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## NEUTRON DIFFRACTION AND MAGNETIC STUDIES OF Nd<sub>2</sub>Fe<sub>17-x</sub>T<sub>x</sub> (T=Si, Mn) ALLOYS

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**Abstract**--We have carried out neutron and magnetic studies on Nd<sub>2</sub>Fe<sub>17-x</sub>T<sub>x</sub> (T=Si, Mn) alloys. The unit cell of the compounds contracts with both Si and Mn substitution. Si atoms avoid the 6c site, prefer the 18h site strongly, fill the 9d site steadily and fill the 18f site only at relatively high Si concentration. Mn atoms avoid the 9d sites but prefer the 6c site strongly, while the 18f site and 18h site fill slowly. The Si site occupancies appear to be dominated by the crystal environment while the Mn site occupancies are dominated by steric considerations. The Curie temperature of the compound Nd<sub>2</sub>Fe<sub>17</sub> increases significantly with Si substitution but is only affected slightly by the Mn substitution. Although the unit cell contracts with increasing Si concentration, the average length of bonds to the Fe(6c) and the Fe(18f) sites increase slightly at  $x < 4$ .

### Introduction

The fact that the Curie temperature,  $T_C$ , of R<sub>2</sub>Fe<sub>17</sub> compound can increase upon some substitution of non-magnetic atoms has attracted much attention [1-6]. To understand the mechanism of this increase with substitution, it is important to know the correct site occupancies of the substituent in the crystal. Neutron diffraction is the most reliable technique to obtain this information.

Silicon is an attractive substituent (T) in the pseudobinary phase R<sub>2</sub>Fe<sub>17-x</sub>T<sub>x</sub>, as it enhances the magnetic properties of R<sub>2</sub>Fe<sub>17</sub> compounds [4,6]. In contrast, the Mn substitution for Fe in 2:14:1 compounds decreases the Curie temperature dramatically [7,10]. However, systematic investigation of Si and Mn substitution for Fe in 2:17 compounds by neutron diffraction have not been reported, although we have previously reported results for Nd<sub>2</sub>Fe<sub>13</sub>Si<sub>4</sub> [6]. As part of a series of studies on the substituted 2:17 compounds, R<sub>2</sub>Fe<sub>17-x</sub>T<sub>x</sub>, we have carried out neutron diffraction and magnetic studies on Nd<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub> and Nd<sub>2</sub>Fe<sub>17-x</sub>Mn<sub>x</sub> alloys.

### Experiment

Nd<sub>2</sub>Fe<sub>17-x</sub>Mn<sub>x</sub> samples used in this research were synthesized by rf induction melting of the constituent elements while Nd<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub> samples used in this research

were synthesized by either rf induction melting or arc-melting. The ingots were annealed under vacuum at temperatures of 980°C for one to three weeks. The annealed ingots were then crushed and ground in an acetone or toluene bath for neutron diffraction and other studies. Neutron diffraction data were collected using the PSD (Position Sensitive Detector) diffractometer at the University of Missouri Research Reactor. Data collection for each sample takes about 24 hours on about 2 grams of the powdered samples in a 3mm diameter vanadium can, at a wavelength of 1.4783Å. Data were collected at 295K.

Neutron diffraction data were analyzed using the program FULLPROF [8], a program for Rietveld analysis of neutron (nuclear and magnetic scattering) or X-ray powder diffraction data collected at constant steps in the scattering angle  $2\theta$  on a conventional instrument. The Curie temperatures,  $T_C$ , were measured using a QUANTUM DESIGN MPMS system.

### Results and Discussion

The refinement results of the neutron diffraction data are summarized in Table 1 and Table 2 for Si and Mn samples, respectively. It is not surprising that the unit cell of the compounds will change with the incorporation of substituents due to the different atomic sizes of Fe, Si and Mn. In Nd<sub>2</sub>Fe<sub>17-x</sub>Si<sub>x</sub>, the unit cell contracts at a rate about  $3.4\text{\AA}^3$  per silicon atom. However, the  $a$  parameter shows a decrease with increasing silicon content, while the  $c$  parameter increases slightly for small  $x$ , reaches a maximum at  $x=3$ , and then decreases. The  $c/a$  ratio shows a similar maximum. However, all Si samples have a larger  $c/a$  ratio than the Nd<sub>2</sub>Fe<sub>17</sub> compound. The more unexpected result is that, although Mn atoms are slightly larger than Fe atoms, the unit cell volume of Nd<sub>2</sub>Fe<sub>17-x</sub>Mn<sub>x</sub> decreases as the Mn content increases (Table 2). While the  $a$  parameter decreases nearly linearly with Mn content, the  $c$  parameter increases slightly at the low  $x$  range, reaches a maximum at  $x=0.5$ , and then decreases. The  $c/a$  ratio increases at low Mn concentration, and decreases at high Mn concentration. This behavior is similar to that observed in Nd<sub>2</sub>Fe<sub>14-x</sub>Mn<sub>x</sub>B compounds but different from what was observed in Er<sub>2</sub>Fe<sub>14-x</sub>Mn<sub>x</sub>B compounds [7].

Table 1 Refinement results for the  $\text{Nd}_2\text{Fe}_{17-x}\text{Si}_x$  solid solutions. (T=295K)

parameter	x=0	x=1.104	x=2.232	x=3.132	x=3.708	x=4.212
a, Å	8.6002(1)	8.5741(2)	8.5524(3)	8.5409(4)	8.5411(3)	8.5325(1)
c, Å	12.4835(2)	12.4907(3)	12.4988(5)	12.5020(7)	12.4604(6)	12.4554(2)
c/a	1.4515	1.4568	1.4614	1.4637	1.4589	1.4587
v, Å <sup>3</sup>	799.631	795.223	791.724	789.804	787.213	785.311
Rw-factor	7.09	7.80	8.33	10.70	6.11	7.71
$\chi^2$	3.11	3.11	3.80	5.98	2.29	2.82
$\mu$ , Nd,6c	2.1(2)	2.5(2)	2.7(3)	2.3(3)	0.5(3)	0.5(3)
$\mu$ , Fe,6c	2.5(2)	2.9(3)	2.5(4)	1.9(3)	0.9(3)	0.7(2)
$\mu$ , Fe,9d	1.7(2)	2.6(4)	2.1(4)	1.5(3)	1.0(3)	0.7(2)
$\mu$ , Fe,18f	2.4(2)	2.6(2)	2.6(3)	2.3(3)	1.4(3)	0.7(2)
$\mu$ , Fe18h	1.7(2)	2.2(3)	2.3(2)	2.4(3)	1.0(3)	0.7(2)
$\mu$ /formula	38.92	45.1	41.03	33.66	15.95	9.96
$\mu(z)/\mu(x)$	0.0	0.0	0.0	1.6	3.1	infinite

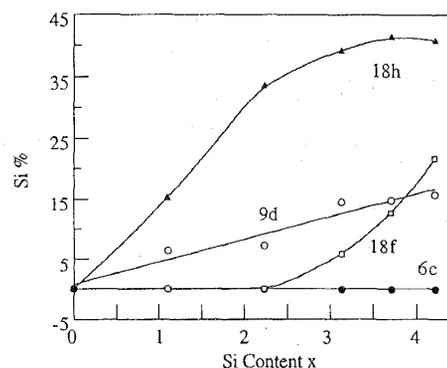
Table 2 Refinement results for  $\text{Nd}_2\text{Fe}_{17-x}\text{Mn}_x$  solid solutions. (T=295K)

parameter	x=0	0.516	1.080	1.476	1.884
a, Å	8.6002(1)	8.5955(3)	8.5920(3)	8.5918(3)	8.5876(4)
c, Å	12.4835(2)	12.4849(4)	12.4788(4)	12.4761(4)	12.4628(5)
c/a	1.4515	1.4525	1.4524	1.4521	1.4513
v, Å <sup>3</sup>	799.631	798.835	797.791	797.586	795.955
Rw-factor	7.09	5.31	5.21	5.36	5.95
$\chi^2$	3.11	1.43	1.45	1.41	1.72
$\mu$ , Nd,6c	2.1(2)	1.3(3)	1.1(3)	1.1(2)	0.3(6)
$\mu$ , Fe/Mn,6c	2.5(2)	1.3(4)	1.0(4)	0.8(4)	0.0(6)
$\mu$ , Fe/Mn,9d	1.7(2)	1.1(3)	0.9(3)	1.1(3)	0.8(6)
$\mu$ , Fe/Mn,18f	2.4(2)	2.2(3)	2.1(3)	1.6(3)	0.9(6)
$\mu$ , Fe/Mn,18h	1.7(2)	1.4(2)	1.4(2)	1.3(2)	1.0(6)
Tc, K	330	345	320	315	310

The compositional dependence of the Si site occupation in  $\text{Nd}_2\text{Fe}_{17-x}\text{Si}_x$  obtained in this study is shown in Fig. 1, in which the uncertainties, 2-5% of the refined occupation, are not shown. It was found that silicon atoms avoid the dumbbell 6c site over the entire Si concentration range. The 18h site has a high initial affinity for Si, but appears to saturate at about 40%. However, the 18h site silicon population is much higher than any other site for silicon content up to  $x=4.212$ , which appears to be the limit of phase stability. In contrast, the 9d site occupancy increases steadily. The 18f site fills only at a relatively high Si concentration ( $x$  greater than 2.3) and then fills very rapidly.

Li and Morrish reported occupancies for the  $\text{Sm}_2\text{Fe}_{17-x}\text{Si}_x$  alloys distinctly different from these on the basis of Mossbauer fitting [4]. They assume that the hyperfine fields are greatest on those sites with the largest number of Fe neighbors. However, our combined neutron-Mossbauer studies suggest that the hyperfine fields scale with the Wigner-Seitz volume[6]. With that assumption their 18f-18h assignment would be switched leading to better agreement. The 9d-6c difference is not so easily explained, but these are low multiplicity sites with a low Si occupancy. Insofar as the neutron diffraction results do not rely on any arbitrary assumptions and are robust and unique,

we are confident in their reliability.

Fig. 1 The percentage Si found on the four Fe sites in the  $\text{Nd}_2\text{Fe}_{17-x}\text{Si}_x$  alloys

The Curie temperature of the compound  $\text{Nd}_2\text{Fe}_{17}$  increases significantly with Si substitution. Although the iron content decreases, the magnetic moment per formula unit at room temperature increases over a limited Si content range (Table 1). The Fe and Nd moments increase slightly in the low Si concentration range and drop rapidly when the

Si content reaches  $x > 3$ . The easy direction of magnetization was found to change from basal at low silicon content to axial at high silicon content. An interesting feature is that the unit cell contracts with increasing Si concentration, but the average length of the bonds to the Fe(6c) (the dumbbell site) and the Fe(18f) sites increase slightly at  $x < 4$  (Fig. 2). While the elongation of these bonds may be partially responsible for the increase of the Curie temperature, theory suggests [9] that the Si substitution also significantly changes the density of states at the Fermi level and thereby affects  $T_c$ .

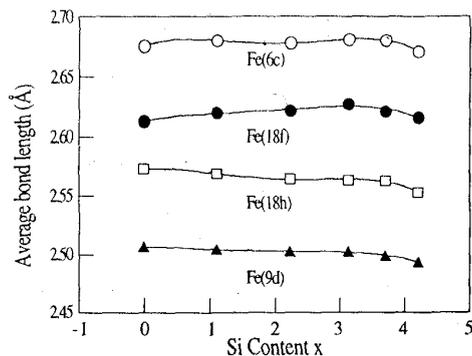


Fig. 2 The compositional dependence of the average bond length to Fe sites in  $Nd_2Fe_{17-x}Si_x$  compounds

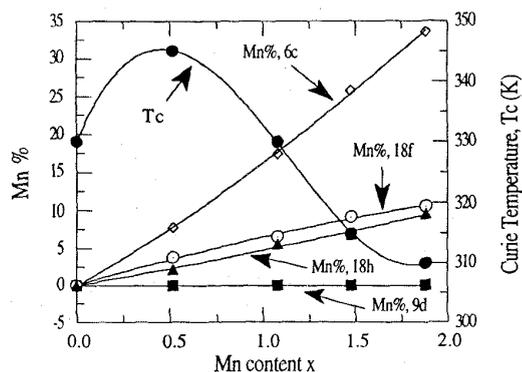


Fig. 3 The compositional dependence of the Mn site occupancies and the Curie temperature in  $Nd_2Fe_{17-x}Mn_x$  compounds

The behavior of Mn site occupations appears to be dominated by the site volume. All Mn atoms avoid the smallest 9d sites. The largest 6c site has a high initial affinity for Mn and fills rapidly, while the 18f site and 18h site fills slowly (Fig. 3). As the Mn content increases, the site moments of all sites decrease, indicating an overall negative contribution of Mn atoms to the magnetic exchange. The largest moment reduction on the 6c site relates to the large Mn occupation on this site. It was reported that the Mn substitution for Fe in 2:14:1 compounds leads to a dramatic drop in Curie temperature by more than 100 degrees per Mn atom per unit formula [10].

However, only a very slight effect of Mn substitution for Fe in 2:17 compounds is observed (Fig. 3). Compared to the Curie temperature of the parent compound  $Nd_2Fe_{17}$ , 330K, the Curie temperature of  $Nd_2Fe_{16.5}Mn_{0.5}$  is even higher. This unexpected behavior is probably due to the fact that most Mn atoms occupy the 6c site which has the largest Wigner-Seitz cell volume and the longest average site bond length. Perhaps in this environment the Mn couples weakly ferromagnetically to Fe.

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