Magnetic phase transition in MnFeP\textsubscript{0.5}As\textsubscript{0.4}Si\textsubscript{0.1}

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Abstract. We have carried out a detailed investigation of the magnetic phase transition in MnFeP\textsubscript{0.5}As\textsubscript{0.4}Si\textsubscript{0.1}. Temperature hysteresis has been observed in the variable temperature magnetization curves (B\textsubscript{appl} = 0.01 T) with T\textsubscript{C} \approx 302 K on warming and T\textsubscript{C} \approx 292 K on cooling. The first order nature of this transition in MnFeP\textsubscript{0.5}As\textsubscript{0.4}Si\textsubscript{0.1} is confirmed by the negative slope obtained from isotherms of M\textsubscript{2} versus B/M around the critical temperature. Linear thermal expansion measurements reveal a large volume change, ΔV/V \sim 8.7 \times 10^{-3}, at the magnetic phase transition and that this magnetovolume effect is suppressed to ΔV/V \sim 5.5 \times 10^{-3} in an applied field of B\textsubscript{appl} = 1.0 T. Analyses of \textsuperscript{57}Fe Mössbauer spectra (4.5 - 300 K) using a random distribution model and taking nearest-neighbour environments into account, indicate that the paramagnetic and ferromagnetic phases coexist over a temperature range of \sim 45 K around the Curie temperature. The Debye temperature for MnFeP\textsubscript{0.5}As\textsubscript{0.4}Si\textsubscript{0.1} has been evaluated as \theta_D = 350 \pm 20 K from the temperature dependence of the average isomer shift.

1. Introduction
The discovery by Pecharsky and Gschneidner in 1997 of a giant magnetocaloric effect (MCE) in Gd\textsubscript{5}Si\textsubscript{2}Ge\textsubscript{2} [1], has led to enhanced scientific interest and search for materials with a large MCE that are operational over technologically relevant temperatures [2]. This in turn has led to the synthesis and observation of a giant MCE in many other intermetallic systems [2] including the transition metal (T) rich systems La(Fe\textsubscript{1-x}Si\textsubscript{x})\textsubscript{13} [3], MnAs\textsubscript{1-x}Sb\textsubscript{x} [4] and MnFeP\textsubscript{1-x}As\textsubscript{x} [5]. An especially important aspect of these discoveries is that they demonstrate that large values of MCE are not restricted to materials with large magnetic moments but that, in the vicinity of a phase transition, the MCE depends strongly on the type of the magnetic phase transition [2].

As summarized by Gschneidner \textit{et al.} [2], recent work has demonstrated giant MCE near a first order magnetic transition which can, by varying material composition and/or applied magnetic field, cause the transition to occur over a wide temperature range and even extend above room temperature. For example, in MnFeP\textsubscript{1-x}As\textsubscript{x} the transition temperature can be tuned from \sim 150 K to 335 K by adjusting the P/As ratio [5]. MnFeP\textsubscript{1-x}As\textsubscript{x} compounds crystallise with the Fe\textsubscript{3}P hexagonal structure and P and As are randomly distributed on the 1b and 2c sites whereas Fe atoms occupy the 3f site and Mn atoms the 3g site [6]. \textsuperscript{57}Fe Mössbauer spectroscopy has previously been used to explore the first-
order character of the ferromagnetic to paramagnetic transition in a systematic study of both the MnFeP_{1-x}As_x and Mn_{1-x}Fe_{0.5}P_{1-x}Ge_x systems [6].

In an earlier study it was reported that while no crystallographic structural changes are associated with the magnetic phase transition, a pronounced volume change was observed along with anomalous behaviour electrical resistance [7]. Here we report a detailed investigation of the magnetic phase transition in MnFeP_{0.5}As_{0.4}Si_{0.1} using magnetic and variable temperature Mössbauer spectroscopy measurements. An aim is to investigate the effects of external field on the magnetovolume effects and further understand the critical magnetic behaviour around transition.

2. Experimental process

A polycrystalline sample of MnFeP_{0.5}As_{0.4}Si_{0.1} was prepared as described previously [5, 7]. The compound was found to crystallise in the Fe_{2}P-type hexagonal structure [7] as expected on the basis of the structure of MnFeP_{1-x}As_x compounds. Magnetic measurements were performed using a Quantum Design Physical Properties Measurement System with a magnetic field sweep rate of 0.005 T/s and amplitude up to 8.5 T. Thermal expansion measurements were performed using a strain-gauge linear differential transformer method over the temperature range 77 – 300 K at Departamento de Física de la Materia Condensada, Universidad de Zaragoza, Spain. As shown in Fig. 1(b), this allows the absolute changes of the length in zero and applied magnetic field to be measured relative to the initial length of the sample. The $^{57}$Fe Mössbauer spectra were obtained between 4.5 K and 300 K using a standard constant-acceleration spectrometer and a $^{57}$CoRh source. The spectrometer was calibrated at room temperature with an $\alpha$-iron foil.

3. Results and discussion

As shown in Fig. 1, the temperature dependence of magnetization for MnFeP_{0.5}As_{0.4}Si_{0.1} as measured in an applied magnetic field of B_{appl} = 0.01 T, exhibits a pronounced magnetic phase transition around 299 K with a temperature hysteresis of around 10 K between the cooling (C) and warming (W) curves - $T_C^W \sim 302$ K or $T_C^C \sim 292$ K respectively. The abrupt change in magnetization and the temperature hysteresis at $T_C$ are characteristic of a first-order magnetic transition.

The changes in linear thermal expansion, $\Delta l/l(T)$, of MnFeP_{0.5}As_{0.4}Si_{0.1} on warming through the transition temperature $T_C$ in zero field and an applied field of B_{appl} = 1 T on warming through the transition temperature $T_C$.

![Figure 1](image-url) (a) Temperature dependence of magnetization in a field of 0.01 T during cooling (triangles) and warming (squares) and (b) Temperature dependence of the linear thermal expansion of MnFeP_{0.5}As_{0.4}Si_{0.1} in zero field and an applied field of B_{appl} = 1 T on warming through the transition temperature $T_C$.

The changes in linear thermal expansion, $\Delta l/l(T)$, of MnFeP_{0.5}As_{0.4}Si_{0.1} on warming through the transition temperature $T_C$ in zero field and an applied field of B_{appl} = 1 T are shown in Figure 1 (b). Using $\Delta V/V(T) = \frac{3}{2} \Delta l/l(T)$ [8], it is clear from Figure 1(b) that MnFeP_{0.5}As_{0.4}Si_{0.1} exhibits a large magnetovolume effect around the transition temperature. Compared with the paramagnetic region above $T_C$, in zero field the unit cell volume in the ferromagnetic (FM) state contracts by $\sim 0.87\%$ ($\Delta V/V \sim 8.7 \times 10^{-3}$) whereas in a magnetic field of B_{appl} = 1 T, the relative contraction of the unit cell volume is only $\Delta V/V \sim 5.5 \times 10^{-3}$. This indicates that the magnetic field suppresses the magnetovolume
effects. Similar behaviour has been detected in the SmMn$_2$Ge$_2$ system where a large magnetovolume effect, $\Delta V/V \sim -0.3\%$, was observed in a canted antiferromagnetic state between $T_C^{\text{Sm}}$ ($\sim 100$ K) and $T_N^{\text{Int}}$ ($\sim 150$ K) in zero field whereas application of a field of $B_{\text{appl}} = 4$ T caused the structural distortion to recover to $\Delta V/V \sim 0$ [9]. For SmMn$_2$Ge$_2$ this behaviour is due to the metamagnetic transition from the zero field antiferromagnetic state to the field-induced ferromagnetic state [9].

**Figure 2** (a) Variation of magnetization with applied magnetic field ($B_{\text{appl}} = 0$–8.5 T) for MnFeP$_{0.5}$As$_{0.4}$Si$_{0.1}$ at the temperatures indicated and (b) Arrot plots ($M^2$ versus $B/M$) derived from the magnetisation data of Fig 2(a).

The order of the magnetic phase transition has been further investigated by Arrot plots (curves of $M^2$ versus $B/M$) derived from the field dependence of the magnetization at temperatures around $T_C$. Figure 2(a) shows typical M-B curves at the temperatures indicated with the corresponding Arrot plots shown in Figure 2(b). It can be seen clearly from the jump in magnetization, that application of a certain magnetic field value above $T_C$, can cause the paramagnetic state to change to a ferromagnetic state. The critical field at which the transition from paramagnetism to ferromagnetism starts can be defined as the field value at which the M-B slope changes (e.g. 2.4 T and 5.2 T at 300 K and 310 K, respectively). In addition, the order of the transition - second-order or first-order – is indicated by a positive or negative slope in the isothermal plots of $M^2$ versus $B/M$, respectively. In the case of MnFeP$_{0.5}$As$_{0.4}$Si$_{0.1}$, the negative slope of the Arrot plot at 300 K and 310 K in Fig. 2(b) indicates the first-order nature of this metamagnetic phase transition from paramagnetism to ferromagnetism.

**Figure 3** $^{57}$Fe Mössbauer spectra of MnFeP$_{0.5}$As$_{0.4}$Si$_{0.1}$ over the temperature range 4.5 - 300 K

Figure 3 shows $^{57}$Fe Mössbauer spectra of MnFeP$_{0.5}$As$_{0.4}$Si$_{0.1}$ at selected temperatures. Given that Si probably enters the 1b and 2c sites to replace P/As [7], the spectra have been fitted with a binomial distribution model while also taking into account the different iron near-neighbour environments (five different iron near-neighbour environments in this system) and the correlation between the hyperfine fields and the number of iron near neighbours [6]. Fig. 4(a) shows the fractions of each state as a function of temperature as determined from the fitting; it is clear that there exists a certain temperature range ($\sim 250$ K to 295 K) over which the ferromagnetic and paramagnetic states co-exist.
The temperature dependences of the Mössbauer hyperfine parameters are shown in Figure 3. The Debye temperature has been determined from the temperature dependence of the isomer shift (IS), \( \langle \delta(T) \rangle \) [6]:

\[
IS(T) = IS_0(T) + IS_{SODS}(T)
\]

\( IS_0(T) \) represents the T dependence of the charge density at the probe nucleus which is generally weakly temperature dependent. The second term, \( IS_{SODS} \), the so-called second-order Doppler shift, can be described in terms of the Debye model for the phonon spectrum by,

\[
IS_{SODS}(T) = -\frac{3kT}{2mc} \left[ \frac{3\theta_D^2}{8T} + 3\left( \frac{T}{\theta_D} \right)^3 \int_{0}^{\infty} \frac{x^3}{e^x - 1} \, dx \right],
\]

where \( m \) is the mass of the \(^{57}\)Fe nucleus, \( k \) Boltzmann’s constant, \( c \) the velocity of light and \( \tau = \theta_D/T \) the reduced temperature [6]. A Debye temperature value of \( \theta_D = 350 \pm 20 \) K has been derived on fitting the mean isomer shift data of Figure 3(b) to equation (2).

Figure 4. (a) The average hyperfine field and the fractional area of the paramagnetic phase as a function of temperature. (b) The temperature dependence of the isomer shift. The solid line is the result of a fit with the Debye model (equation 2).

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