Influence of Co substitution on magnetoelastic properties of Nd$_6$Fe$_{13}$Cu compound

P. Iranmanesh$^1$, N. Tajabor$^{*1}$, M. Rezaee Roknabadi$^1$, D. Fruchart$^2$, F. Pourarian$^3$

$^1$ Department of Physics, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, 91775-1436, Iran.
$^2$ Institut Néel, Département MCMF, Group IICF, BP 166, 38042 Grenoble Cedex 9, France
$^3$ Department of Material Science & Engineering, Carnegie Mellon University, Pittsburgh, PA 15219, USA.

Abstract: In this research the magnetoelastic properties of Nd$_6$Fe$_{13-x}$Co$_x$Cu (x = 0 and 1) intermetallic compounds are investigated. Analysis of X-ray diffraction patterns indicates that a single phase is formed approximately for x = 0 and the x = 1 sample is multi-phase. The lattice parameters were decreased, the Néel temperature of main phase and the Curie temperature of impurity phase was increased with Co content. Due to the presence of Nd$_2$Fe$_{17-y}$Co$_y$ ferromagnetic phase in the sample with x = 1 the change of the anisotropy and increase of exchange effects was observed in the magnetic and magnetoelastic measurements. Thermal expansion, longitudinal ($\lambda_l$) and transverse ($\lambda_t$) magnetostriction were measured using the strain gauge method in the selected temperatures range of 80 - 500 K under applied magnetic fields up to 1.5 T. Anomaly and Invar effect are observed in the linear thermal expansion and $\alpha$(T) curves at the Néel temperature. The linear spontaneous magnetostriction decreases sharply by approaching the Néel temperature and also shows the short-range magnetic ordering effects when antiferromagnetic to paramagnetic transition occurs. In the low field region, the absolute values of anisotropic magnetostriction of Nd$_6$Fe$_{13}$Cu compound are small and then start to increase with applied magnetic field. Each isofield curve of the anisotropic magnetostriction passes through a minimum and then approaches to zero with increasing temperature. This magnetostriction compensation arises from the difference in the magnetoelastic coupling constants of the sublattices in this compound.

Keywords: Intermetallic compound, Nd$_6$Fe$_{13-x}$Co$_x$Cu, Magnetic properties, Magnetoelastic properties.

Introduction

The ternary intermetallic RE$_6$T$_{13}$M compounds (RE = light rare earth, T = Fe or Co, M = Cu, Ag, Au, Si, Ga, etc.) are found as second phase in the M doped RE-Fe-B permanent magnets with enhanced coercivity [1-4]. These compounds crystallize in the tetragonal Nd$_6$Fe$_{13}$Si or La$_6$Co$_{11}$Ga$_3$ structure with the I4/mcm space group. In this structure, the rare earth ions and M atom occupy R$_1$(8f), R$_3$(16l) and (4a) sites and Fe atoms located on the Fe$_7$(4d), Fe$_8$(16k), Fe$_8$(16l) and Fe$_8$(16l2) nonequivalent crystallographic sites [2-7]. In addition, they absorb a large amount of hydrogen without any change in their symmetry [5, 6]. Hence, they may provoke some interests in technological field and fundamental investigations. A complicated crystallographic structure and different competing interactions has induced great debates about their spin configuration and magnetic behaviour [8-12].

Nd$_6$Fe$_{13}$Cu compound with an antiferromagnetic structure and Néel temperature (T$_N$) of 419 K was reported before [10] but to our knowledge the substitution of Co for Fe has not been studied yet. The partial replacement of transition elements for Fe usually affects the effective interactions such as crystalline field and magnetic exchanges. Therefore, interesting

*Corresponding author, Telefax: +98 (0511) 8763647, Email: ntajabor@yahoo.com
phenomena are expected in the magnetic and the
magnetoelastic properties, though just a few
attentions have been paid to the former until now.

Experimental
Nd$_6$Fe$_{13}$Co$_x$Cu ($x = 0$ and 1) compounds were
prepared by arc melting of the pure elements
(99.9%) under purified Ar atmosphere. The
samples were remelted in a high-frequency
induction furnace equipped with a water-cooled
crucible. To assure the homogeneity, the ingots
were subsequently wrapped in a Ta foil, sealed in
an evacuated quartz lump, and annealed for 40
days at 550 °C [5].

The crystal structure of the samples was
determined by X-ray diffraction using Cu-κα
radiation. The analysis of XRD patterns were
carried out using Fullprof software and the weight
percentage of each phase in the samples was
deduced from the intensities of the Bragg’s peaks.

To determine the Curie temperature of samples, the
accurate thermomagnetic measurements were
performed on encapsulated free powder with
heating rate of 5 °C/min at a constant magnetic
field of 0.3 T. The accuracy of the temperature and
magnetisation measurements was 0.1 K and 1*10$^{-3}$
a.u. (Arbitrary unit), respectively. The
magnetisation measurements of compacted powder
were performed at the applied magnetic fields up
to 7 T by using a commercial extracting sample
magnetometer (ESM) in the temperature ranging
from 5 to 300 K.

Linear thermal expansion (LTE) and
magnetostriction measurements were performed on
a disc shape sample with 6 mm diameter and 2 mm
thickness, in a temperature ranging from 80 to 500
K in magnetic fields up to 1.5 T, using the strain
gauge method. No difference was observed
between the strains measured in the plane or
perpendicular to the plane (cooling direction after
the melt) of the disc of the annealed samples,
suggesting the absence of any preferred orientation
effects. The thermal expansion $\Delta l/l = [(l(T) - l(80K))/l(80K)]$ was deduced by
measuring the relative change of length of the
samples versus temperature. The magnetostriction
coefficients were measured (with the accuracy of
2×10$^{-6}$) parallel (longitudinal magnetostriction, $\lambda_l$)
and perpendicular (transverse magnetostriction, $\lambda_t$)
to the field direction, thus allowing to deduce the
anisotropic ($\Delta \lambda = \lambda_l - \lambda_t$) magnetostriction.

Results and Discussion

Structural analysis
Analysis of the XRD patterns of Nd$_6$Fe$_{13}$Co$_x$Cu ($x = 0$ and 1) samples shows that for $x = 0$ an
approximately single phase Nd$_6$Fe$_{13}$Cu compound
(containing ≤ 5 wt% Nd$_2$Fe$_{17}$ phase) with the
expected tetragonal structure (S.G. I4/mcm) is
formed. Upon Co substitution, the second phase
Nd$_2$Fe$_{17-y}$Co$_y$ with $0 < y < 1$ is formed in
the sample (Fig. 1). The data of the X-ray analysis are
given in Table 1, which show that the substitution
of Co for Fe causes the decrease of the lattice
parameters in each individual phase. This is
expected because of the smaller size of the cobalt
ions with respect to that of iron.

Fig. 1 The observed (circles) and calculated (solid lines) X-ray diffraction patterns of the Nd$_6$Fe$_{13}$Co$_x$Cu sample at room
temperature. The vertical bars indicate the position of Bragg reflections and the difference between the observed and
calculated intensities is given at the bottom of the diagram. The first and second rows of vertical lines refer to the
Nd$_6$Fe$_{13}$Co$_x$Cu and Nd$_3$Fe$_{17-y}$Co$_y$ contributions to diffraction patter.
Table 1. The lattice parameters and unit-cell volumes of Nd$_6$Fe$_{13-x}$Co$_x$Cu (x = 0 and 1) samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compound</th>
<th>wt%</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0</td>
<td>Nd$<em>6$Fe$</em>{13}$Cu</td>
<td>≈ 95</td>
<td>8.0962</td>
<td>22.2791</td>
<td>1460.360</td>
</tr>
<tr>
<td>x = 0</td>
<td>Nd$<em>3$Fe$</em>{17}$</td>
<td>≤ 5</td>
<td>8.5782</td>
<td>12.4611</td>
<td>794.108</td>
</tr>
<tr>
<td>x = 1</td>
<td>Nd$<em>6$Fe$</em>{13-y}$Co$_y$Cu</td>
<td>74</td>
<td>8.0957</td>
<td>22.2757</td>
<td>1459.963</td>
</tr>
<tr>
<td>x = 1</td>
<td>Nd$<em>3$Fe$</em>{17-y}$Co$_y$</td>
<td>26</td>
<td>8.5748</td>
<td>12.4573</td>
<td>793.234</td>
</tr>
</tbody>
</table>

**Magnetic properties**

The Curie temperature of the prepared samples with x = 0 and 1 which obtained from the second derivative of magnetisation versus temperature curves, are 325 and 403, respectively. It is believed that these observed Curie temperatures are due to the presence of the impurity phases of Nd$_3$Fe$_{17}$ and Nd$_3$Fe$_{17-y}$Co$_y$ (0 < y < 1) in the samples [13].

The temperature dependence of the magnetisation for x = 0 and 1 samples at selected fields are shown in Fig. 2. It can be seen that the magnetisation curves for x = 0 sample show a hill shape region in a temperature range depending on the strength of the magnetic field. The anomalously rise in magnetisation in the range from 30 to 150 K may attribute to a canting configuration of the moments of sublattices that causes enhancement of the resultant magnetisation. This behaviour is also reported for Pr$_6$Fe$_{13}$Sn compound [3].

![Graph](https://via.placeholder.com/150)

Fig. 2 Temperature dependence of the magnetisation of Nd$_6$Fe$_{13-x}$Co$_x$Cu (a) x = 0 and (b) x = 1 samples at different applied fields.
A low value of magnetisation (M < 8 μ₀/f.u.) at 300 K and 7 T for the sample with x = 0 confirms that the magnetic structure consists of at least two magnetic sublattices which are aligned antiparallel as depicted in Fig. 3. In the RE₆T₁₃M family of compounds, the short-range magnetic orders may originate from the Fe-Fe exchange interactions. These magnetic correlations usually are considered as primary step for expanding a macroscopically ordered magnetic phase over the volume of magnetic materials [16]. Considering structure of the studied compound in Fig. 3, the preliminary short-range magnetic orders can be originated from n_{FeFe} intralayer ferromagnetic exchange interaction. However, the long-range order starts by activation of the Fe (16l₂)-Nd (8f) interlayer planar ferromagnetic interaction (n_{RFe}), and will be completed by the antiferromagnetic arrangement of the blocks separated by the nonmagnetic M slabs. However, we know that the magnetisation curve of the sample with x = 1 represents the total magnetisation of Nd₆Fe₁₃Co₂Cu and Nd₆Fe₁₇Co₇ phases. At low fields, the sample behaves as a ferromagnetic system due to the magnetisation of the Nd₆Fe₁₇-based compound, and then as the magnetic field increases the magnetisation of Nd₆Fe₁₃Cu-based compound also contributes to the total magnetisation.

**Magnetoelastic properties**

Fig. 4 shows linear thermal expansion, Δl/l(T), of samples with x = 0 and 1, as well as the LTE coefficient, α(T) = d/dT[Δl/l(T)], deduced from the slope of the experimental curve of the linear thermal expansion at selected temperatures. The Néel temperatures are indicated by the arrows. It can be seen that, both Δl/l(T) and α(T) curves show anomaly and Invar effect by approaching T_N. The linear thermal expansion coefficient curve beyond the magnetic ordering temperature in the paramagnetic region is almost linear. The observed Néel temperature of Nd₆Fe₁₃Cu is approximately 421 K that is in agreement to the reported value [10]. In Fig. 4(b) for sample with x = 1, there are two anomalies in the linear thermal expansion coefficient curve, the first minimum is about 403 K and the second one is about 452 K. We believe that the first anomaly belongs to the Curie temperature of Nd₆Fe₁₇Co₂ and the second one may refers to the Néel temperature of the Nd₆Fe₁₃Co₂Cu compound.

Below the magnetic ordering temperature, the measured linear thermal expansion (Δl/l(T)) of the magnetic materials is the combination of lattice (Δl/l(T))_{lat} and magnetic (Δl/l(T))_{m} contributions. In order to calculate the lattice contribution, the measured thermal expansion in the paramagnetic region has been fitted using Grüneisen–Debye model with Debye temperature T_D = 314 K [15]. Therefore, the magnetic contribution or the so called linear spontaneous magnetostriction is the difference between experimental and the lattice thermal expansion (Δl/l(T))_{m} = (Δl/l(T))_{exp} − (Δl/l(T))_{lat}, which refers to the change of magnetic energy due to the temperature dependence of the crystallographic unit cell volume. The obtained linear spontaneous magnetostriction for samples with x = 0 and 1 is presented in Fig. 5. Considering the schematic representation of collinear antiferromagnetic structure of Nd₆Fe₁₃Cu compound in Fig. 3, the linear spontaneous magnetostriction of this compound below T_N = 421 K can be attributed to the gradual occurrence of the long-range ordering of the magnetic moments. The small value of linear spontaneous magnetostriction beyond the magnetic ordering temperature may arise from the short-range magnetic ordering that has been observed in several R-T intermetallic compounds [17].

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1- Bohr magneton per formula unit
Fig. 4 Experimental thermal expansion $\Delta l/l(T)$ and linear thermal expansion coefficient $\alpha(T)$ curve of of Nd$_6$Fe$_{13-x}$Co$_x$Cu $(a) \ x = 0$ and $(b) \ x = 1$ samples. The dash line exhibits calculated lattice contribution to the thermal expansion. The arrows indicate the Néel temperature.

Fig. 5 Temperature dependence of the linear spontaneous magnetostriction of Nd$_6$Fe$_{13-x}$Co$_x$Cu $(a) \ x = 0$ and $(b) \ x = 1$ samples. Arrows indicate the beginning of the paramagnetic behaviour.
The anisotropic magnetostriction ($\Delta \lambda$) curves as a function of applied magnetic field are shown in Fig. 6. It can be seen that at first in Fig. 6(a), the absolute value of $\Delta \lambda$ in the Nd$_6$Fe$_{13}$Cu compound is small and then increases with applied field at temperatures below 145 K. Saturation behaviour starts approximately from 200 K. This trend may be attributed to the temperature dependence of the magnetostriction constants behaviour.

The temperature dependence of the anisotropic magnetostriction at selected fields is also represented in Fig 7. All the curves of Nd$_6$Fe$_{13}$Cu compound in Fig. 7(a) have similar behaviour in whole temperature range; the absolute value of $\Delta \lambda$ first increases with temperature up to about 145 K and then decreases to zero at magnetostriction compensation point that occurs above the room temperature.

Pervious results on the R$_6$Fe$_{13}$M compounds show the existence of two rare earth sites with the opposite anisotropy. This means that these two sites have different easy directions (the 16l and 8f sites exhibit uniaxial and nearly planar anisotropy, respectively) [5, 18]. So, the magnetostrictive strain with different sign can be expected at these two Nd sites. It is also found that the compensation point and spin reorientation transition in Nd$_6$Fe$_{13}$Si compound coincide together [19]. Below $T_{SR}$, the overall spin arrangement of the Nd(8f) and Fe atoms is planar. From these experimental facts we can deduced the magnetostrictive strain sign of the two Nd sites and the Fe sublattice. The value of $\Delta \lambda$ in Nd$_6$Fe$_{13}$Si below $T_{SR}$ is negative. Since the anisotropy of the rare earth sublattice dominants at low temperatures, therefore the Nd(8f) site with planar anisotropy creates negative strain. Above $T_{SR}$ and at high temperatures, the Nd(16l) site and Fe sublattice with axial anisotropy have positive contribution to the $\Delta \lambda$ results.

Fig. 6 Isothermal curves of the anisotropic magnetostriction of Nd$_6$Fe$_{13-x}$CoxCu (a) $x = 0$ and (b) $x = 1$ samples as a function of applied field at selected temperatures.
By comparing the anisotropic magnetostriction results of Nd₆Fe₁₃Si with that of the Nd₆Fe₁₃Cu compound in Fig. 7(a), it can be concluded that by increasing the temperature the negative contribution of Nd (8f) site to $\Delta \lambda$ increases up to about 145 K, where $\Delta \lambda$ curves approach minimum. Then, as the temperature increases, the positive contribution of the Fe sublattice in magnetostriction compete more with negative contribution of Nd (8f) site. Finally, these two contributions compensate each other and the anisotropic magnetostriction goes to zero ($T_0 \approx 350$ K). Similar magnetostriction compensation behaviour has also been reported for Pr₆Fe₁₃Ga₃ [16]. After passing the compensation point, the positive value of Fe planar sublattice to $\Delta \lambda$ increases and dominates that of the Nd(8f) site. By approaching ordering temperature, $\Delta \lambda$ becomes zero.

$\Delta \lambda$ in Fig. 7(b) for sample with $x = 1$ follows the same trend as magnetisation curves in Fig. 2(b). Due to the presence of large amount of the second phase of Nd₆Fe₁₇Co₃ in the studied sample it is difficult to precisely analyze the above data.

**Conclusion**

Linear thermal expansion and magnetostriction behaviour of Nd₆Fe₁₃₋ₓCoxCu ($x = 0$ and 1) compounds are studied. From the analysis of XRD patterns and thermomagnetic results it can be concluded that by Co substitution, the lattice parameters of each individual phase are decreased with increase in $T_C$ and $T_N$. The magnetisation curve of the sample with $x = 0$ (Nd₆Fe₁₃Cu compound) shows a hill shape region and this may be attributed to the canting configuration of the magnetic moments of the sublattices. This canting configuration originates from the competition between the magnetic anisotropy and the thermal
energy that changes canting angle between the magnetic moments and the applied magnetic field. The magnetic behaviour of the sample with $x = 1$ at low fields may be dominated by the presence of the Nd$_2$Fe$_{17-y}$Co$_y$ phase. Well defined anomalies and Invar effect are observed in the linear thermal expansion and $\alpha(T)$ curves at the Néel temperature. The linear spontaneous magnetostriction decreases sharply by approaching the Néel temperature and also shows the short-range magnetic ordering effects when antiferromagnetic to paramagnetic transition occurs. In the sample with $x = 1$, there are two anomalies in the $\alpha$ curve, the first one is about 403 K which belongs to the Curie temperature of Nd$_2$Fe$_{17-y}$Co$_y$ compound and the second minimum is about 452 K which may refers to the Néel temperature of the Nd$_2$Fe$_{13-y}$Co$_y$Cu compound.

In the sample with $x = 0$, temperature dependence curves of anisotropic magnetostriction pass through a minimum at about 145 K and then go to zero at compensation temperature ($T_0 \approx 350$K). This behaviour shows that the anisotropy of the Nd and Fe sublattices with different sing compete with each other. In the sample with $x = 1$, due to the presence of large amount of the second phase of Nd$_2$Fe$_{13-y}$Co$_y$ in the studied sample it is difficult to precisely analyze the anisotropic magnetostriction behaviour.

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References