ELSEVIER

Journal of Alloys and Compounds 229 (1995) 257–261

Journal of ALLOYS AND COMPOUNDS

Effects of Si substitution on the magnetic properties of R_2Fe_{17} compounds with $R \equiv Y$ and Tm

Bao-gen Shen, Hua-yang Gong, Bing Liang, Zhao-hua Cheng, Jun-xian Zhang

State Key Laboratory of Magnetism, Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing 100080, People's Republic of China

Received 3 May 1995

Abstract

X-Ray diffraction of $R_2Fe_{17-x}Si_x$ ($R \equiv Y$ and Tm) shows that the prepared samples are single phase, having the rhombohedral Th_2Zn_{17}-type structure and/or the hexagonal Th_2Ni_{17}-type structure. The substitution of Si for Fe in R_2Fe_{17} ($R \equiv Y$ and Tm) leads to a strong increase in the Curie temperature and a reduction in the unit cell volume. The Fe moments derived from $Y_2Fe_{17-x}Si_x$ decrease with increasing Si concentration from 2.0 μ_B for $x = 0$ to 1.73 μ_B for $x = 3$ as a result of magnetic dilution. The Tm moment is 6.0 ± 0.3 μ_B, which is slightly lower than its free ion value. Samples of $Tm_2Fe_{17-x}Si_x$ with $x = 0$–3 have a spin reorientation transition at low temperature. The spin reorientation temperature increases initially, then decreases with Si substitution, having a maximum value of 187.5 K at about $x = 2$.

Keywords: Rare-earth iron compounds; Silicon substitution; Magnetic properties

1. Introduction

Rare earth–iron compounds with the Th_2Ni_{17}- or Th_2Zn_{17}-type structure have high saturation magnetization. The relatively low Curie temperature and the planar magnetocrystalline anisotropy at room temperature make them unattractive for application as permanent magnet materials. The most effective way of increasing T_C of R_2Fe_{17} and modifying its anisotropy is to use interstitial or substitutional additions. Recent attention has been focused on the effect of substitution of Ga, Al and Si for Fe on the magnetic properties of R_2Fe_{17}. Substitution of low concentrations of Ga and Al in R_2Fe_{17} compounds leads to an increase in the Curie temperature and is accompanied by a linear increase in the unit cell volume [1–6]. Some studies on the magnetic properties of $R_2Fe_{17-x}Si_x$ compounds have shown that the Curie temperature of these materials increases with increasing Si concentration, whereas the unit cell volume decreases [7–15]. This surprising property seems to be related to the preferential occupation of Si atoms. Neutron diffraction studies have shown that Si atoms preferentially occupy the 4f site for $Y_2Fe_{14}Si_3$ [10]; however, Si atoms were found to prefer the 18h site for $Nd_2Fe_{13}Si_4$ [11]. A recent Mössbauer effect study on $Sm_2Fe_{17-x}Si_x$ has indicated that Si atoms prefer the 18f sites and are excluded from the 9d site at all concentrations [14]. The dependence of the Curie temperature on the Si content can be interpreted by a model that considers the competition between positive and negative interactions [14]. In this paper, the magnetic properties of $R_2Fe_{17-x}Si_x$ ($x = 0$, 1, 2 and 3) compounds with $R \equiv Y$ and Tm are reported.

2. Experimental details

Samples with the composition $R_2Fe_{17-x}Si_x$ ($R \equiv Y$ and Tm; $x = 0$, 1, 2 and 3) were prepared from 99.9% pure elements by arc melting under a highly purified argon atmosphere. The samples were then annealed in an argon atmosphere at 1000°C for 12 h. X-Ray diffraction was performed to study the dependence of the crystal structure and the unit cell volume on the Si concentration. The saturation magnetization at 1.5 K was measured by an extracting sample magnetometer in a field of 65 kOe. The temperature dependence of the magnetization was measured using an extracting sample magnetometer below room temperature and a vibrating sample magnetometer above room temperature in a magnetic field of 1 kOe. The Curie tempera-

SSDI 0925-8388(95)01891-3

tures were determined from these measurements. The spin reorientation temperatures for $Tm_2Fe_{17-x}Si_x$ were determined from the a.c. susceptibility vs. temperature curves measured in an a.c. magnetic field of less than 1 Oe.

3. Results and discussion

X-Ray diffraction of $R_2Fe_{17-x}Si_x$ ($R \equiv Y$ and Tm) shows a single 2:17 phase structure. Fig. 1 shows the typical X-ray diffraction patterns for $Tm_2Fe_{17-x}Si_x$ with $x = 1$ and 3. The substitution of Si for Fe leads to single-phase samples up to $x = 3$. $Tm_2Fe_{17-x}Si_x$ compounds with $x \leq 3$ have the hexagonal Th_2Ni_{17}-type structure and $Y_2Fe_{17-x}Si_x$ compounds with $x \leq 3$ consist of a mixture of the Th_2Ni_{17}- and Th_2Zn_{17}-type structures. Table 1 summarizes the lattice constants a and c and the unit cell volumes V which were derived from X-ray diffraction analysis. The substitution of Si for Fe leads to a contraction of the unit cell volume. Similar results have been observed in $R_2Fe_{17-x}Si_x$ compounds [7–15].

The saturation magnetization M_S values at 1.5 K for $R_2Fe_{17-x}Si_x$ ($R \equiv Y$ and Tm) compounds are listed in Table 2. Fig. 2 shows the magnetic moment μ_s per formula unit (f.u.) of the $R_2Fe_{17-x}Si_x$ compounds with $R \equiv Y$ and Tm as a function of the Si concentration. As has been shown in $R_2Fe_{17-x}Si_x$ compounds with $R \equiv Ce$ [13] and $R \equiv Er$ [8], the values of μ_s of $Y_2Fe_{17-x}Si_x$ and $Tm_2Fe_{17-x}Si_x$ decrease monotonically with increasing Si concentration, with approximately linear rates of -3.3 μ_B f.u.$^{-1}$ per Si atom and -2.9 μ_B f.u.$^{-1}$ per Si atom respectively. This decrease is faster than for simple magnetic dilution, in contrast with $Nd_2Fe_{17-x}Si_x$ [7]. For $Y_2Fe_{17-x}Si_x$, the Fe magnetic moment μ_{Fe} can be derived from the equation $\mu_s = (17-x)\mu_{Fe}$ because Y is non- magnetic. The values of μ_{Fe} are found to decrease linearly from 2.0 μ_B for $x = 0$ to 1.73 μ_B for $x = 3$, as shown in Table 2. The decrease in the Fe moment is due to magnetic dilution. The antiparallel coupling between the magnetic moments of the Tm and Fe atoms yields ferrimagnetism for $Tm_2Fe_{17-x}Si_x$ compounds. If the Fe moments in $Tm_2Fe_{17-x}Si_x$ are assumed to be equal to the values of μ_{Fe} in $Y_2Fe_{17-x}Si_x$, values for the Tm magnetic moments μ_{Tm} can be obtained. The Tm moment is found to be 6.0 ± 0.3 μ_B, which is slightly lower than the free ion value for Tm^{3+} (7 μ_B) (see Table 2). This may be due to crystal field effects which commonly reduce μ_{Tm}.

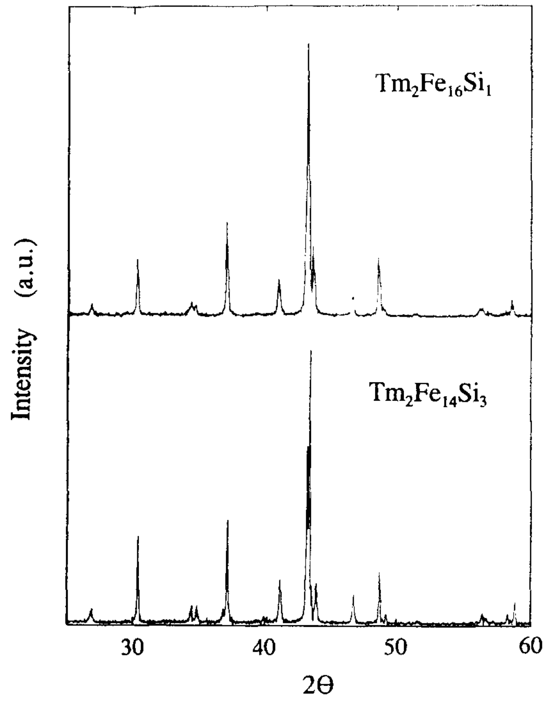

Fig. 1. X-Ray diffraction patterns of $Tm_2Fe_{17-x}Si_x$ compounds with $x = 1$ and 3.

Table 1
Lattice parameters of $R_2Fe_{17-x}Si_x$ compounds with $R \equiv Y$ and Tm

Compound	Structure	a (Å)	c (Å)	V (Å^3)
Y_2Fe_{17}	Th_2Ni_{17}	8.473	8.293	515.6
	Th_2Zn_{17}	8.504	12.379	775.2
$Y_2Fe_{16}Si_1$	Th_2Ni_{17}	8.454	8.296	513.5
	Th_2Zn_{17}	8.489	12.374	772.3
$Y_2Fe_{15}Si_2$	Th_2Ni_{17}	8.437	8.297	511.5
	Th_2Zn_{17}	8.470	12.373	768.6
$Y_2Fe_{14}Si_3$	Th_2Ni_{17}	8.435	8.263	509.1
	Th_2Zn_{17}	8.433	12.395	763.5
Tm_2Fe_{17}	Th_2Ni_{17}	8.422	8.278	510.9
$Tm_2Fe_{16}Si_1$	Th_2Ni_{17}	8.400	8.306	507.5
$Tm_2Fe_{15}Si_2$	Th_2Ni_{17}	8.394	8.275	505.0
$Tm_2Fe_{14}Si_3$	Th_2Ni_{17}	8.373	8.247	500.8

Fig. 3 shows the concentration dependence of the Curie temperature T_C of $R_2Fe_{17-x}Si_x$ ($R \equiv Y$ and Tm) compounds, together with data reported by Lin et al. [10], Gubbens et al. [9] and Valeanu et al. [12]. The Curie temperatures increase monotonically with increasing Si concentration from 324 K for $x = 0$ to 489 K for $x = 3$ when $R \equiv Y$ and from 260 K for $x = 0$ to 480 K for $x = 3$ when $R \equiv Tm$. Numerous investigations have shown that the substitution of low concentrations of non- magnetic atoms, such as Ga, Al and Si, for Fe in R_2Fe_{17} compounds leads to an increase in the Curie temperature [7–15]. The Curie temperature in the rare earth–iron compounds is dominated by the exchange interactions of Fe–Fe atoms. The small difference in T_C between Y and Tm compounds with the same Si concentration, as shown in Table 2, indicates a small contribution of the Tm–Fe exchange interaction to the Curie temperature. The

Table 2
MagNetic parameters of $R_2F_{17-x}Si_x$ compounds with R ≡ Y and Tm

Compound	T_C (K)	M_S (emu g^{-1})	μ_s (μ_B f.u.$^{-1}$)	μ_{Fe} (μ_B)	μ_{Tm} (μ_B)	T_{SR} (K)
Y_2Fe_{17}	324	168.7	34.0	2.00		
$Y_2Fe_{16}Si_1$	424	152.9	30.1	1.88		
$Y_2Fe_{15}Si_2$	470	143.9	27.6	1.84		
$Y_2Fe_{14}S_3$	489	129.5	24.2	1.73		
Tm_2Fe_{17}	260	92.7	21.4	2.00	−6.3	87.3
$Tm_2Fe_{16}Si_1$	429	82.7	18.6	1.88	−5.7	140.9
$Tm_2Fe_{15}Si_2$	467	70.4	15.5	1.84	−6.0	187.5
$Tm_2Fe_{14}Si_3$	480	57.5	12.4	1.73	−5.9	173.1

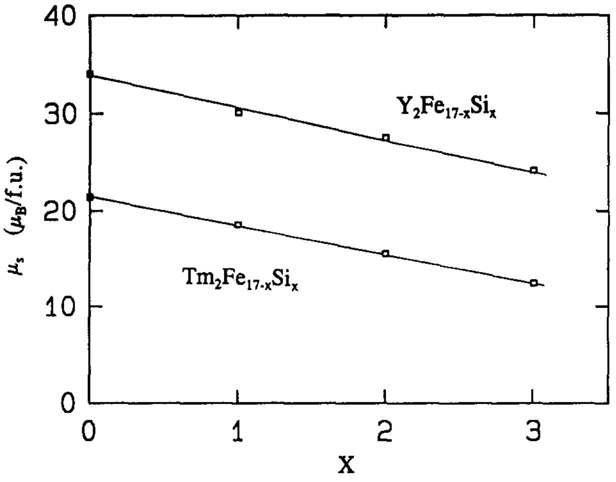

Fig. 2. Magnetic moments μ_s per formula unit for $R_2Fe_{17-x}Si_x$ compounds with R ≡ Y and Tm as a function of Si concentration.

low Curie temperature in R_2Fe_{17} is suggested to be due to an antiferromagnetic exchange interaction associated with the relatively small Fe–Fe distances on some sites. The enhancement of the Curie temperature in rare earth–iron compounds corresponds to an increase in the Fe–Fe exchange interactions as a result of the increasing interatomic Fe–Fe distance. The Ga- and Al-substituted R_2Fe_{17} compounds display an increase in the Curie temperature associated with lattice expansion [1–6]. However, for Si-substituted R_2Fe_{17} compounds, the Curie temperature increases together with a contraction of the unit cell. This indicates that the composition dependence of the Curie temperature cannot be explained on the basis of the variation of the unit cell volume only. It has been found that the Curie temperature enhancement in $R_2Fe_{17-x}Si_x$ is related to the preferential occupation of Si atoms. A neutron diffraction study of $Nd_2Fe_{13}Si_4$ by Long et al. [11] has shown that Si atoms preferentially occupy the 18h site with the largest number of rare earth near-neighbours. They suggest that the increase in Curie temperature is closely related to the lattice expansion in the 9d–18h plane of the unit cell.

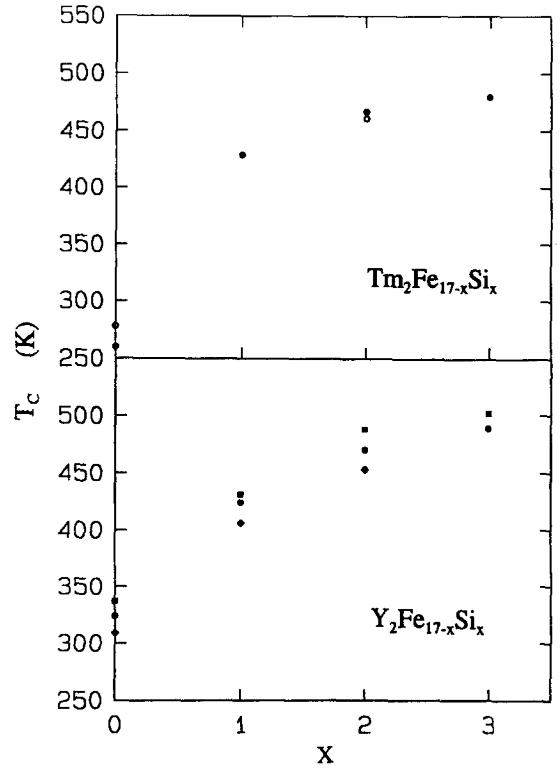

Fig. 3. Curie temperature T_C of $R_2Fe_{17-x}Si_x$ compounds with R ≡ Y and Tm as a function of Si concentration. Data are from this work (●), Ref. [9] (○), Ref. [10] (■) and Ref. [12] (◇).

A recent Mössbauer effect study on $Sm_2Fe_{17-x}Si_x$ compounds has been reported by Li et al. [14] and has shown that the Si atoms prefer the 18f sites at all concentrations. The Curie temperature as a function of Si concentration can be interpreted by a model that considers the competition between the positive and negative exchange interactions [14]. According to the viewpoint of Ref. [14], for $R_2Fe_{17-x}Si_x$, the preferential occupation of Si atoms on the 18f site leads to a strong decrease in the negative interactions between the 9d and 18f atoms, although the positive interactions are also weakened; however, the total Fe–Fe exchange interaction may increase, leading to an increase in the Curie temperature.

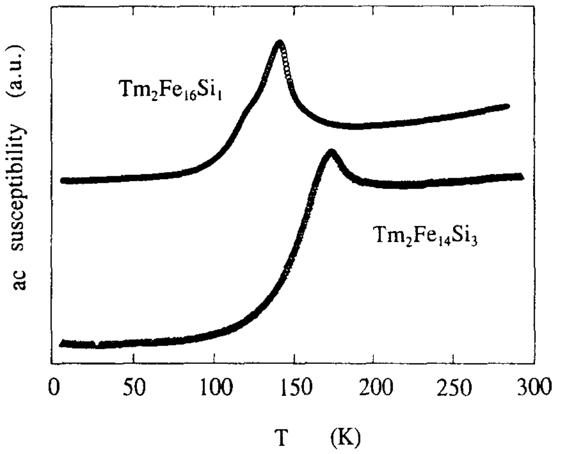

Fig. 4. Temperature dependence of the a.c. susceptibility of $Tm_2Fe_{17-x}Si_x$ compounds with $x = 1$ and 3.

Fig. 4 shows examples of the temperature dependence of the a.c. susceptibility for $Tm_2Fe_{17-x}Si_x$ with $x = 1$ and 3. A sharp peak in the a.c. susceptibility vs. temperature curves clearly indicates a spin reorientation transition, the easy magnetization direction being parallel to the c axis below T_{SR}. The spin reorientation temperature T_{SR} of $Tm_2Fe_{17-x}Si_x$ is shown in Fig. 5 and Table 2 as a function of the Si concentration. The value of T_{SR} increases initially, then decreases with increasing Si concentration; a maximum occurs at an Si content of $x = 2$. The easy magnetization direction in the rare earth–iron compounds is determined by the competition between the Fe sublattice magnetization and the R sublattice magnetization. For $Tm_2Fe_{17-x}Si_x$, the total anisotropy constant is the sum of the Fe sublattice anisotropy constant K_1^{Fe} and the Tm sublattice anisotropy constant K_1^{Tm}. It has been shown that K_1^{Fe} is negative for the R_2Fe_{17} compounds. The rare earth sublattice anisotropy is determined from the product of the second-order crystal field parameter A_{20} and the second-order Stevens coefficient α_J and can be given by

$$K_1^R = (-3/2)\alpha_J \langle r^2 \rangle \langle 3J^2 - J(J+1) \rangle A_{20}$$

where the quantities in angular brackets are expected values. The second-order crystal field parameter A_{20} is negative in the R_2Fe_{17} compounds and depends on the crystal field associated with the surroundings of a given rare earth element. Because α_J is positive for Tm, K_1^{Tm} is positive, which favours an easy magnetization parallel to the c axis. At room temperature, the Tm sublattice anisotropy is too small to overcome the easy plane anisotropy of the Fe sublattice. The Tm sublattice anisotropy becomes stronger at low temperature, and a uniaxial orientation of the magnetization is observed in $Tm_2Fe_{17-x}Si_x$. For samples with $x \leq 2$, the enhancement of T_{SR} with x indicates an increase in the positive value of K_1^{Tm} with increasing Si concentration. Indeed, it has been found from a ^{169}Tm Mössbauer effect study on $Tm_2Fe_{15}Si_2$ [9] that the second-order crystal field parameter A_{20} is shifted towards more negative values than in the parent compound and, simultaneously, the spin reorientation temperature increases. However, for $x > 2$, T_{SR} decreases in $Tm_2Fe_{17-x}Si_x$. Similar results have also been observed in Ga-substituted Er_2Fe_{17} compounds, in which the T_{SR} values first increase and then decrease with increasing Ga concentration [16]. This may be due to the fact that A_{20} is shifted towards less negative values when larger amounts of non-magnetic atoms are substituted for Fe.

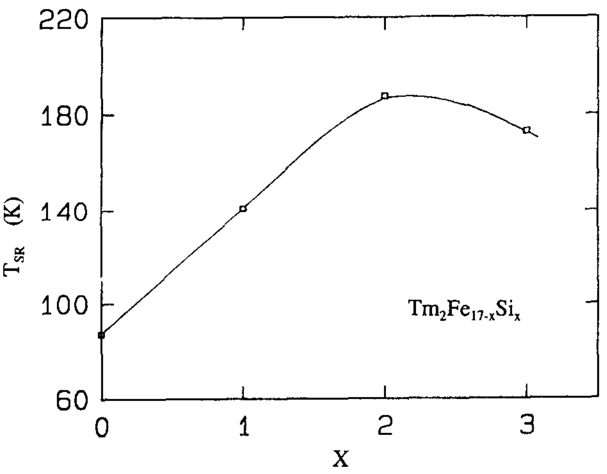

Fig. 5. Spin reorientation temperature T_{SR} of $Tm_2Fe_{17-x}Si_x$ compounds as a function of Si concentration.

Acknowledgment

This work was supported by The National Natural Science Foundation of China.

References

[1] D. McNeely and H. Oesterreicher, *J. Less-Common Met., 44* (1976) 183.
[2] F. Weitzer, K. Hiebl and P. Rogl, *J. Appl. Phys., 65* (1989) 4963.
[3] B.G. Shen, F.W. Wang, L.S. Kong and L. Cao, *J. Phys.: Condensed Matter, 5* (1993) L685.
[4] Z. Wang and R.A. Dunlap, *J. Phys.: Condensed Matter, 5* (1993) 2407.
[5] Z. Hu, W.B. Yelon, S. Mishra, G.J. Long, O.A. Pringle, D.P. Middleton, K.H.J. Buschow and F. Grandjean, *J. Appl. Phys., 76* (1994) 443.
[6] G.J. Long, G.K. Marasinghe, S. Mishra, O.A. Pringle, Z. Hu, W.B. Yelon, D.P. Middleton, K.H.J. Buschow and F. Grandjean, *J. Appl. Phys., 76* (1994) 5383.

[7] R. van Mens, *J. Magn. Magn. Mater., 61* (1986) 24.

[8] E.E. Alp, A.M. Umarji, S.K. Malik, G.K. Shenoy, M.Q. Huang, E.B. Boltich and W.E. Wallace, *Journal, 68* (1987) 305.

[9] P.C.M. Gubbens, A.M. van der Kraan, T.H. Jacobs and K.H.J. Buschow, *J. Less-Common Met., 159* (1990) 173.

[10] C. Lin, Y.X. Sun, Z.X. Liu, H.W. Jiang, G. Jiang, J.L. Yang, B.S. Zhang and Y.F. Ding, *Solid State Commun., 81* (1992) 299.

[11] G.J. Long, G.K. Marasinghe, S. Mishra, O.A. Pringle, F. Grandjean, K.H.J. Buschow, D.P. Middleton, W.B. Yelon, F. Pourarian and O. Isnard, *Solid State Commun., 88* (1993) 761.

[12] M. Valeanu, N. Plugaru and E. Burzo, *Solid State Commun., 89* (1994) 519.

[13] D.P. Middleton and K.H.J. Buschow, *J. Alloys Compounds, 206* (1994) L1.

[14] Z.W. Li, X.Z. Zhou and A.H. Morrish, *Phys. Rev. B, 51* (1995) 2891.

[15] B.G. Shen, B. Liang, F.W. Wang, Z.H. Cheng, H.Y. Gong, S.Y. Zhang and J.X. Zhang, *J. Appl. Phys., 77* (1995) 2637.

[16] B.G. Shen, to be published.