The crystal and magnetic structure of the magnetocaloric compound FeMnP$_{0.5}$Si$_{0.5}$

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Abstract

The crystal and magnetic structure of the magnetocaloric compound FeMnP$_{0.5}$Si$_{0.5}$ have been studied by means of neutron and X-ray powder diffraction. Single phase samples of nominal composition FeMnP$_{0.5}$Si$_{0.5}$ have been prepared by the drop synthesis method. The compound crystallizes in the Fe$_2$P-type structure (P62m) with the magnetic moments aligned along the a-axis. It is found that the Fe atoms are mainly situated in the tetrahedral 3g site while the Mn atoms prefer the pyramidal 3f position. The material is ferromagnetic ($T_C = 382$ K) and at 296 K the total magnetic moment is $4.4 \mu_B$/f.u. It is shown that the magnetic moment in the 3f site is larger ($2.5 \mu_B$) than in the 3g site ($1.9 \mu_B$).

Keywords: Magnetocaloric, Neutron powder diffraction, X-ray diffraction (XRD), Drop synthesis method, Magnetic refrigeration, Magnetic structure

1. Introduction

Magnetocaloric compounds have gained an increased interest since the middle 1990’s due to environmental and energy benefits from magnetic refrigeration and the discovery of the Giant Magnetocaloric Effect (GMCE) [1]. In GMCE compounds rare earth metals are common alloying elements and due to their rareness in nature and high costs, they will be a problem in a future large-scale production. Hence, there is a need to find more common and cheaper compounds not based on rare earth metals that possess the GMCE.

A large number of studies on the compound Fe$_2$P have been performed since the 1960’s and its crystallographic and magnetic properties have been well investigated [2, 3, 4]. The relatively large saturation magnetization, first order nature of the transition and readily tunable transition temperature with various substitutions make the Fe$_2$P system a candidate compound for magnetocaloric applications. Numerous compounds based on Fe$_2$P have been fabricated during the years and compounds of the FeMnP$_{1-x}$M$_x$-type (M = Si, Ge and/or As) have shown improved magnetocaloric properties.

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In this investigation, samples of nominal composition \(\text{FeMnP}_{0.5}\text{Si}_{0.5}\) have been synthesized and the crystal and magnetic structure and the magnitude of the magnetic moments at different temperatures have been determined. There is a controversy about the exact properties of the \(\text{FeMnP}_{1-x}\text{Si}_x\)-system. A previous study by Cam Thanh et al. [5] on samples of nominally the same composition, \(\text{FeMnP}_{0.5}\text{Si}_{0.5}\), prepared by a ball milling technique, had a transition temperature of 332 K with higher preserved magnetocaloric effect. There is a significant difference in the structural and magnetic properties presented by Cam Thanh et al. [5] compared to our results. This dichotomy may be explained by the fact that their samples contained about 18% of a second phase, identified as \(\text{Fe}_2\text{MnSi}\).

Our magnetization measurements on the \(\text{FeMnP}_{0.5}\text{Si}_{0.5}\) sample show a ferromagnetic transition temperature of 382 K and the magnetic entropy change \(-\Delta S_M\) has from magnetization experiments been estimated to about 8 J/kgK in a magnetic field change of 1.8 T [6]. The magnetocaloric effect is slightly lower compared to similar compounds [7, 8] but due to its content of only common, non-toxic, elements \(\text{FeMnP}_{0.5}\text{Si}_{0.5}\) is a promising magnetocaloric compound within the \(\text{FeMnP}_{1-x}\text{M}_x\) alloy system.

2. Experiments

2.1. Sample preparation

\(\text{FeMnP}_{0.5}\text{Si}_{0.5}\) samples were prepared by the drop synthesis method [9] using a high frequency induction furnace at 1623-1673 K in an Ar atmosphere of 40 kPa. Stoichiometric amounts of iron (Leico Industries, purity 99.995%), manganese (Institute of Physics, Polish Academy of Sciences, purity 99.999%), phosphorus (Cerac, purity 99.999%) and silicon (Highways International, purity 99.999%) were used as raw materials. All samples were crushed, pressed into pellets and sealed in evacuated fused silica tubes. Subsequently, the samples were sintered at 1373 K for 1 h, annealed at 1073 K for 65 h and finally quenched in cold water.

2.2. X-ray powder diffraction

Phase analysis and crystal structure characterizations were performed using X-ray powder diffraction (XRD) with a Bruker D8 diffractometer equipped with a Vantec position sensitive detector (PSD, 4 degree opening) using Cu \(K\alpha_1\) radiation, \(\lambda = 1.540598\) Å. The measurements were made using a 2\(\theta\) range of 20-90° at 296 K and 403 K and a 2\(\theta\)-range of 35-60° in the temperature range 373 K to 393 K.

2.3. Neutron powder diffraction

Neutron powder diffraction data were collected on the instrument MEREDIT at the Nuclear Physics Institute in Rez, Czech Republic. The neutron beam was monochromatised by a copper mosaic monochromator (reflection 220) giving a wavelength of \(\lambda = 1.46\) Å. Samples were studied in a 2\(\theta\)-range of 4-148° at 296 K and 450 K.
2.4. Refinements of the crystal and magnetic structure

Structure refinements were performed on the neutron powder profiles by the Rietveld method [10] using the software FULLPROF [11] and unit cell parameters from XRD data were refined using the software UNITCELL [12]. The neutron wavelength was refined by using unit cell parameters determined from XRD data as starting point. The refined wavelength was used to refine the unit cell parameters at 450 K from neutron powder diffraction data. The peak shape was described by a pseudo-Voight profile function and the background was determined by a linear interpolation between chosen points. The following parameters in the 450 K data set were varied: peak shape, unit cell parameters, scale factor, half width parameters, zero point, background, atom occupancies, isotropic temperature parameter and atomic coordinates. The same parameters of the 296 K data set were varied as well as the parameters for the magnetic moments. The magnetic form factors of Fe and Mn were set as shown in Refs. 13, 14, respectively. The occupancies of the P/Si sites were kept at a 50/50 ratio, thus not allowing the actual P and Si content to be determined from these refinements.

3. Results

3.1. Phase analysis and crystal structure

The XRD investigation confirms that FeMnP_{0.5}Si_{0.5} crystallizes in the hexagonal Fe\textsubscript{2}P-type structure, space group P\overline{6}2m 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 Figure 1 which reveals a pattern of a single phase sample. XRD-patterns in the range 363 to 403 K are shown in Figure 2 where it can be seen that FeMnP_{0.5}Si_{0.5} undergoes a structural transition (within the space group) between ~373 K and 393 K. The a-axis has decreased ~2% while the c-axis has increased ~5% compared to 296 K, see Table 1. The factor c/a and the volume have increased ~7% and 1% respectively. The structural transition occurs in the same region as the Curie temperature why it is likely that the transition originate from magnetostriiction effects. Structure refinements of powder neutron diffraction data shows that the Fe and Mn atoms are preferably situated in the 3g and 3f sites respectively which are based on the interatomic distances (see Table 2) and the refined occupancies of the Fe and Mn atoms (see Table 3).

The composition based on the refined occupancies extracted from the neutron powder diffraction data (however assuming fixed ratio P/Si=1) indicates that the acquired composition of the metallic atoms in the sample is (Fe_{1.018(3)}Mn_{0.982(3)})P_{0.5}Si_{0.5}. Also, the synthetic process with stoichiometric amounts of the raw materials showed minor (less than 0.5%) losses.

3.2. Magnetic structure

Refinements of the neutron powder diffraction data at 296 K and 450 K are shown in Figure 3. The magnetic contribution from the ferromagnetic phase at 296 K is distinguished by the higher

| T (K) | a (Å) | c (Å) | V (Å\textsuperscript{3}) | c/a   |
|-------|-------|-------|-----------------|-------|
| 296   | 6.2090(3) | 3.2880(2) | 109.78(2)  | 0.5296(1) |
| 450   | 6.0830(8)  | 3.4507(9)  | 110.58(4)  | 0.5672(1) |

Table 1: Unit cell parameters of FeMnP_{0.5}Si_{0.5} at 296 K and 450 K refined from XRD data, \( \lambda = 1.540598 \) Å.
Figure 1: X-ray powder diffraction pattern of FeMnP\textsubscript{0.5}Si\textsubscript{0.5} at 296 K. The tick marks indicate the Bragg positions of FeMnP\textsubscript{0.5}Si\textsubscript{0.5}, \( \lambda = 1.540598\ \text{Å} \).

Peak-intensities at lower 2-theta angles. The magnetic moments are aligned in the a-direction and are 1.9(1) \( \mu_B \) and 2.5(1) \( \mu_B \) in the M(1) and M(2) site respectively which gives a total magnetic moment of 4.4(2) \( \mu_B \). The magnetic symmetry group was found to be Cm2m.

4. Discussion

The magnitude of the magnetic moments of the Fe atoms and the total magnetic moment per formula unit is confirmed by recent Mössbauer and magnetization studies of FeMnP\textsubscript{0.5}Si\textsubscript{0.5} \[6\]. The total magnetic moment has been reported to be approx. 4.4 \( \mu_B/f.u \) which is in good agreement with our result, where the total magnetic moment is 4.4(2) \( \mu_B/f.u \). The size of the total magnetic moment is higher than the corresponding value for Fe\textsubscript{2}P (2.9(1) \( \mu_B \)) \[15, 12, 17, 18\]. Earlier studies have also shown that there are significant differences in magnitude of the moments between the two Fe sites in Fe\textsubscript{2}P. The Fe atom in the pyramidal 3f site possesses a smaller magnetic moment than the Fe atom in the tetrahedral 3g site, which is illustrated in Figure 4b.

Table 2: Interatomic distances in FeMnP\textsubscript{0.5}Si\textsubscript{0.5} at 296 K.

| Atoms      | Distance (Å) | Atoms      | Distance (Å) |
|------------|--------------|------------|--------------|
| Fe(1) –    | 2 P/Si(2)    | 2.292(2)   | 1 P/Si(2)    | 2.502(6)   |
| 2 P/Si(1)  | 2.342(2)     | 4 P/Si(1)  | 2.506(2)     |
| 2 Mn(2)    | 2.675(5)     | 2 Fe(1)    | 2.675(5)     |
| 4 Mn(2)    | 2.742(4)     | 4 Fe(1)    | 2.742(4)     |
| 2 Fe(1)    | 2.766(3)     | 4 Mn(2)    | 3.275(6)     |
| P/Si(1) –  | 3 Fe(1)      | 2.342(2)   | 6 Fe(1)      | 2.292(2)   |
| 6 Mn(2)    | 2.506(5)     | 3 Mn(2)    | 2.502(3)     |
Table 3: Placement and occupancy of the Fe and Mn atoms in FeMnP_{0.5}Si_{0.5} at 296 K and 450 K. Derived from refinements of neutron powder diffraction data. (0, 0, 0) was chosen as an origin.

| Atom    | Site | 296 K       |          |          | 450 K       |          |          |
|---------|------|-------------|----------|----------|-------------|----------|----------|
|         |      | x    | y    | z   | Occ.   | x    | y    | z   | Occ.   |
| Fe(1)   | 3g   | 0.257(4) | 0    | 1/2 | 0.235(4) | 0.2548(3) | 0      | 1/2 | 0.2353(4) |
| Mn(1)   | 3g   | 0.2572(4) | 0    | 1/2 | 0.0147(4) | 0.2548(3) | 0      | 1/2 | 0.0147(4) |
| Fe(2)   | 3f   | 0.597(1) | 0    | 0   | 0.0193(2) | 0.591(1) | 0      | 0   | 0.0193(2) |
| Mn(2)   | 3f   | 0.597(1) | 0    | 0   | 0.2307(2) | 0.591(1) | 0      | 0   | 0.2307(2) |
| P/Si(1) | 2d   | 1/3 | 2/3 | 1/2 | 0.1667 | 1/3 | 2/3 | 1/2 | 0.1667 |
| P/Si(2) | 1a   | 0   | 0   | 0   | 0.0833 | 0   | 0   | 0   | 0.0833 |

$R_p = 2.37\%, R_{wp} = 3.05\%, \chi^2 = 3.03$  $R_p = 2.59\%, R_{wp} = 3.36\%, \chi^2 = 3.44$

The refinements of the neutron powder diffraction intensities of FeMnP_{0.5}Si_{0.5} indicate that the Mn atoms prefer to be situated in the pyramidal 3f site in the Fe_{2}P-structure. The substitution of Fe with Mn in the 3f site increases the magnetic moment in the site with ~0.8 $\mu_B$ compared to Fe_{2}P. The magnetic moment of the Fe atom in the 3g site of FeMnP_{0.5}Si_{0.5} is also shown to increase ~0.6 $\mu_B$.

The magnetic structures of FeMnP_{0.5}Si_{0.5} and Fe_{2}P are shown in Figure 4. The magnetic moments are aligned in the a-direction while the moments of Fe_{2}P are aligned in the c-direction [4, 19]. A similar alignment of the magnetic moments as in FeMnP_{0.5}Si_{0.5} has also been reported to occur in FeMnP_{0.5}As_{0.5} [20]. It is of interest to note that in FeMnP_{0.7}As_{0.3} the moments deviate

Figure 2: XRD-patterns of FeMnP_{0.5}Si_{0.5} showing the structural transition occurring at approx. 385 K. $\lambda = 1.540598$ Å.
Figure 3: Structure refinements from neutron powder diffraction data of FeMnP<sub>0.5</sub>Si<sub>0.5</sub> at 296 K and 450 K. The differences in intensity and position of the Bragg peaks are due to the ferro- to paramagnetic transition at \( \sim 390 \) K and the structural transition at \( \sim 385 \) K. The peaks with the highest magnetic intensity are marked with an arrow.

from the c-axis by 50°.

Magnetoelastic transitions have been found for the hexagonal system FeMnP<sub>1-y</sub>As<sub>y</sub> (0.15 \( \leq y \leq 0.66 \)) isostructural with FeMnP<sub>0.5</sub>Si<sub>0.5</sub>. A marked increase both in magnetic hyperfine field and in magnetic moment take place on the Fe tetrahedral site (Fe<sub>t</sub>) as compared to the tetrahedral site in Fe<sub>2</sub>P [20, 21]. Table 4 displays the interatomic distances in paramagnetic and ferromagnetic Fe<sub>2</sub>P, FeMnP<sub>0.7</sub>As<sub>0.3</sub> and the presently studied compound FeMnP<sub>0.5</sub>Si<sub>0.5</sub>. As can be seen from the table the cell volume, the average near Fe<sub>t</sub>–X distances and Fe<sub>t</sub>–M<sub>p</sub> do not change significantly between the paramagnetic (PM) and the ferromagnetic (FM) state. However the crystal a- and c-axis decreases and increases, respectively, when passing the first order ferromagnetic transition from lower temperature. A large interatomic difference is however observed for the Fe<sub>t</sub>–Fe<sub>t</sub> distances for the high moment cases of FeMnP<sub>0.7</sub>As<sub>0.3</sub> and FeMnP<sub>0.5</sub>Si<sub>0.5</sub>. The cell volume expansion between the three different compounds is obvious. The overall crystal expansion and the increase in Fe<sub>t</sub>–Fe<sub>t</sub> distances yields a stronger Fe<sub>t</sub> electron localization and results in a larger Fe<sub>t</sub> magnetic moment.

5. Conclusions

The magnetocaloric compound FeMnP<sub>0.5</sub>Si<sub>0.5</sub> has been synthesized and studied regarding the crystallographic and magnetic structure. X-ray and neutron powder diffraction experiments
Table 4: Magnetic state, Fe saturation magnetic moment and interatomic average distances for tetrahedral Fe in FeMX with Fe₂P structure, Mₚ = pyramidal Fe or Mn and X = P, Si and As.

| Compound          | Magn. state (Tₐ) | Fe₉ sat. mom. (µₜ) | V (Å³) | Fe₉-X (Å) | Fe₉-Fe₉ (Å) | Fe₉-Mₚ (Å) | Ref.     |
|-------------------|------------------|--------------------|--------|-----------|-------------|------------|----------|
| Fe₂P              | PM (295 K)       | -                  | 103.1  | 2.255     | 2.610       | 2.682      | [9]      |
|                   | FM (77 K)        | 1.03               | 102.9  | 2.253     | 2.597       | 2.682      | [17]     |
| FeMnP₀.₇As₀.₃     | PM (250 K)       | -                  | 110.7  | 2.311     | 2.638       | 2.755      | [20]     |
|                   | FM (100 K)       | 1.25               | 110.2  | 2.312     | 2.747       | 2.743      | [20]     |
| FeMnP₀.₅Si₀.₅     | PM (450 K)       | -                  | 109.8  | 2.312     | 2.685       | 2.726      | This work|
|                   | FM (296 K)       | 1.65               | 110.6  | 2.317     | 2.766       | 2.708      | This work|

show that the sample is single phase and reveals the magnetic structure of FeMnP₀.₅Si₀.₅. An isotructural phase transition has been observed at about the same temperature as the magnetic phase transition (382 K). The Fe atoms are mainly situated in the tetrahedral 3g site while the Mn atoms prefer the pyramidal 3f position. The magnetic moments derived from neutron powder diffraction are shown to be coordinated along the a-axis with a total moment of 4.4 µₜ. This high value of the magnetic moment goes along with our Mössbauer results [6] and is in accord with a strong increase in the Fe₉-Fe₉ distances. The high magnetic moment and a readily tunable transition temperature make (slightly) off-stoichiometric FeMnP₀.₅Si₀.₅ a promising alloy system for magnetocaloric applications.

Figure 4: The magnetic structure of FeMnP₀.₅Si₀.₅, a), and Fe₂P, b). The magnetic moments in Fe₂P are aligned in the c-direction while the moments in FeMnP₀.₅Si₀.₅ are aligned in the a-direction. The length of the arrows correspond to the magnitude of the magnetic moments.
Acknowledgments

This work was financed by the Swedish Research Council and the Swedish Energy Agency, which is gratefully acknowledged.

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