Structural and magnetic properties of $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta \leqslant 2$)

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Magnetization measurements of $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta = 0-2$) show that the saturation magnetization, M_s, decreases with an increase in Ga content from 40.4 μ_B/f.u. for Nd_2Fe_{17} to 36.1 μ_B/f.u. for $Nd_2Fe_{15}Ga_2$ at 4.2 K. Neutron diffraction data at 25 K show that the magnetic moment of Fe depends on its crystallographic site and decreases in the order Fe(6c)>Fe(18f)$\geqslant$Fe(18h)$\geqslant$Fe(9d). The magnetic moments of Fe(9d), Fe(18f), and Fe(18h) are found to be practically independent of the Ga content. However, the magnetic moment of Fe(6c) decreases from 2.81(9) μ_B in Nd_2Fe_{17} to 2.14(9) μ_B in $Nd_2Fe_{15}Ga_2$. The decrease of the Fe(6c) moment clearly reduces the exchange interaction between Fe(6c)–Fe(6c) dumbbell pairs which explains the decrease in the anomalous thermal expansion with an increase in Ga concentration. The reduced Fe(6c)–Fe(6c) exchange interaction may also play an important role in increasing the Curie temperature, T_C, with Ga content; T_C increases from 327 K in Nd_2Fe_{17} to 535 K in $Nd_2Fe_{15}Ga_2$. [S0021-8979(00)22008-2]

INTRODUCTION

R_2Fe_{17} compounds crystallize in either the rhombohedral Th_2Zn_{17} or the hexagonal Th_2Ni_{17} crystal structures. In both structures Fe atoms occupy four different crystallographic sites, 6c, 9d, 18f, and 18h in the rhombohedral and 4f, 6g, 12j, and 12k in the hexagonal structure. As the interatomic distances between the 6c–6c, 4f–4f (~2.4 Å) and 9d–18f, 6g–12j (~2.44 Å) Fe atoms are less than 2.45 Å the exchange interaction between these Fe–Fe pairs was assumed to be negative[1,2] providing a possible explanation for the low Curie temperatures, T_C, of the R_2Fe_{17} compounds.[1,2] The Fe(6c)–Fe(6c) interaction was also shown to cause an anomalous thermal expansion of the c axis in Nd_2Fe_{17} below T_C.[3] In order to improve the magnetic properties of R_2Fe_{17}, Fe was partially substituted with transition or nontransition elements with an aim of expanding the R_2Fe_{17} unit cell and increase Fe–Fe bond lengths and thus promoting ferromagnetic exchange interactions. However, if Fe was substituted by Si the magnetic properties of R_2Fe_{17} improve although Si does not expand R_2Fe_{17} and does not preferentially substitute Fe in the 6c site.[4,5] Thus, the simple explanation based on distance dependent exchange and preferential substitution is not sufficient for understanding the changes in the magnetic properties of these compounds.

The magnetic properties of R_2Fe_{17} can be improved, T_C increases over 150 K for $R_2Fe_{14}Ga_3$.[5] Moreover, $Sm_2Fe_{17-\delta}Ga_\delta$ ($\delta \leqslant 3$) exhibit uniaxial anisotropy.[6] In $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta \leqslant 2$)~80% of Ga atoms occupy the 18h Fe and the rest substitute for Fe atoms in the 18f site.[3] Thus, the substitution of Ga for Fe will not change the number of the 6c–6c Fe pairs and will only marginally decrease the number of the 9d–18f Fe pairs. However, the anomalous thermal expansion in Nd_2Fe_{17} along the c axis, which is caused by the Fe(6c)–Fe(6c) exchange interaction, decreases due to the presence of Ga in $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta \leqslant 2$).[3] In order to understand the effect of Ga on the magnetic properties of Nd_2Fe_{17}, the saturation magnetization of $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta \leqslant 2$) was measured. The results were then used to constrain the total magnetic moments obtained from neutron diffraction measurements of $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta \leqslant 2$), in order to obtain precise information on the Fe magnetic moments at different crystallographic sites.

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TABLE I. Saturation magnetization and Curie temperatures of $Nd_2Fe_{17-\delta}Ga_\delta$ (δ=0–2) in the temperature range from 4.2 to 300 K.

$Nd_2Fe_{17-\delta}Ga_\delta$	δ=0	δ=0.5	δ=1	δ=1.5	δ=2
M_s (4.2 K) (μ_B/f.u.)	40.4	39.8	38.9	37.5	36.1
M_s (100 K) (μ_B/f.u.)	39.2	39.1	38.0	34.8	⋯
M_s (200 K) (μ_B/f.u.)	35.9	35.4	⋯	32.0	⋯
M_s (300 K) (μ_B/f.u.)	24.1	32.9	32.4	30.4	29.2
T_c (K)	327	380	432	484	535

EXPERIMENTAL TECHNIQUES

The $Nd_2Fe_{17-\delta}Ga_\delta$ ingots of size 25 g were prepared by induction melting. An excess of 1 wt % of Nd was added to compensate for Nd loss during melting and annealing. To ensure homogeneity, all the samples were melted at least four times and then annealed in an Ar atmosphere at 1340 K for several days. T_C of the samples was determined by a thermomagnetic analyzer. T_C increases with an increase of Ga concentration from 327 K for Nd_2Fe_{17} to 535 K $Nd_2Fe_{15}Ga_2$. The values of T_C are listed at the bottom of Table I. Magnetization measurements of $Nd_2Fe_{17-\delta}Ga_\delta$, in the temperature range from 4.2 to 300 K, were determined by an extraction technique in magnetic fields, $\mu_0 H$, of up to 22 T for $\delta=0-1.5$, while superconducting quantum interference device was used to determine the magnetization for $\delta=0$ and 2 in magnetic fields of up to 5.5 T. The neutron diffraction measurements were performed on the C2 DUALSPEC neutron powder diffractometer at Chalk River Laboratories, Ontario, Canada, in the temperature range from 25 to 770 K. Details can be found in an earlier report.[7] The neutron diffraction patterns obtain below T_C are analyzed using the Fullprof fitting procedure.

RESULTS AND DISCUSSION

The saturation magnetizations, M_s, of $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta=0-2$) as a function of temperature are presented in Table I. The M_s values are deduced from the law of approach to saturation, $M(H)=M_s(1-1/H)$. Due to the increase of Ga content in Nd_2Fe_{17}, M_s decreases from 40.4 μ_B/f.u. for Nd_2Fe_{17} to 36.1 μ_B/f.u. for $Nd_2Fe_{15}Ga_2$, at 4.2 K. The value of M_s for Nd_2Fe_{17} is in good agreement with the value 39.6 μ_B/f.u. determined for a single crystal.[8] The sharp decrease in the value of M_s for Nd_2Fe_{17} at 300 K is due to the ferromagnetic-paramagnetic transition which occurs at 327 K for this alloy.

The measured (crosses) and calculated (solid line) neutron diffraction patterns of $Nd_2Fe_{15.5}Ga_{1.5}$ at 25 K are shown in Fig. 1. The refined structural and magnetic parameters of $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta=0-2$) at 25 K, below T_C, and at 535 K, in the paramagnetic state, are presented in Table II. The results show that ~80% of Ga atoms substitute for Fe in the 18*h* site and the rest of the Ga atoms substitute for Fe in the 18*f* site in Nd_2Fe_{17}.[3] The neutron data, below T_C, were refined using Fullprof, subject to a soft constraint on the total magnetic moment, on the iron atoms. The values of the constraints were derived from the total magnetization measurement data, presented in Table I. A small standard deviation for the total moment of 0.1 μ_B was used in the soft constraint. All individual Fe and Nd moments were free to vary under this constraint. Refinements were performed assuming moments along the *c* axis, and in the basal plane, to determine the preferred ordering direction. The results show that the magnetic moments in $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta=0-2$) are in the basal plane, oriented along [100]. The magnetic moment of Fe depends on its crystallographic site and decreases in the order $Fe(6c)>Fe(18f)\geqslant Fe(18h)\geqslant Fe(9d)$. The presence of Ga in Nd_2Fe_{17} does not change the magnetic moments of Fe(18*f*) and Fe(18*h*) and slightly increases the magnetic moment of Fe(9*d*). On the other hand, the magnetic moment of Fe(6*c*) decreases from 2.81(9) μ_B in Nd_2Fe_{17} to 2.14(9) μ_B in $Nd_2Fe_{15}Ga_2$. The total magnetic moments per formula unit obtained for $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta=0$ and 2) are in good agreement with previous neutron diffraction results.[9,10] However, the magnetic moment of Fe(6*c*) was found to be independent on the Ga concentration in Nd_2Fe_{17}.

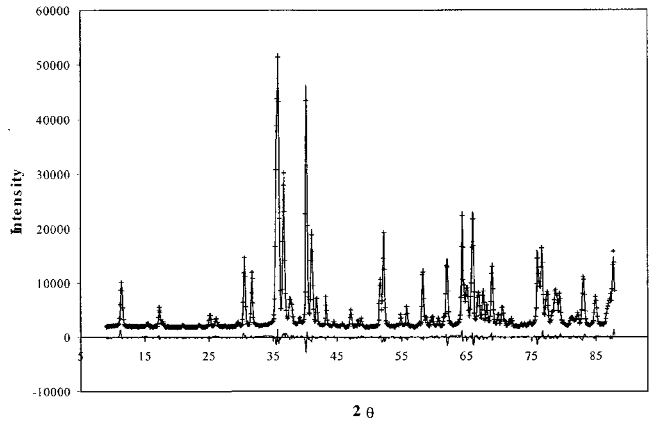

FIG. 1. Neutron powder diffraction pattern of $Nd_2Fe_{15.5}Ga_{1.5}$ at 25 K. The crosses and line refer to the experimental data and calculated Fullprof fit, respectively. The difference pattern is plotted in the lower part of the figure.

The change in the volume of Nd_2Fe_{17} was found to be ~6 Å^3 per Ga atom below T_C, and ~8 Å^3 per Ga atom above T_C. This is in good agreement with the observed ~8 Å^3 increase in volume of Nd_2Fe_{17} per Ga atom.[9] Figure 2 presents the Fe–Fe bond lengths in $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta=0-2$) at 25 K (below T_C) and at 535 K (above T_C). Below T_C, all Fe–Fe bond lengths increase (or do not change) with an increase of Ga content in $Nd_2Fe_{17-\delta}Ga_\delta$ except for Fe(6*c*)–Fe(6*c*) which decreases from 2.416(7) to 2.396(5) Å.[3] Above T_C, the Fe–Fe bond lengths generally increase with an increase of Ga content. The anomalous thermal expansion in Nd_2Fe_{17} along the *c* axis was found to be due to the strong magnetic interaction between Fe(6*c*)–Fe(6*c*) pairs.[3] Substitution of Ga for Fe in Nd_2Fe_{17} decreases the Fe(6*c*) moment and clearly reduces the negative exchange interaction between Fe(6*c*)–Fe(6*c*) pairs. This could explain the decrease in the anomalous thermal expansion with an increase in Ga concentration.[3] The reduced magnitude of negative Fe(6*c*)–Fe(6*c*) exchange interaction may also play an important role in increasing T_C as a function of Ga concentration.

In conclusion, the saturation magnetization of $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta=0-2$) decreases with increasing of Ga

TABLE II. Structural and magnetic parameters for $Nd_2Fe_{17-\delta}Ga_\delta$ (δ=0,1.5,2) obtained from Fullprof (of experimental data obtained at 25 K) and GSAS (of experimental data obtained at 535 K) fits to the neutron diffraction data.

$Nd_2Fe_{17-\delta}$ G_δ	$\delta=0$	$\delta=1.5$	$\delta=2$	$\delta=0$	$\delta=1.5$	$\delta=2$
a (Å)	8.5729(3)	8.6091(7)	8.6197(7)	8.5970(3)	8.6375(3)	8.6535(3)
c (Å)	12.5051(4)	12.5441(6)	12.5580(4)	12.4618(4)	12.5430(4)	12.5757(4)
V (Å^3)	795.9	805.2	808.0	797.4	810.4	815.5
(Nd) $6c,z$	0.3429(4)	0.3418(4)	0.3418(4)	0.3423(4)	0.3418(4)	0.3421(4)
(Fe,X) $6c,z$	0.0966(3)	0.0957(3)	0.0954(3)	0.0963(3)	0.0960(3)	0.0957(3)
(Fe,X) $18f,x$	0.2905(2)	0.2892(2)	0.2887(2)	0.2870(2)	0.2871(2)	0.2866(2)
(Fe,X) $18h,x$	0.5016(1)	0.5022(1)	0.5025(1)	0.5023(1)	0.5028(1)	0.5031(1)
(Fe,X) $18h,z$	0.1575(2)	0.1569(2)	0.1565(2)	0.1550(2)	0.1552(2)	0.1552(2)
R factor %	3.13	3.59	3.48	3.89	3.98	4.21
R_m factor %	4.41	5.56	5.28	⋯	⋯	⋯
μ (Nd) $6c(\mu_B)$	2.71(12)	2.46(12)	2.67(11)	⋯	⋯	⋯
μ (Fe) $6c(\mu_B)$	2.81 (9)	2.33(9)	2.14 (9)	⋯	⋯	⋯
μ (Fe) $9d(\mu_B)$	1.62(8)	1.85(8)	1.86(9)	⋯	⋯	⋯
μ (Fe) $18f$ (μ_B)	2.09(8)	2.20(8)	2.20(8)	⋯	⋯	⋯
μ (Fe) $18h(\mu_B)$	1.98(8)	2.05(8)	1.94(9)	⋯	⋯	⋯
$M_s(\mu_B$/f.u.)	40.33(1.5)	37.50(1.5)	36.08(1.69)	⋯	⋯	⋯
T (K)	25	25	25	535	535	535

content. The magnetic moments of Fe($9d$), Fe($18f$), and Fe($18h$) do not change with Ga substitution while the magnetic moment of Fe($6c$) decreases from 2.81(9) μ_B in Nd_2Fe_{17} to 2.14(9) μ_B in $Nd_2Fe_{15}Ga_2$. This directly reduces the exchange interaction between Fe($6c$)–Fe($6c$) which could explain the decrease in the anomalous thermal expansion with an increase in Ga concentration in $Nd_2Fe_{17-\delta}Ga_\delta$ ($\delta=0-2$).

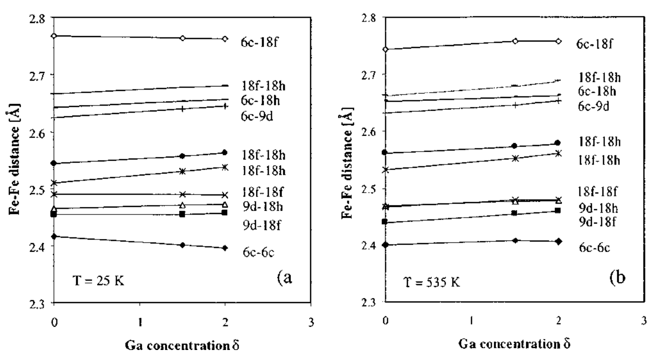

FIG. 2. Fe–Fe bond lengths in the Nd_2Fe_{17} unit cell at (a) 25 and (b) 535 K as a function of the Ga concentration.

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