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# Structural and magnetocaloric properties of $(\text{Mn,Fe})_2(\text{P,Si})$ materials with added nitrogen

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**ABSTRACT** — Amongst magnetic materials that exhibit a giant magnetocaloric effect near room temperature, the  $(\text{Mn,Fe})_2(\text{P,Si})$  system is one of the most promising candidates for magnetic refrigeration. Although the  $(\text{Mn,Fe})_2(\text{P,Si})$  materials hold many advantages, controlling the magnetic entropy change  $\Delta S_m$ , the adiabatic temperature change  $\Delta T_{ad}$ , the thermal hysteresis and the mechanical stability across the ferromagnetic transition requires a delicate tuning of the composition. This work investigates the addition of nitrogen, as an interstitial or substitutional element, as a new parameter to tune the properties of  $(\text{Mn,Fe})_2(\text{P,Si})$  materials. We found that the nitrogen addition results in a decrease of the Curie temperature, consistent with the observed increase in the  $c/a$  ratio. The introduction of nitrogen in  $(\text{Mn,Fe})_2(\text{P,Si})$  materials also results in a strong enhancement of the mechanical stability.

**Keywords:** magnetocaloric effect, magnetic materials, magnetic refrigeration, nitrogen addition

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# 1. Introduction

Recently, magnetocaloric materials have been studied intensively because of their potential application in magnetic refrigeration. Compared to the commonly used vapour-compression refrigeration, magnetic refrigeration, which is based on magnetocaloric effect (MCE), has many advantages. For example, the cooling efficiency of magnetic refrigeration, can reach up to 60% of the Carnot efficiency. This efficiency gain will result in a reduced CO<sub>2</sub> release. In addition, magnetic refrigerators can be built more compactly as the refrigerants are magnetic solids rather than gases. Moreover, magnetic refrigeration generates much less noise due to the absence of an energy-consuming compressor and fewer moving parts. This is also an environmentally friendly technology because of the absence of dangerous and environmentally unfriendly refrigerants such as ozone depleting chemicals (e.g. chlorofluorocarbons), hazardous chemicals (e.g. NH<sub>3</sub>) and greenhouse gases (e.g. hydrochlorofluorocarbons and hydrofluorocarbons). Therefore, magnetic refrigeration is a promising technology with the potential to replace the conventional gas-compression technology [1],[2],[3].

Magnetic materials that display a large MCE near room temperature are a key requirement to realize magnetic refrigeration. In recent years, many novel materials with large MCE have been developed, such as Gd<sub>5</sub>(Si,Ge)<sub>4</sub> [4], Mn(As,Sb) [5],[6], (Mn,Fe)<sub>2</sub>(P,X) (X = As, Ge, Si) [7],[8],[9], LaFe<sub>13-x</sub>Si<sub>x</sub> and their related compounds [10],[11],[12], (Mn,Fe)<sub>2</sub>(P,Si,B) [13] and NiMn-based Heusler alloys [14]. Among the presently known MCE materials with a first-order magnetic transition (FOMT) the (Mn,Fe)<sub>2</sub>(P,Si) compounds fulfill most of the requirements for practical applications of magnetic refrigeration [15]. First, it has a limited thermal hysteresis at the FOMT. Second, the Curie temperatures are in the vicinity of the required working temperature. Third, it has a large MCE at moderate magnetic field. In addition, it is easy to tune the operating temperature by varying the Mn/Fe and/or P/Si ratio. Furthermore, the composition of these compounds does not contain any toxic or expensive elements such as arsenic and germanium, respectively.

Several different approaches have been developed to tailor the properties of the (Mn,Fe)<sub>2</sub>(P,Si)-based materials. It has recently been reported that the introduction of B results into a tunable high-performance MCE material system. In the (Mn,Fe)<sub>2</sub>(P,Si,B) materials, B acts as a substitutional element [15], whereas it is an interstitial element in the (Mn,Fe)<sub>2</sub>(P,As,B) materials [16]. It is well known that the magnetocaloric properties of magnetic materials can be influenced by the application of physical pressure [17],[18]. However, applying physical pressure is an impractical approach for applications. Thus, chemical pressure is commonly employed instead by the introduction of interstitial elements. The introduction of an interstitial element is expected to provide a relatively simple tuning parameter to provide a gradual displacement of the phase transition without a strong impact on the magnetocaloric properties [16]. Interstitial elements may also provide a useful tool to

investigate the role of the magneto-elastic coupling in the FOMT [15]. Nitrogen is an ideal candidate as it has a smaller atomic radius than boron and the same electron configuration as phosphorous.

This work reports on a new approach to tune the magnetocaloric properties of the  $(\text{Mn,Fe})_2(\text{P,Si})$  compounds by adding nitrogen. We demonstrate that N atoms occupy both substitutional and interstitial sites of the hexagonal  $\text{Fe}_2\text{P}$ -type crystal structure. The introduction of nitrogen provides the possibility to tune the Curie temperature, while the magnetocaloric properties are preserved and the mechanical stability is improved.

## 2. Experimental details

All samples were prepared following the same protocol: first high-energy ball milling and then a solid-state reaction was applied. The nitrogen source was introduced in solid form using  $\text{Fe}_{2.4}\text{N}$  iron nitride powder. Stoichiometric mixtures of the starting materials Mn, Fe,  $\text{Fe}_{2.4}\text{N}$ , red P and Si powders were ball milled for 10 h with a constant rotation speed of 380 rpm at room temperature. After milling, the mixture was compacted into small tablets (with a diameter of 12 mm and a height of 5-10 mm) in a hydraulic press. After pressing, the tablets were sealed inside quartz ampoules with 200 mbar of Ar. Then, the samples were sintered at 1373 K for 2 h and annealed at 1123 K for 20 h. The samples were slowly cooled to room temperature before they were re-sintering at 1373 K for 20 h to achieve a homogeneous composition. The thermal treatment was completed by rapidly quenching to room temperature by directly dipping the ampoules into water. The samples were precooled in liquid nitrogen to remove the virgin effect [19], and then crushed using a mortar.

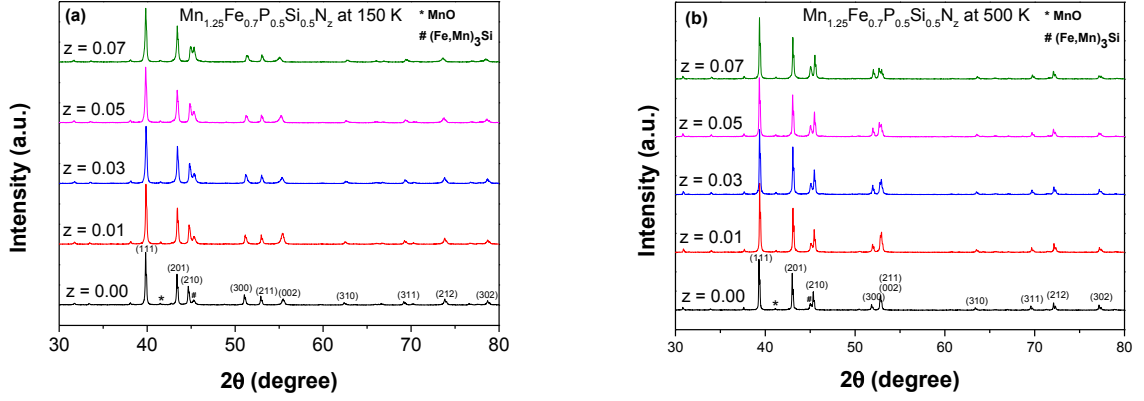
The crystalline structure of the samples was characterized by X-ray diffraction (XRD) using a PANalytical X-pert Pro diffractometer with  $\text{Cu-K}_\alpha$  radiation. The refinements were done using the Fullprof program [20]. A differential scanning calorimeter (DSC) equipped with a liquid nitrogen cooling system was used to measure the specific heat. Magnetic measurements were performed using the Reciprocating Sample Option (RSO) mode in a Superconducting Quantum Interference Device (SQUID) magnetometer (Quantum Design MPMS 5XL). The magnetic entropy change, one of the characteristic parameters for MCE, was derived from the isofield magnetization measurements using the Maxwell relation.

## 3. Results and discussion

### 3.1 Interstitial nitrogen addition

Fig. 1 shows the XRD patterns of  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds measured at 150 K (a) and 500 K (b) (in the ferromagnetic and paramagnetic state, respectively), for samples with a nominal nitrogen composition of  $z = 0.00, 0.01, 0.03, 0.05$  and  $0.07$ . All

samples exhibit the hexagonal  $\text{Fe}_2\text{P}$ -type crystal structure and, as commonly observed in this material family, display a small amount of  $(\text{Mn,Fe})_3\text{Si}$  and  $\text{MnO}$  impurity phases. The  $\text{MnO}$  impurity phase probably originates from the oxidation of  $\text{Mn}$  powder during storage. The XRD pattern gradually changes with an increase in nitrogen content, as the  $a$  and  $c$  lattice parameters evolve. We do not observe any additional reflections, indicating that the nitrogen is fully accommodated in the  $\text{Fe}_2\text{P}$ -type structure.



**Figure 1.** X-ray diffraction patterns measured at 150 K (a) and 500 K (b) for the  $\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5}\text{Si}_{0.5}\text{N}_z$  compounds.

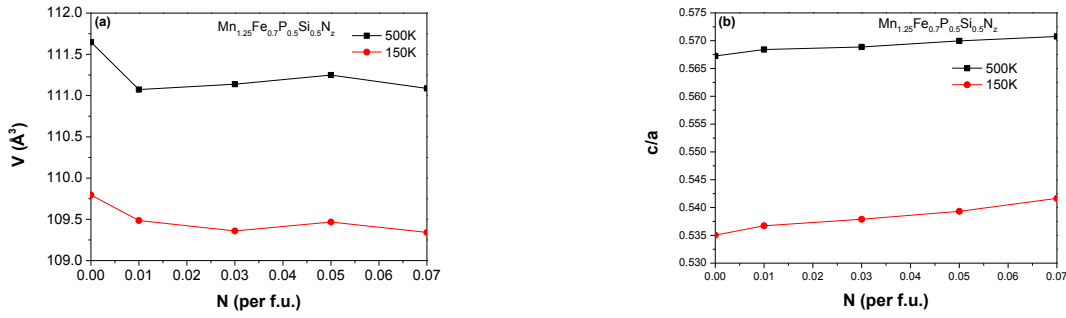
The XRD data were analyzed by the Rietveld refinement method [21] using the Fullprof program. The lattice parameters and unit-cell volume are summarized in Table 1. The results indicate that for an increase in N concentration, the lattice parameter  $a$  decreases, the lattice parameter  $c$  increases, whereas the unit-cell volume hardly changes between 150 and 500 K. A small difference of only 1.3% in volume between these temperatures was observed, which originates from the FOMT and the thermal expansion.

**Table 1.** Lattice parameters and unit-cell volume of the  $\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5}\text{Si}_{0.5}\text{N}_z$  compounds with  $z = 0.00, 0.01, 0.03, 0.05$  and  $0.07$  at a temperature of 150 and 150 and 500 K, respectively.

Compound	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$c/a$
$\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5}\text{Si}_{0.5}\text{N}_z$	(150/500 K)	(150/500 K)	(150/500 K)	(150/500 K)
$z = 0.00$	6.18812/6.10262	3.31082/3.4617	109.795/111.649	0.53503/0.56725
$z = 0.01$	6.17579/6.08798	3.31471/3.46045	109.486/111.073	0.53673/0.56841
$z = 0.03$	6.16894/6.08753	3.31819/3.46299	109.359/111.138	0.53789/0.56887
$z = 0.05$	6.16551/6.08563	3.32517/3.46859	109.467/111.249	0.53932/0.56996
$z = 0.07$	6.15434/6.07985	3.33346/3.47014	109.342/111.087	0.54164/0.57076

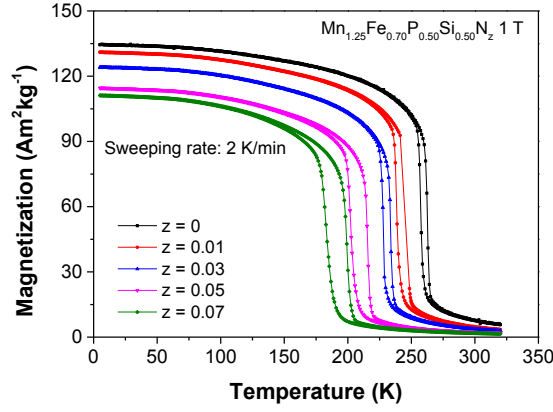
Fig. 2 shows the evolution of the unit-cell volume  $V$  and the  $c/a$  ratio in the ferromagnetic state (150 K) and paramagnetic state (500 K) for the  $\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5}\text{Si}_{0.5}\text{N}_z$

compounds. The addition of nitrogen as an interstitial element leads to two main features. First, there is a gradual increase in the  $c/a$  ratio when  $z$  increases. Second, the unit-cell volume slightly decreases when the N concentration is increased to 1%. A further increase in N concentration up to 7% only causes a slight variation in unit-cell volume in both the paramagnetic and ferromagnetic state (Fig. 2 (a)). It is expected that the unit-cell volume increases when the nitrogen atoms enter the structure as an interstitial element. The addition of nitrogen as a substitutional element should lead to a larger decrease in the unit-cell volume compared to the boron addition, as the radius of a nitrogen atom is smaller than that of boron. The slight variation in unit-cell volume for increasing nitrogen doping suggests that in this case the nitrogen atoms enter the structure partly as substitutional and partly as interstitial element.



**Figure 2.** Unit-cell volume  $V$  (a) and  $c/a$  ratio (b) of the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds in the paramagnetic (500 K) and ferromagnetic state (150 K) as function of the nitrogen content.

In Fig. 3 the temperature dependence of the magnetization is shown for the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds measured during cooling and heating in a magnetic field of 1 T. Two main features were observed. First, the Curie temperature decreases as a function of the nitrogen content, which is consistent with the increase in the  $c/a$  ratio observed in Fig. 2(b). Second, the increase in nitrogen concentration leads to a gradual decrease in the spontaneous magnetization and a slight increase in thermal hysteresis. The presence of thermal hysteresis ( $\Delta T_{hys}$ ) reveals the first-order nature of the transitions, which usually results in a large MCE [1].

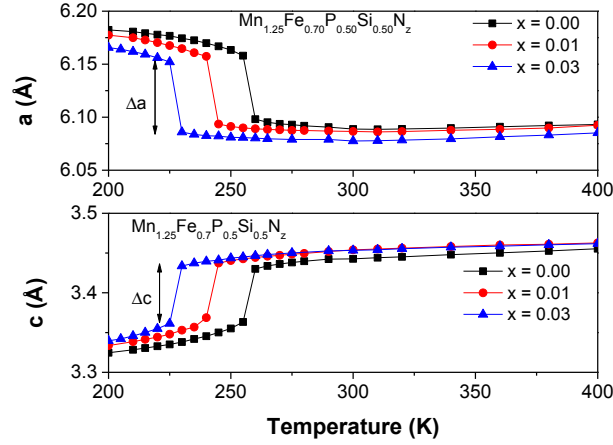


**Figure 3.** Magnetization curves measured on heating and cooling in a magnetic field of 1 T for the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds.

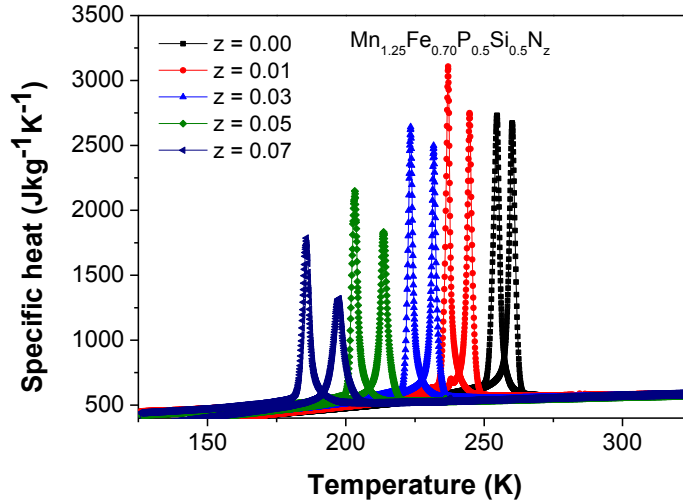
**Table 2.** Curie temperature  $T_C$  in zero-field derived from the DSC data measured on heating; the isothermal entropy change derived from the isofield magnetization curves in a field change of 1 T, thermal hysteresis derived from the DSC data measured in zero field upon cooling and heating and the relative changes in lattice parameter  $|\Delta a/a|$  and  $|\Delta c/c|$  at the transition for the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds.

$\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5}\text{Si}_{0.5}\text{N}_z$	$T_C$ (K)	$ \Delta S_m $ ( $\text{Jkg}^{-1}\text{K}^{-1}$ )	$\Delta T_{hys}$ (K)	$ \Delta a/a $ (%)	$ \Delta c/c $ (%)
$z = 0.00$	260	13.75	4.80	0.97	1.98
$z = 0.01$	245	14.59	5.40	1.04	2.04
$z = 0.03$	232	13.80	5.60	1.08	2.15

Dung and coworkers [22] have pointed out that there is a correlation between the magnitude of the hysteresis and the relative changes in lattice parameters  $|\Delta a/a|$  and  $|\Delta c/c|$  at  $T_C$ . Hence, the XRD patterns as a function of temperature were collected in zero field to investigate the origin of the increase in thermal hysteresis for increasing  $z$ . Fig. 4 shows the temperature dependence of the lattice parameters  $a$  and  $c$  for the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds with  $z = 0.00, 0.01, 0.03$ . As shown in Fig. 4, the same trend in the thermal evolution of the lattice parameters  $a$  and  $c$  has been observed for all samples. Specifically, the lattice parameter  $a$  decreases while the lattice parameter  $c$  increases for increasing temperature. We note that the volume change at  $T_C$  is very small due to the opposite change in the  $a$  and  $c$  parameters. This may contribute to an improvement in mechanical stability for the N-doped materials. In our experiments, we observed that the N-doped materials remain in their physical forms when precooled in liquid nitrogen, whereas the pristine  $(\text{Mn,Fe})_2(\text{P,Si})$  materials are easily fragmented. As presented in Table 2, larger  $|\Delta a/a|$  and  $|\Delta c/c|$  ratios result in a larger  $\Delta T_{hys}$ . This increase in  $\Delta T_{hys}$  is expected to be due to a higher energy barrier to nucleate the new phase. This is in good agreement with the previous report on  $(\text{Mn,Fe})_2(\text{P,Si})$  compounds [22].



**Figure 4.** Lattice parameters  $a$  and  $c$  as a function of temperature derived from the XRD patterns measured in zero field upon heating for the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  ( $z = 0.00, 0.01, 0.03$ ) compounds.

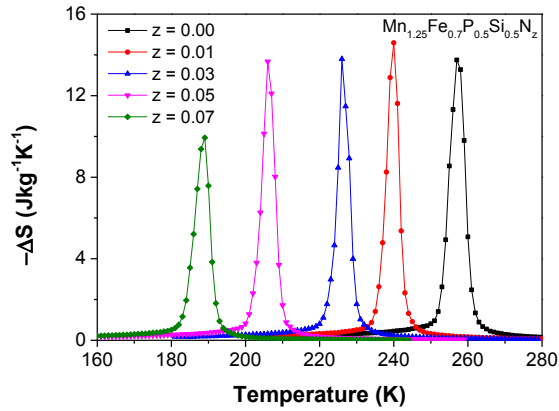


**Figure 5.** Specific heat of the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds measured in zero-field upon cooling and heating.

We note that the sharp first-order magnetic transition of the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds becomes weaker for increasing N concentrations. This is indicated by the lower and broader peak at  $T_C$  in the specific heat curves of Fig. 5.

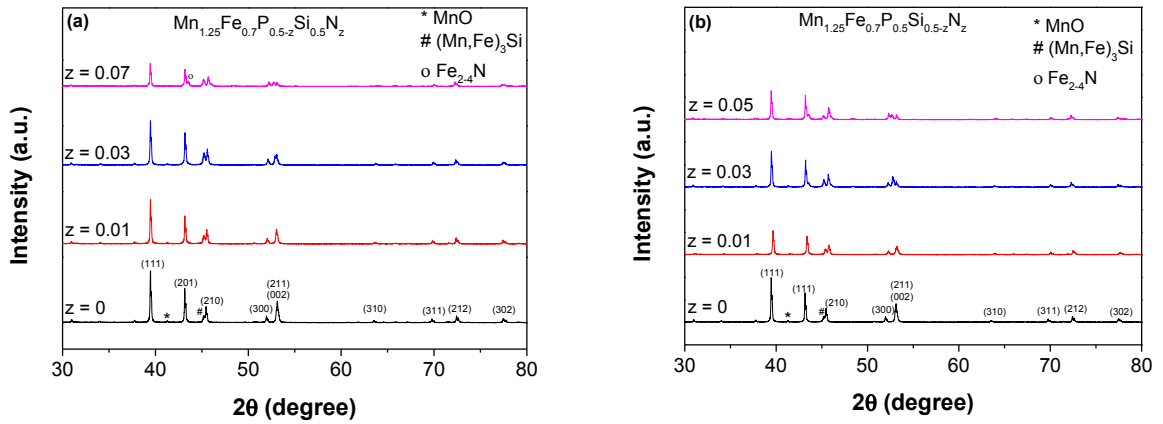
Fig. 6 shows the isothermal entropy change for the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds as a function of temperature for a field change of 1 T. The  $\Delta S_m$  values of the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50}\text{N}_z$  compounds are comparable to those observed for many well-known magnetocaloric materials, such as  $\text{Gd}_5\text{Si}_2\text{Ge}_2$ , Heusler alloys and  $\text{La}(\text{Fe}_x\text{Si})_{13}\text{H}_y$  [2]. The results indicate that a small nitrogen addition offers a new control parameter to tune the Curie temperature, while it hardly influences the magnetic entropy change.





**Figure 6.** Entropy change for the  $\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5}\text{Si}_{0.5}\text{N}_z$  compounds as a function of temperature for a field change of 1 T.

### 3.2 Nitrogen substitution

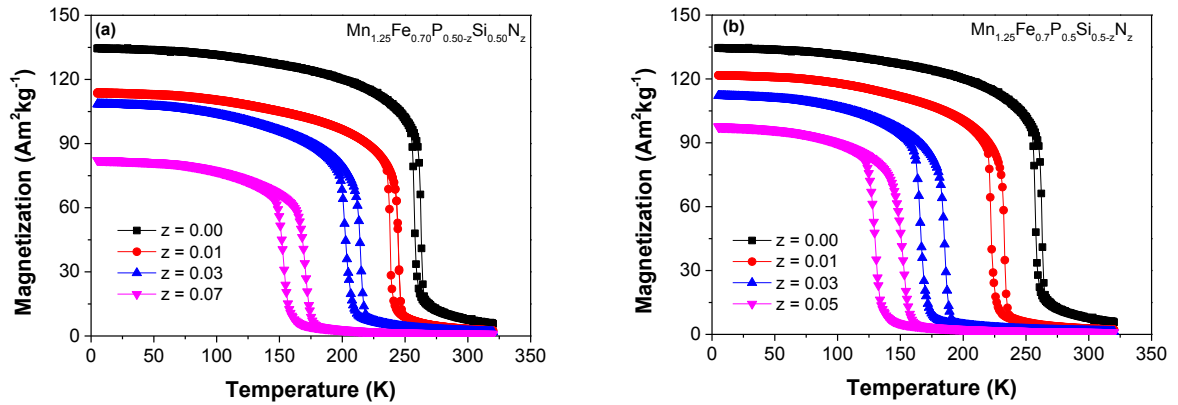


**Figure 7.** X-ray diffraction patterns measured at room temperature for  $\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5-z}\text{Si}_{0.5}\text{N}_z$  compounds (a) and for  $\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5}\text{Si}_{0.5-z}\text{N}_z$  compounds (b).

In Fig. 7, the X-ray diffraction patterns are shown for the  $\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5-z}\text{Si}_{0.5}\text{N}_z$  and  $\text{Mn}_{1.25}\text{Fe}_{0.7}\text{P}_{0.5}\text{Si}_{0.5-z}\text{N}_z$  compounds, where N respectively substitutes P and Si. It is clear that the substitution of P, as well as Si, by N does not result in a structure change for  $z = 0.01$ . However, for  $z \geq 0.03$  a  $\text{Fe}_{2.4}\text{N}$  impurity phase is observed. The lattice parameters and unit-cell volume of these compounds are summarized in Table 3.

**Table 3.** Lattice parameters and unit-cell volume of the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50-z}\text{Si}_{0.50}\text{N}_z$  and  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50-z}\text{N}_z$  compounds with  $z = 0.00, 0.01, 0.03, 0.05$  and  $0.07$  at room temperature.

Compound	$a$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
$\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50-z}\text{Si}_{0.50}\text{N}_z$			
$z = 0.00$	6.09032	3.44543	110.676
$z = 0.01$	6.08425	3.45370	110.721
$z = 0.03$	6.07954	3.46159	110.802
$z = 0.07$	6.06300	3.46996	110.466
$\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50-z}\text{N}_z$			
$z = 0.01$	6.08688	3.46211	111.090
$z = 0.03$	6.06911	3.47201	110.755
$z = 0.05$	6.05927	3.47648	110.538



**Figure 8.** Magnetization curves measured on heating and cooling in a magnetic field of 1 T for the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50-z}\text{Si}_{0.50}\text{N}_z$  (a) and  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50-z}\text{N}_z$  (b) compounds.

In Fig. 8, the temperature dependence of the magnetization, recorded on cooling and heating in a magnetic field of 1 T, is shown for the  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50-z}\text{Si}_{0.50}\text{N}_z$  (a) and for  $\text{Mn}_{1.25}\text{Fe}_{0.70}\text{P}_{0.50}\text{Si}_{0.50-z}\text{N}_z$  (b) compounds. It is obvious that similar to the interstitial nitrogen addition, N substitutions for either P or Si lead to a decrease in  $T_C$  and an increase in thermal hysteresis for an increasing nitrogen content. However, the changes in  $T_C$  and  $\Delta T_{\text{hys}}$  are more pronounced when N substitutes Si rather than P. Interestingly, the spontaneous magnetization of the samples with a substitutional formulation is a little lower than for samples with interstitial formulations at the same nitrogen concentration.

## 4. Conclusions

In this paper, the influence of nitrogen additions on the crystal structure and the magnetocaloric properties of  $(\text{Mn,Fe})_2(\text{P,Si})$  compounds are discussed in detail. The addition of nitrogen leads to a slight variation in the unit-cell volume, indicating that nitrogen atoms enter the structure both as a substitutional and as an interstitial element. The addition of nitrogen leads to a moderate decrease in Curie temperature, while it preserves the magnetocaloric properties and improves the mechanical stability. It is found that the nitrogen addition provides a new control parameter to tune the Curie temperature and improves the mechanical properties of  $(\text{Mn,Fe})_2(\text{P,Si})$  materials.

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