Structural and magnetic properties of \( \text{Nd}_2\text{Fe}_ {17-\delta}\text{Ga}_\delta \) (\( \delta \leq 2 \))

E. Girt

Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720 and Department of Material Science and Mineral Engineering, University of California, Berkeley, California 94720

M. Guillot

Laboratoire des Champs Magnétiques Intenses, CNRS/MPI, 38042 Grenoble, France

I. P. Swainson

Neutron Program for Materials Research, Steacie Institute for Molecular Sciences, NRC, Chalk River, Ontario K0J 1P0, Canada

Kannan M. Krishnan

Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Z. Altounian

Department of Physics, Centre for the Physics of Materials, McGill University, 3600 University Street, Montréal, Québec, H3A 2T8, Canada

G. Thomas

Department of Material Science and Mineral Engineering, University of California, Berkeley, California 94720 and Material Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Magnetization measurements of \( \text{Nd}_2\text{Fe}_ {17-\delta}\text{Ga}_\delta \) (\( \delta = 0 - 2 \)) show that the saturation magnetization, \( M_s \), decreases with an increase in Ga content from 40.4 \( \mu_B/\text{f.u.} \) for \( \text{Nd}_2\text{Fe}_{17} \) to 36.1 \( \mu_B/\text{f.u.} \) for \( \text{Nd}_2\text{Fe}_{15}\text{Ga}_2 \) 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 \( \text{Fe}(6c) > \text{Fe}(18f) > \text{Fe}(18h) \geq \text{Fe}(9d) \). The magnetic moments of \( \text{Fe}(9d), \text{Fe}(18f), \) and \( \text{Fe}(18h) \) are found to be practically independent of the Ga content. However, the magnetic moment of \( \text{Fe}(6c) \) decreases from 2.81(9) \( \mu_B \) in \( \text{Nd}_2\text{Fe}_{17} \) to 2.14(9) \( \mu_B \) in \( \text{Nd}_2\text{Fe}_{15}\text{Ga}_2 \). The decrease of the \( \text{Fe}(6c) \) moment clearly reduces the exchange interaction between \( \text{Fe}(6c) - \text{Fe}(6c) \) dumbbell pairs which explains the decrease in the anomalous thermal expansion with an increase in Ga concentration. The reduced \( \text{Fe}(6c) - \text{Fe}(6c) \) 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 \( \text{Nd}_2\text{Fe}_{17} \) to 535 K in \( \text{Nd}_2\text{Fe}_{15}\text{Ga}_2 \).

INTRODUCTION

\( \text{R}_2\text{Fe}_{17} \) compounds crystallize in either the rhombohedral \( \text{Th}_2\text{Zn}_{17} \) or the hexagonal \( \text{Th}_2\text{Ni}_{17} \) 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 \( 6c-6c, 4f-4f \) (\( \sim 2.4 \) Å) and \( 9d-18f, 6g-12j \) (\( \sim 2.44 \) 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 \( \text{R}_2\text{Fe}_{17} \) compounds.\(^{1,2} \) The \( \text{Fe}(6c) - \text{Fe}(6c) \) interaction was also shown to cause an anomalous thermal expansion of the c axis in \( \text{Nd}_2\text{Fe}_{17} \) below \( T_C \).\(^{3} \) In order to improve the magnetic properties of \( \text{R}_2\text{Fe}_{17} \), Fe was partially substituted with transition or nontransition elements with an aim of expanding the \( \text{R}_2\text{Fe}_{17} \) 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 \( \text{R}_2\text{Fe}_{17} \) improve although Si does not expand \( \text{R}_2\text{Fe}_{17} \) 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 \( \text{R}_2\text{Fe}_{17} \) can be improved, \( T_C \) increases over 150 K for \( \text{R}_2\text{Fe}_{14}\text{Ga}_3 \).\(^{5} \) Moreover, \( \text{Sm}_2\text{Fe}_{17-\delta}\text{Ga}_\delta \) (\( \delta = 3 \)) exhibit uniaxial anisotropy.\(^{6} \) In \( \text{Nd}_2\text{Fe}_{17-\delta}\text{Ga}_\delta \) (\( \delta \leq 2 \)) \( \sim 80\% \) 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 \( \text{Nd}_2\text{Fe}_{17} \) along the c axis, which is caused by the \( \text{Fe}(6c) - \text{Fe}(6c) \) exchange interaction, decreases due to the presence of Ga in \( \text{Nd}_2\text{Fe}_{17-\delta}\text{Ga}_\delta \) (\( \delta \leq 2 \)).\(^{3} \) In order to understand the effect of Ga on the magnetic properties of \( \text{Nd}_2\text{Fe}_{17} \), the saturation magnetization of \( \text{Nd}_2\text{Fe}_{17-\delta}\text{Ga}_\delta \) (\( \delta = 2 \)) was measured. The results were then used to constrain the total magnetic moments obtained from neutron diffraction measurements of \( \text{Nd}_2\text{Fe}_{17-\delta}\text{Ga}_\delta \) (\( \delta = 2 \)), in order to obtain precise information on the Fe magnetic moments at different crystallographic sites.

\(^{a}\)Electronic mail: egirt@lbl.gov
TABLE I. Saturation magnetization and Curie temperatures of Nd$_2$Fe$_{17-\delta}$Ga$_\delta$ ($\delta=0$–2) in the temperature range from 4.2 to 300 K.  

<table>
<thead>
<tr>
<th>Nd$<em>2$Fe$</em>{17-\delta}$Ga$_\delta$</th>
<th>$\delta=0$</th>
<th>$\delta=0.5$</th>
<th>$\delta=1$</th>
<th>$\delta=1.5$</th>
<th>$\delta=2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_s$ (4.2 K) ($\mu_B$/f.u.)</td>
<td>40.4</td>
<td>39.8</td>
<td>38.9</td>
<td>37.5</td>
<td>36.1</td>
</tr>
<tr>
<td>$M_s$ (100 K) ($\mu_B$/f.u.)</td>
<td>39.2</td>
<td>39.1</td>
<td>38.0</td>
<td>34.8</td>
<td>...</td>
</tr>
<tr>
<td>$M_s$ (300 K) ($\mu_B$/f.u.)</td>
<td>35.9</td>
<td>35.4</td>
<td>...</td>
<td>32.0</td>
<td>...</td>
</tr>
<tr>
<td>$T_C$ (K)</td>
<td>327</td>
<td>380</td>
<td>432</td>
<td>484</td>
<td>535</td>
</tr>
</tbody>
</table>

EXPERIMENTAL TECHNIQUES

The Nd$_2$Fe$_{17-\delta}$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$_2$Fe$_{17}$ to 535 K for Nd$_2$Fe$_{17}$Ga$_2$. The values of $T_C$ are listed at the bottom of Table I. Magnetization measurements of Nd$_2$Fe$_{17-\delta}$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 $\delta=2$ 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 4.2 to 770 K. Details can be found in an earlier report. 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$_2$Fe$_{17-\delta}$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, $M(H) = M_s (1 - H/H_C)$. Due to the increase of Ga content in Nd$_2$Fe$_{17}$, $M_s$ decreases from 40.4 $\mu_B$/f.u. for Nd$_2$Fe$_{17}$ to 36.1 $\mu_B$/f.u. for Nd$_2$Fe$_{17}$Ga$_2$, at 4.2 K. The value of $M_s$ for Nd$_2$Fe$_{17}$ is in good agreement with the value 39.6 $\mu_B$/f.u. determined for a single crystal. The sharp decrease in the value of $M_s$ for Nd$_2$Fe$_{17}$ 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$_2$Fe$_{15.5}$Ga$_1.5$ at 25 K are shown in Fig. 1. The refined structural and magnetic parameters of Nd$_2$Fe$_{17-\delta}$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 $\sim$80% of Ga atoms substitute for Fe in the 18f site and the rest of the Ga atoms substitute for Fe in the 18f site in Nd$_2$Fe$_{17}$. 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 $\mu_B$ 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$_2$Fe$_{17-\delta}$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) > Fe(18h) > Fe(9d). The presence of Ga in Nd$_2$Fe$_{17}$ does not change the magnetic moments of Fe(18f) and Fe(18h) and slightly increases the magnetic moment of Fe(9d). On the other hand, the magnetic moment of Fe(6c) decreases from 2.81(9) $\mu_B$ in Nd$_2$Fe$_{17}$ to 2.14(9) $\mu_B$ in Nd$_2$Fe$_{17}$Ga$_2$. The total magnetic moments per formula unit obtained for Nd$_2$Fe$_{17-\delta}$Ga$_\delta$ ($\delta=0$ and 2) are in good agreement with previous neutron diffraction results. However, the magnetic moment of Fe(6c) was found to be independent on the Ga concentration in Nd$_2$Fe$_{17}$.

The change in the volume of Nd$_2$Fe$_{17}$ was found to be $\sim$6 Å$^3$ per Ga atom below $T_C$, and $\sim$8 Å$^3$ per Ga atom above $T_C$. This is in good agreement with the observed $\sim$8 Å$^3$ increase in volume of Nd$_2$Fe$_{17}$ per Ga atom. Figure 2 presents the Fe–Fe bond lengths in Nd$_2$Fe$_{17-\delta}$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$_2$Fe$_{17-\delta}$Ga$_\delta$ except for Fe(6c)–Fe(6c) which decreases from 2.416(7) to 2.396(5) Å. Above $T_C$, the Fe–Fe bond lengths generally increase with an increase of Ga content. The anomalously large thermal expansion in Nd$_2$Fe$_{17}$ along the c axis was found to be due to the strong magnetic interaction between Fe(6c)–Fe(6c) pairs. Substitution of Ga for Fe in Nd$_2$Fe$_{17}$ decreases the Fe(6c) moment and clearly reduces the negative exchange interaction between Fe(6c)–Fe(6c) pairs. This could explain the decrease in the anomalous thermal expansion with an increase in Ga concentration. The reduced magnitude of negative Fe(6c)–Fe(6c) 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$_2$Fe$_{17-\delta}$Ga$_\delta$ ($\delta=0$–2) decreases with increasing of Ga...
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) $\mu_B$ in Nd$_2$Fe$_{17}$ to 2.14(9) $\mu_B$ in Nd$_2$Fe$_{17}$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$_2$Fe$_{17-}\delta$Ga$_\delta$ ($\delta=0$–2).

**ACKNOWLEDGMENTS**

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.