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Tsuyoshi Kajitani
Institute for Materials Research, Tohuku University, Sendai 980, Japan

Yukio Morii and Satoru Funahashi
Department of Physics, Japan Atomic Energy Research Institute, Tokai, Ibaraki 319-11, Japan

Takahiko Iriyama and Kurima Kobayashi
Central Laboratory, Asahi Chemical Industry Co. Ltd., Fuji, Shizuoka 416, Japan

Hiroaki Kato, Yasuaki Nakagawa, and Kenji Hiraya
Institute for Materials Research, Tohuku University, Sendai 980, Japan

High-resolution neutron powder diffraction measurements with $\lambda = 1.8232$ Å and collimation of 6'-20'-6' on Nd$_2$Fe$_{17}$N$_x$ with $x=0$, 2.85, and 2.91 were carried out at room temperature. Structural parameters and magnetic moments were determined by the Rietveld profile-fitting calculation. The magnetic moments of iron atoms increased with increasing nitrogen concentration; e.g., the magnetic moments of iron located at 6c, 9d, 18f, and 18h sites increase from less than 0.7μ_B in the $x=0$ sample to about 2.1μ_B in the $x=2.91$ sample. It is noticed that a local atomic group composed of two Fe(1) atoms at the 6c site plus six Fe(3) atoms at the 18f site keeps its shape against the nitrogen uptake.

I. INTRODUCTION

Novel hard magnetic materials, interstitial ternary nitrides R_2Fe$_{17}$N$_x$, where R refers to rare-earth metals and x runs from about 3 to 6, were recently discovered by a Japanese group[1-3] and a European group.[4] The highest coercivity 30 kOe was achieved by Schnitzke *et al.*[5] for microcrystalline Sm$_2$Fe$_{17}$N$_x$. The measurements of the maximum energy product, $(BH)_{max} = 21$ MG Oe, with coercivity 8.6 kOe, and the magnetic ordering (Curie) temperature at 473 °C for the same material were accomplished by Iriyama *et al.*[6] These values may indicate that the Sm$_2$Fe$_{17}$N$_x$ magnet surpasses the melt-spun Nd–Fe–B alloy magnet, but there are several technical difficulties to be overcome. In R_2Fe$_{17}$ compounds it has been noticed that introduction of interstitial atoms such as carbon,[7,8] hydrogen,[9,10] and nitrogen[4,6] causes an appreciable increase in the magnetic ordering temperature.

The present work aimed to obtain reliable structural parameters and magnetic moments of metal atoms in Nd$_2$Fe$_{17}$N$_x$ with $x=0$, 3.0, and 3.2 (nominal) by high-resolution neutron powder diffraction. Since thermal neutron powder diffraction measurement on the samarium system, which is magnetically most significant, cannot be carried out due to the huge absorption cross section of samarium, the present neodymium system, being isomorphic and magnetically similar, was selected. Recently Jaswal *et al.*[11] carried out a medium-resolution neutron powder diffraction study on nitrogenated Nd$_2$Fe$_{17}$ and Y$_2$Fe$_{17}$. The present work gives a detailed description of the structure of Nd$_2$Fe$_{17}$N$_x$.

II. EXPERIMENTAL PROCEDURES

Nd$_2$Fe$_{17}$ was prepared from pure neodymium and iron (99.9%) by induction melting followed by homogenization annealing at 1150 °C for 40 h in an argon atmosphere. A homogenized ingot of Nd$_2$Fe$_{17}$ was pulverized and then nitrogenated at 465 °C in NH$_3$+H$_2$ mixed gas. Dehydrogenation, i.e., annealing at 465 °C for 0.5 h in an argon atmosphere, proceeded for the nitrogenated samples. Two

Nd$_2$Fe$_{17}$N$_x$ samples were prepared at the nominal nitrogen contents $x=3.0$ and 3.2, which were estimated from the chemical analyses. The residual hydrogen contents were chemically determined as H$_{0.06}$ and H$_{0.05}$ for the N$_{3.0}$ and N$_{3.2}$ samples, respectively. Neutron powder diffraction measurements were carried out on nitrogen-free Nd$_2$Fe$_{17}$ and two nitrogenated samples, using a multidetector-type high-resolution powder diffractometer constructed in the JRR3M reactor hall by Morii *et al.*[12]

The instrument was operated at $\lambda = 1.8232$ Å with collimation of 6'-20'-6' from the first collimator through the third collimator. Each powder sample was stored in a 10ϕ ×40-mm^3 vanadium sample container. The data accumulation was performed stepwise, 0.05° per step. Measured neutron diffraction intensities were analyzed using the Rietveld technique implemented in the program RIETAN.[13] The calculation was carried out assuming the space group $R\bar{3}m$ (No. 166) for Nd$_2$Fe$_{17}$N$_x$ with $x=0$, 3.0, and 3.2. The magnetization directions of the neodymium and iron atoms were assumed to be parallel to the c plane of the hexagonal unit cell.

III. RESULTS

Measured neutron diffraction intensities (dots) and the fitted intensities (lines) of Nd$_2$Fe$_{17}$N$_{3.2}$ are shown in Fig. 1. The profile-fitting calculations for the obtained diffraction patterns were performed from $2\theta = 18°$ through 150° without "excluded regions." The diffraction pattern of the Nd$_2$Fe$_{17}$ sample differs from the other two patterns; e.g., the 110 $(2\theta \sim 24°)$ and 220 $(2\theta \sim 49°)$ peaks grew significantly in the nitrogenated samples. On the other hand, the main peak 223 $(2\theta \sim 60°)$ of Nd$_2$Fe$_{17}$ was lower in Nd$_2$Fe$_{17}$N$_{3.2}$. A small amount (slightly less than 0.4 vol %) of α-Fe was deposited in the Nd$_2$Fe$_{17}$N$_x$ sample as shown in Fig. 1. A small Bragg reflection indicated by an asterisk $(2\theta \sim 51°)$ corresponds to the 220 peak of α-Fe, which was unavoidably high in the N$_2$ gas direct-charged samples.[11]

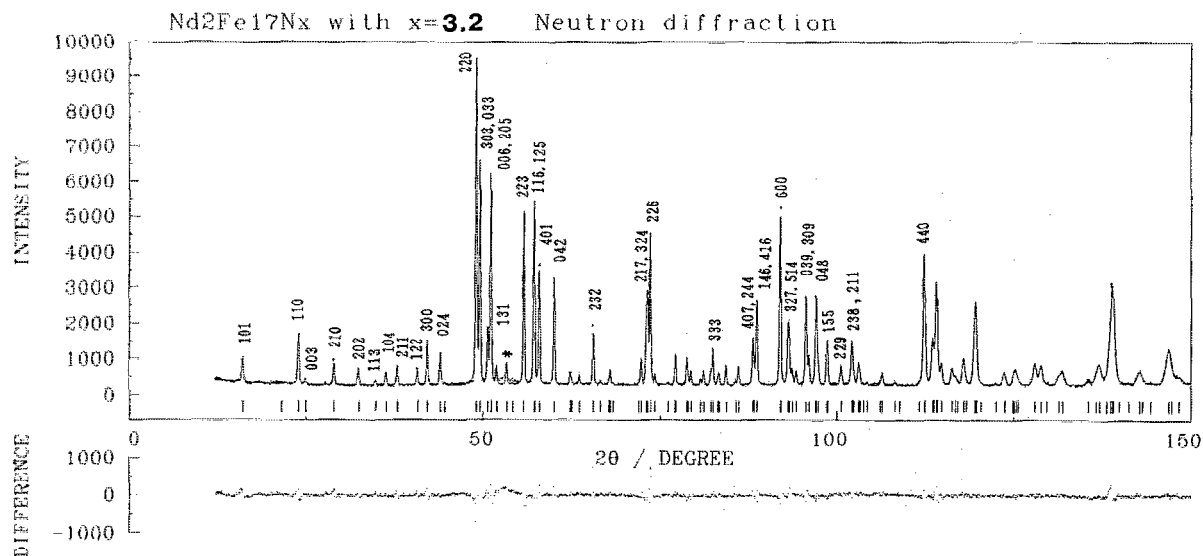Table I shows the determined structural parameters

FIG. 1. Neutron diffraction patterns of $Nd_2Fe_{17}N_{3.2}$.

and magnetic moments of metal atoms. The chemical formulas of the nitrogenated samples estimated from the occupation probabilities at each atom site become $Nd_2Fe_{17}N_{2.85(12)}$ and $Nd_2Fe_{17}N_{2.91(24)}$, respectively. Some discrepancies between the nominal compositions could be discussed in terms of the precipitation of an amorphous rare-earth-metal-rich nitrogenated phase reported[6] previously. Hereafter, we refer to these formulas to distinguish our nitrogenated samples.

Most of the nitrogen atoms have been found in the $9e$ ($\frac{1}{2}$, 0, 0) sites which are sixfold-coordinated by two rare-earth atoms and four iron atoms. The same site was found to be occupied by carbon[8] and deuterium[9,10] in the isomorphic R_2Fe_{17} crystals. On the other hand, the $18g$ (x, $\frac{2}{3}$, $\frac{1}{6}$) sites with $x=0.135$ were partly occupied by deuterium. The present calculations were carried out assuming nitrogen partial occupancies at both the $9e$ ($\frac{1}{2}$, 0, 0) and $18g$ (x, $\frac{2}{3}$, $\frac{1}{6}$) sites. Since a small amount of hydrogen is contained in the present nitrogenated samples, the structural analyses should have taken hydrogen into account. However, we tentatively ignored hydrogen in the calculations to avoid complexity. In the $Nd_2Fe_{17}N_{2.85}$ sample, the occupation probability at the $18g$ site became less than the meaningful level, and then it was ignored. There is some discrepancy between these results and the earlier work.[11] The magnetic moment of Nd was set to zero in the Nd_2Fe_{17} sample because of its low Curie point at 57 °C.[9] The magnetic moments of the iron atoms are estimated to be at low or negligible levels. The magnetic moments of neodymium and iron increase appreciably in the nitrogenated samples.

Table II shows relevant interatomic distances in the present three samples. The small letters c, d, f, and h represent the Wyckoff notations of the $6c$, $9d$, $18f$, and $18h$ sites, respectively. Changes in the local atomic arrangements due to the nitrogenation can be detected from the variations in the interatomic distances. The shortest interatomic distance between a $9e$ ($\frac{1}{2}$, 0, 0) site and an Fe(3)f site, corresponding to a N–Fe(3)f distance in the nitrides,

increases widely from 1.815(6) Å in Nd_2Fe_{17} to 1.912(5) and 1.913(6) Å in $Nd_2Fe_{17}N_{2.85}$ and $Nd_2Fe_{17}N_{2.91}$ samples, respectively. On the other hand, the interatomic distances, Fe(1)c–Fe(1)c ("dumbbell") and Fe(3)f–Fe(3)f ("ring"), are kept almost constant before and after nitrogenation.

IV. DISCUSSION AND SUMMARY

High-resolution neutron powder diffraction measurements done on $Nd_2Fe_{17}N_x$ with $x=0$, 2.85, and 2.91 were carried out at room temperature. The neutron powder diffraction patterns demonstrated the good quality of the present samples, although a small amount, about 0.4 vol %, of α-Fe was deposited in the nitrogenated samples. No extra Bragg line was observed in Nd_2Fe_{17}. The lattice expansion rates of the Nd_2Fe_{17} lattice are 2.66×10^{-3} and 1.83×10^{-3} along the a and c axes, respectively, due to the insertion of one nitrogen in a unit cell. Those values are about 2.5 times higher than the hydrides but are relatively isotropic and more moderate than the carbides such as $Nd_2Fe_{17}C_{0.5}$.[8] The significant increase of the Curie temperature in the nitrides[6] may partly be attributed to local strain and a lattice expansion introduced by the insertion of nitrogen.

The nitrogen location, i.e., the $9e$($\frac{1}{2}$, 0, 0) site, and the occupation probability in that site are successfully determined in $Nd_2Fe_{17}N_{2.85}$ and $Nd_2Fe_{17}N_{2.91}$. A small amount of nitrogen atoms are possibly located in $18g$(x, $\frac{2}{3}$, $\frac{1}{6}$) site with $x=0.189$ in $Nd_2Fe_{17}N_{2.91}$. It is conceivable that the atoms located there are hydrogen instead of nitrogen since some hydrogen atoms coexist in the present nitrogenated samples. Further diffraction work is needed to work on the highly nitrogen (+hydrogen)-charged samples to differentiate the location sites and their occupancies by hydrogen and nitrogen atoms in a unit cell.

The total magnetic moments of $Nd_2Fe_{17}N_{2.85}$ and $Nd_2Fe_{17}N_{2.91}$ determined from the obtained magnetic moments of each metal are $32.5(80)\mu_B$ and $40.2(96)\mu_B$, re-

TABLE I. Structural parameters of $Nd_2Fe_{17}N_x$ with $x=0-3.2$ (nominal) determined by neutron diffraction. Space group $R\bar{3}m$ (No. 166), Th_2Zn_{17}-type structure.

Atoms	Nd_2Fe_{17}	$Nd_2Fe_{17}N_{3.0}$	$Nd_2Fe_{17}N_{3.2}$
Nd	$occ.=1.0$	1.0	1.0
$6c(0\ 0\ z)$	$z=0.3433(10)$	0.3444(11)	0.3446(13)
	$B=0.33(20)A^2$	0.73(26)	0.81(32)
	$m=0.0\ \mu_B$	1.6(5)	1.8(6)
Fe(1)	$occ.=1.0$	1.0	1.0
$6c(0\ 0\ z)$	$z=0.0960(7)$	0.0944(8)	0.0948(9)
	$B=0.36(8)$	0.47(9)	0.38(14)
	$m=0.6(15)$	2.8(6)	2.4(6)
Fe(2)	$occ.=1.0$	1.0	1.0
$9d(1/2\ 0\ 1/2)$	$B=0.36$	0.47	0.38
	$m=0.0(15)$	1.5(6)	2.1(6)
Fe(3)	$occ.=1.0$	1.0	1.0
$18f(x\ 0\ 0)$	$x=0.2884(7)$	0.2821(6)	0.2820(7)
	$B=0.36$	0.47	0.38
	$m=0.5(14)$	1.4(6)	2.0(5)
Fe(4)	$occ.=1.0$	1.0	1.0
$18h(x\ -x\ z)$	$x=0.1689(4)$	0.1725(5)	0.1723(5)
	$z=0.4898(5)$	0.4858(5)	0.4860(5)
	$B=0.32$	0.47	0.38
	$m=0.1(14)$	1.8(4)	2.1(4)
N(1)		$occ.=0.95(4)$	0.95(4)
$9e(1/2\ 0\ 0)$		$B=0.46(29)$	0.28(31)
N(2)			$occ.=0.01(2)$
$18g(x\ 2/3\ 1/6)$			$x=0.189(57)$
			$B=0.28$
Lattice constants(A)			
a axis	8.5782(3)	8.7746(5)	8.7773(4)
c axis	12.4611(5)	12.6570(6)	12.6602(5)
Residuals			
R_p	0.070	0.069	0.072
R_I	0.038	0.031	0.044
R_r	0.025	0.020	0.029
Chemical formulae	Nd_2Fe_{17}	$Nd_2Fe_{17}N_{2.85(12)}$	$Nd_2Fe_{17}N_{2.91(24)}$

TABLE II. Interatomic distances (Å) between nearest atoms in $Nd_2Fe_{17}N_x$ with $x=0-3.2$ (nominal).

| Atom pairs	Nd_2Fe_{17}	$Nd_2Fe_{17}N_{3.0}$	$Nd_2Fe_{17}N_{3.2}$
Nd-Fe(1)c	3.082(21)	3.164(24)	3.163(24)
Nd-Fe(2)d	3.313(12)	3.388(14)	3.390(16)
Nd-Fe(3)f	3.073(15)	3.177(17)	3.178(20)
Nd-Fe(4)h	3.105(20)	3.174(22)	3.172(24)
	3.259(20)	3.390(22)	3.385(24)
	3.205(19)	3.203(21)	3.209(23)
Fe(1)c-Fe(1)c	2.393(17)	2.390(20)	2.400(23)
Fe(1)c-Fe(2)d	2.628(9)	2.693(10)	2.692(11)
Fe(1)c-Fe(3)f	2.748(11)	2.749(11)	2.751(13)
Fe(1)c-Fe(4)h	2.643(10)	2.678(12)	2.679(12)
Fe(2)d-Fe(3)f	2.440(6)	2.477(5)	2.477(6)
Fe(2)d-Fe(4)h	2.463(9)	2.496(10)	2.498(10)
Fe(3)f-Fe(3)f	2.474(6)	2.475(5)	2.475(6)
Fe(3)f-Fe(4)h	2.871(12)	2.998(12)	2.998(13)
	2.681(11)	2.718(11)	2.721(12)
Fe(4)h-Fe(4)h	2.522(9)	2.646(10)	2.643(10)
N(1)-Nd	(2.479(12))	2.537(14)	2.538(16)
N(1)-Fe(3)f	(1.815(6))	1.912(5)	1.913(6)
N(1)-Fe(4)h	(1.950(7))	1.930(8)	1.933(8)
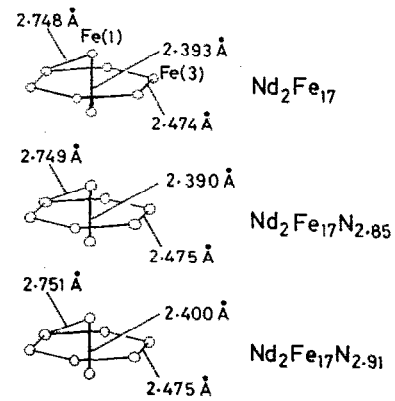
FIG. 2. Local ORTEP drawings of 2Fe(1)-6Fe(3), a dumbbell and a ring.

spectively. We determined the spontaneous magnetic moment of $Nd_2Fe_{17}N_{2.85}$ as $37.6\mu_B$, which was extrapolated from the magnetization measured in the sufficiently high magnetic field up to 250 kOe, being slightly higher than the value determined by the diffraction work. This discrepancy may be within experimental error.

Observed variations in the interatomic distances in the samples indicate that the Fe(1)c–Fe(1)c dumbbell and six-member Fe(3)f ring are stable against nitrogen uptake. Figure 2 shows partial ORTEP drawings of a combination of a dumbbell and a ring contained in a unit cell of Nd_2Fe_{17}, $Nd_2Fe_{17}N_{2.85}$, and $Nd_2Fe_{17}N_{2.91}$. The 2Fe(1)-6Fe(3) group seems to be bound rather tightly relative to the rest of the atoms in a unit cell.

ACKNOWLEDGMENTS

[1] H. Imai and T. Iriyama, Japanese Patent No. 228547/88 (1988).
[2] T. Iriyama, K. Kobayashi, and H. Imai, European Patent Appl. Pub. No. 0-369-097-A1 (1989).
[3] K. Kobayashi, T. Iriyama, N. Imaoka, A. Sudo, and N. Kashiwaya, European Patent Appl. Pub. No. 0-417-733-A2 (1990).
[4] J. M. D. Coey and H. Sun, J. Magn. Magn. Mater. 87, L251 (1990).
[5] K. Schnitzke, L. Schultz, J. Wecker, and M. Katter, Appl. Phys. Lett. 57, 2853 (1990).
[6] T. Iriyama, K. Kobayashi, N. Imaoka, T. Fukuda, H. Kato, and Y. Nakagawa, IEEE Trans. Mag. 28, 2326 (1992).
[7] F. R. de Boer, R. Verhoef, Zhang Zhi-dong, D. B. De Mooij, and K. H. J. Buschow, J. Magn. Magn. Mater. 72, 167 (1988).
[8] R. B. Helmholdt and K. H. J. Buschow, J. Less-Common Met. 155, 15 (1989).
[9] B. Rupp and G. Wiesinger, J. Magn. Magn. Mater. 71, 269 (1988).
[10] O. Isnard, S. Miraglia, J. L. Soubeyroux, and D. Fruchart, Solid State Commun. 81, 13 (1992).
[11] S. S. Jaswal, W. B. Yelon, G. C. Hadjipanayis, Y. Z. Wang, and D. J. Sellmyer, Phys. Rev. Lett. 67, 644 (1991).
[12] Y. Morii, K. Fuchizaki, S. Funahashi, N. Minakawa, Y. Shimojo, and A. Ishida, in Proceedings of the Fourth International Symposium on Advances in Nuclear Engineering Research, February 1992, Mito, Japan, p. 280.
[13] F. Izumi, J. Cryst. Soc. Jpn. 34, 76 (1992) [in Japanese].