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Influence of Co substitution on magnetic properties and thermal expansion of Nd₆Fe₁₃Si intermetallic compound

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ABSTRACT

We studied the effect of Co substitution in Nd₆Fe_{13-x}Co_xSi (x = 0, 1) intermetallic compounds on the crystalline structure, magnetic properties and thermal expansion. The partial Co substitution reduces the lattice parameters of the tetragonal Nd₆Fe₁₃Si structure which enhance (3d–3d) exchange interaction and this causes an increase of the Néel temperature (T_N). The spin reorientation temperature (T_{SR}) of Nd₆Fe₁₂CoSi occurs at a higher temperature with respect to that of the Nd₆Fe₁₃Si compound. Both the linear thermal expansion coefficient $\alpha(T)$ show remarkable anomalies at T_{SR} and the magnetic ordering temperature (T_N). T_{SR} is associated with a shoulder in the linear thermal expansion and near T_N we observe invar-type of behaviour. Both effects are enhanced for the Co substituted sample, giving clear evidence for the enhanced exchange interactions.

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1. Introduction

Intermetallic compounds based on rare-earth (R) and transition (T) metals form a large group of materials which have found many applications and encouraged fundamental research. To improve the properties of the Nd₂Fe₁₄B compound several elements (M), such as Si, Al, Cu, Ga and etc, are added. The pronounced effect of these elements is to increase the coercivity of this compound by forming intergranular Nd₆Fe_{13-x}M_{1+x} phases [1–3].

The magnetic and structural properties of $R_6Fe_{13-x}M_{1+x}$ (R = light rare-earth, M = Si, Al, Cu, Ga ...) compounds and their hydrates that crystallize in the tetragonal Nd₆Fe₁₃Si or La₆Co₁₁Ga₃ structural type (with space group *I4/mcm*) have attracted the interest of many research groups [4–8]. The Nd₆Fe₁₃Si-type structure can be described as a multilayer structure in which the layers are perpendicular to the tetragonal *c*-axis. The layers with Fe atoms at 16*k*, 4*d*, 16*l*₁ and 16*l*₂ sites are separated by layers of rare-earth (8*f* and 16*l* sites) or layers of M (4*a* site) [9,10]. Because of competing intralayer and interlayer ordering mechanisms (3d–3d, 4f–3d and 4f–4f) and complicated magnetic anisotropy, these R₆Fe_{13-x}M_{1+x} intermetallic compounds show a diverse magnetic behaviour with various magnetic ordering schemes [11,12].

The compound $Nd_6Fe_{13}Si$ orders antiferromagnetically around 421 K [12]. A powder neutron diffraction study between 2 and

421 K [13] has shown collinear antiferromagnetic structures with a spin reorientation at about 100 K. Below 100 K, the Nd and Fe magnetic moments are found to be parallel within the basal plane, whereas, above this temperature, they are aligned parallel to the *c*-axis. The antiferromagnetic structure consists of ferromagnetic blocks, separated by Si layers. Thus Nd and Fe moments are coupled locally ferromagnetic and ferromagnetic moments in each block change their direction collectively when going to the next block separated by the Si layer. All moments in neighbouring blocks are aligned antiferromagnetically [13]. The powder neutron diffraction indicates also a large anisotropic change in the unit cell volume associated with a change in the magnetoelastic coupling at the first-order spin reorientation transition. In addition to the neutron diffraction, the Mössbauer spectral studies of Nd₆Fe₁₃Si between 80 and 295 K [13-15] also have shown spin reorientation at 100 K.

The measured magnetisation of $Nd_6Fe_{13}Si$ between 4.2 and 295 K in applied fields of zero to 23 T has shown three regions in the magnetic phase diagram [16]. Below 110 K, the magnetic moments are aligned parallel to the basal plane with two observed critical fields at which a gradual spin canting occurs. Above 160 K, the moments are aligned along the *c*-axis with only one critical field. Between 110 and 160 K, a complex intermediate or mixed magnetic phase with up to three critical fields is observed.

In this work, the influence of Co substitution on the lattice parameters, magnetic properties and thermal expansion of $Nd_6Fe_{13}Si$ especially at the spin reorientation temperature is investigated.





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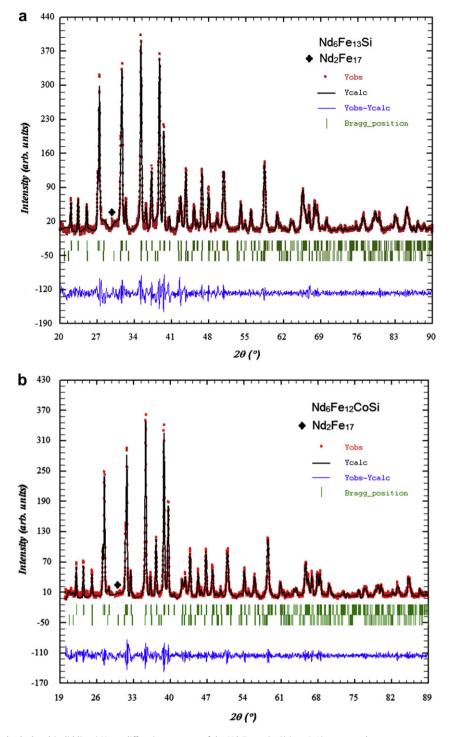


Fig. 1. The observed (circles) and calculated (solid lines) X-ray diffraction patterns of the $Nd_6Fe_{13-x}Co_xSi$ (x = 0, 1) compounds at room temperature. The vertical bars indicate the position of Bragg reflections and the difference between the observed and calculated intensities is given at the bottom of the diagram. The first and second rows of vertical lines refer to the $Nd_6Fe_{13-x}Co_xSi$ (x = 0, 1) and Nd_2Fe_{17} contribution to the diffraction pattern.

2. Experimental

Polycrystalline compounds with nominal stoichiometry of $Nd_6Fe_{13-x}Co_xSi$ (x = 0, 1) were prepared by arc melting of highpurity constituent elements in the purified argon atmosphere in a water-cooled copper crucible. In order to suppress the formation of 2:17 type compound as far as possible, an excess of about 2% of Nd was used. To ensure homogeneity of the ingot the buttons were flipped several times in between arc melting. For further homogenization, the ingots were wrapped in a Ta foil, sealed into an evacuated quartz tube and then annealed at 600 °C for 4 weeks. The samples subsequently were quenched to room temperature by dropping the quartz tube in a jar of water.

X-ray powder diffraction (XRD) experiments using monochromatic Cu-K α radiation ($\lambda = 1.5406$ Å) in the 2θ range of $20-90^{\circ}$ with a step width of 0.017° and Rietveld analysis was performed for the phase identification and also to determine the unit cell parameters of the studied samples. Microstructure and elemental composition of samples were also examined by a Leo 1450VP scanning electron microscope (SEM).

The ordering temperature (T_N) was determined from magnetisation measurements using a vibrating sample magnetometer (VSM) in a field of 1 T with a heating and cooling rate of 10 K/min. The low field magnetisation measurements were performed in the temperature range of 5–370 K by a commercial superconducting quantum interference device (SQUID) magnetometer to find possible spin reorientation (SR) occurring in the compounds. The transition temperatures (T_N and T_{SR}) have been taken at the maximum of the first derivative dM/dT. The field dependence of magnetisation was measured up to a field of 5 T at 5 and 300 K using the SOUID magnetometer.

Thermal expansion measurements were performed in temperatures ranging from 77 to 600 K using the strain gauge method. The samples for measurements were prepared in the form of a disc with 6 mm diameter and 2 mm thickness and the strain gauges were glued on their surface. The linear thermal expansion (LTE) $\Delta l/l(T) = [l(T) - l(77K)]/l(77K)$ was deduced by measuring the relative change of length of the sample versus temperature.

3. Results and discussion

3.1. Structural analysis

X-ray diffraction patterns and Rietveld analysis (Fig. 1) indicate that the Nd₆Fe_{13-x}Co_xSi (x = 0 and 1) samples are approximately single phase (with a small amount of Nd₂Fe₁₇ phase) with the expected tetragonal Nd₆Fe₁₃Si-type structure (S.G. *I4/mcm*), in good agreement with earlier reports on Nd₆Fe₁₃Si [12,13]. A sample with x = 2 was also prepared but not discussed here as it was found not to be single phase.

The refined lattice parameters and the unit cell volume, as calculated by Rietveld analysis, are given in Table 1. We find for both the lattice parameters a and c a decrease with the Co substitution while c/a is approximately constant. This may be attributed to the fact that the metallic radius of cobalt ($r_{Co} = 1.25$ Å) is slightly smaller than that of iron ($r_{\text{Fe}} = 1.26$ Å). The SEM microstructural analysis shows that the prepared samples contain mainly the $Nd_6Fe_{13-x}Co_xSi$ (x = 0 and 1) phase with minor Nd_2Fe_{17} impurity phase, in accordance with the XRD patterns of these samples.

3.2. Magnetic properties

Fig. 2 shows the temperature dependence of magnetisation of the Nd₆Fe_{13-x}Co_xSi (x = 0 and 1) compounds measured on bulk samples using VSM under a field of 1 T. Both compounds display cusp-shaped maxima, the same as those reported in other Nd₆Fe₁₃M compounds [12]. The corresponding Néel temperature which is derived from the above measurements is presented in Table 2. It can be seen that the ordering temperature (T_N) of Nd₆Fe₁₃Si is in agreement with the reported result [12]. A moderate increase in the magnetisation curve of Nd₆Fe₁₃Si compound below

Table 1 The lattice parameters and unit-cell volumes of $Nd_6Fe_{13-x}Co_xSi$ (x = 0, 1) compounds.

Nd ₆ Fe _{13-x} Co _x Si	a (Å)	b (Å)	c (Å)	$V(Å^3)$	c/a
x = 0	8.047(2)	8.047(2)	22.809(3)	1477	2.834
x = 1	8.038(3)	8.038(3)	22.776(2)	1472	2.833

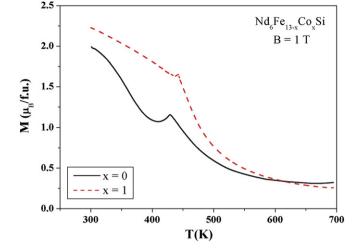


Fig. 2. The magnetisation curves of $Nd_6Fe_{13-x}Co_xSi$ (x = 0, 1) compounds versus temperature at applied field of 1 T using VSM.

340 K can be due to the presence of a small amount of $Nd_2Fe_{17-x}Si_x$ impurity phase [12–14,17].

The Néel temperature peak shifts to a higher temperature by partial replacement of Co for Fe. The ordering temperature is governed by the exchange interaction of sublattices (3d-3d, 4f-3d and 4f-4f) [12,18]. Therefore, the increase of T_N by Co substitution is expected because of enhancement of the 3d-3d exchange interaction due to the reduced cell parameters that causes the increase of exchange coupling constant. A similar shift in the ordering temperature due to the partial Co substitution in other compounds such as: HoFe_{11-x}Co_xTi [19], R₂Fe₁₀Co₄Si₂ [20] and Er₂Fe_{14-x}Co_xB [21] is also observed.

Above T_N , the magnetisation curves show a long tail that goes to zero slowly, the same as in R₆Fe₁₁Al₃ compounds [22,23]. This behaviour may be attributed to the long-range antiferromagnetic ordering that does not shift to the paramagnetic state immediately. But the antiferromagnetic ordering breaks into spin clusters for which the size decreases gradually until the paramagnetic state is reached.

To examine the spin reorientation temperature (T_{SR}) in Nd₆Fe₁₃ _xCo_xSi (x = 0 and 1) compounds, the temperature variation of magnetisation was measured on fine powder in the SQUID magnetometer under a field of 1 T from 5 To 370 K (Fig. 3). It can be seen that magnetisation increases with temperature until it reaches a maximum and then falls off. A similar behaviour is also observed for Pr₆Fe₁₃Sn in the applied field of 1 T [24]. The origin of this behaviour may be attributed to the competition of magnetic anisotropy and thermal energy that causes the change of canting angle between the magnetic moments and the applied field direction. At low temperatures, the anisotropy is so large that the applied field of 1 T is not high enough to affect the temperature dependence of the magnetisation. Below the spin reorientation temperature, all moments prefer basal plane anisotropy whereas above this temperature the easy

Table 2						
The spin reorientation	and	magnetic	ordering	temperatures	of	Nd ₆ Fe _{13-x} Co _x Si
(x = 0, 1) compounds.						

Nd ₆ Fe _{13-x} Co _x Si	T_{SR} (K) ^a	$T_{SR} \left(\mathbf{K} \right)^{\mathbf{b}}$	$T_N (\mathbf{K})^{\mathbf{a}}$	$T_N (\mathbf{K})^{\mathbf{b}}$
<i>x</i> = 0	105	105	426	423
x = 1	170	172	439	442

^a Obtained from magnetic measurements.

^b Obtained from thermal expansion measurements.

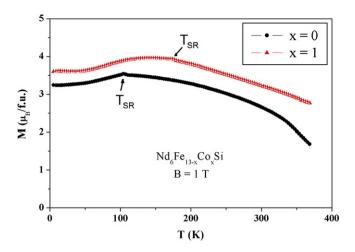


Fig. 3. The temperature dependence of the magnetisation of $Nd_6Fe_{13-x}Co_xSi$ (x = 0, 1) compounds at applied field of 1 T using SQUID magnetometer.

magnetisation direction of moments changes to the *c*-axis. Due to the minimum magnetic anisotropy at T_{SR} where the basal and axial anisotropies cancel each other, the magnetic moments can orientate easily in the presence of the applied field and a peak in magnetisation is observed. When the temperature increases above the spin reorientation temperature, the thermal energy of the magnetic moments causes the decrease of magnetisation thereby changing its behaviour.

In both $Nd_6Fe_{13}Si$ and $Nd_6Fe_{12}CoSi$ compounds, an anomaly due to the spin reorientation is observed at 105 K and 170 K, respectively. The spin reorientation temperature of $Nd_6Fe_{13}Si$ is well reproducing the reported value in the literature [13,14].

The spin reorientation is a result of competing anisotropies of the rare-earth and iron sublattices. At higher temperatures, the dominant iron anisotropy favours axial orientation of the magnetic moments. As the temperature decreases, the anisotropies of the two neodymium sites with opposite sign of anisotropy constants increase and, hence, virtually compensate each other. However, with further temperature decrease, the magnetic anisotropy is governed by the positive fourthorder crystal-field terms of the two neodymium sites which lead to change of magnetic anisotropy [16]. The substitution of Co for Fe gives rise to a substantial shift in SR towards higher temperatures. Therefore, the planar anisotropy dominates over a wider temperature region with Co substitution. In fact, Co atom together with Nd atoms prefers the planar anisotropy. This behaviour indicates that Co site occupation has a strong effect on the local anisotropy of Nd ions and induces a larger positive fourth-order crystal-field parameter. The increase of T_{SR} with Co substitution is also found in other intermetallic compounds such as: $R_2Fe_{14}Si_2$ (with R = heavy rare-earth element) [20].

The field dependence of magnetisation for Nd₆Fe_{13-x}Co_xSi (x = 0 and 1) compounds at temperatures of 5 and 300 K is shown in Fig. 4. There is a hysteresis in the magnetisation versus field behaviour at 5 K in the compounds. In antiferromagnetic heavy rare-earth iron compounds, there is a small hysteresis due to magnetocrystalline anisotropy. However, in light rare-earth iron compounds, the stronger magnetocrystalline anisotropy causes a larger hysteresis [12] as the one observed here. At 5 K, where the compounds have planar anisotropy, a larger hysteresis is observed in the magnetisation curve of Nd₆Fe₁₂CoSi, which indicates that Co substitution for Fe in Nd₆Fe₁₃Si may induce stronger anisotropy within the basal plane.

3.3. Thermal expansion

Linear thermal expansion, $\Delta l/l(T)$, of Nd₆Fe_{13-*x*}Co_{*x*}Si (*x* = 0 and 1) compounds, as well as the LTE coefficient, $\alpha(T) = d/dT[\Delta l/l(T)]$,

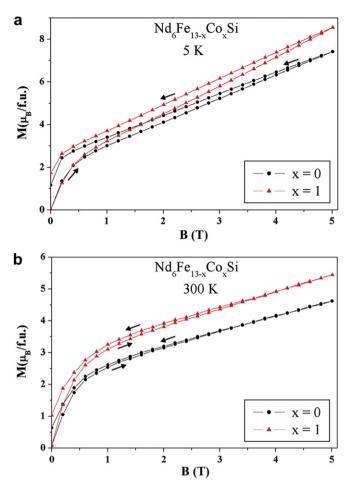


Fig. 4. The magnetisation curves of $Nd_6Fe_{13-x}Co_xSi$ (x = 0, 1) compounds versus applied field at 5 and 300 K temperatures.

deduced from the slope of the experimental curve of the linear thermal expansion at the selected temperatures is shown in Fig. 5. It can be seen that, for both compounds, the $\Delta l/l(T)$ and also $\alpha(T)$ curves display two clear anomalies. At low temperatures, a pronounced shoulder is observed at 105 and 172 K for x = 0 and 1 compounds, respectively, which can be attributed to the spin reorientation transition. The invar-type anomaly is exhibited by approaching T_N . Such an anomaly has been also observed in other compounds such as: RCo₅ and R₂Fe₁₇ [25], R₂Fe₁₄B [26], YFe_{11-x}Co_xTi [27] and R(Fe,Nb)₁₂ [28]. The linear thermal expansion coefficient curve beyond the magnetic ordering temperature in the paramagnetic region is almost linear. The observed Néel temperatures of Nd₆Fe₁₃Si and Nd₆Fe₁₂CoSi compounds are 423 K and 442, respectively (Table 2), which are very close to the values obtained from the magnetic measurements.

Below the magnetic ordering temperature, the measured linear thermal expansion $(\Delta l/l(T))_{exp}$ of the magnetic materials is the combination of lattice $(\Delta l/l(T))_{latt}$ and magnetic $(\Delta l/l(T))_m$ contributions. In order to calculate the lattice contribution, the measured thermal expansion in the paramagnetic region has been fitted using the Grüneisen–Debye model with Debye temperature of $T_D = 368$ K [14], (the dashed line in Fig. 5). Therefore, the magnetic contribution or the so-called linear spontaneous magnetostriction is the difference between experimental and the lattice thermal expansions $(\Delta l/l(T))_m = (\Delta l/l(T))_{exp} - (\Delta l/l(T))_{latt}$; which refers to the change of magnetic energy due to the temperature dependence of the crystallographic unit cell volume. Assuming that the linear

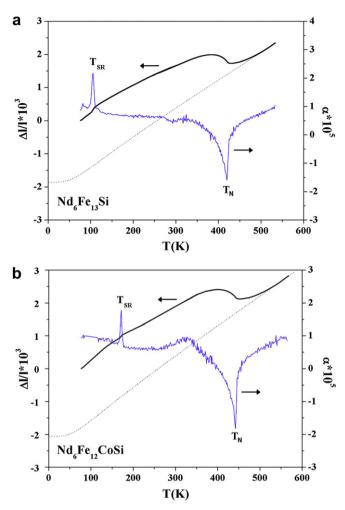


Fig. 5. Experimental thermal expansion $\Delta l/l(T)$ and linear thermal expansion coefficient $\alpha(T)$ curves of Nd₆Fe_{13-x}Co_xSi (x = 0 and 1) compounds. The dashed line exhibits the calculated lattice contribution to the linear thermal expansion.

thermal expansion $\Delta l/l(T)$ is isotropic, the obtained spontaneous volume magnetostriction, $\omega_s = 3(\Delta l/l(T))_m$, of compounds is presented in Fig. 6.

A positive spontaneous volume magnetostriction (ω_s) exists below T_N in both compounds and it is well seen from $\Delta l/l(T)$ and

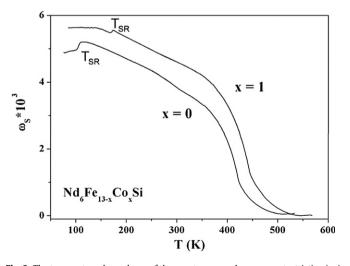


Fig. 6. The temperature dependence of the spontaneous volume magnetostriction (ω_s) of Nd₆Fe_{13-x}Co_xSi (x = 0 and 1) compounds.

also $\alpha(T)$ curves, that ω_s displays an anomaly around zero-field spin reorientation transition. A nearly zero value of spontaneous volume magnetostriction is observed above the magnetic ordering temperature which may arise from the short-range magnetic ordering that has been observed in several R-T intermetallic compounds [25–27].

The neutron diffraction study of Nd₆Fe₁₃Si [13] shows a significant change in the lattice parameters at the spin reorientation temperature of the magnetic moments. The first-order spin reorientation is accompanied by large magnetostriction strains. The significant change of lattice parameters at zero-field T_{SR} corresponds to an anomaly in the temperature dependence of the spontaneous volume magnetostriction. The reported neutron diffraction result also shows that the neodymium magnetic moments are much more sensitive to the temperature changes than the iron magnetic moments. Upon cooling, a substantial increase of Nd moments is observed near the spin reorientation temperature, whereas, the iron moments have a smooth temperature variation. So, the anomaly of ω_s at the spin reorientation is due to a significant change of the magnetic moments of the rareearth sublattice at this temperature. The Co substitution leads to the increase of ω_s due to the variation of exchange interactions which also cause the increase of T_N .

4. Conclusion

The influence of Co substitution for Fe in the Nd₆Fe₁₃Si compound on lattice parameters, ordering temperature, spin reorientation temperature and spontaneous volume magnetostriction has been investigated. The partial Co substitution causes the decrease of lattice parameters as well as the increase of the Néel temperature. The enhancement of T_N is due to the increase of the 3d-3d exchange interactions. The shifting of the spin reorientation towards higher temperatures (105 K for Nd₆Fe₁₃Si and 170 K for Nd₆Fe₁₂CoSi) by Co substitution is discussed in terms of the strong effect of Co on the local anisotropy of Nd which modifies the overall anisotropy of the compound. A well defined anomaly at T_{SR} and invar effect at the Néel temperature are observed in the linear thermal expansion and $\alpha(T)$ curves. A considerable change of the lattice parameters corresponds to the variation of the spontaneous volume magnetostriction at the zero-field spin reorientation temperature due to the significant change of the Nd magnetic moments at this point. The observed increase in spontaneous volume magnetostriction with partial Co substitution is explained by the enhanced exchange interactions which also cause a shift in T_N towards a higher temperature.

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