
01 Aug 1998

Neutron Diffraction and Mössbauer Spectral Study of Nd₂Fe₁₆Ti and Its Nitride

Fernande Grandjean

Missouri University of Science and Technology, grandjeanf@mst.edu

Peter C. Ezekwenna

Gary J. Long

Missouri University of Science and Technology, glong@mst.edu

Oran Allan Pringle

Missouri University of Science and Technology, pringle@mst.edu

et. al. For a complete list of authors, see https://scholarsmine.mst.edu/chem_facwork/778

Follow this and additional works at: https://scholarsmine.mst.edu/chem_facwork

 Part of the [Chemistry Commons](#), and the [Physics Commons](#)

Recommended Citation

F. Grandjean et al., "Neutron Diffraction and Mössbauer Spectral Study of Nd₂Fe₁₆Ti and Its Nitride," *Journal of Applied Physics*, vol. 84, no. 4, pp. 1893-1900, American Institute of Physics (AIP), Aug 1998. The definitive version is available at <https://doi.org/10.1063/1.368317>

This Article - Journal is brought to you for free and open access by Scholars' Mine. It has been accepted for inclusion in Chemistry Faculty Research & Creative Works by an authorized administrator of Scholars' Mine. This work is protected by U. S. Copyright Law. Unauthorized use including reproduction for redistribution requires the permission of the copyright holder. For more information, please contact scholarsmine@mst.edu.

Neutron diffraction and Mössbauer spectral study of $\text{Nd}_2\text{Fe}_{16}\text{Ti}$ and its nitride

F. Grandjean^{a)}

Institute of Physics, B5, University of Liège, B-4000 Sart-Tilman, Belgium

P. C. Ezekwenna, Gary J. Long, and O. A. Pringle

Departments of Chemistry and Physics, University of Missouri-Rolla, Rolla, Missouri 65409-0010

Ph. l'Héritier and M. Ellouze

Laboratoire des Matériaux et du Génie Physique, ENS de Physique de Grenoble, F-38402 Saint-Martin d'Hères Cédex, France

H. P. Luo and W. B. Yelon

University of Missouri Research Reactor, University of Missouri-Columbia, Columbia, Missouri 65211

(Received 3 March 1998; accepted for publication 14 May 1998)

The 295 K powder neutron diffraction patterns and the temperature dependence of the Mössbauer spectra of $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x$ and $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x\text{N}_y$ have been measured. A Rietveld refinement of the neutron diffraction patterns yields the $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ stoichiometries for the two compounds and indicates that titanium occupies only the $6c$ crystallographic site and nitrogen only the $9e$ site in the rhombohedral $\text{Th}_2\text{Zn}_{17}$ structure. The insertion of interstitial nitrogen into $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ produces a 6.8% increase in the unit cell volume. The relative areas of the Mössbauer spectral components indicate that iron–iron, iron–titanium, and titanium–titanium $6c$ – $6c$ dumbbell pairs exist in both of these materials. The magnetic hyperfine fields observed for the iron on the $6c$ site in the iron–titanium dumbbell pair in both compounds is substantially reduced from that found in $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ because of the titanium dumbbell near neighbor. For all the remaining hyperfine parameters there is a good correlation with those observed in $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$. A linear increase is observed for the weighted average isomer shift with increasing unit cell volume for $\text{Nd}_2\text{Fe}_{17}$, $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$, $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$, and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$, because of the decreasing s -electron density at the iron-57 nucleus. © 1998 American Institute of Physics. [S0021-8979(98)07116-3]

I. INTRODUCTION

The crystallographic and magnetic properties of the pseudobinary $\text{Nd}_2\text{Fe}_{17-x}\text{M}_x$ solid solutions, where M is a metal or a metalloid, have been studied extensively^{1–5} because the substitution of iron by a nonmagnetic atom, M, increases the Curie temperature of the material, at least for x values smaller than ~ 3 . The substitution of iron by aluminum, gallium, titanium, vanadium, and niobium, leads to an expansion of the unit cell volume, whereas substitution by silicon, copper, and zirconium leads to a contraction of the unit cell volume. Hence, in the various compounds, the increase in Curie temperature cannot result solely from the unit cell expansion as has been proposed earlier.^{6–8}

The substitutional patterns of the M atom on the four different crystallographic sites of the $\text{Th}_2\text{Zn}_{17}$ structure have been determined by neutron diffraction. For x less than 2, aluminum, silicon, and gallium show^{1–4} a strong preference for the $18h$ site, whereas titanium, vanadium, and niobium show⁵ a strong preference for the $6c$ site. The Mössbauer spectra of the $\text{Nd}_2\text{Fe}_{17-x}\text{M}_x$ solid solutions, where M is aluminum and silicon, have been analyzed^{2,4} in terms of a binomial distribution of near neighbors based upon the site

occupancies determined from neutron diffraction studies. Hence, it is of value to study the Mössbauer spectra of the $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x$ solid solutions, in which titanium is expected to substitute for iron on the $6c$ site. A preliminary study of an earlier sample of $\text{Nd}_2\text{Fe}_{16}\text{Ti}$ has already been reported.⁹

$\text{Nd}_2\text{Fe}_{17}$ and all the pseudobinary $\text{Nd}_2\text{Fe}_{17-x}\text{M}_x$ solid solutions crystallize in the $\text{Th}_2\text{Zn}_{17}$ rhombohedral structure⁶ with the $R\bar{3}m$, No. 166 space group. This structure has been extensively described in the literature^{6–8} and only the structural features, which are important for the following discussion, are described herein. The neodymium atoms occupy the $6c$ site and the iron atoms occupy the four crystallographically different $6c$, $9d$, $18f$, and $18h$ sites. The iron atoms on the $6c$ site form a dumbbell pair, situated at the center and perpendicular to a hexagon of iron $18f$ atoms. When titanium replaces iron on the $6c$ site in $\text{Nd}_2\text{Fe}_{17}$, the iron–titanium distance is 2.435 Å, a distance which is both 0.3 Å smaller than the sum of the atomic radii of iron and titanium, and 0.055 Å smaller than the sum of their covalent radii. Hence, it might be difficult to accommodate both an iron and a titanium atom in a $6c$ dumbbell pair and even more difficult to accommodate two titanium atoms in such a dumbbell pair. In contrast, from the reported^{5,9} 38% titanium occupancy on the $6c$ in $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x$, a random binomial distribution of iron and titanium on the $6c$ dumbbell pair

^{a)}Electronic mail: fgrandjean@ulg.ac.be

yields 38% iron–iron pairs, 47% iron–titanium pairs, and 14% titanium–titanium pairs. Because of the potential steric crowding on the $6c$ site, we have speculated that one titanium atom might replace one dumbbell pair by occupying the $3a$ site at the center of the dumbbell and the center of the $18f$ hexagon in the $\text{Th}_2\text{Zn}_{17}$ structure. In order to investigate this hypothesis, we have prepared a sample of nominal stoichiometry $\text{Nd}_2\text{Fe}_{15}\text{Ti}$, a sample which has been subsequently nitrated. Herein, we report on a neutron diffraction and Mössbauer spectral study of the resulting samples.

II. EXPERIMENT

The stoichiometric amounts of neodymium, iron, and titanium required to form $\text{Nd}_2\text{Fe}_{15}\text{Ti}$ were arc melted and the resulting ingot annealed at 1270 K for 72 h. The powder x-ray diffraction patterns of the resulting materials were measured with a Guinier–Hagg camera and chromium K_α radiation. The results reveal the $\text{Th}_2\text{Zn}_{17}$ structure with $a = 8.6006 \text{ \AA}$, $c = 12.5099 \text{ \AA}$, and $V = 801.4 \text{ \AA}^3$. Traces of α -iron were also observed by x-ray diffraction, and its presence, as well as the absence of any traces of $\text{NdFe}_{11}\text{Ti}$, was also confirmed by thermal magnetic analysis.

The nitridation of the presumed $\text{Nd}_2\text{Fe}_{15}\text{Ti}$ sample was carried out under nitrogen gas at a pressure of 13 MPa at 700 K for 22 h. The introduction of 3.8 nitrogen atoms per formula unit was indicated by the weight increase upon nitridation. The lattice expansion upon titanium substitution might be sufficient to permit some nitrogen to occupy the $18g$ interstitial site within the iron $18h$ hexagon, but neutron diffraction results (see below) indicate that this is not the case.

The powder x-ray diffraction pattern indicates that the presumed $\text{Nd}_2\text{Fe}_{15}\text{TiN}_{3.8}$ sample crystallizes in the $\text{Th}_2\text{Zn}_{17}$ structure with $a = 8.8173 \text{ \AA}$, $c = 12.7033 \text{ \AA}$, and $V = 855.3 \text{ \AA}^3$. The volume expansion upon nitridation is 6.3%, a value which is identical to that measured for $\text{Nd}_2\text{Fe}_{17}$ upon nitridation.⁸

The powder neutron diffraction patterns were measured by using a linear position sensitive detector and neutrons with a wavelength of 1.7675 \AA . The data for each sample were collected over ~ 24 h at 295 K between 2θ angles of 5° and 105° on approximately 2 g of finely powdered sample placed in a thin wall vanadium container. Refinements of the neutron diffraction data were carried out with the FULLPROF¹⁰ computer code which permits multiple phase refinement as well as a magnetic structure refinement for each of the coexisting phases. The goodness-of-fit parameters given by this program include the pattern R factor, R_p , the weighted pattern R factor, R_{wp} , the magnetic R factor, $R_{magnetic}$, and the goodness-of-fit indicator, χ^2 . These parameters, as well as the thermal parameter, B , are defined in Refs. 11 and 12. The results are discussed in detail below.

The Mössbauer spectra were obtained between 78 and 295 K on a constant-acceleration spectrometer which utilized a room temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with α -iron foil. The Mössbauer absorbers, which were $\sim 30 \text{ mg/cm}^2$, were prepared from powdered samples which had been sieved to a 0.045 mm or smaller particle diameter. The resulting spectra

TABLE I. Neutron diffraction results for the $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x$ and $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x\text{N}_y$ solid solutions.

	$\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x$		$\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x\text{N}_y$	
	Best fit	Consistent fit	Best fit	Consistent fit
x	0.80(8)	0.68(6)	0.70(8)	0.68(6)
y	2.73(4)	2.70(4)
$a, \text{ \AA}$	8.6027(3)	8.6027(3)	8.8205(5)	8.8205(6)
$c, \text{ \AA}$	12.5174(5)	12.5173(5)	12.7130(8)	12.7131(9)
c/a	1.4551(1)	1.4550(1)	1.4413(2)	1.4413(2)
$V, \text{ \AA}^3$	802.26(9)	802.26(9)	856.6(1)	856.6(1)
Nd, $6c, z$	0.3448(4)	0.3448(4)	0.3459(5)	0.3460(6)
Fe/Ti, $6c, z$	0.0995(5)	0.0996(5)	0.0978(5)	0.0979(7)
Fe/Ti, $18f, x$	0.2932(2)	0.2933(2)	0.2824(2)	0.2823(3)
Fe/Ti, $18h, x$	0.1677(1)	0.1677(1)	0.1713(2)	0.1714(2)
Fe/Ti, $18h, z$	0.4921(2)	0.4921(2)	0.4859(2)	0.4860(2)
% Ti, $6c$	33.9(3)	33.9(3)	24.3(3)	33.9
% Ti, $9d$	0.0	0.0	0.0	0.0
% Ti, $18f$	1.9(4)	0.0	0.0	0.0
% Ti, $18h$	0.0	0.0	3.5(4)	0.0
R_p factor	4.30	4.38	4.47	5.21
R_{wp} factor	5.55	5.71	5.64	6.51
R_m factor	4.41	4.68	6.52	13.9
χ^2	2.42	2.57	1.94	2.58
$\mu_{\text{Nd}, 6c}, \mu_B$	1.3(2)	1.3(2)	1.8(1)	1.6(1)
$\mu_{\text{Fe}, 6c}, \mu_B$	1.65	1.65	2.22	2.22
$\mu_{\text{Fe}, 9d}, \mu_B$	1.40	1.40	2.19	2.19
$\mu_{\text{Fe}, 18f}, \mu_B$	1.27	1.27	1.73	1.73
$\mu_{\text{Fe}, 18h}, \mu_B$	1.22	1.22	1.95	1.95
$B_{\text{Nd or Fe/Ti}}, \text{ \AA}$	1.08(4)	1.08(4)	1.03(5)	1.06(6)
$B_N, \text{ \AA}$	0.65(16)	0.61(18)
Fe ₂ Ti, vol. %	5.1(1)	5.1(1)	0.0	0.0
α -Fe, vol. %	1.3(1)	1.3(1)	8.1(2)	7.9(2)

have been fit as discussed below and the estimated errors are $\pm 1 \text{ kOe}$ for the hyperfine fields, $\pm 0.005 \text{ mm/s}$ for the isomer shifts, and $\pm 0.01 \text{ mm/s}$ for the quadrupole shifts.

III. NEUTRON DIFFRACTION RESULTS

The results of the Rietveld refinement of the 295 K powder neutron diffraction patterns for the nominal $\text{Nd}_2\text{Fe}_{15}\text{Ti}$ sample immediately indicated that the compound crystallized with the $\text{Th}_2\text{Zn}_{17}$ structure and that titanium did not occupy the $3a$ site. Thus the two compounds were reformulated as $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x$ and $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x\text{N}_y$, and the stoichiometric variables, x and y , were determined from Rietveld refinements. The results are given in Table I and the refined patterns are shown in Figs. 1 and 2, respectively. Thus, for the purposes of this article, the two compounds are formulated as $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$.

For both solid solutions, it was immediately obvious from the initial refinements that there was a very high correlation between the refined values of x , the small amount of titanium on the $18f$ and/or $18h$ sites, and the iron magnetic moments. To overcome the difficulties associated with these correlations, in all subsequent fits the iron magnetic moments were constrained to be consistent with the magnetic hyperfine fields obtained from the Mössbauer spectral analysis discussed below. With only this constraint, the “best fit” refinements given in Table I were obtained. It should be noted that there are some unusual differences in these two refine-

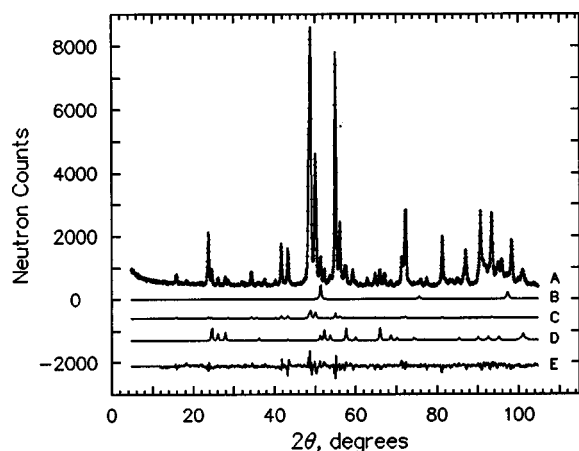


FIG. 1. The 295 K powder neutron diffraction pattern and refinement (A), α -iron (B), magnetic contribution (C), Fe_2Ti nuclear contribution (D), and the residual (E) for $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$. The contribution of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ is not shown separately.

ments, differences that seem quite inconsistent with the use of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ as the starting material for the preparation of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$. First, there is a completely unexpected change in the titanium occupancy found for the $18f$ and $18h$ sites in the two compounds, a change that seems physically unreasonable in view of the temperatures used for the nitridation. It was not possible to obtain a viable refinement of the diffraction data in which the same small amount of titanium was on the same $18f$ and/or $18h$ sites, or on both sites, in both $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$. Second, there has been a totally unexpected and physically unreasonable change in x upon nitridation. Third, the amount of α -iron has increased and the amount of Fe_2Ti has decreased upon nitridation.

Because of the first two difficulties mentioned above, an alternative refinement was carried out in which no titanium was allowed to occupy either the $18f$ or $18h$ sites in either compound and the stoichiometric amount of titanium, x , was constrained to be the same in each compound. The resulting refinements are given as the "consistent fits" in Table I. It

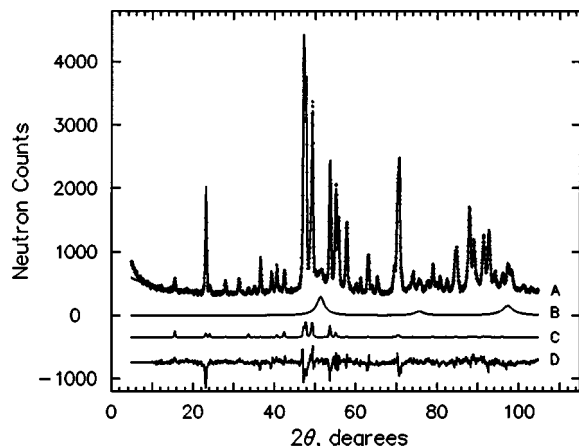


FIG. 2. The 295 K powder neutron diffraction pattern and refinement (A), broadened α -iron (B), magnetic contribution (C), and the residual (D) for $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$. The contribution of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ is not shown separately.

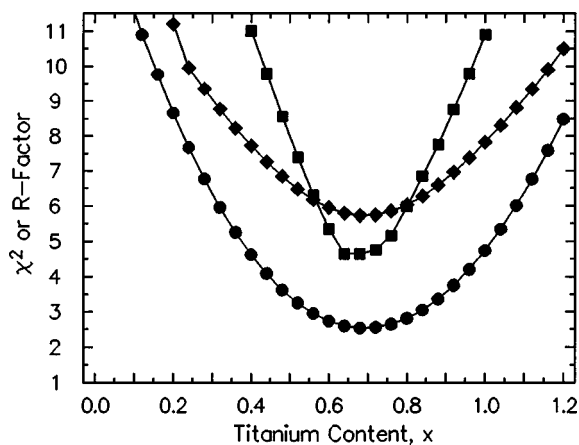


FIG. 3. The dependence of χ^2 (●) and the $R_{\text{wp-}}$ (◆) and $R_{\text{m-}}$ (■) factors, as a function of x , the amount of titanium on the crystallographic $6c$ site, in $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x$.

was immediately obvious that, in the case of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$, the consistent fit is virtually identical to and as valid as the best fit. Further, the titanium occupancy of the $6c$ site is well determined as is shown in Fig. 3, which reveals a well defined minimum in the R factors and χ^2 .

All attempts at a refinement that replaced the two $6c-6c$ dumbbell atoms with a single titanium atom at the $3a$ site lead to unreasonable, substantially higher, R factors and χ^2 values than those shown in Fig. 3. Thus, we are forced to conclude that titanium cannot occupy the $3a$ site in this structure.

In the case of $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x\text{N}_y$ (as is shown in Fig. 4), the consistent fit indicated by the arrow is not quite as good as the best fit, but we believe that this is the most physically reasonable fit in view of the thermal properties of $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x$. The refined y value of 2.7 and the 6.8% lattice expansion are virtually the same as that found for the nitridation^{9,13} of $\text{Nd}_2\text{Fe}_{17}$ and related¹⁴ R_2Fe_{17} compounds, where R=rare earth. The powder neutron diffraction pattern of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ does not show the presence of any Fe_2Ti because the latter compound is decomposed under the

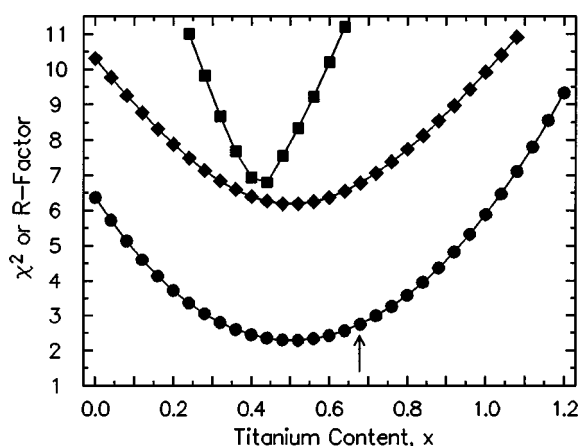


FIG. 4. The dependence of χ^2 (●) and the $R_{\text{wp-}}$ (◆) and $R_{\text{m-}}$ (■) factors, as a function of x , the amount of titanium on the crystallographic $6c$ site, in $\text{Nd}_2\text{Fe}_{17-x}\text{Ti}_x\text{N}_{2.7}$. The arrow indicates the values for the most "consistent fit" reported in Table I.

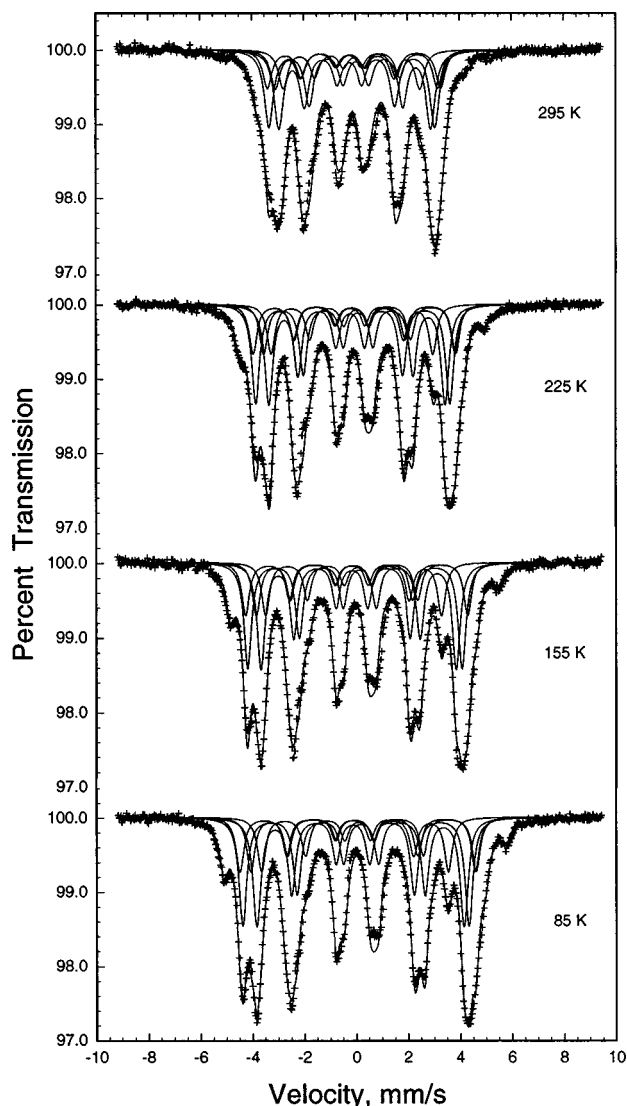


FIG. 5. The Mössbauer spectra of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ obtained at the indicated temperatures.

conditions of the preparation into α -iron and noncrystalline titanium nitride. This accounts for the increase in the amount of α -iron in the nitrated compound.

An attempt to place nitrogen on the tetrahedral interstitial 18g site led to a slightly, but not significantly, better refinement with at most 3% nitrogen occupancy of the 18g site. The neglect of this nitrogen has no influence upon the remaining parameters given in Table I. Thus, in spite of the nominal 3.8 nitrogen atoms per formula unit, the neutron diffraction results indicate that nitrogen is found virtually only on the octahedral 9e site to the extent of 2.7 nitrogen atoms per formula unit. This is the amount of nitrogen typically found^{7,13,15} on the 9e site, and it is believed that the additional nitrogen uptake may be associated with the decomposition of Fe_2Ti to form amorphous titanium nitride and α -iron.

IV. MÖSSBAUER SPECTRAL RESULTS

The Mössbauer spectra of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$, obtained between 85 and 295 K, are shown in Fig. 5. The analysis of

these spectra is based both on the titanium site occupancy determined from the neutron diffraction results and the analysis of the Mössbauer spectra^{13–15} of $\text{Nd}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}$. If there is any titanium present on the 18f site, it is a very small amount, as indicated in Sec. III. Hence, we have assumed that titanium occupies only the 6c site at 33.9% and the actual composition of the sample is $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$, as determined from the most “consistent fit” neutron diffraction results presented in Table I. With this assumption, the expected relative areas of the 6c, 9d, 18f, and 18h contributions to the Mössbauer spectrum are 8.2%, 18.4%, 36.8%, and 36.8%, respectively. Furthermore, because of both the basal orientation of the magnetization and the 9d, 18f, and 18h site symmetry, the contributions of these sites are divided^{13–15} into two sextets with relative areas of two to one. Hence, at least seven sextets are required to fit the spectra.

A close examination of the 85 K spectrum of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ indicates that the peak observed at 5.8 mm/s, which is usually assigned^{13–15} to the 6c site, has a relative area of at most 4.5%, i.e., approximately one-half the expected area of 8.2%. If titanium randomly occupies the 6c site, a binomial distribution would indicate the presence of 44% iron–iron dumbbell pairs, 45% iron–titanium dumbbell pairs, and 11% titanium–titanium dumbbell pairs. Of course only the first two pairs, noted herein as 6c and 6c', would be observed in the Mössbauer spectrum and thus two sextets of equal relative areas of 4.1% are expected. Consequently, eight sextets with relative areas of 4.1%, 4.1%, 12.3%, 6.1%, 24.5%, 12.3%, 24.5%, and 12.3%, assigned to the 6c, 6c', 9d₆, 9d₃, 18f₁₂, 18f₆, 18h₁₂, and 18h₆ sites, respectively, have been used to fit the Mössbauer spectra of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$. In addition, a spectral absorption of 5.1% is assigned to the Fe_2Ti impurity observed in the neutron diffraction pattern. Thus, a ninth sextet with hyperfine parameters compatible with those¹⁶ of Fe_2Ti was also fit and its relative area amounts to ~3% of the total absorption area. No α -iron could be detected in the Mössbauer spectra in contrast with the neutron diffraction measurements which indicated the presence of 1.3% α -iron. The deconvolution and assignment of the different sextets is based on the previous analysis of the Mössbauer spectra^{13–15} of $\text{Nd}_2\text{Fe}_{17}$ and $\text{Pr}_2\text{Fe}_{17}$. The linewidth of the eight sextets is equal to 0.36 mm/s at 85, 155, and 225 K and 0.42 mm/s at 295 K. These linewidths are larger than the calibration linewidth of 0.25 mm/s and the observed^{13–15} linewidth of ~0.3 mm/s in the R_2Fe_{17} compounds. The slight broadening at 85, 155, and 225 K is probably due to the distribution of the titanium atoms in the near-neighbor environment of the four crystallographic iron sites and the additional broadening at 295 K is related to the proximity of the Curie temperature. The quality of the fits with this model is excellent as is indicated by the solid lines in Fig. 5 and the Mössbauer spectral hyperfine parameters deduced from this analysis are given in Table II. It should be noted that the analysis of the previously published⁸ Mössbauer spectrum of $\text{Nd}_2\text{Fe}_{16}\text{Ti}$ with the same model is also excellent.

In $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ the observed sequence of isomer shifts, $6c > 18f > 18h > 9d$, parallels the sequence of

TABLE II. Mössbauer spectral hyperfine parameters for $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$.

	T (K)	$6c$	$6c'$	$9d_6$	$9d_3$	$18f_{12}$	$18f_6$	$18h_{12}$	$18h_6$	W. Av.
H (kOe)	85	336	273	282	313	253	268	264	223	266
	155	319	258	265	293	240	251	249	210	251
	225	293	235	241	264	216	229	226	193	228
	295	248	198	203	223	186	197	193	163	194
δ^a (mm/s)	85	0.346	0.296	0.000	0.000	0.050	0.050	0.030	0.030	0.056
	155	0.316	0.260	-0.040	-0.040	0.020	0.020	-0.008	-0.008	0.021
	225	0.270	0.220	-0.095	-0.095	-0.030	-0.030	-0.050	-0.050	-0.027
	295	0.230	0.180	-0.150	-0.150	-0.085	-0.085	-0.095	-0.095	-0.077
QS (mm/s)	85	-0.04	0.40	0.12	-0.10	0.38	0.40	-0.30	-0.18	
	155	-0.04	0.40	0.12	-0.10	0.38	0.40	-0.30	-0.18	
	225	-0.04	0.40	0.08	-0.10	0.35	0.38	-0.30	-0.18	
	295	-0.04	0.40	0.08	-0.12	0.28	0.38	-0.24	-0.11	
Area (%)		4.1	4.1	12.2	6.2	24.5	12.2	24.5	12.2	

^aRelative to room temperature α -iron foil.

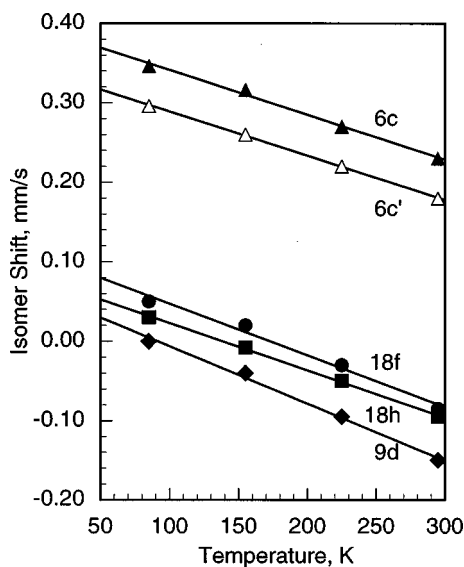
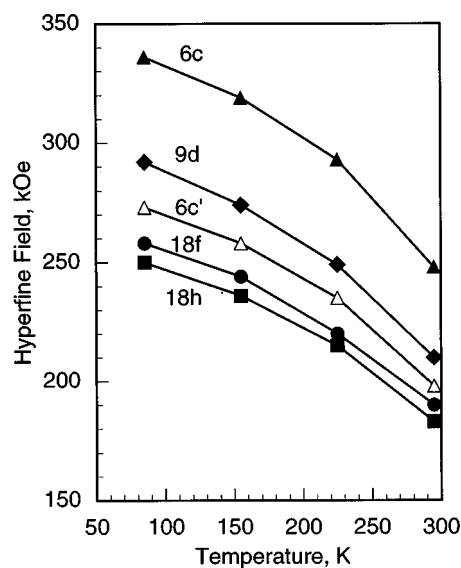
Wigner–Seitz cell volumes observed^{13–15,17,18} in many R_2Fe_{17} compounds. The isomer shift of the $6c'$ site is smaller than the isomer shift of the $6c$ site, in agreement with the presence of one titanium near neighbor. Indeed, iron in titanium has a negative¹⁹ isomer shift of -0.04 mm/s relative to α -iron. As shown in Fig. 6, the temperature dependence of the five isomer shifts is linear, in agreement with the second-order Doppler shift. From the slopes of the straight lines, effective masses of 74, 75, 58, 64, and 70 g/mol are obtained²⁰ for iron on the $6c$, $6c'$, $9d$, $18f$, and $18h$ sites, respectively.

As has previously been observed^{13–15,17,18} in many R_2Fe_{17} compounds, the sequence of site weighted average hyperfine fields, $6c > 9d > 18f > 18h$, follows the sequence of the number of iron near neighbors for the different sites. All the hyperfine fields are smaller or equal to those observed^{13,15} in $\text{Nd}_2\text{Fe}_{17}$, in agreement with the presence of titanium in the near-neighbor environment of all the sites. The $6c'$ hyperfine field is substantially smaller than the $6c$ hyperfine field, because of the presence of one titanium near

neighbor on the dumbbell pair. The smooth temperature dependence of the hyperfine fields in $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ is shown in Fig. 7 and mimics the temperature dependence of the magnetization, which is characterized by a Curie temperature of 391 K.

The values of the quadrupole shift are all consistent with the $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ structure but are somewhat different from those observed^{13,15} in $\text{Nd}_2\text{Fe}_{17}$, because of the presence of titanium in the near-neighbor environment of all the sites. The rather large value observed for the $6c'$ site is certainly related to the presence of one titanium near neighbor on the dumbbell pair. Finally, the position of the $9d_3$ line at -5 mm/s, in a fashion similar to that observed⁹ in $\text{Pr}_2\text{Fe}_{17}$, may indicate that the magnetization has rotated by 60° in the basal plane relative to its orientation in $\text{Nd}_2\text{Fe}_{17}$.

The Mössbauer spectra of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ measured at 78 and 295 K are shown in Fig. 8. The analysis of these spectra was also based upon the neutron diffraction results and the analysis of the spectra^{13,15} of $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$. A nomi-

FIG. 6. The temperature dependence of the isomer shifts in $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$.FIG. 7. The temperature dependence of the site weighted average hyperfine fields in $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$.

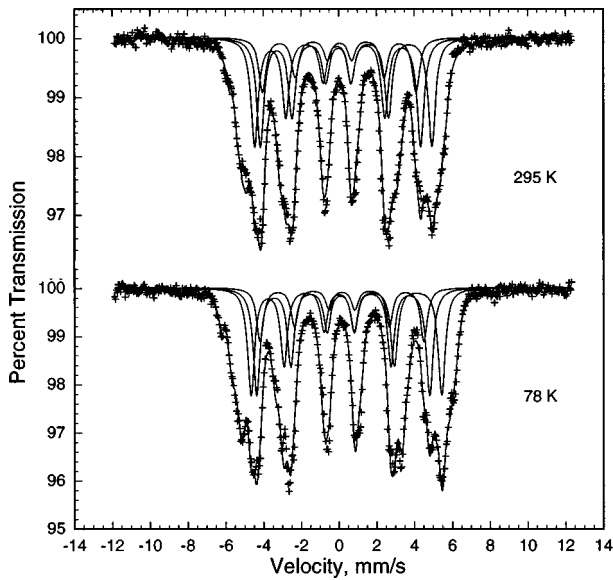


FIG. 8. The Mössbauer spectra of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ obtained at 78 and 295 K.

nal composition of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ was assumed in agreement with the neutron diffraction results discussed in Sec. III. Different spectral fits indicated that the Mössbauer spectra were insensitive to the low, $\sim 3\%$, occupancy of the $18h$ site by titanium and that equally good fits could be obtained by placing titanium only on the $6c$ site, a conclusion which is in agreement with the neutron diffraction results presented in Sec. III. Hence, titanium was assumed to occupy only the $6c$ site. Consequently, in a model similar to that used for $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$, eight sextets were used to fit the Mössbauer spectra of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ at 78 and 295 K. The linewidth of all components of the eight sextets was 0.44 mm/s. This broadening results both from the distribution of titanium atoms in the near-neighbor environment of the four sites and from the distribution of nitrogen on the $9e$ sites. In addition, a ninth sextet with the α -iron hyperfine parameters and a relative area of 8.5% was added to the fit.

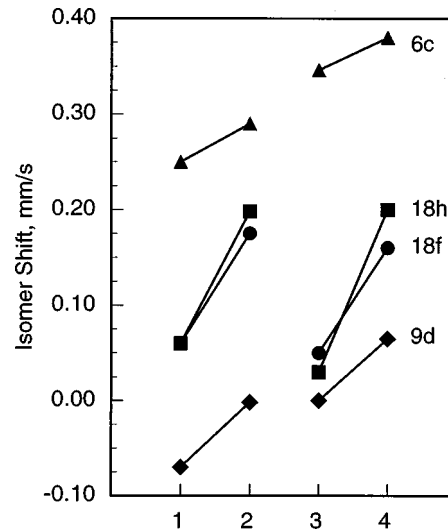


FIG. 9. The changes in the isomer shifts in $\text{Nd}_2\text{Fe}_{17}$ (1), $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (2), $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ (3), and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ (4).

The hyperfine parameters deduced from these fits are given in Table III together with the corresponding parameters^{13,15} for $\text{Nd}_2\text{Fe}_{17}$, $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.7}$, and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$, for comparison. The changes in isomer shifts and hyperfine fields from 78 to 295 K are normal.

The changes in isomer shift for the four crystallographic sites in $\text{Nd}_2\text{Fe}_{17}$, $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$, $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$, and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ are shown in Fig. 9. It is very clear that the changes upon nitridation are very similar in the two pairs of compounds i.e., in $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$, and in $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$. The general increase in isomer shift results from the unit cell expansion upon nitridation, a unit cell expansion which decreases the s -electron density at the iron nucleus. This effect is best illustrated in Fig. 10, in which the weighted average isomer shift is plotted as a function of the unit cell volume.¹⁵ It should be noted that the weighted average isomer shift for $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ has been calculated

TABLE III. Hyperfine parameters for $\text{Nd}_2\text{Fe}_{17}$ (1), $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (2), $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ (3), and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ (4).

	Cpd	T (K)	$6c$	$6c'$	$9d_6$	$9d_3$	$18f_{12}$	$18f_6$	$18h_{12}$	$18h_6$	W. Av.
H (kOe)	1	85	350	...	300	274	283	314	271	266	292
	2	85	360	...	381	366	299	315	326	332	334
	3	85	336	273	284	315	254	267	264	222	266
	4	78	348	336	358	383	284	269	313	317	313
	4	295	329	323	320	353	263	252	291	295	289
δ^a (mm/s)	1	85	0.250	...	-0.070	-0.070	0.060	0.060	0.065	0.065	0.061
	2	85	0.290	...	-0.002	-0.002	0.175	0.175	0.198	0.198	0.164
	3	85	0.340	0.290	-0.030	-0.030	0.032	0.032	0.002	0.002	0.056
	4	78	0.380	0.340	0.065	0.065	0.160	0.160	0.200	0.200	0.174
	4	295	0.290	0.250	-0.045	-0.045	0.040	0.040	0.080	0.080	0.058
QS (mm/s)	1	85	-0.06	...	-0.10	0.34	0.43	-0.10	-0.42	0.48	
	2	85	-0.38	...	-0.18	0.36	0.10	0.38	-0.20	0.38	
	3	85	-0.04	0.40	0.12	-0.10	0.38	0.40	-0.30	-0.18	
	4	78	-0.40	0.25	0.10	-0.14	0.12	0.00	0.38	-0.36	
	4	295	-0.40	0.25	0.12	-0.14	0.12	0.00	0.32	-0.36	

^aRelative to metallic α -iron foil at room temperature.

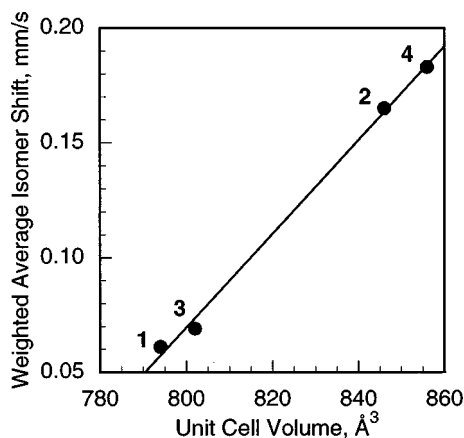


FIG. 10. The relationship between the weighted average isomer shift and the unit cell volume in $\text{Nd}_2\text{Fe}_{17}$ (1), $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (2), $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ (3), and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ (4).

ignoring the $6c'$ site and with site weights equal to their crystallographic degeneracies. The linear relation between the weighted average isomer shift and the unit cell volume indicates that the unit cell expansion is responsible primarily for the increase in isomer shift.

A more detailed examination of Fig. 9 indicates that the $18f$ and $18h$ isomer shifts actually decrease between $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ and between $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$. We believe that the presence of titanium on the $6c$ as a near neighbor is responsible for this decrease.¹⁹ In particular, the presence of titanium–titanium and titanium–iron dumbbell pairs on both sides of the $18f$ hexagon must influence the $18f$ isomer shift.

The changes in site weighted average hyperfine field in $\text{Nd}_2\text{Fe}_{17}$ (1), $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (2), $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ (3), and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ (4) are shown in Fig. 11. Here too, the similarity in the changes in the two pairs of compounds, i.e., between $\text{Nd}_2\text{Fe}_{17}$ and $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$, and between $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ is striking.

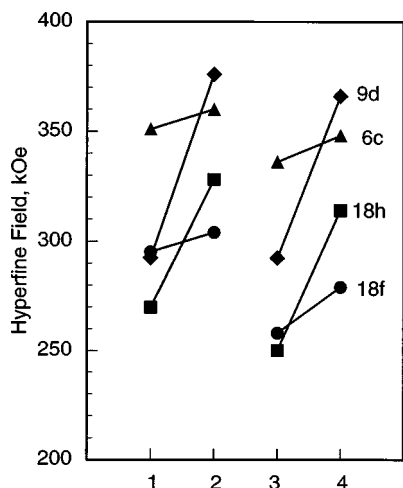


FIG. 11. The changes in the site weighted average hyperfine fields in $\text{Nd}_2\text{Fe}_{17}$ (1), $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$ (2), $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ (3), and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ (4).

V. CONCLUSIONS

The first conclusion drawn from this work is that it is not possible, at least with the synthesis method reported herein, to replace the $6c-6c$ iron–iron dumbbell pair in the $\text{Nd}_2\text{Fe}_{17}$ structure with a single titanium atom on the $3a$ site, the site which bisects the dumbbell. The 802.3 \AA^3 unit cell volume of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ is one of the largest for the R_2Fe_{17} series of compounds and is 1.0% larger than the 794 \AA^3 unit cell volume¹⁵ of $\text{Nd}_2\text{Fe}_{17}$. Apparently, a much larger increase in unit cell volume would be required to permit the placement of a titanium atom on the more crowded $3a$ site. If one uses the 1.26 \AA atomic radius or the 8.38 \AA^3 atomic volume of iron and the 1.47 \AA atomic radius or the 13.31 \AA^3 atomic volume of titanium to calculate the expected increase in the unit cell volume in going from $\text{Nd}_2\text{Fe}_{17}$ to $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$, one obtains an expected expansion of 10.2 \AA^3 , a value which is slightly larger than the observed expansion of 8.3 \AA^3 . The reduced observed expansion no doubt results because of strong covalent interactions of titanium with its near neighbors and especially with the second titanium when two titanium atoms occupy the $6c-6c$ dumbbell sites. This is no doubt the reason why titanium–titanium dumbbell pairs can form in $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$. The Mössbauer spectral results confirm the presence of the unexpected titanium–titanium $6c-6c$ dumbbell pairs in both $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ and $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$.

In contrast, it should be noted that the replacement of some of the iron on the $6c$ dumbbell site, to form $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$, yields a nitrated compound whose unit cell volume of 856.6 \AA^3 is 1.3% larger than the 846 \AA^3 unit cell volume¹⁵ of $\text{Nd}_2\text{Fe}_{17}\text{N}_{2.6}$. The 54.3 \AA^3 expansion upon nitridation of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}$ to form $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ is much larger than the calculated expansion of 26.4 \AA^3 obtained by using an atomic radius of 0.92 \AA or atomic volume of 3.26 \AA^3 for nitrogen. Thus, one might expect that the expanded lattice of $\text{Nd}_2\text{Fe}_{16.32}\text{Ti}_{0.68}\text{N}_{2.7}$ might permit the placement of some nitrogen on the tetrahedral interstitial $18g$ site in the $\text{Nd}_2\text{Fe}_{17}$ structure. Our neutron diffraction results do not rule out this possibility, but the amount of nitrogen on the $18g$ site is very small.

ACKNOWLEDGMENTS

The authors acknowledge, with thanks, the financial support of the Division of Materials Research of the U.S. National Science Foundation for Grant Nos. DMR-9521739 and DMR-9614596, the Ministère de la Communauté Française de Belgique for A.R.C. Grant No. 94/99-175, and NATO for a Cooperative Scientific Research Grant. F.G. thanks the Fonds National de la Recherche Scientifique for travel support to work at the University of Missouri-Rolla. Finally, the authors thank D. Hautot for help in measuring the Mössbauer spectra.

¹W. B. Yelon, H. Xie, G. J. Long, O. A. Pringle, F. Grandjean, and K. H. J. Buschow, *J. Appl. Phys.* **73**, 6029 (1993).

²G. 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**, 761 (1993).

³Z. Hu, W. B. Yelon, S. Mishra, G. J. Long, O. A. Pringle, D. P. Middle-

- ton, K. H. J. Buschow, and F. Grandjean, *J. Appl. Phys.* **76**, 443 (1994).
- ⁴G. 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**, 5383 (1994).
- ⁵W. B. Yelon, Z. Hu, W. J. James, and G. K. Marasinghe, *J. Appl. Phys.* **79**, 5939 (1996).
- ⁶R. Skomski, S. Brennan, and S. Wirth, in *Interstitial Intermetallic Alloys*, edited by F. Grandjean, G. J. Long, and K. H. J. Buschow (Kluwer Academic, Dordrecht, the Netherlands, 1995), p. 371; J. F. Herbst, J. S. Croat, R. W. Lee, and W. B. Yelon, *J. Appl. Phys.* **53**, 250 (1982).
- ⁷J. M. D. Coey and H. Sun, *J. Magn. Magn. Mater.* **87**, L251 (1990).
- ⁸S. Miraglia, J. L. Soubeyroux, C. Kolbeck, O. Isnard, and D. Fruchart, *J. Less-Common Met.* **171**, 51 (1991).
- ⁹G. K. Marasinghe, P. C. Ezekwenna, W. J. James, G. J. Long, O. A. Pringle, Z. Hu, W. B. Yelon, and F. Grandjean, *J. Appl. Phys.* **79**, 4587 (1996).
- ¹⁰J. Rodriguez-Carjaval, FULLPROF Rietveld refinement written code (Institute Laue Langevin, Grenoble, France).
- ¹¹J. Rodriguez-Carjaval, "FULLPROF: A program for Rietveld refinement and pattern matching analysis," in Abstracts of the Satellite Meeting on Powder Diffraction of the XVth Congress of the International Union of Crystallography Toulouse, France, 1990, p. 127.
- ¹²R. A. Young, in *The Rietveld Method*, edited by R. A. Young (International Union of Crystallography, Oxford University Press, Oxford, 1995), p. 1.
- ¹³G. J. Long, O. A. Pringle, F. Grandjean, and K. H. J. Buschow, *J. Appl. Phys.* **72**, 4845 (1992).
- ¹⁴G. J. Long, O. A. Pringle, F. Grandjean, W. B. Yelon, and K. H. J. Buschow, *J. Appl. Phys.* **74**, 504 (1993).
- ¹⁵F. Grandjean, G. J. Long, S. Mishra, O. A. Pringle, O. Isnard, S. Miraglia, and D. Fruchart, *Hyperfine Interact.* **95**, 571 (1995).
- ¹⁶E. Galvão da Silva, C. A. Samudio Peres, and M. McElfresh, *Hyperfine Interact.* **94**, 2317 (1994).
- ¹⁷G. J. Long, O. A. Pringle, F. Grandjean, T. H. Jacobs, and K. H. J. Buschow, *J. Appl. Phys.* **75**, 2598 (1994).
- ¹⁸G. J. Long, S. Mishra, O. A. Pringle, F. Grandjean, and K. H. J. Buschow, *J. Appl. Phys.* **75**, 5994 (1994).
- ¹⁹R. Ingalls, F. Van der Woude, and G. A. Sawatzky, in *Mössbauer Effect Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), p. 361.
- ²⁰R. D. Ernst, D. R. Wilson, and R. H. Herber, *J. Am. Chem. Soc.* **106**, 1646 (1984).