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The Magnetic Structures of YMn_2Si_2 and $LaMn_2Si_2$

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Abstract

Time of flight powder neutron diffraction has been used to confirm the antiferromagnetic structure of YMn_2Si_2 (magnetic space group $I_p4/m'm'm'$) in agreement with previous investigations. YMn_2Si_2 has a total magnetic moment at 10 K of $\mu_{Mn} = 2.21$ (3) μ_B. On the other hand, in agreement with the recent findings of Venturini and co-workers, $LaMn_2Si_2$ is found to exhibit a canted magnetic structure below the ferromagnetic transition temperature T_C rather than collinear c-axis ferromagnetism as accepted previously. At T = 10 K, $LaMn_2Si_2$, of magnetic space group Im', has a total magnetic moment of $\mu_{Mn} = 2.608$ (9) μ_B and a canting angle $\angle_{(001)} = 49.8$ (2)°. Similarly the new high temperature antiferromagnetic region, also reported for $LaMn_2Si_2$ for $T > T_C$ by Venturini *et al.*, has been confirmed. $LaMn_2Si_2$ at 305 K is found to have an I4/m'm'm space group with a magnetic moment $\mu_{Mn} = 1.222$ (8) μ_B.

Introduction

Compounds based on the rare earth (R) transition metal (T) systems with the tetragonal $ThCr_2Si_2$ - type structure (space group I4/mmm) continue to attract a great deal of interest. This reflects the wide range of magnetic phenomena exhibited by such RT_2X_2 compounds (see [1] for a review), including the heavy fermionic and superconducting behaviour of some members of this series [e.g. 2, 3]. Our overall interest is centred on the details of the magnetic interactions which occur in the $La_{1-x}Y_xMn_2Si_2$ series as the antiferromagnetism of YMn_2Si_2 gives way to the ferromagnetism of $LaMn_2Si_2$ at a critical concentration $x_C \sim 0.2$ [4]. The intermediate region between established antiferromagnetism and established ferromagnetism exhibits a range of magnetic behaviours, with features indicative of cluster glass or spin glass - like magnetism also having been observed [5]. This transition from ferromagnetism to antiferromagnetism has been investigated by ^{57}Fe Mössbauer effect measurements with distinct changes being observed in the hyperfine interaction parameters for a series of $La_{1-x}Y_xMn_2Si_2(^{57}Fe)$ samples, above and below the critical concentrations $x_C \sim 0.15$ at 4.2 K and $x_C \sim 0.25$ at room temperature respectively [6,7].

Here we present aspects of a complementary neutron diffraction study of the magnetic structures of a series of $La_{1-x}Y_xMn_2Si_2$ compounds. The behaviour of the limiting $LaMn_2Si_2$ and YMn_2Si_2 compounds at 10 K , room temperature (RT) and 305 K is described, with details of the variable temperature investigation of the remaining samples in this series (x = 0.1, 0.15, 0.25 and 0.5) presented elsewhere [8]. This investigation is particularly pertinent in light of the revision of the

magnetic structures and behaviour of the Mn sublattice in $LaMn_2Si_2$ and related $ThCr_2Si_2$ - type structures reported recently [9-11].

Experimental

The samples were prepared by standard argon arc melting in a partial pressure of purified argon. The starting materials were of high purity (Mn 99.99 % - Goodfellow Metals, La 99.99 % - Aldrich Chemical Company Inc., Y 99.99 % - Aldrich Chemical Company Inc. and Si 99.7 % - Research Organic/Inorganic Chemical Corp.). The starting materials contained ~ 3 % excess Mn to compensate for Mn loss due to evaporation during melting, and each ingot was melted at least 5 times for improved homogeneity. As our argon arc furnace can only cope with relatively small charges, ~ 3 g, the final samples examined in the neutron experiments were a combined mixture of fine powders obtained from 4 ingots each of $LaMn_2Si_2$ and YMn_2Si_2. X - ray diffraction established the presence of all of the reflections of the tetragonal $ThCr_2Si_2$ structure. No impurities were observed in the $LaMn_2Si_2$ compound, although a small fraction (~ 6%) of YSi_2 and an, as yet unknown, impurity phase were present in the YMn_2Si_2 compound. The neutron diffraction measurements were carried out on the POLARIS time of flight diffractometer, using the pulsed neutron source at the ISIS facility, Rutherford Appleton Laboratory, DRAL, UK. As discussed below, Rietveld refinements of the neutron data were carried out using the GSAS program package [12].

	YMn_2Si_2 T = 10 K	**$LaMn_2Si_2$ T = 305 K**	**$LaMn_2Si_2$ T = 10 K**
Cell constants:			
a [Å]	3.91195(6)	4.10977(3)	4.09848(8)
c [Å]	10.4287(2)	10.59779(11)	10.56325(8)
U_{iso} [Å^2]:			
Y,La	0.370(11)	0.545(12)	0.241(6)
Mn	0.337(18)	0.425(13)	0.351(7)
Si	0.459(20)	0.545(11)	0.412(5)
z_{Si} (0,0,z)	0.3839(1)	0.38067(5)	0.38010(1)
Magnetic space group:	*$I_p4/m'm'm'$*	*$I4/m'm'm$*	*Im'*
M_x [μ_B]			1.993(7)
M_z [μ_B]	2.21(3)	1.222(8)	1.682(10)
$M_{tot.}$ [μ_B]	2.21(3)	1.222(8)	2.608(9)
$\angle_{(001)}$			49.8(2)°
$f_{corr.(001)}$	1.020(1)	1.064(4)	1.066(1)
R_{wp} (%)	4.9	2.93	2.74
$R_{int.}$ (%)	3.69	3.19	2.22

Table 1 Results of the Rietveld refinements of YMn_2Si_2 at T = 10 K, and $LaMn_2Si_2$ at T = 10 K and T = 305 K. (The errors represent the uncertainties in the parameters as determined by the refinement).

Results and Discussion

The time of flight neutron diffraction patterns obtained for the YMn_2Si_2 sample (T_N = 410 K [1]) confirmed that the sample crystallises in the I4/mmm space group as expected. The additional magnetic reflections in the RT and 10 K patterns can be indexed on the basis of the chemical cell as (111), (113), (201) and (203). The absence of *(00l)* type reflections indicates the alignment of the magnetic moments along the c-axis. These features are consistent with the antiferromagnetic structure described by Siek *et al.* [13] and the Rietveld refinements were therefore carried out in the magnetic space group $I_p4/m'm'm'$. The magnetic structure, as shown in Figure 1a, consists of ferromagnetic (001) Mn planes coupled antiferromagnetically along the c-axis. Full details of the structural and magnetic parameters are given in Table 1. All the data were corrected for sample attenuation and an additional absorption parameter was included in the refinements, while effects due to preferred orientation (f_{corr}) were modelled using a correction procedure as formulated by Dollase [14].

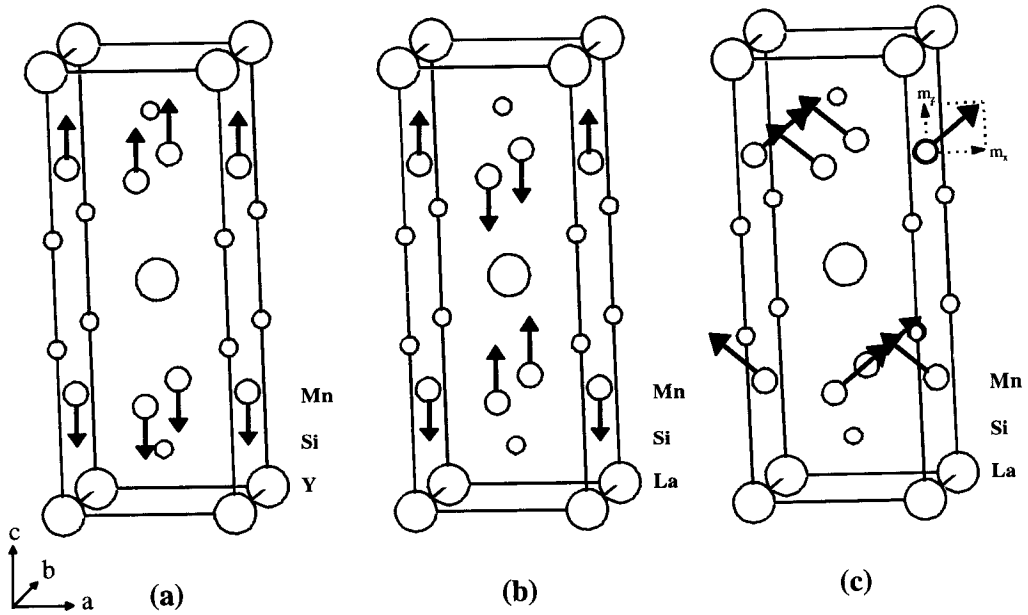

Figure 1 (a) The antiferromagnetic structure of YMn_2Si_2 at 10 K (magnetic space group $I_p4/m'm'm'$; cf [13]) (b) The high temperature antiferromagnetic structure of $LaMn_2Si_2$ at 305 K (magnetic space group I4/m'm'm; cf [10]) (c) The ferromagnetic structure of $LaMn_2Si_2$ at 10 K (magnetic space group Im'; cf [10]).

The moment on the Mn atoms at 10 K, μ_{Mn} = 2.21 (3) μ_B (Table 1), is in good agreement with that obtained for YMn_2Si_2 previously (μ_{Mn} = 2.40(14) μ_B at 80 K [13, 1]. The intralayer Mn - Mn separation distance of $d_{Mn\text{-}Mn}$ = 2.766 Å is consistent with the occurrence of antiferromagnetic (001) Mn planes when $d_{Mn\text{-}Mn}$ < 2.865 Å [15,1].

The main interest in the present investigation focuses on the $LaMn_2Si_2$ sample for which previous studies have concluded the magnetic space group I4/mm'm' with ferromagnetic coupling between ferromagnetic (001) Mn - Mn planes of separation $d_{Mn-Mn} > 2.865$ Å [15, 1] below the ordering temperature $T_C \sim 303\text{-}310$ K [1]. On the other hand, as noted above, the recent series of investigations of $ThCr_2Si_2$ - type compounds [e.g. 16, 9 - 11] have included a revision of the magnetic behaviour of the Mn sublattice, leading to antiferromagnetic ordering for $LaMn_2Si_2$ above T_C, with a canted rather than a c - axis collinear ferromagnetic structure below T_C [10].

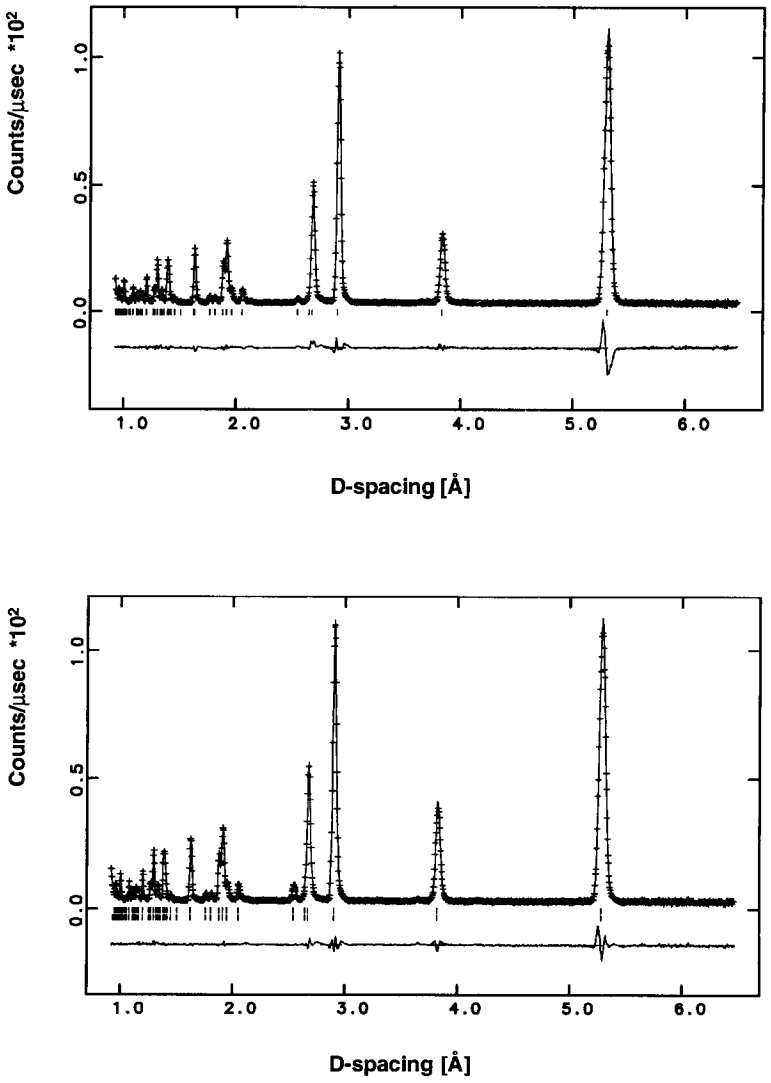

Figure 2 Neutron diffraction patterns of $LaMn_2Si_2$ (Top:305 K, Bottom: 10 K). Tick marks are for 10 K: Top - magnetic reflections (Im'), Bottom - nuclear reflections (I4/mmm).

The neutron diffraction patterns obtained for $LaMn_2Si_2$ at 10 K and 305 K are shown in Figure 2. The key feature in the analysis of the 305 K pattern is that the intensities of the (211) and, particularly, the (101) peaks are significantly enhanced compared with those expected on the basis of scattering from a magnetically disordered paramagnetic phase. Correspondingly, the refinement (Table 1) leads to the magnetic structure shown in Figure 1b in which the Mn - Mn layer are coupled antiferromagnetically. This structure, of magnetic space group I4/m'm'm confirms the results of Venturini *et al.* [10], who first reported this new high temperature antiferromagnetic structure for both $LaMn_2Si_2$ and $LaMn_2Ge_2$.

In a similar manner the Rietveld plot for $LaMn_2Si_2$ at 10 K shows an increase in intensity for both the (101) and (112) reflections. The increase in the (112) reflection is indicative of a ferromagnetic alignment along the c-axis while the strong (101) reflection is consistent with the existence of antiferromagnetically coupled Mn - Mn layers as noted above. The resulting magnetic structure (magnetic space group Im'), is a canted ferromagnet with moments aligned along the 001 direction (Figure 1c). This analysis confirms the canted magnetic structure reported recently for $LaMn_2Si_2$ below T_C [10]. The present analysis of 10 K data leads to a net magnetic moment μ_{Mn} = 2.608 (9) μ_B and a canting angle of $\angle_{(001)}$ = 49.8 (2)° in good agreement with the 50 K values of μ_{Mn} = 2.44 (12) μ_B and $\angle_{(001)}$ = 49° obtained by Venturini *et al.* [10]. It is noted however, that there are slight distortions in the shape of the (101) peak at 3.8 Å. Such distortions, indicative of possible satellite reflection, may suggest a helical rather than a canted magnetic structure. In any event the effect is slight and awaits further analysis [8].

The intralayer separation distance for $LaMn_2Si_2$ at 10 K is $d_{Mn\text{-}Mn}$ = 2.898 Å compared with the value at 305 K of $d_{Mn\text{-}Mn}$ = 2.906 Å. Whereas the intralayer spacing in antiferromagnetic YMn_2Si_2 fits in with the tendency for antiferromagnetic coupling between Mn -Mn layers when $d_{Mn\text{-}Mn}$ < 2.865 Å, the $d_{Mn\text{-}Mn}$ value for $LaMn_2Si_2$ does not appear to meet the corresponding relationship of ferromagnetic order when $d_{Mn\text{-}Mn}$ > 2.865 Å [15]. In fact, the occurrence of antiferromagnetic planes at high temperature in $LaMn_2Si_2$ rather indicates that this effect is the main feature and that the occurrence of ferromagnetism at low temperature results from secondary effects [10]. Our current investigations of a series of samples over a wide temperature range (T = 10 - 400 K) will enable this question of the dependence of the magnetic order on intralayer spacing, to be examined in detail [8].

Given that the present 305 K pattern for $LaMn_2Si_2$ was obtained around the ordering temperature reported for T_C ~ 303 - 310 K [1], attempts to refine the neutron diffraction pattern (Figure 2 top) were also carried out based on the canted magnetic structure (Im') appropriate to the 10 K pattern of Figure 2 (bottom). In the event the trend of the refinements was always towards the antiferromagnetic structure (I4/m'm'm) with a canted structure (which would exhibit nominally only a very slight canting angle at such a high temperature) unable to produce a stable refinement. This behaviour will be investigated more fully with our continuing measurements at higher temperatures T > 305 K [8].

Evidence in support of a high temperature antiferromagnetic region above T_C in a series of related 1:2:2 Mn based compounds, has recently been obtained by Mössbauer spectroscopy using ^{57}Fe as a dilute probe in the materials [17, 18]. Nowik *et al.* [17] reported antiferromagnetism for $RMn_2Si_{2-x}Ge_x$ (R = La, Sm, Gd) compounds above T_C ~ 320 K, with a Neel temperature of typically T_N ~ 450 K. Similarly Li *et al.* [18] observed distinct changes in the magnetic hyperfine and quadrupole splitting in $La_{0.85}Y_{0.15}Mn_2Si_2$ (^{57}Fe) at the ferromagnetic transition temperature T_C ~ 300 K, with evidence for antiferromagnetic order persisting to T_N ~ 435 K. In particular the transferred hyperfine field which acts at the ^{57}Fe atoms located at the Si 4e site, was found to reduce to zero above T_C as a result of the antiparallel alignment of the moments in the (001) planes, whereas the hyperfine field as measured by ^{57}Fe atoms (~ 90% fraction) at the Mn 4d sites persisted to T_N ~ 435 K.

Conclusions

Neutron diffraction measurements have been carried out on YMn_2Si_2 and $LaMn_2Si_2$ at 10 K, room temperature and 305 K. The present refinements on YMn_2Si_2 at 10 K agree with the established antiferromagnetic structure (magnetic space group $I_p4/m'm'm'$, [1]). The present YMn_2Si_2 sample has an intralayer Mn - Mn separation distance of d_{Mn-Mn} = 2.766 Å at 10 K, below the distance of 2.865 Å considered necessary for antiferromagnetic order in such compounds [15, 1]. On the other hand, in agreement with the recent magnetic structural studies of $LaMn_2Si_2$ by Venturini *et al.* [10], (see also [16, 9, 11] for related $ThCr_2Si_2$ - type compounds), a canted magnetic structure is observed for $LaMn_2Si_2$ below the ferromagnetic transition temperature T_C rather than collinear c-axis ferromagnetism [1]. The magnetic space group of $LaMn_2Si_2$ at 10 K is Im' with a canting angle $\angle_{(001)}$ = 49.8 (2)° and a net magnetic moment μ_{Mn} = 2.608 (9) μ_B (Table 1; Figure 1c). Likewise the new high temperature ($T > T_C$) antiferromagnetic structure proposed recently for $LaMn_2Si_2$ and $LaMn_2Ge_2$ [10] is confirmed. Refinement of the present $LaMn_2Si_2$ sample at 305 K (Figure 2) leads to the structure shown in Figure 1b (magnetic space group I4/m'm'm). Our continuing investigation of a series of $La_{1-x}Y_xMn_2Si_2$ compounds (x = 0, 0.1, 0.15, 0.25, 0.5 and 1.0) over the temperature range T = 10 - 400 K will help to clarify further the magnetic interaction and structures present in this system, particularly around the critical concentration $x_C \sim 0.2$, and their dependence on the Mn - Mn intralayer separation distance (cf [15] and [10]).

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