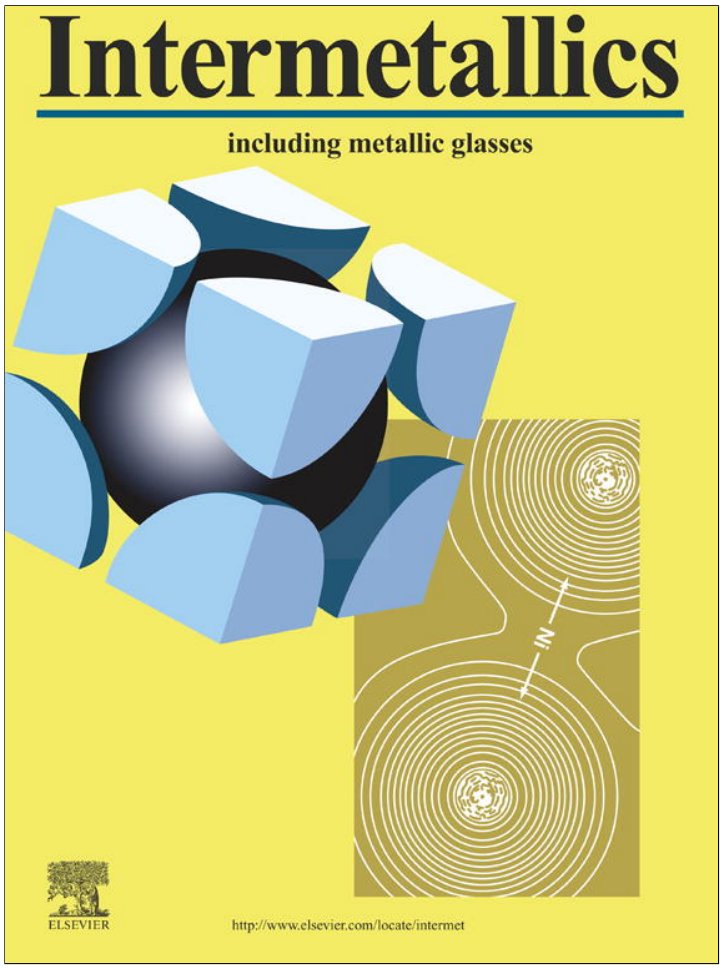

Intermetallics 42 (2013) 180–183

Contents lists available at SciVerse ScienceDirect

Intermetallics

journal homepage: www.elsevier.com/locate/intermet

Magnetostriction effect of Co substitution in the $Nd_6Fe_{13}Si$ intermetallic compound

P. Iranmanesh [a,b,*], N. Tajabor [b], F. Pourarian [c]

[a] Department of Physics, Vali-e-Asr University of Rafsanjan, 77139-36417 Rafsanjan, Iran
[b] Department of Physics, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad 91775-1436, Iran
[c] Department of Material Science & Engineering, Carnegie Mellon University, Pittsburgh, PA 15219, USA

ARTICLE INFO

Article history:
Received 29 January 2013
Received in revised form
15 June 2013
Accepted 19 June 2013
Available online

Keywords:
A. Magnetic intermetallics
B. Magnetic properties
B. Elastic properties

ABSTRACT

We studied the magnetostriction of $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) intermetallic compounds with tetragonal $Nd_6Fe_{13}Si$-type structure, using the strain gauge method in the temperature range of 77–600 K under applied magnetic fields up to 1.5 T. The anisotropic magnetostriction ($\Delta\lambda$) versus temperature of the studied samples has shown almost similar field-dependence behavior. Below the spin reorientation temperature (T_{SR}), $\Delta\lambda$ changes its sign from positive to negative value at an applied threshold field which increases with decreasing temperature. This behavior may originate from the reduction of the magnetocrystalline anisotropy with temperature. It is also observed that absolute value of $\Delta\lambda$ increases by Co substitution. On the other hand, the volume magnetostriction ($\Delta V/V$) versus field shows different behavior. The $\Delta V/V$ curves of $Nd_6Fe_{12}CoSi$ tend to have a nearly quadratic dependence on applied field near magnetic ordering temperature as expected for the parastrictive behavior. The temperature dependence of magnetostriction values is discussed based on the magnetostriction relation of the tetragonal structure to determine the signs of some of magnetostriction constants for these polycrystalline compounds.

1. Introduction

The ternary intermetallic compounds of $Nd_6Fe_{13}Si$-type $R_6Fe_{13}M$ (R = Nd, Pr and M = Si, Ag, Au, Cu,…) have been widely studied as secondary phase in the Nd–Fe–B permanent magnet that causes an increasing effect in the coercivity [1–3]. The crystallographic structure of tetragonal $Nd_6Fe_{13}Si$ (space group *I4/mcm*) contains only one Si site at 4*a*, while 8*f* and 16*l* sites for Nd and 4 nonequivalent (16*k*, 4*d*, $16l_1$ and $16l_2$) sites for Fe [4,5]. The structure of $R_6Fe_{13}M$ compounds in half of the unit cell can be described as layers of rare-earth, iron and metal stacked along the *c*-axis in the sequence of M-R(16*l*)-R(8*f*)-Fe($16l_2$)-Fe($16l_1$)-Fe(4*d*,16*k*)-Fe($16l_1$)-Fe($16l_2$)-R(8*f*)-R(16*l*)-M [6–9]. These intermetallic compounds have attracted considerable attention because of the outstanding variety of magnetic interactions originating from complex interplay between the different exchange interactions (3d–3d, 4f–3d and 4f–4f) as well as competing magnetocrystalline anisotropies of the two rare-earth sites [10,11].

$Nd_6Fe_{13}Si$ compound is found to be antiferromagnetic below 420–430 K [11,12]. Various studies of this compound such as Mössbauer spectroscopy in the temperature range of 80–295 K [13,14], the powder neutron diffraction in the temperature range of 2–421 K [15] and high field magnetization between 4.2 and 295 K in applied fields up to 23 T [16] exhibit a collinear antiferromagnetic structure with an observed spin reorientation at about 100 K. This means that below 100 K, the alignment of Nd and Fe magnetic moments are in the basal plane whereas, by increasing temperature, they prefer to align along the *c*-axis.

In the pervious investigation, we studied the effect of Co substitution for Fe on the structure, magnetic properties and thermal expansion of $Nd_6Fe_{13}Si$ [12]. It is found that lattice parameters decrease and the Néel temperature (T_N) increases due to the increase of 3d–3d exchange interaction. The spin reorientation (*SR*) also shifts to higher temperature with Co substitution. This may arise due to the strong effect of Co on the local anisotropy of Nd atoms. Both linear thermal expansion and linear thermal expansion coefficient $\alpha(T)$ of the studied compounds show a remarkable anomaly at T_{SR} and invar behavior near T_N. However, it is interesting to study the influence of Co substitution on the magnetostrictive properties especially at the vicinity of spin reorientation temperature, so, the magnetoelastic properties of $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) compounds are investigated in this work.

* Corresponding author. Department of Physics, Vali-e-Asr University of Rafsanjan, 77139-36417 Rafsanjan, Iran. Tel.: +98 915 511 7584; fax: +98 391 320 2429.
E-mail addresses: p.iranmanesh@vru.ac.ir, p.iranmanesh@gmail.com (P. Iranmanesh).

0966-9795/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.intermet.2013.06.004

2. Experimental

The starting polycrystalline compounds with nominal stoichiometry $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) were prepared by arc melting of high-purity 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 amount of about 2% of Nd was used. To obtain single phase samples, the ingots were turned over and melted again several times. After arc melting the ingots wrapped in the tantalum foil, sealed into evacuated quartz tube, then annealed at temperature of 600 °C for 4 weeks and subsequently quenched to room temperature by immersing the quartz tube in a water vessel.

X-ray powder diffraction (XRD) experiments using monochromatic Cu-Kα radiation ($\lambda = 1.5406$ Å) in the 2θ range of 20–90° with a step width of 0.017° were performed. For phase identification and structural characterization, the analysis of XRD profiles of samples was performed using the Fullprof software, which is based on Rietveld method. Microstructure and elemental composition of samples were also checked by scanning electron microscopy (SEM). Both XRD and SEM microstructural analysis revealed the formation of single phase $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) samples [12].

Magnetostriction measurements were performed in magnetic fields up to 1.5 T and temperature ranging from 77 to 600 K using the strain gauge Wheatstone bridge technique on disc-shaped samples with 6 mm diameter and 2 mm thickness. The magnetostriction of the samples was measured (with an accuracy of 2×10^{-6}) parallel (longitudinal magnetostriction, λ_l) and perpendicular (transverse magnetostriction, λ_t) to the applied magnetic field direction. The anisotropic magnetostriction ($\Delta\lambda$) and volume magnetostriction ($\Delta V/V$) were deduced from the relations of $\Delta\lambda = \lambda_l - \lambda_t$ and $\Delta V/V = \lambda_l + 2\lambda_t$, respectively.

3. Results and discussion

Fig. 1 shows the field dependence of anisotropic magnetostriction ($\Delta\lambda$) of $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) samples at some selected temperatures. It can be seen that $\Delta\lambda$ shows different behaviors at different ranges of applied fields and temperatures. The behavior of $\Delta\lambda$ curves versus the applied magnetic field below the spin reorientation temperature (T_{SR}) of about 105 and 172 K for $Nd_6Fe_{13}Si$ and $Nd_6Fe_{12}CoSi$ compounds, respectively, is completely different from the other curves. The $\Delta\lambda$ curves at temperatures below T_{SR} show a sign change from positive to negative at some threshold filed ($\mu_oH < 0.8$ T at 77 K), which increases with decreasing temperature. This behavior may be originated from the reduction of magnetocrystalline anisotropy with temperature. In other hand, at low temperature where the anisotropy is large, a larger applied field is needed to overcome the magnetic anisotropy. Beyond the spin reorientation temperature, $\Delta\lambda$ values are small; this may be attributed to the reduction of the magnetization with increasing temperature as seen in the magnetization measurements [12].

The temperature dependence of anisotropic magnetostriction ($\Delta\lambda$) for $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) compounds at some typical selected fields is shown in Fig. 2. It is clear that the two compounds show almost similar field-dependence behaviors in whole temperature range. Meanwhile, the absolute values of $\Delta\lambda$ increase by Co substitution for Fe in $Nd_6Fe_{13}Si$ (Fig. 2(b)) especially below T_{SR}. The absolute values of $\Delta\lambda$ decrease with increasing temperature up to T_{SR} and then the rate of decreasing reduces and $\Delta\lambda$ goes toward zero. The $\Delta\lambda$ curves of $Nd_6Fe_{13}Si$ (Fig. 2(a)) show a compensation point (T_0) at about 380 K. This behavior may be due to the magnetostriction compensation of the two Nd and Fe sublattices contributing in the magnetostriction effect. The values of $\Delta\lambda$ at temperatures above T_0 where the iron anisotropy is dominant

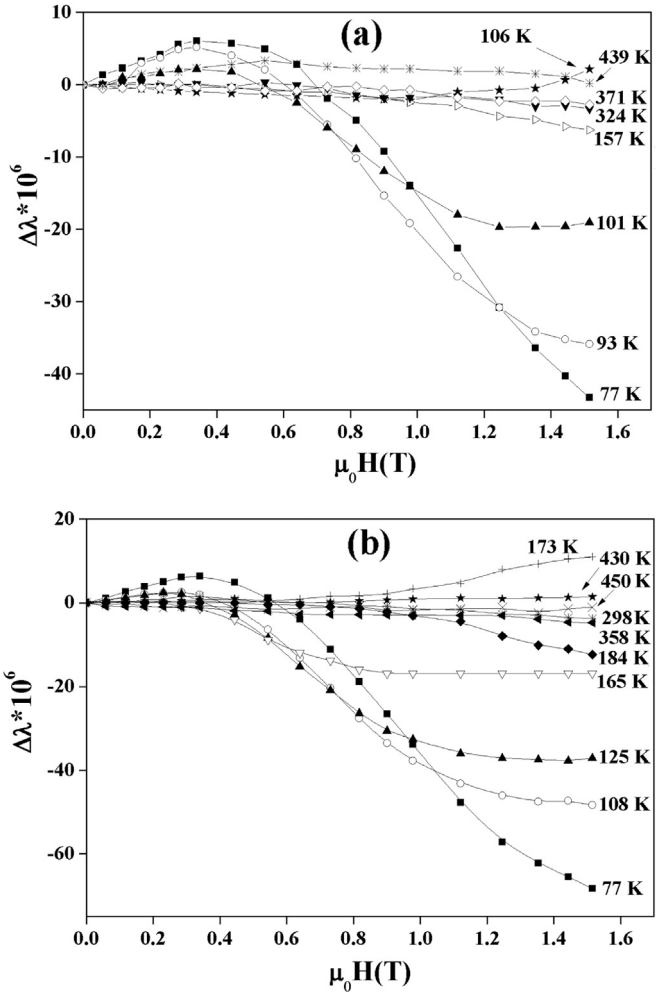

Fig. 1. Field dependence of anisotropic magnetostriction ($\Delta\lambda$) of $Nd_6Fe_{13-x}Co_xSi$ samples with (a) $x = 0$ and (b) $x = 1$ at some selected temperatures.

[16] are positive. This may indicate that the magnetostriction may also arise from the low anisotropy of iron sublattice and so, it can be concluded that the sign of the anisotropy of Fe sublattice is positive.

For further discussion, we use the standard model of magnetostriction for systems with axial symmetry that presents different crystal electric field (CEF) contributions of any orders [17]

$$\lambda_{CEF}(T) = \lambda_2(0)m_{RE}^3 + \lambda_4(0)m_{RE}^{10} + \lambda_6(0)m_{RE}^{21} \quad (1)$$

here m_{RE} is the reduced rare-earth sublattice magnetization. Neutron diffraction results show that at higher temperatures, the dominant iron anisotropy favors axial orientation of the magnetic moments. As the temperature decreases, the anisotropy of the two neodymium sites with opposite sign anisotropy constants increases and, hence, virtually compensates each other. However, with further temperature decrease, the magnetic anisotropy is governed by the positive fourth-order crystal-field terms of the two neodymium sites which lead to change of magnetic anisotropy [16]. Therefore, using these results it can be concluded that in addition to the second order crystal field term, the forth order one is important below the spin reorientation temperature. So, the rare-earth sublattice magnetization becomes larger in this temperature range and causes the observed increase in the absolute value of $\Delta\lambda$ by further decreasing temperature from T_{SR}. In this low temperature and weak applied field region, the present compounds have easy plane anisotropy with high anisotropy field.

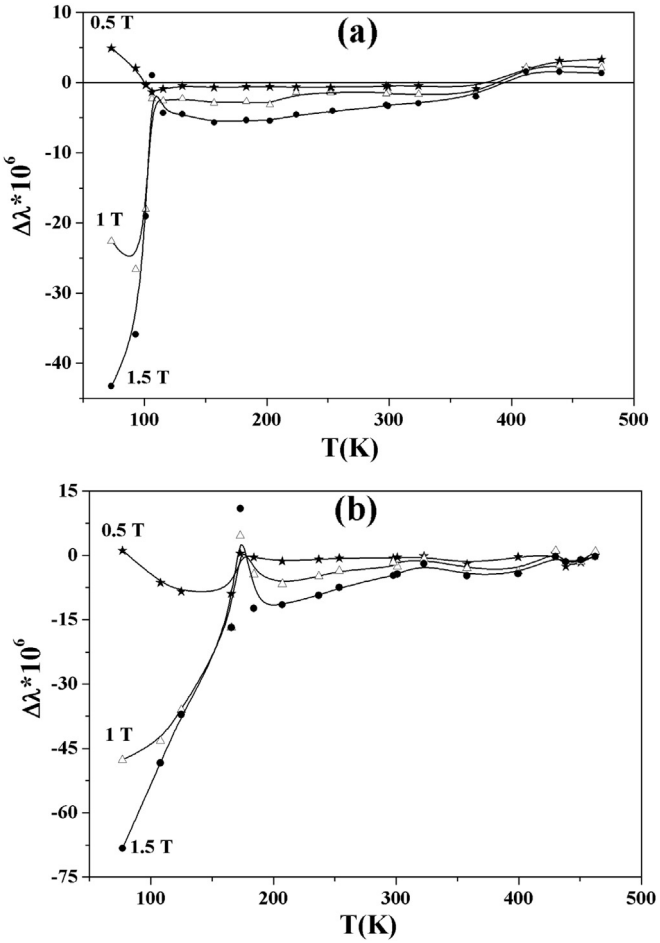

Fig. 2. Temperature dependence of anisotropic magnetostriction ($\Delta\lambda$) for $Nd_6Fe_{13-x}Co_xSi$ samples with (a) $x = 0$ and (b) $x = 1$ at typical selected fields up to 1.5 T.

Now consider the relation of anisotropic magnetostriction for a polycrystalline material with axial symmetry (as the present compounds with tetragonal structure) in terms of irreducible magnetoelastic constants [18], calculated by averaging over all directions within a sphere [17],

$$\Delta\lambda = \frac{2}{15}\left(\sqrt{3}\lambda_{22}^{\alpha} + 3\lambda^{\gamma} + 2\lambda^{\varepsilon}\right) + \text{higher order termes} \qquad (2)$$

where λ_{22}^{α}, λ^{γ} and λ^{ε} denote the c/a ratio distortion for the fixed volume upon the magnetization rotation from the basal plane to the c-axis due the effect of applied magnetic field and temperature, the breaking of the cylindrical symmetry of the basal plane by magnetization rotation and the shear tilting of c-axis, respectively. It is said that for materials with the strong planar anisotropy under the action of weak magnetic fields in comparison with the anisotropy field of the sample, λ^{γ} is the dominant mode [19,20]. So, regarding the $\Delta\lambda$ results (Fig. 2), it can be deduced that, λ^{γ} being the dominant term in the low temperature and field conditions, is negative. As temperature increases above T_{SR}, the planar anisotropy field decreases and thus the axial anisotropy becomes more favorable and just the second-order crystal filed contributes in the anisotropy. Consequently, at higher temperatures, $\lambda_{22}^{\alpha} + \lambda^{\varepsilon}$ are positive and the dominant mode in $\Delta\lambda$. Therefore,λ_{22}^{α}, λ^{γ} and λ^{ε} with their different signs cause the decreasing of $\Delta\lambda$ and the occurrence of magnetostriction compensation in $Nd_6Fe_{13}Si$ compound. It is worth noting that in the $\Delta\lambda$ expression, the single-ion crystal field modes contribute in the anisotropic magnetostriction of polycrystalline and no exchange striction term (λ_{11}^{α} and λ_{12}^{α}) are present in $\Delta\lambda$.

The Co substitution for Fe in $Nd_6Fe_{13}Si$ increases the absolute values of $\Delta\lambda$. This behavior may be attributed to the enhancement of contribution of the rare-earth sublattice that induces the larger anisotropic magnetostriction in $Nd_6Fe_{12}CoSi$ compound.

As mentioned above, $Nd_6Fe_{13}Si$ is antiferromagnetic. According to the magnetic structure of this compound it is confirmed that there is two magnetic sublattices for Nd sites with opposite anisotropy. The Nd (16l) and Nd (8f) sites exhibit uniaxial and nearly planar anisotropies respectively. This means that these two sites have different easy directions. So the observed low anisotropic magnetostriction values (order of $\sim 10^{-6}$) for $Nd_6Fe_{13-x}Co_xSi$ in the magnetic ordering region may attribute to the effect of competing magnetoelastic coupling (strain reduction) of the two Nd sublattices. The magnetic strains due to the Fe sites (with low magnetic anisotropy) are considered to be low.

The field dependence of volume magnetostriction ($\Delta V/V$) of $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) samples at some selected temperatures is presented in Fig. 3. It is clear that the Co substitution causes the change of the volume magnetostriction behavior of these compounds. In $Nd_6Fe_{13}Si$ compound (Fig. 3(a)), apart from the different trends observed for different isotherms at low field region (below about 0.5 T), $\Delta V/V$ increases monotonically with the applied field. However, in $Nd_6Fe_{12}CoSi$ compound (Fig. 3(b)), below T_{SR} (172 K) $\Delta V/$

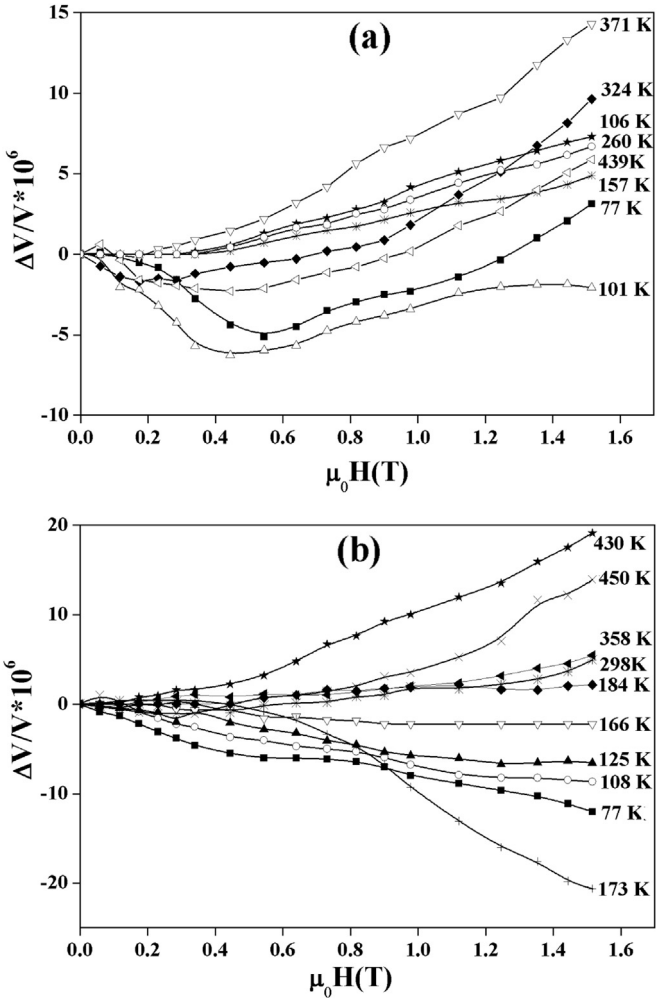

Fig. 3. Field dependence of volume magnetostriction ($\Delta V/V$) of $Nd_6Fe_{13-x}Co_xSi$ samples with (a) $x = 0$ and (b) $x = 1$ at some selected temperatures.

V decreases with increasing applied field and above this temperature the increasing behavior is observed. At T_{SR}, the volume magnetostriction of $Nd_6Fe_{13}Si$ compound has positive value, whereas, $\Delta V/V$ for $Nd_6Fe_{12}CoSi$ compound is negative indicating the different values of volume changes are related to the magnetostrictive coupling constants at these two compounds. The $\Delta V/V$ curves have nearly quadratic field-dependence near magnetic ordering temperature ($T_N = 426$ and 439 K for the compounds with $x = 0$ and 1, respectively [12]) as expected for the parastrictive behavior [21].

Fig. 4 shows the temperature dependence of volume magnetostriction ($\Delta V/V$) for $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) compounds at selected applied fields. It can be seen that apart from the anomalous behavior around the spin reorientation transition (at $T_{SR} = 105$ and 172 K for the samples with $x = 0$ and 1, respectively), $\Delta V/V$ isofield curves show an increasing trend in the whole ordered range. At the ordering region, it shows an anomalous and strongly field-dependent behavior once again up to about T_N where it shows rapid field dependence. The peak at T_{SR} which is accompanied by the considerable increase in unit-cell volume [14] can be originated from the decrease of magnetic anisotropy and the enhancement of magnetization induced by magnetic field at this temperature. The increase of volume magnetostriction beyond T_{SR} can be ascribed by the change of magnetic anisotropy which leads the rotation of magnetic moments from basal plane to tetragonal c-axis. The volume magnetostriction of these compounds has negative and positive values below and above T_{SR}, respectively, which indicates the volume expansion of these compounds is due to the change of magnetic anisotropy.

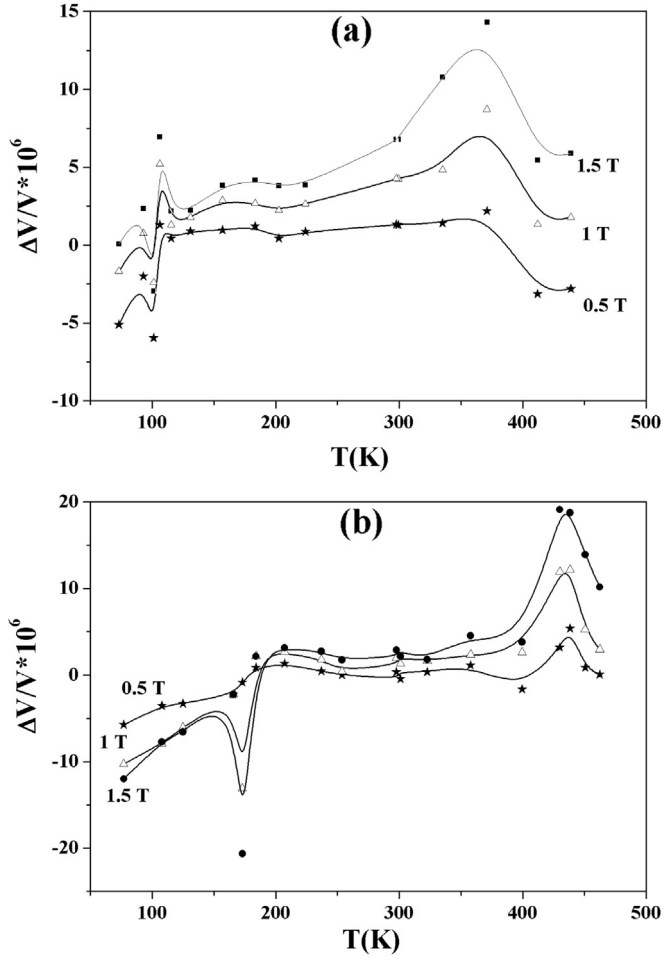

Fig. 4. Temperature dependence of volume magnetostriction ($\Delta V/V$) for $Nd_6Fe_{13-x}Co_xSi$ samples with (a) $x = 0$ and (b) $x = 1$ at typical selected fields up to 1.5 T.

For further discussion, one can describe the volume magnetostriction of these polycrystalline compounds in terms of the irreducible magnetoelastic coupling constants, the same as $\Delta\lambda$. In this way, the volume magnetostriction is in the form of $\Delta V/V = \lambda_{11}^{\alpha}$ [18], which is the uniform exchange striction mode. λ_{11}^{α} represents the volume changes that originate from two-ion isotropic exchange depending only on the magnitude of magnetization (or the applied magnetic field) and not its direction. It can be seen that the volume magnetostriction of $Nd_6Fe_{12}CoSi$ compound (Fig. 4(b)) is larger than in $Nd_6Fe_{13}Si$ (Fig. 4(a)) especially at the maximum applied field. As mentioned above, considering the $\Delta V/V$ expression, one can conclude that the increase of volume magnetostriction may arise from the volume dependence of the magnetic exchange interactions enhanced by Co substitution for Fe in $Nd_6Fe_{13}Si$ compound.

4. Conclusion

The magnetostriction of polycrystalline $Nd_6Fe_{13-x}Co_xSi$ ($x = 0, 1$) compounds were investigated. The study of anisotropic and volume magnetostriction has been performed in the temperature range of 77–600 K. The isofields of anisotropic and volume magnetostriction exhibit the drastic change of their behavior around T_{SR} that can be ascribed to the effect of weakness of the magnetocrystalline anisotropy above this temperature. The Co substitution for Fe in $Nd_6Fe_{13}Si$ increases the absolute values of magnetostriction especially below the spin reorientation temperature, which may be attributed to the enhancement of the contribution of the rare-earth sublattice. The experimental results of the temperature dependence of the magnetostriction were discussed in the framework of the magnetostriction relation of tetragonal structure to determine the signs of some of magnetostriction constants for these compounds.

References

[1] Weitzer F, Leithe-Jasper A, Rogl P, Hiebl K, Noël H, Wiesinger G, et al. J Solid State Chem 1993;104:368–76.
[2] Leithe-Jasper A, Rogl P, Wiesinger G, Rainbacher A, Hatzl R, Forst huber M. J Magn Magn Mater 1997;170:189–200.
[3] de Groot CH, de Kort Kees. J Appl Phys 1999;85:8312–6.
[4] Bessais L, Djega-Mariadassou C, Ky VH, Phuc NX. J Alloys and Comp 2006;426:22–5.
[5] Allemand J, Letant A, Morea JM, Nozieres JP, Perrier De La Bathie R. J Less-Common Met 1990;I66:73–9.
[6] Schobinger-Papamantellos P, Buschow KHJ, de Groot CH, de Boer FR, Böttger Grit, Ritter C. J Phys Condens Matter 1999;11:4469–81.
[7] Wang Jing-yun, Wang Fang-wei, Shen Bao-gen, Yan Qi-wei, Zhan Wen-shan, Lin Chin. J Appl Phys 1999;85:4690–2.
[8] Wang Fang-Wei, Zhang Pan-Lin, Shen Bao-Gen, Yan Qi-Wei. Chin Phys Soc 2004;13:918–23.
[9] Benbow Evan M, Dalal Naresh S, Latturner Susan E. J Solid State Chem 2009;182:3055.
[10] Schobinger-Papamantellosa P, Ritterb C, Buschow KHJ. J Alloy Compd 2003;260:156–72.
[11] de Groot CH, Buschow KHJ, Boer FR. Phys Rev B 1998;57:11472–82.
[12] Iranmanesh P, Tajabor N, Rezaee Roknabadi M, Pourarian F, Brück E. Intermetallics 2011;19:682–7.
[13] Hautot Dimitri, Long Gary J, Grandjean F, de Groot CH, Buschow KHJ. J Appl Phys 1998;83:1554–62.
[14] Hautot Dimitri, Long Gary J, Grandjean F, de Groot CH, Buschow KHJ. J Appl Phys 1997;81:5435–7.
[15] Isnard Olivier, Long Gary J, Hautot Dimitri, Buschow KHJ, Grandjean Fernande. J Phys Condens Matter 2002;14:12391–409.
[16] Grandjean F, Lon GJ, Guillo M, Isnard O, Buschow KHJ. Phys Condens Matter 2004;16:4347–55.
[17] Algarabel PA, Del Moral A, Ibarra MR, Marquina C. J Magn Magn Mater 1992;114:161–75.
[18] Callen ER, Callen HB. Phys Rev A 1965;129:455–71.
[19] Garcia-Landa B, Ibarra MR, Algarabel PA, Kayzel FE, Anh TH, Franse JJM. Phys B 1992;177:227–32.
[20] Garcia-Landa B, Algarabel PA, Ibarra MR, Kayzel FE, Anh TH, Franse JJM. J Appl Phys 1993;73:6147–9.
[21] Sanavi Khoshnoud D, Tajabor N, Pourarian F, Salamatia H. J Magn Magn Mater 2009;321:3847–53.