Site dependence of the magnetocaloric effect in Mn$_{5-x}$Fe$_x$Si$_3$

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The nuclear and magnetic structures of Mn$_3$Fe$_2$Si$_3$ are investigated in the temperature range from 20 to 300 K. The magnetic properties of Mn$_3$Fe$_2$Si$_3$ were measured on a single crystal. The compound undergoes a paramagnetic to antiferromagnetic transition at $T_{N2}' \approx 120$ K and an antiferromagnetic to antiferromagnetic transition at $T_{N1}' \approx 69$ K. A similar sequence of magnetic phase transitions is found for the parent compound Mn$_5$Si$_3$ upon temperature variation, but the field-driven transition observed in Mn$_5$Si$_3$ is not found in Mn$_3$Fe$_2$Si$_3$, resulting in a strongly reduced magnetocaloric effect. Structurally, the hexagonal symmetry found for both compounds under ambient conditions is preserved in Mn$_3$Fe$_2$Si$_3$ through both magnetic transitions, indicating that the crystal structure is only weakly affected by the magnetic phase transition, in contrast to Mn$_5$Si$_3$ where both transitions distort the nuclear structure. Both compounds feature a collinear high-temperature magnetic phase AF2 and transfer into a non-collinear phase AF1 at low temperature. While one of the distinct crystallographic sites remains disordered in the AF2 phase in the parent compound, the magnetic structure in the AF2 phase involves all magnetic atoms in Mn$_3$Fe$_2$Si$_3$. These observations imply that the distinct sites occupied by the magnetic atoms play an important role in the magnetocaloric behaviour of the family.

1. Introduction

Magnetocaloric cooling has become one of the most promising candidates for energy-efficient and environmentally friendly refrigeration and can potentially replace the conventional vapour-compression-based technologies (Yu et al., 2003; Brück, 2005; Gschneidner & Pecharsky, 2008; Takeuchi & Sandeman, 2015). The magnetocaloric refrigeration cycle is based on materials which exhibit the magnetocaloric effect (MCE), that is, a change of temperature upon adiabatic magnetization/demagnetization (Pecharsky & Gschneidner, 1999).

The series of compounds in the system Mn$_{5-x}$Fe$_x$Si$_3$ are well known for their magnetocaloric properties (Songlin et al., 2002; Gourdon et al., 2014; Hering et al., 2015; Maraytta et al., 2019; Singh et al., 2020). The crystal structure of the parent compound Mn$_5$Si$_3$ can be described in space group $P\bar{6}_3/mcm$ (Bińczycka et al., 1973). Within the crystal structure two non-equivalent sites are available for the paramagnetic atoms. The M1 site is surrounded by Si atoms in the form of a distorted octahedron, which shares common faces with its analogues, forming infinite chains along the c axis. The atoms on the M2...
site form empty \([\infty (M2)_6]\) octahedra, which also form infinite chains of face-shared octahedra along the \(c\) direction. Neighbouring \(\infty ((M1)Si)_3\) chains share common edges with each other and form channels which are occupied by chains of empty octahedra of composition \(\infty (M2)_6\). It is well known that Fe atoms preferentially occupy the \(M1\) site and Mn atoms are preferentially incorporated onto the \(M2\) site (Songlin et al., 2002; Hering et al., 2015).

The compounds of this series are ideal for studying the underlying mechanism of the magnetocaloric effect for various reasons:

(i) The nature of the magnetic ordering changes depending on the composition. While for small values of \(x\) antiferromagnetic structures are reported, ferromagnetism is observed for \(x > 3\) (Narasimhan et al., 1970; Songlin et al., 2002; Vinokurova et al., 1995; Hering et al., 2015; Singh et al., 2020).

(ii) Compounds with an Fe content \(x \geq 3\) show a direct MCE (the magnetic entropy decreases with the application of the magnetic field and the material heats up), while the parent compound \(\text{Mn}_5\text{Si}_3\) shows an inverse MCE, i.e. the magnetic entropy rises with the application of the field and the material cools down. The inverse MCE is observed at the transition from a collinearly ordered arrangement of the spins to a non-coplanar arrangement (Gottschilch et al., 2012; Biniskos et al., 2018; Luccas et al., 2019), while in the compound with \(x = 4\) a direct MCE is observed at the paramagnetic to ferromagnetic transition (Gourdon et al., 2014; Hering et al., 2015; Maraytta et al., 2019).

(iii) The availability of two significantly different sites for the paramagnetic atoms within the structure gives the opportunity to elucidate the role of magnetic atoms occupying multiple sites in magnetocaloric materials.

(iv) In addition, large single crystals of the compounds up to 10 cm in length and 1–2 cm diameter are readily available. This is of advantage when it comes to elucidating the underlying crystal and magnetic structures, the magnetic anisotropy, or the spin and/or lattice dynamics (Biniskos et al., 2017, 2018; Maraytta et al., 2020).

The compound investigated here, \(\text{Mn}_3\text{Fe}_2\text{Si}_3\), is special within the series, as the stoichiometry would allow perfect site order, i.e. all \(M1\) sites occupied by Fe atoms and all \(M2\) sites occupied by Mn. Like the parent compound \(\text{Mn}_5\text{Si}_3\), \(\text{Mn}_3\text{Fe}_2\text{Si}_3\) is known to have two different antiferromagnetic phases, yet their magnetic structures are still unknown.

In this work we study the details of the crystal structure of \(\text{Mn}_3\text{Fe}_2\text{Si}_3\) as a function of temperature using high-resolution synchrotron single-crystal diffraction and determine for the first time the magnetic structure of \(\text{Mn}_3\text{Fe}_2\text{Si}_3\) in the AF1 and AF2 phases using neutron powder diffraction. We compare the direction-dependent macroscopic magnetic and magnetocaloric properties of single-crystalline \(\text{Mn}_3\text{Fe}_2\text{Si}_3\) and the parent compound \(\text{Mn}_5\text{Si}_3\), and discuss the differences in the light of the structural investigations.

2. Experimental procedures

2.1. Sample preparation

Single crystals of \(\text{Mn}_5\text{Si}_3\) and \(\text{Mn}_3\text{Fe}_2\text{Si}_3\) were obtained according to the method described by Hering et al. (2015). Chemical analysis using inductively coupled plasma with optical emission spectroscopy showed no deviations from the ideal stoichiometry (see Table S1 in the supporting information).

2.2. Magnetization

Fragments of the oriented single crystal with a mass of 6–12 mg were cut using spark erosion. Measurements of the magnetization parallel and perpendicular to the hexagonal \([001]\) direction with varying temperature and magnetic field were carried out in the temperature region between 5 and 380 K and magnetic fields in the range \(-9 \text{T} \leq \mu_0 H \leq 9 \text{T}\) using the vibrating sample magnetometer (VSM) option of a PPMS and PPMS Dynacool from Quantum Design, respectively. Isothermal measurements were performed to identify the magnetic phases for the different directions of the applied field and to determine the magnetic entropy change \(\Delta S_m\). As the magnetization curves became featureless for \(H \parallel [001]\) for \(T > T_{\text{N1}}\), isotherms were only recorded up to 73 K for this field direction. In the case of \(\text{Mn}_5\text{Si}_3\), the field-dependent magnetization was measured in sweep mode, i.e. the field was varied at a rate of 5 mT s\(^{-1}\) and the magnetization was recorded continuously. For \(\text{Mn}_3\text{Fe}_2\text{Si}_3\), preliminary measurements had shown that the measured magnetization changes with the thermomagnetic history. Therefore, we employed the following temperature protocol: The samples were initially cooled to 140 K. Subsequently a field of 9 T was applied and the sample was cooled to the target temperature at a rate of 5 K min\(^{-1}\), and then a field loop between 9 T and \(-9 \text{T}\) was recorded. At the end of the loop, the sample was again heated to 140 K and cooled to the next target temperature to ensure as identical starting conditions for the magnetization loop as possible.

2.3. Neutron powder diffraction

Time-of-flight neutron powder diffraction data on about 5 g of \(\text{Mn}_3\text{Fe}_2\text{Si}_3\) powder were recorded using the POWGEN diffractometer at Oak Ridge National Laboratory (Huq et al., 2011) at temperatures of 20, 50, 90, 105 and 300 K. Data were recorded using two different bands, one with central...
wavelength $\text{CWL} = 0.8 \, \text{Å} (d \, \text{spacing coverage} \, 0.1340–8.200 \, \text{Å})$ and the other with $\text{CWL} = 2.665 \, \text{Å} (1.0701–22.9342 \, \text{Å})$.

2.4. Synchrotron single-crystal diffraction

Synchrotron single-crystal diffraction data were measured on beamline P24 of PETRA III at DESY (Hamburg, Germany) at a wavelength of $\lambda = 0.44279 \, \text{Å}$ using a MarCCD165 detector. Data sets were collected upon cooling ($T = 300, 250, 200, 150, 100, 80, 60, 40$ and $20 \, \text{K}$) using an open-flow helium cryostat. Data were reduced with the CrysAlisPro software (Rigaku Oxford Diffraction, 2015). All refinements of the powder and single-crystal data of Mn$_3$Fe$_2$Si$_3$ were performed with the program JANA2006 (Petríček et al., 2014).

3. Results

3.1. Magnetization measurements

Isothermal magnetization measurements at selected temperatures in AF1, AF2 and the paramagnetic state (Fig. 2) for Mn$_5$Si$_3$ and Mn$_3$Fe$_2$Si$_3$ for a field applied perpendicular to [001] and parallel to [001] exhibit a plethora of features, which are only visible as small kinks. The field derivatives $\partial M/\partial H$ emphasize the slope changes and visualize the temperature dependence of the different features (Fig. 3).

In Mn$_5$Si$_3$, the features labelled (i) and (ii) have been reported in the various magnetization studies on single crystals and powders (Sürgers et al., 2017; Vinokurova et al., 1990; Al-Kanani & Booth, 1995; Songlin et al., 2002; Das et al., 2019) and are related to the field-driven transition from the field-induced antiferromagnetic phase $\text{AF1}^*$ to AF2 and from AF1 to AF1*. In contrast to the results obtained by Sürgers and co-workers, we observe the feature related to the transition from AF1 to AF1* only if the field is applied parallel to the orthorhombic [001] direction.$^1$ The splitting that is observed for feature (ii) below 25 K is hysteretic, i.e. when the field is varied from $-9 \, \text{T}$ to $9 \, \text{T}$ it splits at approximately 6 T. In the vicinity of $T_{\text{N1}} \approx 66 \, \text{K}$ we observe a slightly elevated $\partial M/\partial H$ for the field applied parallel to [001] and the formation of two sharp kinks labelled (iii) for $H \parallel [001]$. Below $\approx 30 \, \text{K}$, we observe for both field directions a nearly constant $\partial M/\partial H$ for $|\mu_0 H| < 0.6 \, \text{T}$, labelled (iv). This feature has already been observed in the literature but has not been discussed in detail (Sürgers et al., 2017; Vinokurova et al., 1990; Al-Kanani & Booth, 1995; Songlin et al., 2002; Das et al., 2019). It resembles the magnetization of a soft ferromagnet that has not been corrected for the demagnetization field. Recently it has been proposed that the linear increase in the magnetization can be explained as a longitudinal variation of the moment on the M1 site (Biniskos et al., 2022), which explains the behaviour observed here. Feature (iv) narrows down above 30 K for both field directions. For a field parallel to [001] it becomes an open hysteresis loop, which is indicated by the small peak at positive field for increasing field and at negative field for decreasing fields (Fig. S1 in the supporting information). This feature disappears for the field parallel to [001] at $T_{\text{N1}}$ but persists even beyond $T_{\text{N2}}$ for the perpendicular direction.

Mn$_3$Fe$_2$Si$_3$ exhibits a much lower slope $\partial M/\partial H$ (compare the range of the colour bars on the right-hand side of the panels). In the low-temperature phase AF1 ($T < T_{\text{N1}} = 69 \, \text{K}$), we observe the features labelled (c) and (a) for the field parallel and perpendicular to the [001] direction. For both field

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$^1$The orthorhombic low-temperature phase of Mn$_5$Si$_3$, space group $\text{Cmmm}$, is obtained from the hexagonal phase according to the transformation $a_{\text{orth}} \approx a_{\text{hex}}, b_{\text{ortho}} \approx a_{\text{hex}} + 2d_{\text{hex}}, c_{\text{ortho}} \approx c_{\text{hex}}$. 

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Figure 2
Isothermal magnetization data: full hysteresis loops at selected temperatures in AF1 and AF2 for the field direction (left) $\parallel$ and (right) $\perp$ [001] for (top) Mn$_5$Si$_3$ and (bottom) Mn$_3$Fe$_2$Si$_3$. The line colour indicates the temperature of the isothermal measurement.
In Mn5Si3, the strong increase in magnetization when entering the magnetic transition was due to the coexistence of two magnetic phases. Larson & Von Dreele (2004) studied the atomic coordinates and preferred orientation according to the March–Dollase model. A correction for the background points was used. An absorption correction function and a background described by ten terms of the neutron powder data, a pseudo-Voigt profile, were employed. The magnetic entropy changes for a field change $\Delta B = 5$ T from isothermal magnetization measurements for (left) Mn5Si3 and (right) Mn3Fe2Si3. Note that the MCE is underestimated due to the coarse temperature steps of 3 and 5 K, respectively. Dashed vertical lines indicate the transition temperatures $T_{N1}$ and $T_{N2}$.

**Figure 4**
Magnetic entropy changes for a field change $\Delta B = 5$ T from isothermal magnetization measurements for (left) Mn5Si3 and (right) Mn3Fe2Si3. Note that the MCE is underestimated due to the coarse temperature steps of 3 and 5 K, respectively. Dashed vertical lines indicate the transition temperatures $T_{N1}$ and $T_{N2}$.

For this composition, the slope of the magnetization versus temperature is nearly a factor of 10 smaller. Here a clear direction dependence of the MCE is visible. If the field is applied $\parallel [001]$, an inverse MCE is observed in a narrow temperature region around 60 K. For the direction $\perp [001]$, $-\Delta S_{iso}$ is more negative upon heating in the temperature region between 20 and 55 K and then turns positive above approximately 70 K. Within the AF2 phase, the MCE does not differ strongly for the different field directions.

**3.2.2. Temperature dependence of the crystal structure of Mn3Fe2Si3**
Refinement of the synchrotron single-crystal diffraction data shows that Mn3Fe2Si3 crystallizes in the hexagonal space group $P6_3/mcm$ at all measured temperatures with unit-cell parameters $a = 6.8534$ (3) Å and $c = 4.7556$ (2) Å [$V = 193.437$ (15) Å$^3$] at room temperature, in good agreement with the literature (Bińczycka et al., 1973). Atomic positions and interatomic distances of Mn3Fe2Si3 refined from synchrotron single-crystal diffraction data as a function of temperature are presented in Tables S4 and S5, respectively.

To determine the distribution of the Mn and Fe atoms on the distinct crystallographic sites, a combined refinement of the synchrotron single-crystal and the room-temperature neutron powder data was performed. It shows that the M1 (Wyckoff position 4d) site in the $[(M1)Si]_2$ octahedra is occupied by 76.5 (1) at.% Fe and 23.4 (1) at.% Mn, while the M2 (Wyckoff position 6g) site is occupied by 15.6 (1) at.% Fe and 84.4 (1) at.% Mn. This preferential incorporation of Fe and Mn atoms onto the two sites is in agreement with earlier observations (Bińczycka et al., 1973; Hering et al., 2015).

**Figure 5**
Unit-cell parameters $a$ and $c$ and unit-cell volume of Mn3Fe2Si3 as a function of temperature obtained from synchrotron X-ray single-crystal diffraction data measured during cooling. The figure at the bottom right shows the values of $a (b)$, $c$, the $c/a$ ratio and the unit-cell volume of Mn3Fe2Si3 normalized to the values at 300 K. Temperatures corresponding to the AF1–AF2 and AF2–PM transitions are indicated by dashed lines. Estimated standard deviations are smaller than the size of the symbols.

**3.2. Structural refinement**
Refinement of the nuclear structure of Mn3Fe2Si3 was carried out with SHELXL. In comparison, the isothermal entropy change $S_{iso}$ in Mn3Fe2Si3 is nearly a factor of 10 smaller. Here a clear direction dependence of the MCE is visible. If the field is applied $\parallel [001]$, an inverse MCE is observed in a narrow temperature region around 60 K. For the direction $\perp [001]$, $-\Delta S_{iso}$ is more negative upon heating in the temperature region between 20 and 55 K and then turns positive above approximately 70 K. Within the AF2 phase, the MCE does not differ strongly for the different field directions.

**3.2.1. Refinement of the nuclear structure**
In Mn3Si3, the strong increase in magnetization when entering the AF2 phase from the AF1 phase results in the rather strong inverse MCE (Fig. 4). The resulting $S_{iso}$ varies only slightly for the different directions and is in agreement with the powder results obtained by Songlin et al. (2002). The observed small direction dependence can basically be attributed to the different temperature steps chosen in the measurement for Mn3Si3.

In comparison, the isothermal entropy change $\Delta S_{iso}$ in Mn3Fe2Si3 is nearly a factor of 10 smaller. Here a clear direction dependence of the MCE is visible. If the field is applied $\parallel [001]$, an inverse MCE is observed in a narrow temperature region around 60 K. For the direction $\perp [001]$, $-\Delta S_{iso}$ is more negative upon heating in the temperature region between 20 and 55 K and then turns positive above approximately 70 K. Within the AF2 phase, the MCE does not differ strongly for the different field directions.

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The unit-cell parameters and unit-cell volume of Mn$_3$Fe$_2$Si$_3$ decrease smoothly as the temperature decreases, with the slope decreasing towards lower temperatures (Fig. 5; see also Table S3).

Within the standard deviations, all interatomic distances between paramagnetic atoms in Mn$_3$Fe$_2$Si$_3$ decrease with decreasing temperature, with no clear sign of a response to the transition from the antiferromagnetic AF1 to the antiferromagnetic AF2 phase, or to the transition from the antiferromagnetic AF2 phase to the paramagnetic PM phase (Fig. 6; see also Fig. S2 and Table S5 in the supporting information). The interatomic distances between metal atoms located on the same sites are reduced more significantly than the distances between metal atoms located on different sites (interatomic M1—Si and Si—Si distances decrease in general less than M—M distances; Fig. S3).

If one compares the temperature dependence of the structure of Mn$_3$Fe$_2$Si$_3$ with that of Mn$_5$Si$_3$ (Brown & Forsyth, 1995; Brown et al., 1992; Gottschilch et al., 2012) some major differences can be identified:

(i) While the symmetry remains hexagonal in Mn$_3$Fe$_2$Si$_3$ over the whole investigated temperature range, i.e. in the stability fields of the AF2 and AF1 phases, in Mn$_5$Si$_3$ the PM–AF2 transition is accompanied by a reduction of the symmetry from hexagonal to orthorhombic. In addition, for Mn$_5$Si$_3$ a further decrease of the symmetry to monoclinic was observed by Gottschilch et al. (2012) for the AF1 phase, which was, however, not reported by Brown et al. (1992).

(ii) The M1—M1 distance in Mn$_5$Si$_3$ is clearly changed at the AF2–AF1 transition, while this is not observed for Mn$_3$Fe$_2$Si$_3$. Assuming that the monoclinic model from the literature for the AF1 phase of Mn$_5$Si$_3$ is correct (Gottschilch et al., 2012), the M1 position is split into two symmetrically independent positions, which in turn leads to two different M1—M1 distances parallel to c, one of them being significantly increased at the transition while the second one is significantly decreased (Fig. 6).

(iii) At the AF2–AF1 transition, the M2—M2 distances in Mn$_5$Si$_3$ clearly show a change of slope, a trend that is not observed for Mn$_3$Fe$_2$Si$_3$.

To compare the temperature-dependent behaviour of both compounds further, the normalized angular distortion $\Sigma$ and distance distortion $\Delta$ of the $[(M1)Si_6]$ and $[(M2)Si_6]$ octahedra were calculated using the program Octadist (Ketkaew et al., 2021)$^2$ and normalized to the values at 300 K. Estimated standard deviations are smaller than the size of the symbols. Temperatures of the AF1–AF2 and AF2–PM transitions are indicated by dashed lines.

$^2$ For these calculations a dummy atom at position (0, 0, 0) at the central point of the empty octahedra was introduced.
visible. For the derivation of the magnetic space-group symmetries the built-in algorithms of JANA2006 (Petříček et al., 2014) were used. Starting from the space group $P6_3/mcm$ of the nuclear structure (Tables S6 and S7) and assuming one magnetic propagation vector $[k_{\text{hex}} = (1/2)00]$ or $[k_{\text{ortho}} = (010)]$, eight different orthorhombic models with different magnetic moment directions are derived (Table S8).

For the refinements, the nuclear structure of Mn$_2$Fe$_2$Si$_3$ was transformed to the orthohexagonal setting ($[a_{\text{ortho}} = a_{\text{hex}}, \ b_{\text{ortho}} = a_{\text{hex}} + 2b_{\text{hex}}, \ c_{\text{ortho}} = c_{\text{hex}}$), space group $Ccmm$. Magnetic atoms occupying the same site were restricted to have identical magnetic moments. Only magnetic moments and polynomial background parameters, which were combined with a manual background, were refined, while all other parameters were fixed to the values obtained from the refinement of the nuclear structure.

From the eight refined models, the one in magnetic space group $P_{\text{C}2\text{nan}}$ clearly gives the best agreement factor, both at 90 and 20 K (Table S9). Figs. 9(a) and 9(b) show the corresponding Rietveld refinements.

For the data at 90 K (and 105 K), which correspond to the stability region of the AF2 phase ($T_{\text{AF1-AF2}} \simeq 70 \, \text{K} < T < T_{\text{AF2-PM}} \simeq 120 \, \text{K}$) the model in magnetic space group $P_{\text{C}2\text{nan}}$ fits the measured neutron diffraction pattern very well. The only exception is the 010 reflection [see inset in Fig. 9(a)] which is significantly broader than all other magnetic peaks and only disappears completely at 150 K.

At 20 K, that is in the stability field of the AF1 phase ($T_{\text{AF1-AF2}} \simeq 70 \, \text{K}$), the intensities of the newly arising magnetic peaks are underestimated in the refinement based on magnetic space group $P_{\text{C}2\text{nan}}$. In particular, the 230 reflection, which is weak but clearly visible, has an intensity that is calculated to be zero in this model [see inset in Fig. 9(b)]. We therefore decided to lower the magnetic symmetry for the 20 K data further. For this, the nuclear structure was transformed to the different maximum translationalengleiche subgroups of $Ccmm$, while still restricting the nuclear structure to hexagonal symmetry. For each of the different subgroups, the different magnetic models were then derived and refined. On the basis of the agreement factors (Tables S10 and S11), the model in magnetic space group $P_{\text{C}2\text{221}}$ (derived from the $C22_1$ space group) clearly appears to be the best of the 40 refined models. The Rietveld refinement of this model is shown in Fig. 9(c).

3.2.4. Magnetic structures of Mn$_2$Fe$_2$Si$_3$. The refinements of the magnetic structures of Mn$_2$Fe$_2$Si$_3$ based on the neutron diffraction data at 105, 90, 50 and 20 K show two different antiferromagnetic structures: the AF2 phase corresponding to the temperature range $T_{\text{AF1-AF2}} \simeq 70 \, \text{K} < T < T_{\text{AF2-PM}} \simeq 120 \, \text{K}$ and the AF1 phase corresponding to the temperature range $T < T_{\text{AF1-AF2}} \simeq 70 \, \text{K}$, in accordance with the heat capacity and magnetization data.

In the centrosymmetric AF2 phase (magnetic space group $P_{\text{C}2\text{nan}}$), no components of magnetic moments are allowed parallel to the $c$ axis (Table S8). Magnetic moments on the Mn1/Fe1 sites are aligned along the [010] direction. Moments are allowed along the [100] direction for the Fe21/Mn21 site, and in the $ab$ plane for Fe22/Mn22. However, at 105 and 90 K, all refined $M_1$ components for these sites are zero within error (Table 1) and consequently the AF2 structure is collinear, with all the spins aligned parallel or antiparallel to the $b$ axis (Fig. 10). The Fe1/Mn1 and Fe22/Mn22 sites have refined

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Footnote: Note that in the orthohexagonal description, the Wyckoff position $6g$ ($Fe_{22}/Mn_{22}$) splits into two Wyckoff positions, $4f$ ($Fe_{21}/Mn_{21}$) and $8g$ ($Fe_{22}/Mn_{22}$). As the synchrotron data clearly show that the structure of Mn$_2$Fe$_2$Si$_3$ remains hexagonal down to the lowest temperature, restrictions corresponding to the higher symmetry were applied in all refinements of the magnetic structure using local symmetry operators.
magnetic moments of similar size, 0.70 (7) \( \mu_B \) and 0.66 (7) \( \mu_B \) at 105 K, respectively. When taking into account the standard deviations, the ordered moment on the Fe21/Mn21 sites is not significantly different from zero. Thus, of the Fe/Mn sites forming the empty octahedra, only two-thirds carry an ordered moment in the AF2 phase. Within these octahedra, the atoms at the same height \( z \) have their spins aligned in an antiparallel way. At 90 K, the observed magnetic ordering of the AF2 phase is very similar to the structure at 105 K and only the magnitude of the refined magnetic moments on Fe1/Mn1 and Fe22/Mn22 is slightly increased, with values of 0.82 (8) \( \mu_B \) and 0.76 (8) \( \mu_B \), respectively (Table 1).

At temperatures below \( T_{AF1-AF2} \cong 70 \) K, the magnetic structure changes to that of the AF1 phase with symmetry \( P_{c22} \), (Fig. 11). The most significant difference between the AF2 and AF1 phases is that the magnetic moments on the Fe22/Mn22 sites acquire a component in the \( c \) direction and leads to the non-collinearity of the magnetic structure has a reduced symmetry. In both Mn5Si3 and Mn3Fe2Si3, the moments on the \( M_{22} \) site are 1.0 (5) \( \mu_B \) at 20 K. Moments on the \( M1 \) sites (now split into two magnetically independent Wyckoff positions Fe11/Mn11 and Fe12/Mn12) keep their orientation parallel to the \( b \) axis, and all allowed \( M_z \) components on the \( M21/M22 \) sites are still refined to zero within their standard deviation (Table 2).

### Table 1

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### Table 2

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<td>Fe22/Mn22</td>
<td>-0.12 (51)</td>
<td>-0.78 (3)</td>
<td>-0.67 (3)</td>
</tr>
</tbody>
</table>

4. Discussion: comparison of the magnetic structures of Mn5Fe2Si3 and Mn3Fe2Si3

The magnetic structure of Mn5Si3 and that of Mn3Fe2Si3 determined here share common features. Cooling from high temperature leads to the development of the collinear antiferromagnetic structure AF2 at 99 and 120 K, respectively, with the moments aligned parallel to the crystallographic \( b \) direction (referring to the orthorhombic/orthohexagonal setting).

In Mn3Si3, the PM–AF2 transition is accompanied by a structural phase transition from hexagonal to orthorhombic, while in Mn5Fe2Si3, the structure remains hexagonal and only the magnetic structure has a reduced symmetry. In both Mn5Si3 and Mn3Fe2Si3, the moments on the \( M22 \) site are...
ordered, while the Mn21 site shows no ordered moment. A major difference is the order on the M1 sites, which are preferentially occupied by Fe atoms in Mn5Fe2Si3: here they carry an ordered moment in the AF2 phase which is aligned along b, while in Mn5Si3 no ordered moment is observed on the M1 site in the AF2 phase. Upon further cooling a non-collinear structure is formed in both compounds below the temperature $T_{N2} \approx 70$ K. The structure of this phase has been extensively discussed for Mn5Si3 in the past. The structures as described by Brown et al. (1992) and Gottschilch et al. (2012) both feature an ordered moment on the M1 site with a fairly large $M_z$ component. In the work of Brown et al. (1992), moments on the M2 site lie mainly in the bc plane, while according to Gottschilch et al. (2012) these moments align in the ab plane.

In Mn5Fe2Si3 the moments on the M11/M12 site increase slightly and stay parallel to the b direction, while the moments on the M22 site are co-planar in the bc plane. Note that this structure agrees exactly with a recent proposal for the Mn5Si3 ground state based on band structure calculations (Biniskos et al., 2022).

It is striking that in Mn5Fe2Si3, both magnetic transitions (PM–AF2 and AF2–AF1) are hardly reflected in any abrupt changes of the crystal structure [only the angular distortions of the [(M1)Si3] octahedra decrease slightly at the PM–AF2 transition]. This is significantly different in Mn5Si3, where the AF2–PM transition is combined with a change of space-group symmetry and where at the AF2–AF1 transition the interatomic $M_1$–$M_1$ distances change drastically and the octahedral distortions also show a pronounced change.

In earlier work it was assumed that the absence of an ordered moment on the M1 site in Mn5Si3 in the AF2 phase was in particular due to the Mn1–Mn1 distance being too short (2.397 Å), which was supposed to be below the critical distance that would permit magnetic ordering on the manganese (Brown & Forsyth, 1995; Shiga, 1988). The sudden increase in this distance at the AF2–AF1 transition as observed by Gourdon et al. (2014) (Fig. 6) would bring this distance above the critical distance, opening the possibility for an ordered moment on the M1 site. However, in reality the data from the literature do not provide such a uniform picture. According to Brown et al. (1992) and Brown & Forsyth (1995) the M1–M1 distance is 2.3967 Å in the AF2 phase at 70 K and increases slightly to 2.4021 Å at 4.2 K in AF1, so the critical distance should lie within this range. However, according to Gottschilch et al. (2012) things are more complicated, as here the AF2–AF1 transition is coupled to a structural transition into a monoclinic phase. In this monoclinic phase the M1 site splits, leading to two distinct M1–M1 distances: the first is 2.349 Å at 60 K (2.359 Å at 12 K) and the second is 2.448 Å at 60 K (2.457 Å at 12 K). So, if one assumes the monoclinic model to be correct, only half of these distances are above the critical distance. The substitution of Mn atoms with Fe atoms on the M1 site leads to an even smaller M1–M1 distance of 2.371 Å at the PM–AF2 transition, but ordering of the spins on these sites might well be permitted. The orbitals of the smaller Fe atoms – which predominantly occupy the M1 site – overlap less and hence the bandwidth is narrower, allowing the formation of an ordered moment (Shiga, 1988) already at $T_{N2}$.

The coupling between the magnetic structure and the crystal structure in Mn5Si3 is obvious by the strong rise in the distance distortions for the [(M1)Si3] octahedra and the formation of an ordered moment on the M1 sites at the AF2–AF1 transition. We argue that the site disorder in Mn5Fe2Si3 and the substitution of Mn atoms with the smaller Fe atoms provide additional space for the magnetic atoms, so that the magnetic order affects the crystal structure only weakly. The only pronounced effect that we observe on the crystal structure is the reduction of the angular distortions in the [(M2)3] octahedra, which are mainly built by the larger Mn atoms.

The various magnetic features in both Mn5Si3 and Mn5Fe2Si3, which cannot easily be explained by the zero-field magnetic structure, require detailed single-crystal neutron diffraction in modestly strong magnetic fields of several tesla. While the magnetic response of the compounds is complex and difficult to interpret, we can state that the strongly reduced MCE in Mn5Fe2Si3 at the AF2–AF1 transition is related to the order on the M1 site, which hardly changes at this temperature. This is in excellent agreement with the recent observation that the inverse MCE associated with the AF2–AF1 transition in Mn5Si3 is due to a change in the excitation spectrum from well defined spin waves in the AF1 phase to a fluctuation-dominated excitation spectrum in the AF2 phase (Biniskos et al., 2018).

5. Conclusion

In conclusion, we have determined the crystal and magnetic structure of Mn5Fe2Si3 by means of synchrotron single-crystal diffraction and neutron powder diffraction, and compared the single-crystal magnetic response of Mn5Fe2Si3 and the parent compound Mn5Si3. We find strong similarities in the magnetic structures with a distinct difference in the ordering on the M1 site. We associate these differences with the magnetocaloric properties of the compounds based on isothermal magnetization measurements, shining a spotlight on the influence of the different magnetic sites.

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