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Original article

Spin correlations in $(\text{Mn,Fe})_2(\text{P,Si})$ magnetocaloric compounds above Curie temperature



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ABSTRACT

The longitudinal-field muon-spin relaxation (LF- μ SR) technique was employed to study the spin correlations in $(\text{Mn,Fe})_2(\text{P,Si})$ compounds above the ferromagnetic transition temperature (T_C). The $(\text{Mn,Fe})_2(\text{P,Si})$ compound under study is found to show itinerant magnetism. The standard deviation of the magnetic field distribution of electronic origin increases with a decrease in temperature, which is attributed to the development of spin correlations. The anomalously low magnetic fluctuation rate is suggested to be another signature of the spin correlations. The development of pronounced magnetic fluctuations is in agreement with the observed deviation of the paramagnetic susceptibility from Curie–Weiss behavior. Our study sheds light on the magneto-elastic transition and the mixed magnetism in $(\text{Mn,Fe})_2(\text{P,Si})$ compounds.

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1. Introduction

Magnetic refrigeration, based on the magnetocaloric effect (MCE), has been considered to be the most promising technology to replace vapor-compression for near room temperature refrigeration applications (e.g. refrigerator, air-conditioner) [1–6]. It has been demonstrated that the cooling efficiency of magnetic refrigeration systems can reach up to 60% of the theoretical limit, compared to about 45% in the best gas compression refrigerators [1–6]. Cooling systems based on magnetocaloric principles operate with less noise due to the absence of a compressor. Additionally, magnetic refrigeration makes use of water-based coolants instead of ozone depleting or greenhouse gases, which makes it an environmentally friendly technology.

Following the discovery of a sub-room temperature giant MCE in the ternary system Gd–Ge–Si [7], great efforts have been made to search for new classes of materials, which can be used for near room-temperature magnetic refrigeration applications. Some

examples of these materials are: $\text{La}(\text{Fe,Si})_{13}$ -based compounds [8,9], MnAs-based compounds [10], MnCoGe-based compounds [11], Heusler-type alloys [12–16], and $(\text{Mn,Fe})_2(\text{P,As,Ge,Si})$ -based compounds [17–25]. Among the diverse classes of magnetocaloric materials, the $(\text{Mn,Fe})_2(\text{P,Si})$ -based [21–25] compounds have been considered as the most promising materials for near room-temperature refrigeration and energy conversion applications due to their combination of a giant MCE, a tunable working temperature, low hysteresis and low material cost.

$(\text{Mn,Fe})_2(\text{P,Si})$ compounds crystallize in a hexagonal Fe_2P -type structure (space group $P-62m$), which contains two metallic ($3f$ and $3g$) and two non-metallic ($2c$ and $1b$) sites. Neutron diffraction [26,27], atomic-scale scanning transmission electron microscopy [28] and density functional theory (DFT) calculations [23,29,31] indicate a preferential occupation of the two 2 transition-metal atoms in the hexagonal structure. Mn prefers the $3g$ site with five non-metal nearest neighbors forming a square pyramid, while Fe favors the $3f$ site surrounded by four non-metal coordination atoms forming a tetrahedron. The distribution of Si and P atoms on the non-metallic $2c$ and $1b$ sites has also been investigated using neutron diffraction [26]. Si prefers to occupy the $2c$ site, and this preference is more pronounced for the higher Si-containing compositions.

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The giant MCE in $(\text{Mn,Fe})_2(\text{P,Si})$ compounds originates from a magneto-elastic transition, where a para-ferromagnetic (PM-FM) transition is coupled to a structure change without altering the symmetry [26]. As indicated by DFT calculations [23], $(\text{Mn,Fe})_2(\text{P,Si})$ compounds show mixed magnetism during the magneto-elastic transition. The Mn atoms on the 3g sites do not undergo a significant reduction in magnetic moment above the ferromagnetic transition temperature (T_C). In contrast, the magnetic moment of Fe is significantly reduced in the PM state, due to a strong electronic redistribution around the 3f site. The size of the Fe moment on the 3f site strongly depends on the effective exchange field created by the magnetic moments on the 3g site [29,30]. The presence and development of magnetic correlations in the PM state are expected to enhance the effective exchange field, promote the formation of Fe moment, and finally result in long-range magnetic order.

In the present work, the spin correlations in the PM state of the $(\text{Mn,Fe})_2(\text{P,Si})$ compounds were investigated by means of muon-spin relaxation (μSR) technique [32–37]. In the μSR technique, polarized muons are implanted into the sample, where the muon-spin evolves in the local magnetic field until the muons decay into positrons. The created positrons are emitted preferentially along the final muon-spin direction. As a result, the time dependence of muon-spin polarization can be reconstructed by collecting the emitted positrons, which in turn reflects the static and dynamic properties of the local magnetic field. This study provides new insight into the mixed magnetism and the magneto-elastic phase transition in the $(\text{Mn,Fe})_2(\text{P,Si})$ compounds.

2. Experimental

The studied $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound was prepared by ball milling, using Mn, Fe, red P, and Si powders as starting materials. The obtained fine powder was pressed into tablets and sealed in quartz ampoules. The sample was sintered at 1373 K for 2 h and then annealed at 1123 K for 20 h before being oven cooled to room temperature. To improve the homogeneity of the sample, the annealed sample was again heated to 1373 K and kept for 20 h before being quenched into water.

X-ray diffraction, on a PANalytical X-pert Pro diffractometer with $\text{Cu } K_\alpha$ radiation, confirms the high purity of the as-prepared sample. Magnetization measurements were performed using the reciprocating sample option mode (RSO) in a superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS 5XL).

μSR experiments were carried out on the general purpose surface-muon instrument (GPS) at the Swiss muon source (SmS) of the Paul Scherrer Institute (PSI), Switzerland. Longitudinal-field (LF) muon-spin relaxation signals were collected for the powder sample (≈ 1 g) in the temperature range between 50 and 450 K using a closed cycle refrigerator. The μSR data was analyzed using the *musfit* package [38].

3. Results and discussion

3.1. Magnetization measurement

Fig. 1 shows the magnetic phase diagram for the $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound, derived from thermomagnetic measurements. Below T_C , the Mn and Fe atoms are ferromagnetically coupled. After crossing the FM to PM transition, the magnetic coupling between them is significantly weakened due to the thermal fluctuations and the increase of the interlayer Fe(3f)-Mn(3g) distance [39].

The ferromagnetic transition temperature T_C shifts to higher temperatures when the applied magnetic field is increased, which

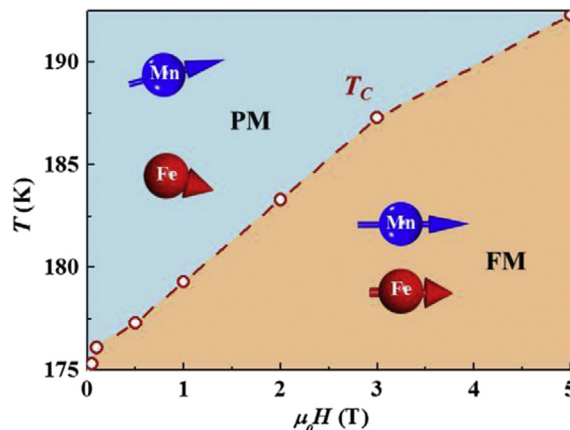


Fig. 1. Magnetic phase diagram for $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ derived from magnetization measurements.

implies an enhanced stability of the FM state in applied magnetic fields. The sensitivity of the magnetic states to external variables is attributed to the existence of a very sharp peak in the density of states (DOS) at the Fermi level for the Fe_2P -type compounds [40,41].

The inverse susceptibility is plotted as a function of temperature in Fig. 2. Above T_C , the PM susceptibility deviates from the Curie–Weiss law up to about 300 K. The deviations are more pronounced for temperatures closer to T_C , which suggests the presence of short-range magnetic correlations in the PM state [39,42–45].

A Curie–Weiss fit of the inverse susceptibility above 300 K gives a Curie constant of $C = 2.47(1) \times 10^{-4} \text{ Km}^3 \text{ kg}^{-1}$. The effective PM moment per formula unit ($\mu_{\text{eff-PM}}$) can be derived from the Curie constant using [46]:

$$C = \frac{\mu_0 N \mu_{\text{eff-PM}}^2}{3k_B} \quad (1)$$

where μ_0 is the permeability of vacuum, N is the number of formula units per unit of mass, and k_B is the Boltzmann constant. An effective magnetic moment per formula unit of $4.6(1) \mu_B$ is deduced from Eq. (1).

The saturation magnetic moment per formula unit for the FM state ($\mu_{\text{eff-FM}} \approx 3.0 \mu_B$) is obtained from the saturation

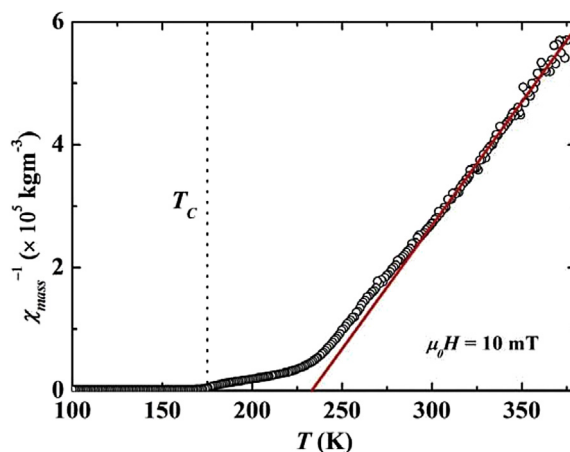


Fig. 2. Temperature dependence of the inverse susceptibility for $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ measured on cooling.

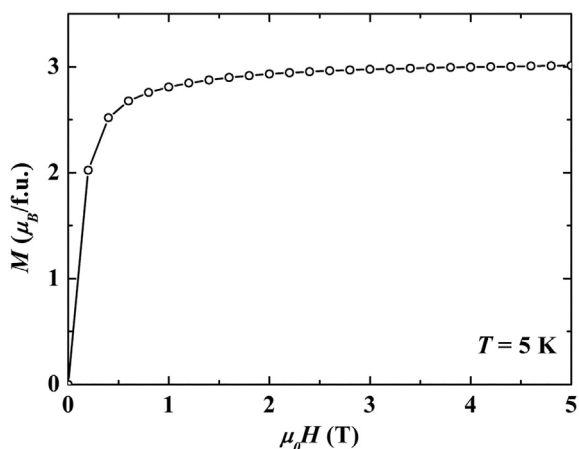


Fig. 3. Isothermal magnetization as a function of field for $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ measured at 5 K.

magnetization measurements at 5 K, as presented in Fig. 3. The ratio between $\mu_{\text{eff-PM}}$ and $\mu_{\text{eff-FM}}$ is about 1.5. According to the Rhodes-Wohlfarth model [47,48], this indicates itinerant magnetism for the $(\text{Mn,Fe})_2(\text{P,Si})$ compounds, which is in agreement with previous studies on the Fe_2P parent compound [33,45,49,50]. The itinerant magnetism in the Fe_2P -based compounds reflects the instability of the Fe moment on the $3f$ site. In the PM state, the Fe electrons are delocalized, causing a pronounced hybridization with neighboring P/Si atoms. As a result, the Fe moment is partially quenched in the PM state. However, in the FM state, Fe carries a large magnetic moment instead of forming chemical bonds, due to the redistribution of electron density around Fe atoms.

3.2. μSR measurement

For many itinerant magnets, spin correlations have been experimentally detected above T_C , e.g. Fe [51–53], Ni [52,54], Fe–Ni invar alloy [55], ErCo_2 [34], and Fe_2P [45,49]. Here we report μSR studies on the spin correlations of $(\text{Mn,Fe})_2(\text{P,Si})$ system in the PM regime.

The μSR spectra were recorded in a longitudinal-field $\mu_0 H_{\text{LF}} = 10$ mT for the $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound. Mn and P carry large nuclear magnetic moments. As a result, the local magnetic field sensed by the implanted muons in the $(\text{Mn,Fe})_2(\text{P,Si})$ compound is a combination of the nuclear magnetic fields, the external magnetic field, and the magnetic fields created by the unpaired electrons of Mn and Fe. The nuclear magnetic field is considered to be static in μSR experiments, since the relaxation time of nuclear spins is much longer than the muon life time [56]. In a previous zero-field μSR experiment [57], the standard deviation of the nuclear field distribution in the $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound was estimated to be 0.13 mT, which is about two orders of magnitude smaller than the applied longitudinal field. Consequently, the nuclear magnetic field is decoupled from the applied LF field in the current LF- μSR experiments, and hence it will not contribute to the observed muon-spin relaxation.

Fig. 4 shows the LF- μSR spectra measured at different temperatures. At 180 K (above $T_C \approx 175$ K), the spectrum displays a slow-dynamics behavior with a dip at about 0.5 ms. This feature becomes less noticeable with an increase in temperature. The previous zero-field μSR study [57] revealed that muons in the $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound hop fast above 325 K, while they become static below 325 K. In the following analysis, we focus on the LF- μSR spectra measured below 325 K to avoid the muon-hopping. Below T_C , the initial asymmetry in the spectrum drops

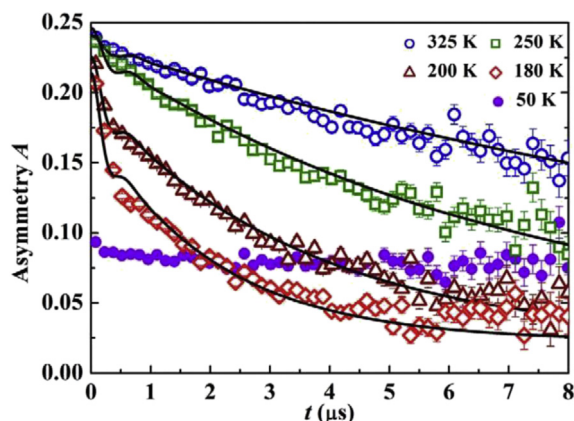


Fig. 4. LF- μSR spectra for the $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound. The solid lines represent fits to the data.

significantly, compared to that in the PM state. The absence of oscillation signals reflects a broad distribution of local magnetic fields experienced by the muons at different stopping sites inside the magnetically-ordered polycrystalline sample.

The LF- μSR spectra measured above T_C were fitted using the dynamical-LF Kubo-Toyabe model [58–60], where the local magnetic field is assumed to show a Gaussian distribution. The derived spin fluctuation rate n is around 2 ms^{-1} in the temperature range between 180 and 325 K. The observed spin fluctuation rate is significantly smaller than the characteristic fluctuation rate estimated for the uncorrelated magnetic moments ($\approx 10^{-13} \text{ s}^{-1}$) [33]. The anomalously slow spin dynamics observed in the present study is another signature of correlations between the magnetic moments in the paramagnetic regime for the $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound. A similar phenomenon has been recently observed in other magnetic systems [35].

The standard deviation of the magnetic field distribution of electronic origin, *i.e.* Δ_e , was derived from the fits to the LF- μSR spectra. The Δ_e , presented in Fig. 5, rises significantly with a decrease in temperature. The increase in Δ_e can be attributed to the development of short-range magnetic correlations at temperatures close to T_C . This is in agreement with the magnetic susceptibility measurements.

In the PM regime of $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound, the Mn atoms still carry large magnetic moments [23]. At high

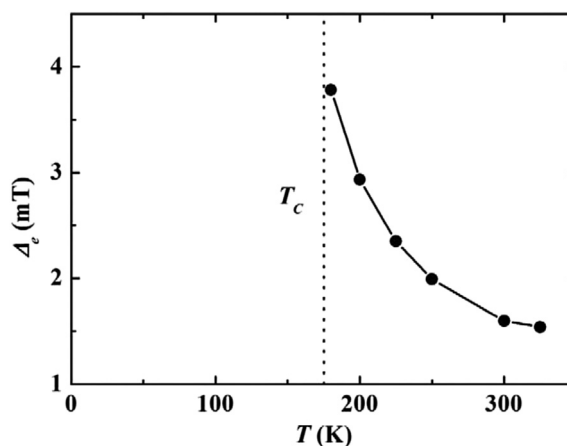


Fig. 5. The standard deviation of the magnetic field distribution created by unpaired electrons at different temperatures for the $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.05}\text{Si}_{0.05}$ compound.

temperatures, the Mn moments are magnetically disordered due to the large thermal energy. As a result, the local magnetic fields are averaged out at different muon stopping sites and a small value for the Δ_e is observed. With the decrease in temperature, short-range spin correlations appear and become much stronger in the vicinity of T_C . The development of spin–spin correlations, which leads to a rise in the standard deviation of the local field distribution, as well as the deviations from the Curie–Weiss behavior for the paramagnetic susceptibility.

Consequently, our LF- μ SR results reveal the presence and development of short-range spin correlations above T_C in the $\text{Mn}_{1.70}\text{Fe}_{0.25}\text{P}_{0.50}\text{Si}_{0.50}$ compound, which is commonly found in many itinerant magnets [34,45,49,51–55]. The short-range spin correlations play a crucial role in the unique mixed magnetism and magnetoelastic transition in the $(\text{Mn,Fe})_2(\text{P,Si})$ compounds. The short-range magnetic correlations between the Mn moments in the PM state enhance the effective exchange field experienced by the Fe atoms, which boosts the metamagnetic transition of the Fe atoms. The metamagnetic transition of Fe is accompanied with a strong electronic reconstruction, which leads to the electronic contribution to entropy change in the $(\text{Mn,Fe})_2(\text{P,Si})$ materials. Consequently, the presence of short-range spin correlations in the PM regime effectively enhances the mixed magnetism and the resultant the magnetocaloric effect in the $(\text{Mn,Fe})_2(\text{P,Si})$ materials.

4. Conclusions

The spin correlations in the paramagnetic regime of the studied $(\text{Mn,Fe})_2(\text{P,Si})$ compound was investigated by means of longitudinal-field μ SR experiments. The slow magnetic fluctuations and the increasing standard deviation of the local field distribution, detected by the implanted muons, reflect the presence and development of short-range magnetic correlations. These correlations are responsible for the deviations from Curie–Weiss behavior observed in the paramagnetic susceptibility.

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