure with the unit cell parameters a = 6.2090(3) Å and c = 3.2880(3) Å.

- The Fe atoms are mainly situated in the pyramidal 3g site while the tetragonal 3f site is prefered by the Mn atoms.

- The magnetic moments derived from neutron powder diffraction are shown to be coordinated along the a-axis with a total moment of 4.4 μ_B.

Introduction

Room temperature magnetic refrigeration, based on the magnetocaloric effect (MCE) has attracted attention due to its energy saving potentials and being friendly to the environment because of the magnetic refrigeration cycle, see Fig. 1. The compound $FeMnP_{0.5}Si_{0.5}$, based on the Fe_2P-system, has showed promising magnetocaloric properties and due to its rather cheap and non toxic elements it is proposed that these type of compounds may be a future for magnetic refrigeration.

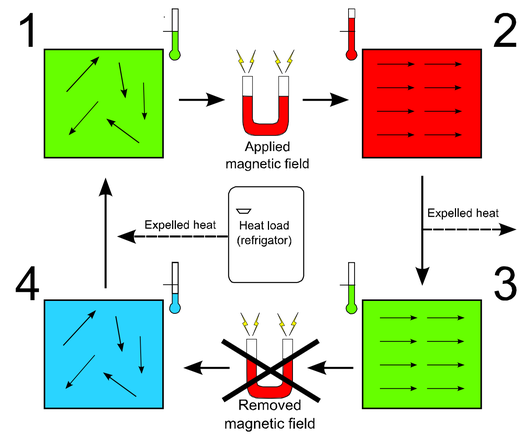

Fig. 1: Scheme of the magnetocaloric cycle.

Results

Phase analysis

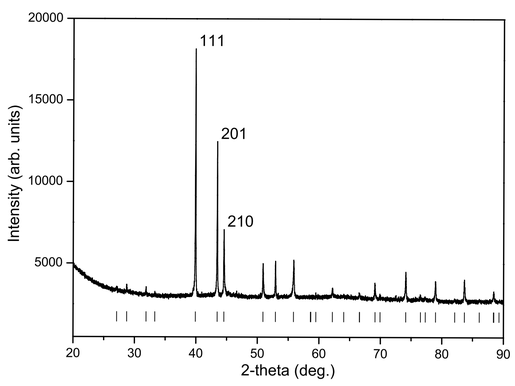

Fig. 2: X-ray powder diffraction pattern of $FeMnP_{0.5}Si_{0.5}$ at 296 K. The tick marks indicate the Bragg positions of $FeMnP_{0.5}Si_{0.5}$.

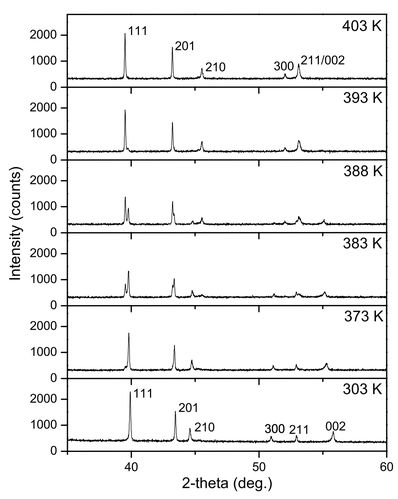

Fig. 3: XRD-patterns of $FeMnP_{0.5}Si_{0.5}$ showing the structural transition occurring at approx. 385 K.

The XRD investigation confirms that $FeMnP_{0.5}Si_{0.5}$ crystallizes in the hexagonal Fe_2P-type structure, space group P-62m and unit cell parameters a=6.2090(3) Å, c=3.2880(3) Å. The XRD pattern for $FeMnP_{0.5}Si_{0.5}$ at 296 K is shown in Fig. 2 which reveals a pattern of a single phase sample. XRD-patterns in the range 363–403 K are shown in Fig. 3 where it can be seen that $FeMnP_{0.5}Si_{0.5}$ undergoes an isostructural transition between 373 and 393 K. The a-axis has decreased 2% while the c-axis has increased 5% compared to 296 K.

The structural transition occurs in the same region as the Curie temperature why it is likely that the transition originate from magnetostriction effects.

Structure refinements

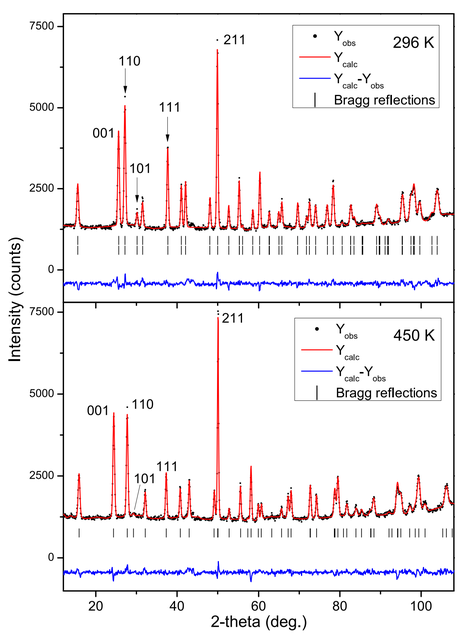

Fig. 4: Structure refinements from neutron powder diffraction data of $FeMnP_{0.5}Si_{0.5}$ at 296 and 450 K. The peaks with the highest magnetic intensity are marked with an arrow.

Structure refinements of neutron powder diffraction data of $FeMnP_{0.5}Si_{0.5}$ at 296 K and 450 K can be seen in Fig. 4. The data from the refinements are summarized in Table 1 and it can be seen that the tetragonal 3g site is mainly occupied by the Fe atoms and has a magnetic moment of 1.9 μ_B. The Mn atoms are mainly situated in the pyramidal 3f site and has a magnetic moment of 2.5 μ_B. The total magnetic moment per unit cell is thus approx 4.4 μ_B.

This high value of the magnetic moment is confirmed by Mössbauer results [2]. The magnetic structures of $FeMnP_{0.5}Si_{0.5}$ and Fe_2P are shown in Fig. 5. The magnetic moments are aligned in the a-direction while the moments of Fe_2P are aligned in the c-direction [3]. The composition based on the refined occupancies extracted from the neutron powder diffraction data (at fixed ratio P/Si=1) indicates that the acquired composition of the metallic atoms in the sample is close to $FeMnP_{0.5}Si_{0.5}$ ($Fe_{1.02(1)}Mn_{0.98(1)}P_{0.5}Si_{0.5}$, namely).

Table 1: Placement and occupancy of the Fe and Mn atoms in $FeMnP_{0.5}Si_{0.5}$ at 296 and 450 K. Derived from refinements of neutron powder diffraction data.

Atom	Site	x	y	z	occ	M [μ_B]
Fe1	3g	0.25683	0	0.5	0.95333	1.9(1)
Mn1	3g	0.25683	0	0.5	0.04667	1.9(1)
Fe2	3f	0.59764	0	0	0.03535	2.5(1)
Mn2	3f	0.59764	0	0	0.96465	2.5(1)

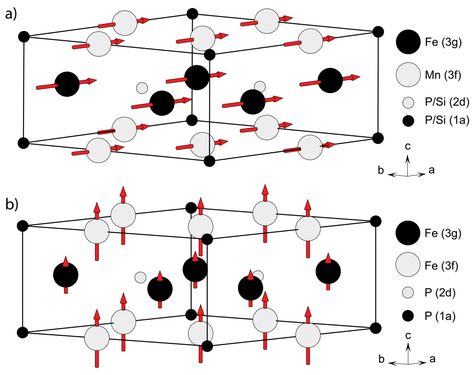

Fig. 5: The magnetic structure of $FeMnP_{0.5}Si_{0.5}$ (a) and Fe_2P (b). The magnetic moments in Fe_2P are aligned in the c-direction while the moments in $FeMnP_{0.5}Si_{0.5}$ are aligned in the a-direction. The length of the arrows corresponds to the magnitude of the magnetic moments.

Experiments

Sample preparation

Samples of stoichiometric $FeMnP_{0.5}Si_{0.5}$ were prepared by the drop synthesis method using a high frequency induction furnace, see Fig. 6. Raw materials were high purity pieces of iron, manganese. phosphorous and silicon. All samples were crushed, pressed into pellets and sealed in evacuated fused silica tubes. Subsequent, the samples were sintered at 1373 K for 1 h, annealed at 1073 K for 65 h and finally quenched in cold water. The synthetic process showed minor (less than 0.5 weight%) losses.

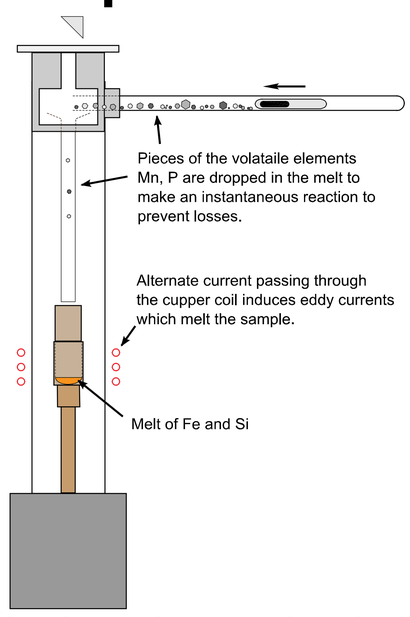

Fig. 6: Experimental setup for the drop synthesis method using an induction furnace

Structure analysis

Phase analysis and structure characterizations were performed using X-ray and neutron powder diffraction in the temperature range of 296 - 450 K. Neutron powder diffraction data were collected on the instrument MEREDIT at the Nuclear Physics Institute in Rez, Czech Republic.

Structure refinements were performed on the neutron powder profiles by the Rietveld method using the software FULLPROOF and unit cell parameters from XRD data were refined using the software UNITCELL

This work is funded by

Swedish Energy Agency

Vetenskapsrådet

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