2011

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2011 J. Phys.: Conf. Ser. 303 012022

(http://iopscience.iop.org/1742-6596/303/1/012022)

Neutron diffraction study of the magnetic order in $NdMn_2Ge_{1.6}Si_{0.4}$

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Abstract. Here we report a detailed investigation of $NdMn_2Ge_{1.6}Si_{0.4}$; this forms part of our investigation of the magnetic order across the $NdMn_2Ge_{2-x}Si_x$ (x = 0–2.0) series by magnetometry, x-ray diffraction and neutron diffraction over the temperature range 6–465 K. On decreasing the temperature from 465 K, $NdMn_2Ge_{1.6}Si_{0.4}$ exhibits four magnetic transitions: (i) from paramagnetism to intralayer antiferromagnetism AFl at $T_N^{intra} \sim 430$ K; (ii) AFl to canted ferromagnetism Fmc at $T_C^{inter} \sim 330$ K; (iii) Fmc to conical magnetic ordering of the Mn sublattice Fmi at $T_{cc} \sim 178$ K and (iv) Fmi(Mn) to Fmi(Mn)+F(Nd) at $T_C^{Nd} \sim 72$ K.

1. Introduction

The tetragonal intermetallic compounds RT_2X_2 (R = rare-earth; T = transition metal and X = Si or Ge) have been studied extensively and present a wide range of magnetic behaviours. Of particular interest are those compounds with T = Mn which is the only T element to order magnetically, generally well above room temperature. The RT_2X_2 compounds form in the $ThCr_2Si_2$ structure (space group I4/mmm, #139) and the naturally layered nature of this crystal structure leads to an extreme sensitivity of the magnetic order to the interatomic distances. In particular, there is a critical intralayer Mn–Mn distance of ~2.87 Å above which the magnetic order is ferromagnetic (FM) and antiferromagnetic (AF) below. At least nine magnetic structures have been identified in the T = Mn compounds [1], encompassing collinear, canted, conical and incommensurate FM and AF order. Throughout this paper we will use the notation introduced by Venturini et al. [1] to describe our magnetic structures.

From a more practical viewpoint, the discovery of a giant magnetocaloric effect (MCE) near room temperature in the layered rare earth compound $Gd_5Si_2Ge_2$ [2] has led to increased efforts in the search for materials with a large MCE. $NdMn_2Ge_2$ and related compounds offer interesting prospects for enhanced magnetocaloric behaviour because the naturally layered crystal structure allows control of the intrinsic magnetism via inter- and intra-planar separations of the Mn atoms

with the Nd atoms contributing to larger magnetization due to ferromagnetic coupling between the Mn and Nd sublattices below the Nd ordering temperature T_C^{Nd}.

We have carried out an extensive neutron powder diffraction study of the entire $NdMn_2(Ge, Si)_2$ system with the aim of determining the magnetic structures across the phase diagram from $NdMn_2Ge_2$ to $NdMn_2Si_2$. The two end-member compounds have previously been studied by Welter et al. [3, 4]. A tentative magnetic phase diagram for the $NdMn_2(Ge, Si)_2$ series has been proposed by Wang et al. [5, 6] on the basis of magnetometry measurements. In this paper, we present a detailed determination of the intrinsic magnetism of $NdMn_2Ge_{1.6}Si_{0.4}$. The magnetism of this Si-doped compound is found to be similar to that of $NdMn_2Ge_2$ [4].

2. Experimental Methods

The $NdMn_2Ge_{1.6}Si_{0.4}$ sample was prepared by arc melting stoichiometric amounts of the pure elements (Nd 99.9 wt.%; Mn, Si, Ge 99.99 wt.%). The sample was turned and remelted several times to ensure homogeneity. The alloyed button was then sealed under vacuum in a quartz tube, annealed for 1 week at 900 °C and quenched in water. Cu-Kα x-ray diffraction confirmed the majority phase to be the intended tetragonal $ThCr_2Si_2$–like $NdMn_2Ge_{1.6}Si_{0.4}$ phase. Magnetic characterization was carried out on a Quantum Design PPMS susceptometer/magnetometer operated down to 5 K.

Neutron diffraction experiments were carried out on the *Wombat* high-intensity powder diffractometer at the OPAL reactor in Sydney, Australia [7]. The neutron wavelength was 2.41726(2) Å. Temperatures down to 6 K were obtained using a closed-cycle refrigerator. All refinements of the x-ray and neutron diffraction patterns employed the FullProf/WinPlotr package [8, 9].

3. Results and Discussion

3.1. Basic characterisation and magnetometry

The tetragonal $ThCr_2Si_2$-type structure of $NdMn_2Ge_{1.6}Si_{0.4}$ has Nd atoms in the 2a site (0, 0, 0) while the Mn atoms occupy the 4d site (0, $\frac{1}{2}$, $\frac{1}{4}$) and the Si, Ge atoms occupy the 4e site (0, 0, z_e), with $z_e = 0.392$ at room temperature. The magnetization measurements (Figure 1) show that the temperature dependence of the magnetic behaviour of $NdMn_2Ge_{1.6}Si_{0.4}$ comprises five distinct regions:

- $T > T_N^{Intra} \sim 430$ K
- $T_C^{Inter} \sim 330$ K $< T < T_N^{Intra} \sim 430$ K
- $T_{cc} \sim 178$ K $< T < T_C^{Inter} \sim 330$ K
- $T_C^{Nd} \sim 72$ K $< T < T_{cc} \sim 178$ K
- $T < T_C^{Nd} \sim 72$ K

Magnetization measurements at 10 K in fields up to 5 T yield a saturation magnetization of 70 $JT^{-1}kg^{-1}$, indicating substantial FM order. To determine the magnetic order in $NdMn_2Ge_{1.6}Si_{0.4}$ we have carried out neutron powder diffraction experiments in each of these temperature regions.

4. Neutron powder diffraction

4.1. T > 430 K

Figure 2 shows examples of the refined neutron powder diffraction patterns of $NdMn_2Ge_{1.6}Si_{0.4}$ obtained over the temperature range 6 K to 465 K. An expanded view of the neutron diffraction pattern of $NdMn_2Ge_{1.6}Si_{0.4}$ at 6 K from $2\theta = 20°$ to $2\theta = 60°$ is shown in Figure 3. In Table 1

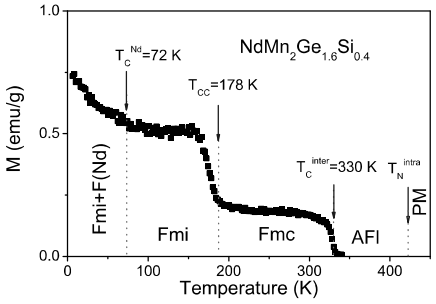

Figure 1. Temperature dependence of the magnetization of $NdMn_2Ge_{1.6}Si_{0.4}$ obtained in a field of 10 Oe. $T_N^{Intra} \sim 430$ K is derived from the temperature dependence of the intensity of the (101) neutron diffraction peak. The easy magnetization is along the c-axis for $T > T_{cc}$, while the direction of easy magnetization turns into the ab-plane with $T < T_{cc}$.

we present a summary of the crystallographic and magnetic parameters determined from our refinements and in Figure 4 we show the temperature dependence of three key diffraction peaks (002), (101) and (112). As discussed below, these reflections allow us to follow the thermal evolution of the intrinsic magnetic behaviour of $NdMn_2Ge_{1.6}Si_{0.4}$. The $NdMn_2Ge_{1.6}Si_{0.4}$ phase is paramagnetic at 465 K with the refined diffraction pattern purely nuclear, as expected.

4.2. 330 K < T < 430 K

Upon cooling, the magnetic contributions to the $NdMn_2Ge_{1.6}Si_{0.4}$ diffraction patterns arising from the AF ordering of the Mn sublattice appear at $T_N^{Intra} \sim 430$ K. In figure 2 we show the refinement to the neutron diffraction pattern obtained at 405 K. At 405 K the magnetic contributions occur only at nuclear peak positions ($\mathbf{k} = [0\ 0\ 0]$). The effect is most clearly seen in the increase in the (101) peak at $2\theta = 38°$. We find no evidence for additional magnetic-only peaks from the $NdMn_2Ge_{1.6}Si_{0.4}$ phase at 405 K. The Mn moments order in the tetragonal basal plane and form an AFl magnetic structure.

4.3. 178 K < T < 330 K

The magnetization measurements (Figure 1) show a sudden increase at 330 K corresponding to a rearrangement of the Mn order, resulting in a ferromagnetic component. In the neutron diffraction patterns, this rearrangement manifests as an increase in the (112) peak at $2\theta = 57°$, together with the continuing increase in the (101) intensity. The presence of both (101) and (112) magnetic intensities shows that the Mn order comprises both AF and FM contributions. The 4d special position of the Mn moments is effectively a 'C' symmetry position so the Mn nuclear/FM structure factor for the (101) peak is zero and non-zero for (112). Our refinement of the patterns in the temperature range 178 K < T < 330 K indicates that the Mn sublattice magnetic order is Fmc, i.e. a canted ferromagnet with the FM order along the tetragonal c-axis. The pattern at 300 K is shown in Figure 2 as a typical example of the behaviour in this region.

4.4. 72 K < T < 178 K

The magnetization measurements show a second dramatic increase at 178 K; this corresponds to a further rearrangement of the Mn order, resulting in a stronger FM component. In the neutron

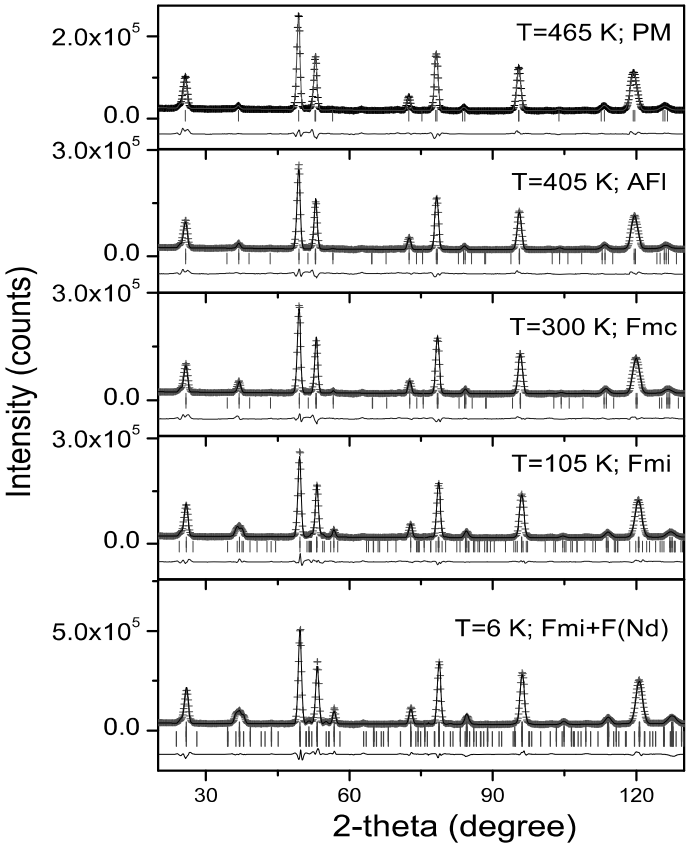

Figure 2. Neutron diffraction patterns of $NdMn_2Ge_{1.6}Si_{0.4}$ at the temperatures indicated (neutron wavelength $\lambda = 2.41726(2)$Å). Refinements to the magnetic structures indicated are given by the full lines and peak markers in the usual way.

diffraction patterns this rearrangement manifests as a sudden increase in the intensities of the (101) and (002) peaks (see Figure 4). The increase in the nuclear-allowed (002) peak intensity shows that the FM component of the Mn order has reoriented from the c-axis to the basal plane. Our refinement of the patterns in the temperature range 72 K < T < 178 K indicates that the Mn sublattice magnetic order is Fmi, i.e. a conical ferromagnet with the FM order perpendicular to the tetragonal c-axis. The incommensurate propagation vector is [0 0 0.111(1)] at 105 K.

4.5. T < 72 K

Below 72 K, the Nd sublattice orders magnetically in the tetragonal basal plane while the Mn order remains Fmi, albeit with a larger propagation vector component [0 0 0.159(1)] at 6 K. The effect of the FM ordering of the Nd sublattice is seen in the magnetization curve as a pronounced upturn in magnetization (see Figure 1). The change in the propagation vector describing the

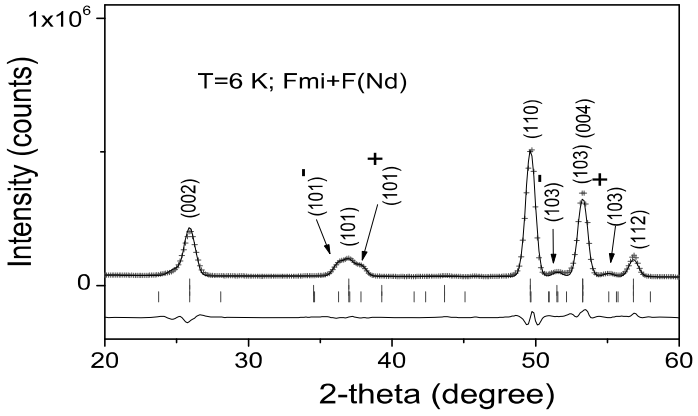

Figure 3. Expanded view of the neutron diffraction pattern of $NdMn_2Ge_{1.6}Si_{0.4}$ at 6 K.

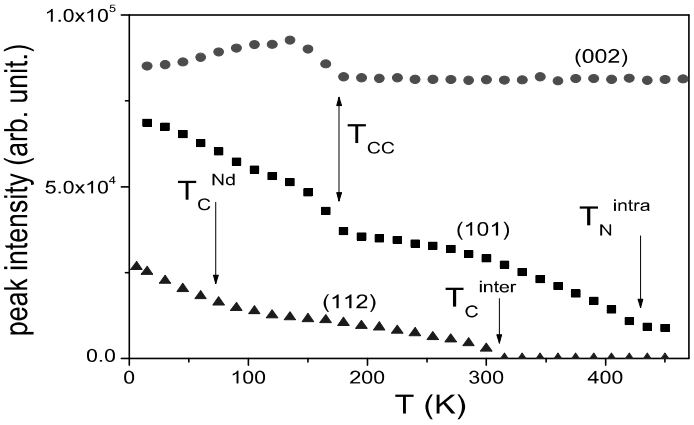

Figure 4. Temperature dependence of the (101), (112) and (002) neutron diffraction peak intensities of $NdMn_2Ge_{1.6}Si_{0.4}$.

ordering of the Mn sublattice is clearly seen in the broadening of the (101) peak as the **k**-vector satellites progressively separate from the central peak. The Nd and Mn magnetic moments at 6 K are 2.8(2) μ_B and 3.7(1) μ_B, respectively.

5. Conclusions

We have determined the various magnetic structures of $NdMn_2Ge_{1.6}Si_{0.4}$ by neutron powder diffraction over the temperature range 6–465 K. The magnetic ordering temperature is $T_N^{Intra} \sim 430$ K, involving AF order of the Mn sublattice. Upon cooling, the Mn order reorients at $T_C^{Inter} \sim 330$ K and $T_{cc} \sim 178$ K. At $T_C^{Nd} \sim 72$ K, the Nd sublattice orders ferromagnetically.

Table 1. Structural and magnetic parameters derived from Rietveld refinements of the neutron diffraction patterns for $NdMn_2Ge_{1.6}Si_{0.4}$. The errors are shown for T = 6 K as a typical example.

T (K)	6 K	15 K	105 K	300 K	405 K	465 K
Magnetic state	Fmi+F(Nd)	Fmi+F(Nd)	Fmi	Fmc	AFl	PM
a (Å)	4.071(1)	4.071	4.072	4.078	4.084	4.085
c (Å)	10.798(2)	10.798	10.796	10.829	10.863	10.879
z_e	0.384(1)	0.383	0.385	0.392	0.395	0.397
μ_{ab} (μ_B)	2.95(2)	2.94	2.65	1.42	0.98	–
μ_c (μ_B)	2.27(2)	2.29	2.31	0.54	–	–
Canting angle	38(2)	38	41	62	90	–
μ_{total} (μ_B)	3.7(1)	3.7	3.5	1.5	1.0	–
k_z	0.159(3)	0.157	0.111	–	–	–
μ_{Nd} (μ_B)	2.8(2)	2.8	–	–	–	–
R_{wp}	5.29	5.56	6.08	6.59	7.99	9.22
R_p	3.84	4.13	4.18	4.61	5.80	6.82

The behaviour of $NdMn_2Ge_{1.6}Si_{0.4}$ is similar to that of $NdMn_2Ge_2$ [4]. Replacement of Ge with 20% of Si leads to a reduction in the transition temperatures and the k_z propagation vector component compared with the behaviour shown by $NdMn_2Ge_2$.

Acknowledgments
Financial support for this work was provided by the Australian Research Council and the Australian Institute for Nuclear Science and Engineering. This work is supported by a joint agreement between ANSTO and UNSW. Finally, JMC acknowledges support from the Canada Research Chairs programme.

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