Magnetocaloric Mn$_5$Si$_3$ and MnFe$_4$Si$_3$ at variable pressure and temperature

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Abstract

The influence of hydrostatic high pressure on the crystal structures and magnetic properties of magnetocaloric Mn$_5$Si$_3$ and MnFe$_4$Si$_3$ was studied with temperature dependent synchrotron powder diffraction, neutron single-crystal diffraction and magnetization measurements. Mn$_5$Si$_3$ shows no indication for any pressure-induced structural phase transition up to 24.2 GPa at room temperature. MnFe$_4$Si$_3$ exhibits no clear indication for any pressure-induced structural phase transition up to 24.2 GPa at room temperature. Anomalies in the lattice parameter at low temperatures indicate a structural response to magnetic ordering. The gradient of decreasing magnetic transition temperature with increasing pressure is d$T_C$/dP ≈ -15 K GPa$^{-1}$. The transition temperature in MnFe$_4$Si$_3$ can be tuned by pressure in the temperature range relevant for applications, while pressure has hardly any detrimental influence on other key features relevant to magnetocaloric applications (the width of hysteresis, saturation magnetization, magnetocrystalline anisotropy).

1. Introduction

Magnetic refrigeration is a potential alternative to conventional vapor compression refrigeration since it offers reduced energy consumption and greenhouse gas emissions [1]. Basis for this technology is the magnetocaloric effect (MCE), which is characterized as a change in temperature of a material due to an adiabatic change in magnetization. For applications, a material, where an (ideally constant) MCE occurs over a wide temperature range, would be of major benefit, as it would give access to various target temperatures. A series of strategies has been proposed to optimize the refrigerant capacity and tune the operation range of materials. For example, it is known that for a one-compound material the degree of (dis)order, comprising chemical disorder or defects, gives rise to a distribution of transition temperatures [2, 3]. However, the controlled design of disorder via quenching, annealing, or aging is in general difficult. Therefore, usually, the change in the magnetic transition temperature is tuned by building composite materials made of components with slightly different compositions and operating temperatures (see [4–8] and references therein).

Another possibility to tune the transition temperature and the MCE in a one-phase system is to apply hydrostatic pressure, as pressure strongly affects interatomic distances and magnetic exchange interactions [9–11]. In most of the cases, the application of hydrostatic pressure on a magnetic system leads to a decrease in
the magnetic transition temperature. This also holds for the majority of magnetocaloric materials [12–14]. However, in individual cases, the opposite effect is also observed [15–17], especially when the application of pressure (e.g., GdSi4Ge2) leads to a magnetically ordered phase with a lower unit cell volume when compared to the volume of the paramagnetic phase. In these cases, it is possible to induce the magnetostructural transition by hydrostatic pressure [17]. There are—to our knowledge—few attempts to use hydrostatic pressure as tuning parameter for refrigerating applications at present. For many of the possible candidate materials, the pressures, which would have to be applied to produce the desired shifts in transition temperatures, are fairly low (up to 0.5 GPa) and routinely used in large-scale industrial process e.g. for the food industry (see [18, 19] and references therein).

In this work, we are interested in the system Mn5−xFexSi3. The materials are well suited for commercial applications, as manganese, iron and silicon are abundant, cheap and non-toxic elements. Although the MCEs in this system are in general not particularly large, MnFe4Si3 is of major interest as it has a magnetic transition around room temperature [20]. In addition, pulsed field experiments have shown that the compound can be easily and reliably cycled [21].

The parent structure of all compounds in the system Mn5−xFexSi3 can be generally described in the space group P63/mcm (Z = 2) [22]. The metal atoms occupy the two sites M1 (Wyckoff position 4d, 1/3, 2/3, 0, site symmetry 32) and M2 (Wyckoff position 6g, x, 0, 1/4, site symmetry mm). For the mixed-element compounds, Fe preferentially occupies the M1 positions, which are coordinated by six Si atoms in the form of a distorted octahedron (figure 1). The octahedra share common faces in a staggered arrangement, forming infinite \[ \sqrt{3} \]M1Si3 chains along the c axis. The M2 atoms form the corners of an empty octahedron. They also share common faces and form infinite \[ \sqrt{3} \]M2 chains also along c. A recent neutron diffraction study on MnFe4Si3 shows that, in contrast to the parent structure, a partial ordering of Mn and Fe takes place at the M2 site, leading to a lowering of the symmetry to P \[ \bar{5} \] [20].

Mn5Si3 has a structural phase transition from P63/mcm to Ccmm at 100 K [23]. The transformation coincides with the magnetic transition from a paramagnetic to an antiferromagnetic state [23]. In the Fe-rich compounds of the system, no temperature-induced structural phase transitions are observed. In MnFe4Si3, the MCE is associated with a transition from the paramagnetic to the ferromagnetic state [24]. While the symmetry does not change, the phase transition is clearly reflected in the lattice parameters. In particular, the a lattice parameter shows a sudden increase at the onset of magnetic ordering [20].

Few studies have been conducted up to now regarding the high-pressure behavior of the crystal and magnetic structures in the Mn5−xFexSi3 system [25]. Only for Fe5Si3, the bulk modulus is known (167 GPa) and pressure-dependent investigations show the absence of any structural phase transition up to at least 96 GPa [25].

The objective of this work is the study of the influence of pressure on the crystal structures of Mn5Si3 and MnFe4Si3 based on \textit{in situ} synchrotron powder diffraction data. In addition, the influence of pressure on the magnetic properties and the magnetic phase transition in MnFe4Si3, associated with the MCE effect, is investigated with \textit{in situ} single-crystal neutron diffraction and macroscopic magnetization measurements. Ultimately, we would like to know whether the pressures required to tune the magnetic transition temperature are in an easily accessible range for potential applications.
2. Experimental methods

2.1. Synthesis
Samples of Mn$_5$Si$_3$ and MnFe$_4$Si$_3$ were synthesized from stoichiometric mixtures of the elements Mn (Aldrich, 99.99%), Fe (Aldrich, 99.99%) and Si (Aldrich, 99.99%) by cold crucible induction melting in an argon atmosphere [26]. The melting-crystallization process was repeated three times to maximize the sample homogeneity. From the polycrystalline samples, single crystals were grown using the Czochralski method according to the procedure described by Hering et al [20].

2.2. Synchrotron x-ray diffraction
High-pressure synchrotron diffraction experiments on polycrystalline Mn$_5$Si$_3$ ($\lambda = 0.2905$ Å) were carried out at room temperature at the beamline P02.2 at Petra III, DESY (Hamburg, Germany) equipped with a Perkin Elmer XRD1621 detector. The sample was loaded in a membrane-driven diamond anvil cell (DAC) with a rhenium gasket and neon as a pressure-transmitting medium.

The diffraction experiments on polycrystalline MnFe$_4$Si$_3$ ($\lambda = 0.414\ 038$ Å) with simultaneous temperature variation were performed at the ID09a beamline at the European Synchrotron Radiation Facility (Grenoble, France) using the MAR555 detector. The sample was loaded in a membrane-driven DAC. Neon was used as a pressure medium for the measurements at room and high temperatures (296 K, 324 K, 348 K, and 373 K), while helium was the pressure medium for the experiments at low temperatures (100 K, 150 K, 200 K, and 250 K). Helium is not used at the higher temperatures due to its increased diffusion into the cell material and the diamonds.

The pressures in all high-pressure diffraction experiments were determined using the ruby luminescence method [27]. All recorded powder diffraction patterns of Mn$_5$Si$_3$ and MnFe$_4$Si$_3$ were integrated with the FIT2D software [28]. Subsequently, all powder patterns were refined with the Le Bail and Rietveld methods using the program JANA2006 [29]. Since the elements Mn and Fe have very similar atomic scattering factors which are indistinguishable by x-ray diffraction, the powder diagrams of MnFe$_4$Si$_3$ were analyzed assuming symmetry $P6_3/mmc$ ($Z = 2$). For both compounds, the lattice parameters $a$ and $c$, anisotropic strain broadening, peak-shape parameters (GW and LX in a Pseudo-Voigt model for Mn$_5$Si$_3$, LX in a Lorentzian model for MnFe$_4$Si$_3$), and March-Dollase preferred orientation ([100]) were refined. The background was modeled manually. In addition, the free atomic coordinates of the sites M2 and Si1 were refined in both compounds, as well as the atomic displacement parameters (ADP) for Mn and Si in Mn$_5$Si$_3$. ADPs were not refined for MnFe$_4$Si$_3$; instead, a linear model based on previous temperature-dependent data [20] was used to determine the ADPs for the different temperatures. In all refinements, the correction according to Bérar and Lelann [30] was applied. The calculation of coordination polyhedra was carried out with the IVTON program [31].

2.3. Neutron diffraction
The temperature dependences of the $(1\ 1\ 1)$ reflection and two symmetry equivalent reflections (($\ 1\ 2\ 1$), $(2\ 1\ 1)$) at ambient pressure were determined from a single crystal of MnFe$_4$Si$_3$ (crystal volume of approx. 10 mm$^3$) on the hot diffractometer HEiDi at MLZ [32]. This reflection group was chosen as the nuclear contribution to the reflections is close to zero and their intensities contain mainly the magnetic contributions. The reflections were measured at a wavelength of 1.165 Å in the temperature region from 2.4 K near to 270.8 K in 5 K steps and additionally in closer steps of 2.5 K in the region around the phase transition from 270.8 K to 319.5 K.

The temperature dependence of the $(1\ 1\ 1)$ reflection was studied with single-crystal neutron diffraction ($\lambda = 0.895$ Å) on the polarized hot neutron diffractometer POLI (MLZ, Garching, Germany) [33] at 1 GPa and temperatures between 3.9 K and 340 K using a panoramic diamond anvil cell [34] placed in a Janis cryostat. The cell was loaded with a crystal of MnFe$_5$Si$_3$ (crystal volume of 0.2 mm$^3$) and a 4:1 mixture of deuterated methanol and ethanol.

2.4. Magnetization
Pressure dependent magnetization measurements were performed on a Quantum Design MPMS XL between 3 K and 350 K using a home-made CuBe piston-cylinder type cell. A small oriented single-crystalline slab (3.6 mg) was mounted using GE varnish and then loaded into a teflon capsule filled with mineral oil as a pressure transmitting medium. For the measurements with H||[100], the slab was mounted on a long and narrow Cu strip. In the case of H⊥[100], the slab was mounted flat on a teflon coin that fits snugly inside the teflon capsule. A piece of pure Sn mounted next to the sample on the Cu strip/teflon coin worked as a manometer [35]. The pressure values reported in this manuscript are corrected for the pressure drop occurring between room temperature and the superconducting transition of Sn ($\approx 3.7$ K at ambient pressure). The pressure drop was
The synchrotron powder diffraction data on Mn$_5$Si$_3$, measured up to 24.2 GPa at room temperature, show no indication of any pressure-induced structural phase transition. The order Murnaghan equation of state is estimated to be about 0.2 GPa and obtained from a separate calibration measurement using the $T_c$ of pure MnAs [36]. No corrections were made to the field for shape anisotropy.

3. Results and discussion

3.1. Synchrotron x-ray diffraction

The synchrotron powder diffraction data on Mn$_5$Si$_3$, measured up to 24.2 GPa at room temperature, show no indication of any pressure-induced structural phase transition. The P-V data could be fitted by a single third-order Murnaghan equation of state [37] (EoS) with $K_{0.4 \text{ GPa}} = 96.5(8)$ GPa, $K'_{0.4 \text{ GPa}} = 6.53(11)$ and $V_{0.4 \text{ GPa}} = 198.83(4)$ Å$^3$, where $K_{0.4 \text{ GPa}}, K'_{0.4 \text{ GPa}}$, and $V_{0.4 \text{ GPa}}$ are the bulk modulus, its first derivative, and the unit cell volume at the lowest pressure in the DAC (0.4 GPa), respectively (figure 2). The experimental volume measured at the lowest pressure (0.4 GPa) is $V_{0.4 \text{ GPa,exp}} = 198.83(4)$ Å$^3$. As seen from figure 2, Mn$_5$Si$_3$ is more compressible along the c direction than along the a direction. At 24.2 GPa, the c lattice parameter shows with a relative change of 5.9% a higher compressibility than a with 4.3%.

The results of the Rietveld refinements on Mn$_5$Si$_3$ (a representative refinement is given in the supporting material which is available online at stacks.iop.org/MRX/6/096118/mmedia) indicate that the atomic coordinates not restricted by the symmetry ($x_{\text{Mn2}}$ and $x_{\text{Si1}}$) are within errors not affected by pressure. Hence, the change in interatomic distances can be attributed entirely to the change in the lattice parameters. While the [M1Si$_3$] polyhedron is larger in volume than the [☐(M2)$_3$] polyhedron, the volumes ($V_{\text{CP}}$) of both coordination polyhedra decrease linearly with the unit cell volume and exhibit within errors the same relative change as the unit cell volume (see the supporting material). However, the [M1Si$_3$] polyhedron shows a larger volume distortion $\nu$—calculated as the ratio of the measured to the idealized polyhedron volume [38]—than the [☐(M2)$_3$] one. For both coordination polyhedra the volume distortion is constant with pressure and does not change on compression (see the supporting material).

The analysis of the powder diffraction patterns of MnFe$_4$Si$_3$ measured at various pressures and temperatures does not indicate any change in symmetry within the resolution of our powder diffraction data. At temperatures between 296 K and 373 K as well as at 100 K and 150 K, the unit cell volumes decrease monotonously (figure 3): the curves for 100 K and 296 K are representative for the low (100 K, 150 K) and high (296 K–373 K) temperature range, respectively. At ambient pressure, the c lattice parameter increases with increasing temperature, while a does not show any significant temperature dependence. This is in good agreement with the temperature behavior observed by Hering et al [20]. Anomalies in the unit cell volumes are observed for the pressure runs at 250 K and 200 K at 1.15 GPa and at 1.31 GPa, respectively (figure 3). They are visible in the anomalous changes of the a and c lattice parameters at these temperatures, where clear deviations from the behavior at other temperatures are observed (see the supporting material). At higher pressures of about 5 GPa, an additional change is seen in the c parameters. We argue that the change in the a lattice parameter observed at 250 K and 1.15 GPa as well as at 200 K and 1.31 GPa reflects the magnetic phase transition from the paramagnetic to the ferromagnetic state. This is supported by the fact that in the ferromagnetic phase at ambient...
pressure (where the magnetic moments of the Mn and Fe atoms at site M2 order in the $a,b$-plane) the ferromagnetic ordering is also accompanied by an increase in the $a$ lattice parameter [20]. This increase in turn is closely correlated to the increase in the $M2-M2'$ distance between two coupled M2 atoms in the $a,b$-plane inside the $[\Box (M2)_3]$ polyhedra.

MnFe$_4$Si$_3$ differs from Mn$_5$Si$_3$ in its $c/a$ ratio: this ratio decreases with pressure in Mn$_5$Si$_3$, while it increases in MnFe$_4$Si$_3$ (figure 4). This suggests that the anisotropic compressibility is related to the amount of incorporated iron. Since iron preferably occupies the M1 site and the interactions between neighboring M1 sites are essentially confined to the $c$ direction (figure 1), the influence of the iron is larger along this direction, which leads to a lowering of the axial compressibility along the $c$ axis. Figure 5 shows selected fits of the $P$-$V$ data for MnFe$_4$Si$_3$ to Murnaghan equations of state at different temperatures. A comparison of the bulk moduli at room temperature for Mn$_5$Si$_3$ and MnFe$_4$Si$_3$ (96.5 GPa and 124.4 GPa, respectively) with those for Fe$_5$Si$_3$ (167 GPa) [25] demonstrates that the room-temperature bulk modulus increases with the amount of Fe incorporated into the structure.

For MnFe$_4$Si$_3$ at high temperatures (296 K–373 K), at each temperature one equation of state is sufficient to fit the whole respective pressure range. At all low temperatures (100 K–250 K) an anomalous behavior is

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**Figure 3.** Pressure dependence of the unit cell volume in MnFe$_4$Si$_3$ at selected temperatures. The inset shows the pressure range from 0.5 GPa to 3.3 GPa. Arrows mark the onset of the anomalies at 1.15 GPa at 250 K (red) and 1.31 GPa at 200 K (blue). The dashed lines are guides for the eye.

**Figure 4.** Pressure dependence of the $c/a$ ratios in MnFe$_4$Si$_3$ normalized to their values at 1.6 GPa, the lowest common pressure of all measurements, at selected temperatures. The $c/a$ ratio of Mn$_5$Si$_3$ at RT normalized to ambient pressure is shown in black. The dashed lines are guides for the eye. The errors are shown when larger than the data points.
observed in the measured compression curves as two equations of state are necessary to fit the whole pressure range at each temperature (figure 5). At 100 K and 150 K, the need of two equations of state possibly indicates additional phase transitions at about 5 GPa without a change of the crystal system or a significant change in the anisotropic compressibility. On decompression, the anomalies are reversible. The obtained EoS parameters in different pressure ranges are given in the supporting material. The lower the temperature, the higher the pressure associated with the phase transition. The bulk moduli obtained for the high-pressure phases at 200 K and 250 K are significantly higher than those for the low-pressure phases.

The results of a representative Rietveld refinement for MnFe$_4$Si$_3$ are shown in the supporting material. The pressure dependence of the $x_{\text{Mn}2}$ and $x_{\text{Si}1}$ atomic coordinates at different temperatures is not constant, however, there is no clear general trend with either temperature or pressure observed in their behavior. The interatomic distances are thus determined by both the unit cell volume reduction and the changes in the coordinates on compression.

At room temperature the [M1Si$_3$] polyhedra in MnFe$_4$Si$_3$ are more distorted ($\nu \approx 0.07$) than the [□(M2)$_3$] polyhedra ($\nu \approx 0$), but the compressibility is within error the same for both. Furthermore, the distortion and the relative change with pressure correlate well with the ones observed for Mn$_5$Si$_3$. In addition, the distortions of the coordination polyhedra in both compounds are not pressure dependent within the errors of our Rietveld refinements. At higher temperatures as well as at 100 K, 150 K and 200 K, the pressure behavior is the same. At 250 K, however, the [□(M2)$_3$] polyhedra show a larger relative change in volume than [M1Si$_3$] as consequence of the decrease in M2–M2' distance. In addition, the distortion of the [□(M2)$_3$] polyhedra is nearly temperature and pressure independent, while the distortion of the [M1Si$_3$] polyhedra is not constant as a function of pressure, but no clear trend with temperature is observable. The same is true for the relative volume changes of both polyhedra.

![Figure 5. P-V data for MnFe$_4$Si$_3$ at selected temperatures. The solid lines are third-order Murnaghan equations of state. The solid symbols indicate the unit cell volume at ambient conditions. The dashed lines show the extrapolation of the obtained equations of state to ambient pressure.](image-url)
3.2. Neutron diffraction

The temperature dependence of selected magnetic peaks in MnFe₄Si₃ at ambient pressure and at 1 GPa measured with single-crystal neutron diffraction are shown in Figure 6. In general, the peak intensities increase with decreasing temperature. Although the intensity data at 1 GPa are affected by large errors (mainly due to the elevated background scattering in the experiment and a very small size of the crystal), it is clearly noticeable that the intensity of the (1 1 1) reflection starts to increase around 303 K at ambient pressure, while the same is observed at lower temperatures (≈ 275 K) when pressure is increased. This clearly indicates that the temperature of the magnetic phase transition is decreased upon compression.

3.3. Magnetization

The magnetization data under hydrostatic pressure measured both with H // [100] (easy plane) and H ⊥ [100] (hard axis) confirm this observation (Figure 7). dTₐ / dP is negative over the whole pressure range and is fairly constant within the measured pressure range for all experiments at ≈ −15 K GPa⁻¹. At the highest pressure reached in the magnetization experiment (1.11 GPa) the transition temperature is reduced to Tₐ = 282 K (Figure 7). The transition temperature measured along the hard axis is slightly lower than the one measured in the easy plane (see the supporting material). This is expected as the field has not only to order the material, but also to counter the magnetocrystalline anisotropy. It is worth noting that pressure—within the measured range—has very little effect on the width and thermal hysteresis of the magnetostructural phase transition, meaning that it has little (if any) effect on the energy barrier and consequently on the order of the phase transition.

Figure 8 shows the pressure dependence of the transition temperature comprising the data from all investigations conducted in this work. The decrease in Tₐ of a magnetic transition with increasing pressure is expected for paramagnetic to ferromagnetic phase transitions, where the volume decreases monotonously with increasing pressure. Since pressure destabilizes the ordered state, the phase transition takes place at lower temperatures [39, 40]. Qualitatively, the magnetic phase transition of MnFe₄Si₃ exhibits a pressure dependence comparable to various other materials, where Tₐ decreases linearly with a relatively small |dTₐ / dP| and abruptly changes to a large |dTₐ / dP| at high pressures until the transition is suppressed [41–43].

Pressure also affects the saturation magnetization in MnFe₄Si₃ at 10 K, which shows a small decrease upon increasing pressure. When measured in the easy plane, this decrease is approximately 2.5% of the ambient...
pressure value per GPa. Comparing the saturation magnetization at 10 K measured in the easy plane (figure 7(b)) and along the hard axis (figure 7(d)), one can notice that the moment after saturation along the hard axis is lower than in the easy plane, which is a clear evidence for magnetization anisotropy. Pressure does not strongly affect the magnetocrystalline anisotropy, and the anisotropy field is kept fairly constant around 5.5 T for the measured pressure range. However, the anisotropy field seems to be approached more slowly with increasing pressure.

The effect of pressure is more pronounced in magnetostructural phase transitions, such as those occurring in magnetocaloric materials exhibiting first-order phase transitions, and is larger in materials exhibiting a large volume change at the magnetic transition induced at ambient pressure. The measured $dT_{C}/dP$ of $-15$ K GPa$^{-1}$ in MnFe$_4$Si$_3$ is rather small compared to the effect observed for other magnetocaloric materials, e.g. $-40$ K GPa$^{-1}$ in

Figure 7. Magnetization measurements on MnFe$_4$Si$_3$ at different pressures: (a) Temperature dependence at 0.01 T and (b) Field dependence at 10 K of the magnetization with $H||[100]$ (easy plane); (c) Temperature dependence at 0.01 T and (d) Field dependence at 10 K of the magnetization with $H\perp[100]$ (hard axis).

Figure 8. Pressure dependence of the ferromagnetic to paramagnetic phase transition temperature of MnFe$_4$Si$_3$ determined by different experimental methods.
Mn$_5$Si$_3$ shows no indication for a structural phase transition up to 24.2 GPa at room temperature. MnFe$_4$Si$_3$ is stable on compression above 296 K. The bulk moduli of the system Mn$_{5-x}$Fe$_x$Si$_3$ increase with increasing iron content. The composition also affects the pressure dependent behavior of the $c/a$ ratio, which decreases in Mn$_5$Si$_3$ with pressure, whereas it increases in MnFe$_4$Si$_3$.

For MnFe$_4$Si$_3$ at low pressures (slightly above 1 GPa), structural anomalies, which we attribute to a response of the crystal lattice to the magnetic transition, are observed at 200 and 250 K. No change in symmetry within the resolution of our powder diffraction data can be detected. The trend of decreasing magnetic transition temperature with increasing pressure agrees with neutron single-crystal diffraction and macroscopic resolution of our powder diffraction data can be detected. The trend of decreasing magnetic transition of the crystal lattice to the magnetic transition, are observed at 200 and 250 K. No change in symmetry within the resolution of our powder diffraction data can be detected. The latter show that pressure hardly changes the width and thermal hysteresis of the magnetostructural transition and leads only to a small decrease of the saturation magnetization. In addition, the hysteresis, saturation magnetization and magnetocrystalline anisotropy of the material are hardly influenced. Hence, pressure can be used to modify the temperature range in which the MCE occurs without introducing either disorder in one-component materials or using composite materials with various components that have different chemical compositions and operating temperatures. This would make MnFe$_4$Si$_3$ an advantageous material for refrigeration applications that combine the magnetic field and high pressure.

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