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Revised magnetic phase diagram for $\text{Fe}_x\text{Mn}_{5-x}\text{Si}_3$ intermetallics

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The magnetic and crystal structures of the series $\text{Fe}_x\text{Mn}_{5-x}\text{Si}_3$ ($x=4,3.5,3,2,1$) have been reinvestigated by neutron powder diffraction between 315 and 8 K. Fe atoms are found to preferentially occupy the 4d site of the hexagonal D_{8h} structure ($P6_3/mcm$). The compound Fe_4MnSi_3 orders ferromagnetically below 300 K. Refinement of the neutron data for this compound indicates that the moments are aligned at $\sim 40^\circ$ off the c axis. A high moment at the 6g site is due to a large Mn moment which is forced into a ferromagnetic alignment with the Fe moments. Associated with this moment is a moderate magnetic entropy change, with a maximum value of $4 \text{ J kg}^{-1} \text{ K}^{-1}$ for a magnetic field change of 5 T. The magnetic structure of $\text{Fe}_{3.5}\text{Mn}_{1.5}\text{Si}_3$ is similar to that of Fe_4MnSi_3 , but the Curie point is lower, below 240 K. A feature for this composition is the appearance of a spiral structure below 60 K. The compounds with $x=1, 2$, and 3 are all antiferromagnets with a spiral structure observed for $\text{Fe}_3\text{Mn}_2\text{Si}_3$ at all temperatures up to the Néel point of 150 K. Two separate antiferromagnetic structures exist for $\text{Fe}_2\text{Mn}_3\text{Si}_3$, one between 120 and 45 K and another structure for temperatures below 45 K. Similar features in the magnetic ordering are exhibited by FeMn_4Si_3 . At temperatures between 70 and 95 K, the magnetic structure is similar to that of the low temperature phase of $\text{Fe}_2\text{Mn}_3\text{Si}_3$. Accompanying the magnetic transition at 70 K is a structural distortion to space group $Cmcm$, a feature also observed for Mn_5Si_3 . © 2004 American Institute of Physics. [DOI: 10.1063/1.1688219]

I. INTRODUCTION

The magnetic phase diagram and magnetocaloric properties of the pseudobinary system $\text{Fe}_x\text{Mn}_{5-x}\text{Si}_3$ have recently been reinvestigated.¹ The series crystallizes in the binary D_{8h} structure (Nowotny phase, space group $P6_3/mcm$) reported by Amark *et al.*² for Mn_5Si_3 with Mn located at 4d (1/3, 2/3, 0) and 6g ($x, 0, 1/4, x \approx 0.24$) sites while Si is located at a further 6g site ($x, 0, 1/4, x \approx 0.6$). The atomic ordering and magnetic properties were first investigated by Narasimhan *et al.*,³ who reported that atomic ordering varied with Fe content. In contrast, Johnson *et al.*⁴ determined that Fe atoms preferentially occupy the 4d site. Neutron diffraction data for ferromagnetic Fe_5Si_3 were reported by Johnson *et al.*⁵ who determined Fe moments of $1.05 \mu_B$ and $1.55 \mu_B$ at the 4d and 6g sites, respectively. Magnetic interactions in Mn_5Si_3 are extremely sensitive to Mn–Mn interatomic distances and give rise to a complex antiferromagnetic structure which has been extensively investigated by both powder and single crystal neutron

diffraction.^{6–10} Transitions from antiferromagnetic to ferromagnetic ordering across the series were investigated by Binczycka *et al.*¹¹ In particular, in the Fe rich region of the phase diagram, these authors reported a helical spin structure for $\text{Fe}_3\text{Mn}_2\text{Si}_3$ with a spiral period of 30 Å along the c axis and a collinear c axis ferromagnetic alignment for Fe_4MnSi_3 . A moderate magnetic entropy change of $4 \text{ J kg}^{-1} \text{ K}^{-1}$ reported for Fe_4MnSi_3 ¹ has prompted us to reinvestigate in detail the magnetic phase diagram by neutron powder diffraction.

II. EXPERIMENT

Polycrystalline ingots of $\text{Fe}_x\text{Mn}_{5-x}\text{Si}_3$ with $x=4, 3.5, 3, 2$, and 1 were prepared by arc melting at least 3 N purity Fe, Mn, and Si. The resulting ingots were annealed at 1225 K for 5 days, followed by a rapid quench in iced water. X-ray diffraction measurements indicated that all prepared compounds crystallize in the D_{8h} structure, with traces of a cubic FeSi impurity for samples with $x=2, 3$. Neutron powder diffraction measurements were performed between 8 and 315 K on the ROTAX powder diffractometer installed at the ISIS spallation source.¹²

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FIG. 1. Manganese occupancies of the 4d and 6g sites for the series $\text{Fe}_x\text{Mn}_{5-x}\text{Si}_3$, as determined from the presently reported neutron powder diffraction data. Lines are only guides to the eye.

III. RESULTS AND DISCUSSION

A. Crystal structure

All samples were measured in the paramagnetic phase in order to determine the degree of site occupancies by Fe and Mn atoms at the 4d and 6g sites. The refined Mn occupancies of these sites are displayed in Fig. 1. These results concur exactly with previous determinations by Mössbauer spectroscopy⁵ and neutron diffraction.¹¹ The preference of Fe for the 4d site is possibly due to a more stable Fe metal-metal bond at this site.⁵ The room temperature lattice parameters display an approximately linear increase with increasing Mn concentration (≈ 0.022 Å/Mn atom for a and ≈ 0.017 Å/Mn atom for c), in good agreement with the lattice parameters quoted by Johnson *et al.*⁵ and Aronsson.¹³

B. Magnetic structure

1. Fe_4MnSi_3

This compound orders ferromagnetically just below 300 K¹ and neutron measurements in the magnetic regime for this compound were performed at 8 K. A feature of the neutron data is the presence of magnetic intensity for the (002) reflection, a sign that there is also a basal plane component of the magnetic structure, in addition to the c -axis order. The data were refined by fixing the moments at both sites to be collinear and then refining the site moments as a function of the tilt angle off the c axis. The best fit was obtained with moments aligned at approximately 40° to the c axis, a detail of the magnetic order that has not been reported previously.¹¹ The average refined moments at 8 K for the 4d and 6g sites are $1.4 \mu_B$ and $2.5 \mu_B$, respectively. These moments are substantially higher than the site moments for Fe_5Si_3 . The high moment at the 6g site in particular, which is 30% occupied by Mn, is due to a substantial Mn moment which is forced into a ferromagnetic alignment with Fe moments. Associated with this large moment is a moderate magnetic entropy change.¹

FIG. 2. Sections of the neutron powder diffraction patterns at 315, 150, and 8 K (intermediate detector bank) for $\text{Fe}_{3.5}\text{Mn}_{1.5}\text{Si}_3$. Arrows indicate the reflections which correspond to the spiral structure.

2. $\text{Fe}_{3.5}\text{Mn}_{1.5}\text{Si}_3$

The observation by Binczycka *et al.*¹¹ of a helical spin structure in $\text{Fe}_3\text{Mn}_2\text{Si}_3$ below 77 K with a spiral period of 30 Å prompted us to see if a low temperature spiral phase exists for compositions richer in Fe. The Curie temperature is 265 K and at 150 K the magnetic structure is similar to that of Fe_4MnSi_3 , with moments of $0.9 \mu_B$ and $1.9 \mu_B$ for 4d and 6g sites, respectively. An observation is the appearance of a spiral structure below 60 K, evidenced by satellites around fundamental (100) and (111) reflections and an estimated turn angle of 24° between successive planes along the axis of the spiral (Fig. 2). The spiral phase coexists with the ferromagnetic phase, as there remains a substantial magnetic contribution to the fundamental reflections at 8 K. The 6g site for $x=3.5$ is already occupied by Mn at 50% and antiferromagnetic interactions have clearly set in at low temperatures for this Fe rich compound.

3. $\text{Fe}_3\text{Mn}_2\text{Si}_3$

Magnetization and neutron data reported¹¹ for $\text{Fe}_3\text{Mn}_2\text{Si}_3$ imply that magnetic order occurs below 77 K. The magnetization data of Songlin *et al.*¹ however give a higher Curie point, at about 250 K, followed by a low temperature transition at 50 K. The present neutron results are in contrast with both of these findings. There is no difference between the patterns in the paramagnetic phase and at 200 K. Below 150 K, a magnetic peak is observed at approximately 2.15 Å. The intensity of this peak increases down to 8 K. On

the basis of the observed data, the magnetic structure of $\text{Fe}_3\text{Mn}_2\text{Si}_3$ is most likely that of an incommensurate antiferromagnet.

4. $\text{Fe}_2\text{Mn}_3\text{Si}_3$

The neutron data reported for in this present work are in agreement with the bulk measurements of Songlin *et al.*¹ There are two transitions, with the first corresponding to a paramagnetic to antiferromagnetic ordering at 125 K followed by a successive transition below 45 K. Between 125 and 50 K, magnetic peaks at 11.84, 3.29, and 2.1 Å were observed. These can be indexed as (1/2 0 0), (1/2 1 1), and (1/2 1 2) with respect to the hexagonal cell and therefore the high temperature phase corresponds to a commensurate antiferromagnet with an ordering wave vector of [1/2 0 0]. The diffraction patterns below 50 K are characterized by the aforementioned peaks with the additional appearance of a peak at around 4.5 Å, which can be indexed as [1/2 1 0]. This transition is probably based on a spin reorientation of the moments from the hexagonal axis, to a low temperature planar configuration.

5. FeMn_4Si_3

At temperatures between 70 and 95 K, the magnetic structure of FeMn_4Si_3 is of the same type as that of the low temperature phase of $\text{Fe}_2\text{Mn}_3\text{Si}_3$ observed below 50 K. These peaks are however split, with regard to the commensurate peak positions. For example, the (1/2 0 0) magnetic reflection splits into two peaks occurring at 11.2 and 12.6 Å. Similar distortions are observed for the other magnetic peaks. Below 70 K, nuclear reflections such as (2 0 0), (3 0 0) are also split, suggesting a distortion to an orthorhombic cell. Further analysis showed that this distortion is to the orthorhombic space group *Cmcm*, as observed for Mn_5Si_3 , which undergoes two magnetic transitions at 100 (AF1) and 66 K (AF2).⁸ However, while the orthorhombic structure is observed at all temperatures up to the Néel temperature of 100 K for Mn_5Si_3 , in FeMn_4Si_3 this distortion occurs only in the low temperature phase.

IV. CONCLUSION

The newly revised and updated magnetic phase diagram for the $\text{Fe}_x\text{Mn}_{5-x}\text{Si}_3$ series, is shown in Fig. 3. Antiferromagnetic interactions are observed to set in even for high Fe compositions, as evidenced by the observation of the spiral structure for $\text{Fe}_{3.5}\text{Mn}_{1.5}\text{Si}_3$ at low temperatures. The behavior of the phase diagram is most likely a consequence of the effects of: (a) a strong distance dependence of Mn–Mn exchange interactions and (b) competing interactions at the 4*d* and 6*g* sites. For example, the transition from the spiral to the ferromagnetic phase for $\text{Fe}_{3.5}\text{Mn}_{1.5}\text{Si}_3$ is accompanied by a small, but perceptible, increase in the cell volume, suggesting that magnetoelastic effects may play a role. For Mn rich compounds, the magnetic phase diagram is complex and rich. In particular the low temperature transition observed in FeMn_4Si_3 is similar to that of Mn_5Si_3 and additional arguments concerning the instability of Mn moments in a frustrated crystal environment¹⁴ invoked for Mn_5Si_3 ,¹⁰ could ar-

FIG. 3. Magnetic phase diagram for $\text{Fe}_x\text{Mn}_{5-x}\text{Si}_3$ compounds, based on the findings of the neutron diffraction data presented here.

guably be extended to $\text{Fe}_x\text{Mn}_{5-x}\text{Si}_3$ compounds in the Mn rich region, where the Mn moments, due to the nature of their occupancy of 4*d* and 6*g* sites, can be regarded as existing in a frustrated state.

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