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## The magnetic structure of Nd<sub>6</sub>Fe<sub>13</sub>Si

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**Abstract.** The magnetic structure of Nd<sub>6</sub>Fe<sub>13</sub>Si has been studied by magnetization measurement, the singular point detection technique and neutron powder diffraction. It was found that the Nd<sub>6</sub>Fe<sub>13</sub>Si is ferrimagnetic with a compensation temperature of 357 K and a Curie temperature of 441 K. The spontaneous magnetization values are 12.9 J T<sup>-1</sup> kg<sup>-1</sup> at 5 K and 7.4 J T<sup>-1</sup> kg<sup>-1</sup> at 300 K. There are two values  $B_0^{cr1}$  and  $B_0^{cr2}$  of the magnetic phase transition field below 225 K:  $B_0^{cr1} = 6.2$  T and  $B_0^{cr2} = 8.2$  T at 77 K and  $B_0^{cr} = 5.3$  T at 300 K. The atomic magnetic moments are ordered in an antiparallel manner, and the two magnetosublattices are  $M_I \uparrow \{8f(\text{Nd}), 16l(\text{Nd}), 4d(\text{Fe}), 16l_2(\text{Fe})\}$  and  $M_{II} \downarrow \{16k(\text{Fe}), 16l_1(\text{Fe})\}$ .

### 1. Introduction

In recent years, a new series of ternary rare-earth–iron compounds R<sub>6</sub>Fe<sub>14-x</sub>M<sub>x</sub> (R = La, Pr, Nd or Sm; M = Al, Ga, Ge, Cu, Si or Sb;  $x = 1-4$ ) has attracted much attention [1–4]. These 6:14 phases often appear in the M-doped Nd–Fe–B permanent magnets and may have an effect on the coercivity [3–5]. The crystallographic structure is Nd<sub>6</sub>Fe<sub>13</sub>Si type [3, 4] or La<sub>6</sub>Fe<sub>11</sub>Ga<sub>3</sub> type [6]. They have the same tetragonal symmetry with the space group *I4/mcm*. The rare earth occupies two sites 8f and 16l and the iron occupies four sites 4d, 16l<sub>1</sub>, 16l<sub>2</sub> and 16k. The third element occupies the 4a site when  $x = 1$  and shares the 16l<sub>2</sub> site with Fe besides 4a when  $x > 1$  [3, 6]. The magnetization measurements revealed that the atomic magnetic moments of Fe in the four crystallographic sites are antiparallel collinearly coupled [2–4]. Two spin configurations were proposed by Hu *et al* [2] on the basis of magnetization and Mössbauer study of La<sub>6</sub>Fe<sub>11</sub>Al<sub>3</sub>. The non-collinear magnetic structure of Nd<sub>6</sub>Fe<sub>13</sub>Cu, concluded from the comparison of the x-ray diffraction pattern and the Mössbauer spectrum on an oriented sample by Knoch *et al* [4], may not be true. The reason is that, when the magnetocrystalline anisotropy or the magnetization is very small, the x-ray diffraction pattern is much more sensitive to the sample texture than is the Mössbauer spectrum. For example, on an oriented sample, NdFe<sub>10.5</sub>Mo<sub>1.5</sub> shows easy *c*-axis anisotropy in the x-ray diffraction pattern [7] but this is not seen clearly in the Mössbauer spectrum [8]. In this work, we investigated the magnetic structure of Nd<sub>6</sub>Fe<sub>13</sub>Si in detail. The results are discussed together with previous published work, and the spin configuration in Nd<sub>6</sub>Fe<sub>13</sub>Si will be concluded on the assumption of a collinear coupling scheme.

## 2. Experimental details

The  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  alloy was prepared by arc melting Nd (99.99% purity), Fe (99.9% purity) and Si (99.9% purity), sealed in a quartz tube and annealed at 800 °C for about 3 days. The ingot was then ground into fine powder. The x-ray diffraction pattern shows that the sample is almost single phase (figure 1).

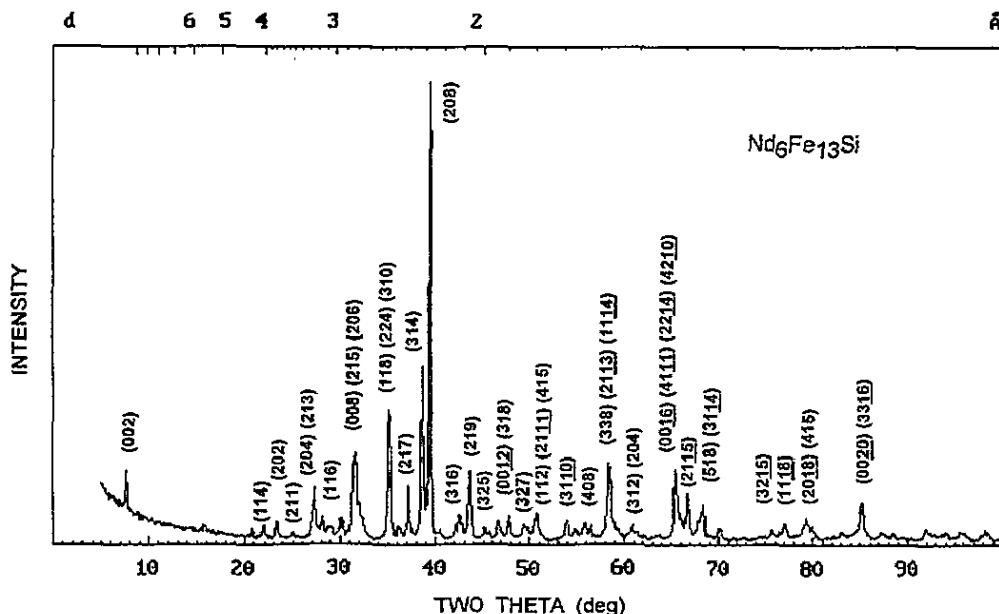


Figure 1. X-ray diffraction pattern of  $\text{Nd}_6\text{Fe}_{13}\text{Si}$ . It is indexed using the lattice parameters from the refinement of neutron diffraction data (see table 1).

The magnetization as a function of temperature was measured on a vibrating-sample magnetometer in an applied field of 0.04 T and on a magnetic balance in an applied field of 1.2 T on the ingot pieces. The magnetization curve was measured at 5 and 300 K with a SQUID magnetometer on the free powder. The magnetic phase transition field from 77 to 300 K was determined by the singular point detection (SPD) technique [9].

Neutron powder diffraction data at 300 K were collected on the triple-axis spectrometer at the China Institute of Atomic Energy, Beijing. The wavelength was 1.541 Å. The data were analysed with the Rietveld structure refinement program RIETAN [10]. The parameters of crystallographic structure of the  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  compound were taken from [3] to start the refinement. The collinear magnetic structure was used during the refinement.

## 3. Results and discussion

The neutron diffraction pattern (dots) with the fitting (lines) of the  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  compound is shown in figure 2. The parameters of the final refined structure are listed in table 1. The final goodness is  $R(F^2) = 0.063$  and  $R(F) = 0.038$ . The lattice parameters  $a = 0.80299(3)$  nm and  $c = 2.2706(3)$  nm and the structural parameters are quite close to those determined

by x-ray diffraction [3]. The magnetic moments of all atoms lie in the fourfold axes and four iron sites exhibit an antiparallel coupling structure. Since the magnetic contribution in diffraction pattern is small, the values of the atomic magnetic moment are not precise. The alignment of the atomic magnetic moments is quite sensitive during the refinement. The spin configuration of the four iron sites ( $4d \uparrow$ ,  $16k \downarrow$ ,  $16l_1 \downarrow$ ,  $16l_2 \uparrow$ ) is close to that proposed by Hu *et al* [2]. The assignment of hyperfine fields of  $^{57}\text{Fe}$  Mössbauer spectra to the iron sites in the 6:14 structure was considered according to the number of nearest-neighbour atoms [2]. It is not easy to distinguish definitely the  $16l_1$  and  $16l_2$  sites, since they both have the same nearest-neighbour atoms of iron and one rare-earth atom difference. In switching  $16l_1$  and  $16l_2$  assignments of the hyperfine fields, the spin configuration of the four iron sites would be the same as that derived from neutron diffraction, and also the sequence of hyperfine fields in the four iron sites  $4d > 16k > 16l_2 > 16l_1$  is the same as that of the absolute values of the atomic magnetic moment in table 1. The atomic magnetic moments of Nd in both 8f and 16l sites are parallel to those of Fe in 4d and  $16l_2$  sites. The magnetic structure in  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  consists of two magnetosublattices:  $M_{\text{I}} \uparrow \{8f(\text{Nd}), 16l(\text{Nd}), 4d(\text{Fe}), 16l_2(\text{Fe})\}$  and  $M_{\text{II}} \downarrow \{16k(\text{Fe}), 16l_1(\text{Fe})\}$ . According to the crystallographic position (figure 3), the 4d and 16k Fe sites are in the same atomic layer with the shortest distance of 0.2398 nm so that they couple antiparallel to each other. The 4d site has distances of 0.2460 nm and 0.2568 nm to the  $16l_1$  and  $16l_2$  sites, respectively, and the magnetic moment at 4d may couple antiparallel to that at  $16l_1$  and parallel to that at  $16l_2$ .

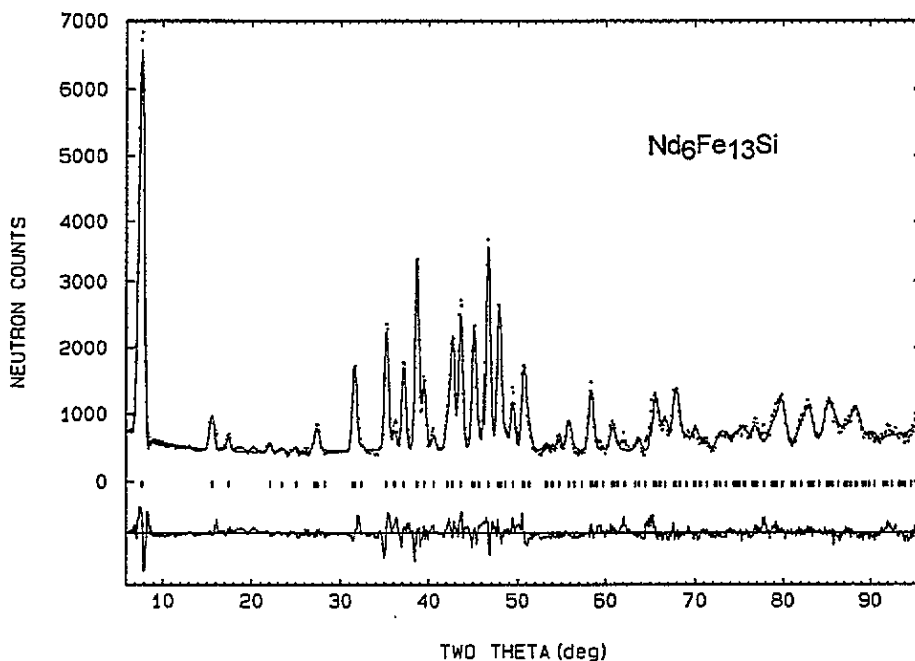
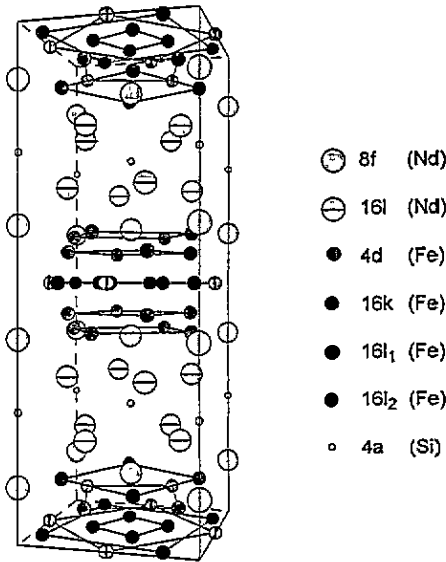
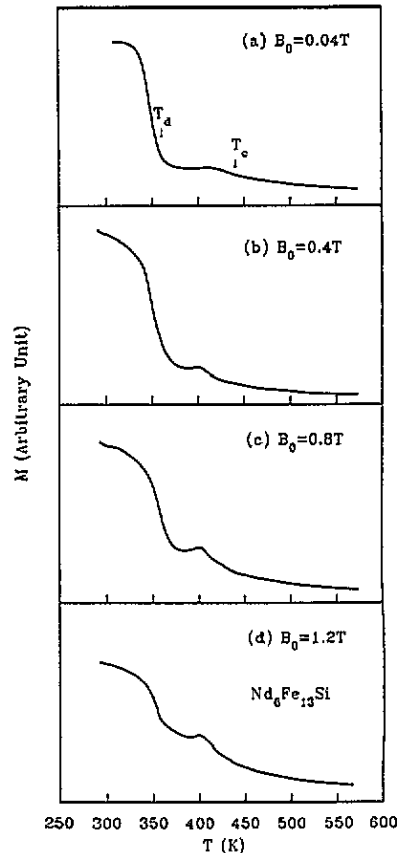


Figure 2. Neutron diffraction pattern of  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  powder at a temperature of 300 K:  $\cdots$ , observed profiles;  $\text{—}$ , calculated curves; calculated positions are indicated at the bottom. The differences between the observed data and calculated values are also given.

Figure 4 shows the thermomagnetic scans in different applied magnetic fields  $B_0$ . They clearly exhibit ferrimagnetic ordering in the  $\text{Nd}_6\text{Fe}_{13}\text{Si}$ . According to the results of neutron

**Table 1.** Crystallographic and magnetic parameters of  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  (tetragonal cell; space group,  $I4/mcm$ ;  $a = 8.0299(3)$  Å and  $c = 22.760(3)$  Å).

	$x$	$y$	$z$	$B$	$o.f$	$M(\mu_B)$
Nd(8f)	0	0	0.1090(2)	1.0(2)	1.0	0.5(2)
Nd(16l)	0.1678(3)	0.6678(3)	0.1912(3)	1.1(2)	1.0	0.5(2)
Si(4a)	0	0	$\frac{1}{4}$	0.4(1)	1.0	0
Fe(4d)	0	$\frac{1}{2}$	0	1.2(2)	1.0	1.3(3)
Fe(16k)	0.0645(5)	0.2084(6)	0	1.2(2)	1.0	-0.9(3)
Fe(16l <sub>1</sub> )	0.1783(5)	0.6783(4)	0.0614(4)	0.6(1)	1.0	-0.5(2)
Fe(16l <sub>2</sub> )	0.3855(4)	0.8855(4)	0.0973(6)	1.0(2)	1.0	0.8(3)

**Figure 3.** Crystallographic structure of  $\text{Nd}_6\text{Fe}_{13}\text{Si}$ .**Figure 4.** Magnetization as a function of temperature for  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  in different applied fields.

diffraction above,  $M_I > M_{II}$  at 300 K. Both  $M_I$  and  $M_{II}$  decrease as the temperature increases and are compensated at  $T_d$  and vanish at  $T_C$ . During the temperature range between the compensation temperature  $T_d$  and the Curie temperature  $T_C$ ,  $M_I < M_{II}$ . The values of  $T_d = 357$  K and  $T_C = 441$  K were derived from the  $M-T$  curve at  $B_0 = 0.04$  T. In our data we did not see any anomalies above 550 K, which does not agree with what was reported by Allemand *et al* [3].

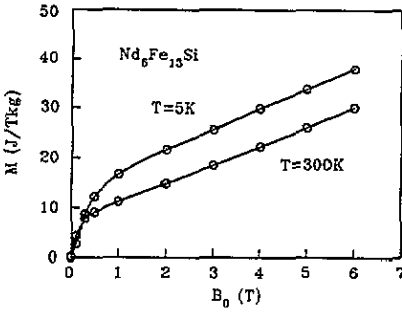


Figure 5. Magnetization curves of  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  at temperatures of 5 and 300 K.

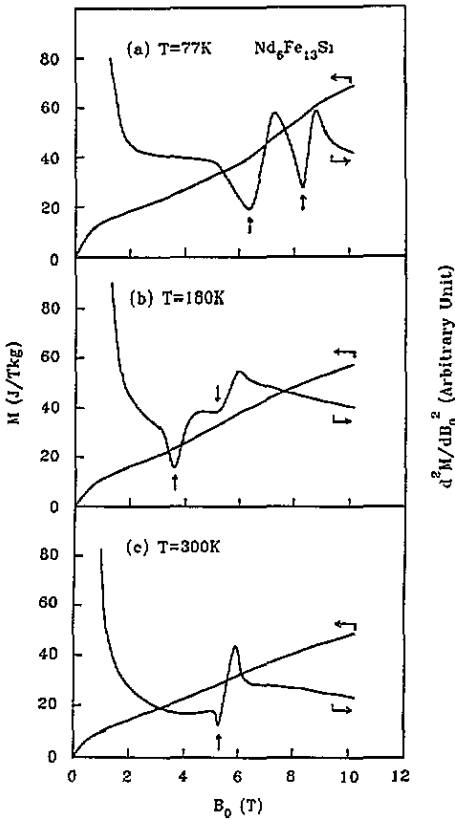


Figure 6. Magnetization curves of  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  in a pulsed field up to 10 T at different temperatures with the corresponding  $d^2M/dB_0^2$  traces, on which the arrows indicate the magnetic phase transition positions.

The magnetization curves of  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  at temperatures of 5 and 300 K are shown in figure 5. The magnetization saturates in applied fields of about 1 T and 0.5 T at 5 K and 300 K respectively. The magnetization increases linearly with increasing applied field in the higher-field range and the susceptibilities are quite high. By extrapolating the linear parts of the magnetization to zero field, the spontaneous magnetization values are derived as  $12.9 \text{ J T}^{-1} \text{ kg}^{-1}$  at 5 K and  $7.4 \text{ J T}^{-1} \text{ kg}^{-1}$  at 300 K. These values are much higher than those reported by Allemand *et al* [3]. The magnetization value of  $6.6 \text{ J T}^{-1} \text{ kg}^{-1}$  at 300 K derived from the atomic magnetic moments of neutron diffraction fitting is consistent with

the magnetization measurement. The small spontaneous magnetization at 5 K indicates that  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  is ferrimagnetic the same as at room temperature.

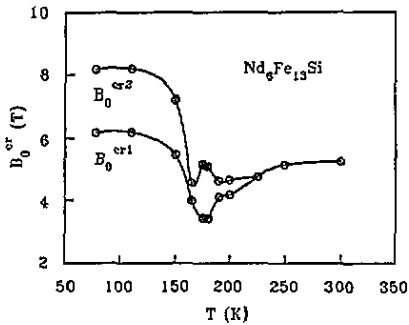


Figure 7. Temperature dependence of the magnetic phase transition field.

At present, the SPD technique is probably the best method for determining the anomalous change in the magnetization curve for polycrystalline samples [9], such as the first-order magnetization process, the magnetocrystalline anisotropy field and the second-order magnetization process. The magnetization curves in the pulsed field up to 10 T with their SPD traces are shown in figure 6. The arrows in the figure indicate where the magnetic phase transitions occur. The values of the critical field  $B_0^{cr}$  at the magnetic phase transition were derived by taking the average values of the marked field positions in the magnetizing and demagnetizing SPD traces. Figure 7 shows that the magnetic phase transition field  $B_0^{cr}$  varies with the temperature. At this field the antiparallel coupling of the magnetic moments in  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  breaks down. It is interesting to note that  $B_0^{cr}$  has two branches below 225 K:  $B_0^{cr1} = 6.2$  T and  $B_0^{cr2} = 8.2$  T at 77 K. The minimum of 3.4 T for  $B_0^{cr1}$  appears at 180 K. The value of  $B_0^{cr} = 5.3$  T at 300 K is close to that found by Allemand *et al* [3] but the features of the  $B_0^{cr}$ - $T$  curve are quite different. In [3] there is no explanation about the determination of  $B_0^{cr}$ .

The discrepancies between our magnetic measurement data and those of Allemand *et al* [3] may be caused by the different sample qualities or different methods of magnetic measurement. Our sample was almost a single phase but their sample was obtained by selecting particles after crushing the 93 wt.% Nd-7 wt.% Fe alloy which is a mixture [3].

#### 4. Conclusion

The ternary rare-earth-iron intermetallic compound  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  is ferrimagnetic below its ordering temperature of 441 K. The compensation temperature of the two antiparallel coupling magnetosublattices is 357 K. The spontaneous magnetization values are  $12.9 \text{ J T}^{-1} \text{ kg}^{-1}$  at 5 K and  $7.4 \text{ J T}^{-1} \text{ kg}^{-1}$  at 300 K. There are two values  $B_0^{cr1}$  and  $B_0^{cr2}$  of the magnetic phase transition field below 225 K:  $B_0^{cr1} = 6.2$  T and  $B_0^{cr2} = 8.2$  T at 77 K;  $B_0^{cr} = 5.3$  T at 300 K. The magnetic structure of  $\text{Nd}_6\text{Fe}_{13}\text{Si}$  has the following spin configuration:  $\{8f(\text{Nd})\uparrow, 16l(\text{Nd})\uparrow, 4d(\text{Fe})\uparrow, 16k(\text{Fe})\downarrow, 16l_1(\text{Fe})\downarrow, 16l_2(\text{Fe})\uparrow\}$ .

#### Acknowledgment

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