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Magnetic properties of the $LaMn_{2-x}Fe_xGe_2$ solid solution ($0 \leqslant x \leqslant 1$) and magnetic structures of $LaMn_{1.5}Fe_{0.5}Ge_2$ from neutron diffraction study

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Abstract

The magnetic properties of the $ThCr_2Si_2$-type structure $LaMn_{2-x}Fe_xGe_2$ solid solution have been studied in the composition range $0 \leqslant x \leqslant 1$. For $x \leqslant 0.4$, all samples exhibit an easy-axis ferromagnetic behaviour while an easy plane occurs when $0.4 \leqslant x \leqslant 0.7$. The Curie temperatures and the saturation magnetization values (4.2 K, $H_{appl.} = 1.5$ T) decrease continuously with the Mn substitution rate from 325 K and 1.45 μ_B per Mn atom for $x = 0$, to 65 K and 0.62 μ_B for $x = 0.7$. The Fe rich compounds ($0.8 \leqslant x \leqslant 1$) do not exhibit ferromagnetism. At 2 K, $LaMn_{1.5}Fe_{0.5}Ge_2$ ($T_c = 162$ K) exhibits a canted ferromagnetic structure characterized by an antiferromagnetic component ($\mu_{Mn}(AF) \sim 2.7$ μ_B) aligned along the c-axis and a ferromagnetic component ($\mu_{Mn}(F) \sim 1.1$ μ_B) lying in the (001) plane. Moreover, at 300 K, the neutron diffraction study clearly shows that $LaMn_{1.5}Fe_{0.5}Ge_2$ is a purely easy-plane antiferromagnet (not detected by bulk magnetic measurements) characterized by a stacking of antiferromagnetic (001) Mn planes. The thermal dependence of the magnetic moment yields an ordering temperature $T_N \sim 385$ K. These results are discussed and compared with those obtained for the RMn_2Ge_2 (R = Ca, Ba, La–Nd) series.

Keywords: $LaMn_{2-x}Fe_xGe_2$; Magnetic properties; Neutron diffraction

1. Introduction

Previous studies of $ThCr_2Si_2$-type structure (*I4/mmm*) $LaMn_2Si_2$ and RMn_2Ge_2 (R = La–Nd) compounds have shown their unusual magnetic behaviour [1,2]. In these ferromagnetic compounds, a large part of the Mn moment is quenched into an antiferromagnetic component within the (001) Mn layers. It has been shown that such antiferromagnetic Mn planes occur in compounds characterized by large Mn–Mn intralayer distances ($d_c > 2.87$ Å) [2]. Furthermore, this antiferromagnetic component persists at T_c suggesting the occurrence of purely antiferromagnetic (001) Mn layers above this temperature in these compounds [2]. This assumption is corroborated by a recent Mössbauer study of Nowik et al. on ^{57}Fe doped RMn_2Ge_2 and RMn_2Si_2 samples [3]. According to these workers, the thermal variation of the transferred hyperfine field on the ^{57}Fe nucleus evidences the persistence of a magnetic ordering above the Curie point in $LaMn_2Si_2$ and in the RMn_2Ge_2 (R = La–Sm) series. However, a neutron diffraction study of the alkaline earth $CaMn_2Ge_2$ and $BaMn_2Ge_2$ compounds has shown that they are characterized by purely antiferromagnetic (001) Mn layers in the whole temperature range $T_N - 2$ K [4].

Owing to these results, the appearance of ferromagnetism in the $LaMn_2Si_2$ and RMn_2Ge_2 compounds seems to be correlated to the temperature as well as to the valence of the R element. In order to clarify the role played by electronic effects, we have decided to investigate the $La_{1-x}Ca_xMn_2Ge_2$ and $LaMn_{2-x}T_xGe_2$ (T = Cr,Fe,Co) solid solutions.

In this paper, we report on the magnetic properties of the $LaMn_{2-x}Fe_xGe_2$ ($0 \leqslant x \leqslant 1$) solid solution studied by bulk magnetization measurements between 4.2 and 800 K and on the magnetic structure of $LaMn_{1.5}Fe_{0.5}Ge_2$ determined by neutron diffraction.

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2. Experimental procedures

Pellets of stoichiometric amounts of the elements were melted in an induction furnace with the cold crucible apparatus. The samples were ground and melted again several times for better homogenization and then annealed for two weeks at 1273 K. The purity of the final products was checked by powder X-ray diffraction technique (Guinier Cu Kα) which confirms the $ThCr_2Si_2$-type structure of the whole $LaMn_{2-x}Fe_xGe_2$ ($0 \leqslant x \leqslant 1$) series. The lattice parameters were determined by a least squares fitting procedure from the Guinier patterns recorded with Si as internal standard (Table 1). They yield T–T intralayer separation largely greater than $d_c = 2.87$ Å in the whole series.

The magnetic measurements were carried out using a Faraday balance (above 300 K) and a MANICS magneto-susceptometer (between 4.2 and 300 K) in fields up to 1.6 T.

Neutron experiments were carried out at the Siloe reactor of the Centre d'Etudes Nucléaires de Grenoble (CENG). The diffraction patterns were recorded with the one-dimension curved multidetector DN5 at a wavelength $\lambda = 2.4970$ Å. In order to correct texture effects, following a procedure largely described in [5], we used during the refinements a fitted coefficient (r_{cor}) which reflects the importance of preferential orientation.

Using the scattering lengths: $b_{Ge} = 8.185$ fm, $b_{Mn} = -3.73$ fm, $b_{La} = 8.24$ fm, $b_{Fe} = 9.45$ fm and the form factor for Mn given in ref. [6], the scaling factor, the z_{Ge} atomic position, r_{cor} and the Mn magnetic moment were refined by the mixed crystallographic executive for diffraction (MXD) least squares fit procedure [7]. The MXD program allows simultaneous fitting of the nuclear and magnetic intensities to the observed intensities.

In the $ThCr_2Si_2$-type structure (*I4/mmm*), the La and Ge atoms occupy the 2(a), (0,0,0) and 4(e) (0,0,$z \sim 0.38$) sites respectively, whereas the transition metal T (Mn or Fe) atoms occupy the special position 4(d) (0,1/2, 1/4), i.e. with an additional C translation mode. Thus, it is important to stress that the magnetic contributions to the observed intensities affect only the nuclear lines obeying the limiting reflection condition: (a) (*hkl*) with $h+k=2n$ for ferromagnetic ordering of the Mn sublattice, (b) (*hkl*) with $h+k=2n+1$ for an antiferromagnetic arrangement of the Mn moments within the (001) planes.

3. Experimental results

3.1. Magnetic measurements

Nine $LaMn_{2-x}Fe_xGe_2$ compounds have been investigated. The main magnetic data are given in Table 1.

The isotherm curves at 4.2 K (Fig. 1) clearly provide evidence for the occurrence of a spontaneous magnetization for the samples with x less than 0.8. For $x < 0.4$, the saturation is not reached at 1.6 T and the shape of the magnetization curves is characteristic of a rather hard magnetic behaviour. As observed in $LaMn_2Ge_2$ [1], these results are in agreement with a ferromagnetic component aligned along the c-axis. For $x \geqslant 0.4$, saturation is clearly reached above 0.5 T, which suggests an easy-plane ferromagnetic component in the corresponding compounds.

The maximum magnetization value (M_{max}) strongly decreases with the Mn substitution rate (x) from ~ 2.4 μ_B per f.u. for $x = 0.1$ to about 0.8 μ_B per f.u. for $x = 0.7$ (Table 1). It is noteworthy that $M_{max.} = 1.45$ μ_B per Mn atom in $LaMn_2Ge_2$ [1] and that no local moment was detected at the iron site in $LaFe_2Ge_2$ [8] and in ^{57}Fe doped RMn_2Ge_2 compounds [3]. Bearing these results

Table 1
Lattice parameters and magnetic data for $LaMn_{2-x}Fe_xGe_2$ ($0 < x < 1$) compounds

x	a (Å)	c (Å)	θ_P (K)	μ_{eff} (μ_B/mole)	T_C (K)	M_{Max} (μ_B/mole) (4.2 K, 1.6 T)	M_{Max} (μ_B/Mn atom) [b]
0	4.204(2)	10.996(6)	225	4.79	325	2.90	1.45
0.1	4.190(2)	10.971(6)	231	4.11	286	2.38 [a]	1.25
0.2	4.183(2)	10.949(6)	215	3.99	263	2.39 [a]	1.33
0.3	4.176(1)	10.929(4)	192	3.97	224	2.40 [a]	1.41
0.4	4.169(1)	10.911(5)	179	3.81	172	1.99	1.24
0.5	4.165(2)	10.896(5)	175	3.88	162	1.83	1.22
0.6	4.160(1)	10.894(4)	140	3.80	103	1.33	0.95
0.7	4.154(2)	10.870(4)	115	3.89	65	0.81	0.62
0.8	4.151(3)	10.831(8)	110	3.41			
0.9	4.144(1)	10.823(4)	89	3.45			
1.0	4.137(1)	10.799(4)	71	3.39			

[a] Saturation not reached.
[b] Assuming a zero net moment on the iron atoms.

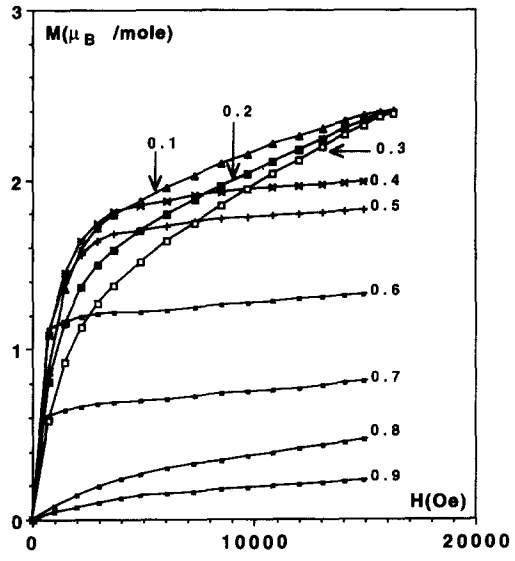

Fig. 1. Field dependence of the magnetization in $LaMn_{2-x}Fe_xGe_2$ compounds at 4.2 K.

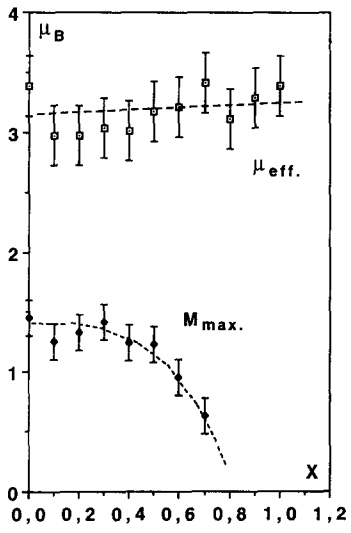

Fig. 2. Variation of the magnetization $M_{max.}$ (T=4.2 K) and the effective paramagnetic moment μ_{eff} per Mn atom versus x in $LaMn_{2-x}Fe_xGe_2$ compounds (see text).

in mind, Fig. 2 displays $M_{max.}$ versus x which reflects the variation of only the Mn moments.

The thermomagnetic curves are shown in Fig. 3. They confirm the ferromagnetic behaviour previously described and show a strong decrease of the Curie temperatures when x is increased (Table 1). The thermomagnetic curve of $LaMn_{1.6}Fe_{0.4}Ge_2$ exhibits an anomaly around T=80 K, probably due to a spin reorientation process. This phenomenon has to be related to the magnetization measurement data which suggests a change of the easy magnetization direction in the $LaMn_{2-x}Fe_xGe_2$ series around this composition range. The Mn concentration dependence of T_c (Fig. 4) shows a quasi-linear variation with a slope $\Delta T/\Delta x$ of about −370 K.

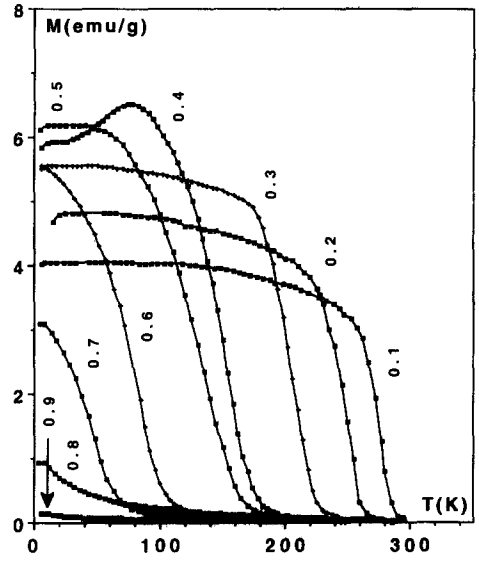

Fig. 3. Temperature dependence of magnetization (H_{app}=1 kOe) in $LaMn_{2-x}Fe_xGe_2$ compounds.

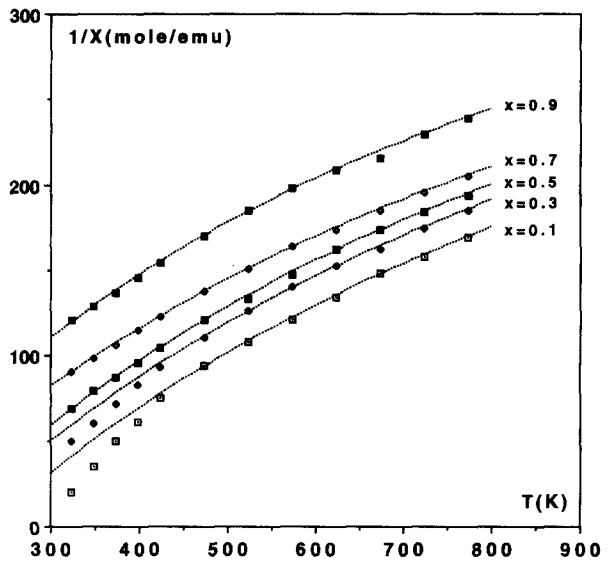

Fig. 4. High temperature dependence of the inverse molar susceptibility in $LaMn_{2-x}Fe_xGe_2$ compounds (for clarity only the odd values of x are shown).

Above room temperature, the thermal variation of the inverse susceptibility is well described by the following equation:

$$\chi=\chi_0+\frac{C}{T-\theta}$$

where the temperature independent susceptibility χ_0 has been estimated to be 5×10^{-6} e.m.u. g^{-1} in $LaMn_{1.1}Fe_{0.9}Ge_2$, which has been used also for the other compounds.

The thermal variation of the inverse susceptibility for several compounds is shown in Fig. 4. For $x<0.4$ (i.e. Mn rich compounds), the inverse susceptibility slightly departs from the calculated curve at temper-

atures around 400 K. Bearing the high temperature magnetic behaviour of $LaMn_2Ge_2$ in mind (see Section 1), these anomalies may be attributed to the Néel points of the corresponding compounds.

Compared to T_c, the paramagnetic Curie temperatures exhibit a slower decrease with Mn substitution and remain positive in the whole series (Fig. 5). However, one observes a continuous decrease of the effective moment (Table 1) while $\mu_{eff.}$ per Mn atom remains almost constant (Fig. 2).

3.2. Neutron diffraction study of $LaMn_{1.5}Fe_{0.5}Ge_2$

As shown in Fig. 3, this compound is characterized by a ferromagnetic transition at $T_c = 162$ K. At 2 K, the magnetization curve suggests an easy-plane anisotropy with a Mn moment saturation value of about 1.2 μ_B (Table 1).

Neutron diffraction patterns recorded between 2 K and 450 K clearly show three characteristic temperature ranges.

3.2.1. $T \geqslant T_c$

(1) At 400 K (Fig. 6), the pattern is characterized by the purely nuclear Bragg peaks which can be well accounted for by the extinction condition $(h+k+l=2n+1)$ of the space group *I4/mmm*. This confirms unambiguously the $ThCr_2Si_2$-type structure for $LaMn_{1.5}Fe_{0.5}Ge_2$. According to our results, any possible interchange of Mn/Fe and Ge on their crystallographic sites is excluded. The March factor $r_{cor} = 1.03(1)$ indicates the presence of very light texture effects. The value of the occupancy factor of the 4(d) transition metal site $f_{occ} = 0.73(1)$ is in fair agreement with the $LaMn_{1.5}Fe_{0.5}Ge_2$ formula. The magnetic refinements were performed using these values.

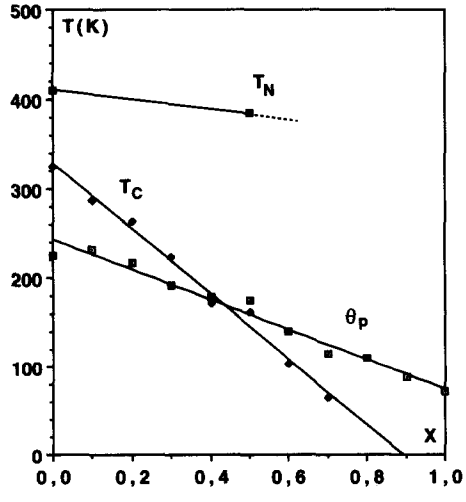

Fig. 5. Variation of T_c, θ_p and T_N versus x in $LaMn_{2-x}Fe_xGe_2$ compounds.

(2) At room temperature (Fig. 6), the pattern shows magnetic contributions only for the nuclear lines which obey the rule: (hkl) with $h+k=2n+1$. This is particularly obvious for the (101) reflection for which the observed intensity is much greater than the purely nuclear calculated intensity. This result indicates an anti-C ordering, giving evidence of an antiferromagnetic arrangement of the moments within the (001) planes. Similar magnetic Mn sublattice orderings have been observed in $CaMn_2Ge_2$, $BaMn_2Ge_2$ and $LaMn_2Si_2$ [1,4]. According to the observed relative magnetic contributions to the intensities of the (101) and (103) lines, the best refinement leads moment directions in the (001) plane. The magnetic structure is sketched in Fig. 7. As in the case of $LaMn_2Ge_2$, it is noteworthy that this purely antiferromagnetic behaviour is not detected in the bulk susceptibility measurements.

Fig. 8 shows the thermal variation of the (101) line intensity. It indicates the onset of the antiferromagnetic order at about 385(5) K.

3.2.2. $T \leqslant T_c$

At 2 K (Fig. 6), the intensities of the previous lines have increased and new magnetic contributions to the intensities of the nuclear lines which obey the rule (hkl) with $h+k=2n$ are observed. This implies that an additional ferromagnetic (see Section 3.1) component occurs at 2 K, in agreement with the magnetometric measurements. From these observations, refinements were performed to account for a canted ferromagnetic structure in which the Mn moments are antiparallel to each other in the (001) Mn planes and are canted between the Mn layers. The occurrence of a magnetic contribution to the (002) line intensity indicates that the ferromagnetic component lies in the basal plane whereas the best refinements lead to an antiferromagnetic component aligned along the c-axis (i.e. a spin reorientation process occurs for this component at T_c). The magnetic structure is shown in Fig. 7.

3.2.3. Magnetic moment values

At 300 K, the best refinements give a moment value of 1.94(6) μ_B per transition metal atom at the equivalent 4(d) position whereas, at 2 K, they yield moment values of 2.03(8) μ_B and 0.85(31) μ_B for the antiferro- and ferromagnetic components respectively (i.e. a canting angle of ~67° from the basal plane, Fig. 7).

Assuming a zero net moment value on the iron atoms (see Section 3.1), one obtains total resulting moment values of ~2.6 μ_B and ~2.9 μ_B per Mn atom at 300 K and 2 K respectively. This is in good agreement with those measured in $LaMn_2Ge_2$ [1]. It is noteworthy that, as also encountered in the RMn_2Ge_2 (R = La–Sm) series [2], the reduced Mn moment values deduced from the

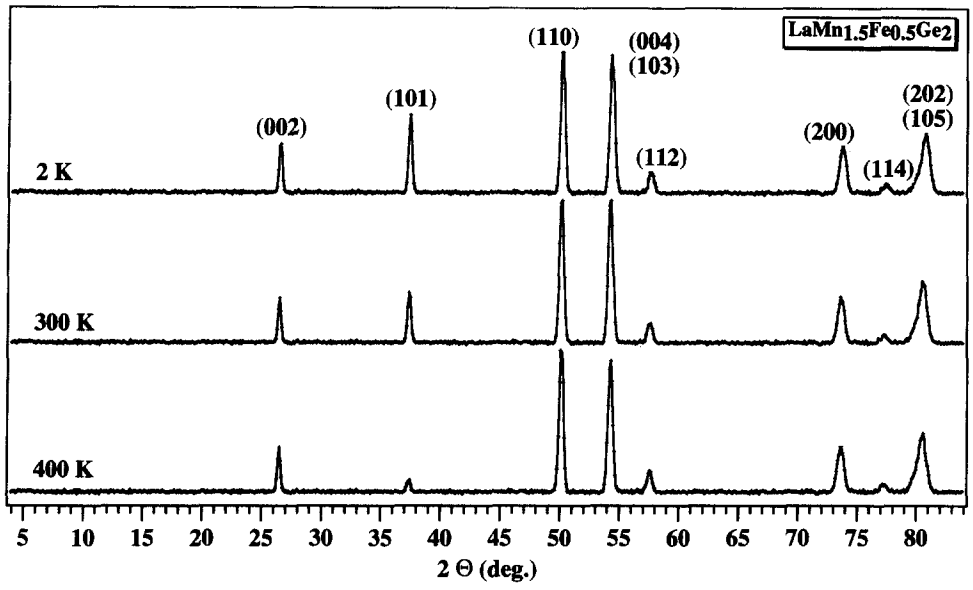

Fig. 6. Neutron diffraction patterns of $LaMn_{1.5}Fe_{0.5}Ge_2$ compounds at 400 K, 300 K and 2 K.

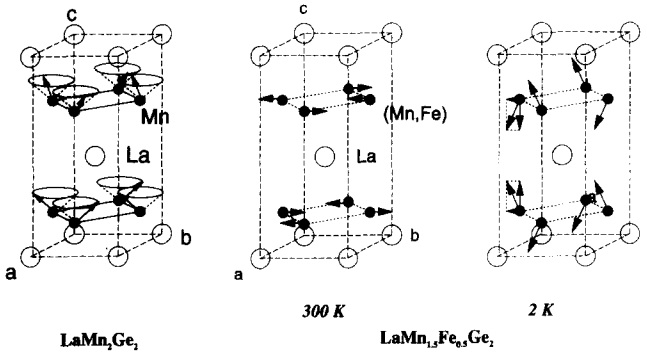

Fig. 7. Magnetic structure of $LaMn_2Ge_2$ and of $LaMn_{1.5}Fe_{0.5}Ge_2$ at 300 K and 2 K.

low temperature magnetization measurements (Table 1) clearly correspond to the purely ferromagnetic component of the magnetic structure, the antiferromagnetic component being obscured, at least below $H_{appl.} = 1.6$ T.

Table 2 gives the observed and calculated intensities together with the lattice constants and the various adjustable parameters at 300 and 2 K.

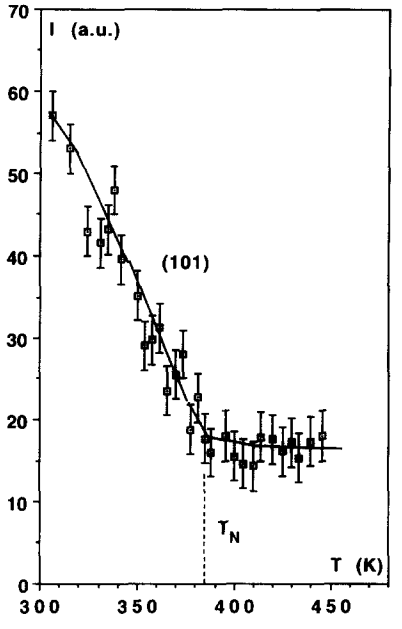

Fig. 8. Thermal variation of the (101) line intensity between 300 K and 450 K.

4. Discussion

According to ferromagnetic behaviour deduced from bulk magnetization measurements, the $LaMn_{2-x}Fe_xGe_2$ compounds ($x < 0.8$) can be described and analyzed as pure ferromagnets. However, the neutron diffraction study of $LaMn_{1.5}Fe_{0.5}Ge_2$ leads us to strongly revise this conclusion.

Below T_c (162 K), this compound is characterized by mixed (001) Mn planes where ferro- and antiferromagnetic components coexist. Moreover, in the whole temperature range below T_c, the antiferromagnetic component is always much larger than the ferromagnetic component. It is noteworthy that a similar magnetic behaviour is encountered in the whole series $LaMn_2Si_2$, RMn_2Ge_2 (R = La–Nd) and $La_{0.3}Y_{0.7}Mn_2Ge_2$ compounds [1,2,9].

However, the present study shows that, above T_c, magnetic order persists and $LaMn_{1.5}Fe_{0.5}Ge_2$ is a purely colinear easy-plane antiferromagnet (not detected by magnetometric measurements) characterized by a stacking of antiferromagnetic (001) Mn planes until $T_N = 385$ K, the moments being antiferromagnetically coupled

Table 2
Calculated and observed intensities, lattice constants and adjustable parameters in $LaMn_{1.5}Fe_{0.5}Ge_2$ at 300 and 2 K

h k l	300 K		2 K	
	I_c	I_o	I_c	I_o
0 0 2	10.5	11.3(3)	15.5	15.0(4)
1 0 1	31.1	31.1(6)	53.9	53.8(7)
1 1 0	165.3	164(2)	188.7	185.6(2)
0 0 4 1 0 3	205.7	207(2)	235.7	243(2)
1 1 2	41.4	42.5(9)	49.4	53.8(8)
2 0 0	157.4	158(3)	176.3	170(4)
1 1 4	29.5	29(1)	36.9	32(1)
2 0 2 1 0 5	273.1	263(4)	273.2	268(6)
a (Å)	4.165(2)		4.158(2)	
c (Å)	10.892(7)		10.864(6)	
r_{cor}	1.03(1)		1.03(1)	
z_{Ge}	0.379(1)		0.379(1)	
f_{occ}	0.73(1)		0.73(1)	
$\mu_{Mn}(\mu_B)$ F	0		1.13 [0.85(31)]	
$\mu_{Mn\ atom}(\mu_B)$ AF	2.58		2.70	
[ ] per 4(d) site	[1.94(6)]		[2.03(8)]	
$\mu_{Mn\ atom}(\mu_B)$	2.58		2.93	
[ ] per 4(d) site	[1.94(6)]		[2.20(15)]	
R (%)	2.5		3.2	

with their direct neighbours situated in each adjacent plane along the c-axis. Such magnetic ordering occurs in the $CaMn_2Ge_2$ and $BaMn_2Ge_2$ compounds [4]. It is worth noting that the occurrence of high temperature magnetic order in these compounds has been observed also for $LaMn_2Si_2$ [1] and has been suggested for the RMn_2Ge_2 series [2,3].

The magnetic properties of the $LaMn_{2-x}Fe_xGe_2$ solid solutions deduced from bulk magnetic measurements provides new information on the Mn sublattice magnetic behaviour in this series.

The replacement of Mn by Fe drastically influences the occurrence of a ferromagnetic component which vanishes for $x \geqslant 0.8$. Increasing x yields a strong quasi-linear decrease of T_c together with the large decrease of the maximum magnetization value $M_{max.}$ (Figs. 2 and 5).

According to the refined manganese moment values, the angle ϕ between the Mn moment direction and the ferromagnetic component direction is 58° in $LaMn_2Ge_2$ [1] and increases to 68° in $LaMn_{1.5}Fe_{0.5}Ge_2$ ($\phi = 90°$ for a zero net ferromagnetic component). It is noteworthy that a helical arrangement of the antiferromagnetic component occurs in $LaMn_2Ge_2$ (and RMn_2Ge_2 (R = Ce–Nd) at low temperature) while a canted one occurs in $LaMn_{1.5}Fe_{0.5}Ge_2$ (and $LaMn_2Si_2$) (Fig. 7).

Bearing these data in mind, increasing x probably yields a continuous decrease of ϕ in the $LaMn_{2-x}Fe_xGe_2$ series and suggests that a purely antiferromagnetic structure occurs in the Fe rich compounds ($x \geqslant 0.8$). In order to check this hypothesis, neutron diffraction studies of some other members of the series are in progress.

The last remark concerns the Néel temperatures. The Fe substitution seems to affect this parameter very slightly. According to the Mössbauer studies of Nowik et al. [3], $LaMn_2Ge_2$ ($T_c = 325$ K) becomes paramagnetic above 420 K whereas $LaMn_{1.5}Fe_{0.5}Ge_2$ ($T_c = 162$ K) behaves antiferromagnetically until 385 K (this work). The purely antiferromagnetic domain is therefore largely enhanced in $LaMn_{1.5}Fe_{0.5}Ge_2$. These data suggest that the antiferromagnetic in-plane Mn–Mn interactions are always very strong in all these compounds, the ferromagnetic component arising from other interactions of which intensity decreases when the Fe content increases (i.e. electronic factor).

Since the antiferromagnetic transition cannot be detected by magnetometric measurements, a systematic ^{57}Fe Mössbauer study of the solid solutions $LaMn_{2-x}Fe_xGe_2$ has to be used in order to determine the x dependence on T_N and the limit of the occurrence of a magnetic order in this series.

5. Conclusions

A neutron diffraction study of $LaMn_{1.5}Fe_{0.5}Ge_2$ has revealed the occurrence, of a purely antiferromagnetic state, characterized by antiferromagnetic (001) Mn planes, between $T_N = 385$ and $T_c = 162$ K, not detected by magnetometric measurements. Moreover, a dominant antiferromagnetic component within these planes persists below T_c, in agreement with the Mn–Mn intralayer separation (2.94 Å). These results clearly show that a better understanding of the magnetic properties of the $ThCr_2Si_2$-type RMn_2X_2 compounds obviously requires the use of the neutron technique.

The reduction of the ferromagnetic range and the corresponding increase of the antiferromagnetic one suggests that the occurrence of the ferromagnetic component is very critical in the whole $LaMn_{2-x}Fe_xGe_2$ series. From this point of view, it would now be interesting to investigate other members of this series as well as other solid solutions. These studies are under way.

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