Magnetic properties of interstitially modified $Nd_3(Fe,Ti)_{29}X_y$ compounds ($X=H$, C, and N)

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The effects of light atom intercalation on the magnetic properties of the monoclinic compound $Nd_3(Fe,Ti)_{29}$ have been studied by Mössbauer spectroscopy and thermogravimetric analysis. Maximum contents of 4 nitrogen atoms and 6 hydrogen atoms per formula unit have been achieved, consistent with structural calculations. The associated lattice expansion ranges from 2% in the hydride to 6.5% in the nitride. Attempts to introduce carbon were unsuccessful as the material decomposed rapidly during the reaction. Both hydrogen and nitrogen additions lead to substantial increases in the magnetic ordering temperature, but only the nitrogen leads to an increase in the iron moment.

I. INTRODUCTION

The search for high-performance magnetic materials, which was revived by the discovery of the $R_2Fe_{14}B$ system, has been expanded greatly by the observation that significant improvements can be obtained through the intercalation of alloys by a variety of light atoms. Often this intercalation process can be used to transform otherwise useless materials into highly promising permanent magnet candidates. The most striking examples of this are the R_2Fe_{17} alloys, which have ordering temperatures only slightly above room temperature, but the addition of either carbon or nitrogen by gas-phase reaction leads to a greatly enhanced T_c and, in the case of the Sm alloy, substantial uniaxial anisotropy.[1]

In 1992, Collocott *et al.* reported the existence of a new, iron-rich, phase in the Nd-Fe-Ti phase diagram.[2] Subsequent x-ray[3] and neutron[4] diffraction measurements showed that the alloy structure belonged to the monoclinic $P2_1/c$ space group, and that the correct stoichiometry was $Nd_3(Fe,Ti)_{29}$. The composition lies between the tetragonal $Nd(Fe,Ti)_{12}$ and rhombohedral $Nd_2(Fe,Ti)_{17}$ phases, and the 3-29 structure can be viewed as an alternating stack of these 1-12 and 2-17 units.[3] The magnetic ordering temperatures of the 3-29 compounds are in the range 411–486 K.[5] Previous work has shown that this phase absorbs nitrogen readily, exhibiting large increases in both T_c and magnetization.[6]

In this paper we report a more extensive study of the effects of H, C, and N interstitial modification on the magnetic properties of $Nd_3(Fe,Ti)_{29}$.

II. EXPERIMENTAL METHODS

$Nd_3(Fe,Ti)_{29}$ samples were prepared by arc melting appropriate amounts of 99.9% purity Nd, Ti, and Fe under Ti-gettered argon. Single-phased alloys were obtained by annealing at 1373 K for 72 h under argon in sealed quartz tubes, followed by water quenching. Structural measurements were made using Cu-K_α radiation on an automated Nicolet–Stoe diffractometer. Ordering temperatures were determined on a Perkin–Elmer TGA-7 by recording the apparent mass as a function of temperature in a small field gradient. ^{57}Fe Mössbauer spectra were obtained on a conventional constant acceleration spectrometer using a 25-mCi $^{57}CoRh$ source. Low-temperature spectra were obtained using a vibration-isolated closed-cycle He fridge. Calibration and isomer shifts are referred to α-Fe at room temperature. The $Nd_3(Fe,Ti)_{29}$ unit cell contains 6 Nd atoms on two sites, and 58 Fe atoms distributed among 15 distinct sites, one being a $2d$ and the remaining 14 being $4e$ sites. It is clear from the spectra in Figs. 1 and 2 that few of the subspectra arising from the 15 Fe sites are resolved, especially at room temperature. We have therefore fitted the spectra using the minimum number of subspectra needed to reproduce the most obvious features of the spectra. The number used varied from 3 in the case of the as-annealed material at room temperature, to 6 in the cases of the nitride and hydride at 12 K.

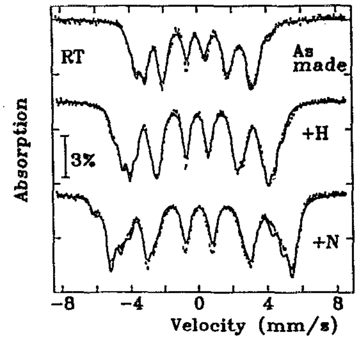

FIG. 1. Room-temperature Mössbauer spectra of $Nd_3(Fe,Ti)_{29}$ as-annealed, and with hydrogen and nitrogen added.

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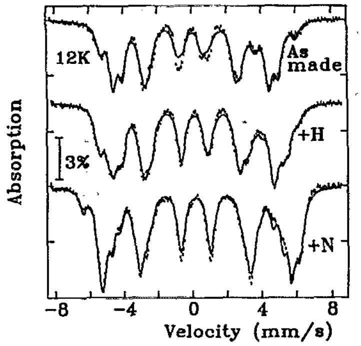

FIG. 2. Mössbauer spectra of $Nd_3(Fe,Ti)_{29}$ as-annealed, and with hydrogen and nitrogen added measured at 12 K.

The intercalation reactions were carried out at various temperatures in a thermopiezic analyzer (TPA) using hydrogen, nitrogen, and acetylene as sources of H, N, and C, respectively.

III. RESULTS AND DISCUSSION

Substantial amounts of hydrogen are absorbed readily by $Nd_3(Fe,Ti)_{29}$. Heating to 300 °C at 40 °C/min in ~1.6 bar of H_2 leads to a hydrogen uptake of over 6 H/formula unit (f.u.), with no evidence of decomposition. While the hydride appears stable at room temperature (no evolution of the material was apparent on the ~1-day timescale needed to record a Mössbauer spectrum), it decomposed rapidly on heating, making an accurate determination of T_c problematic. The value of 548 K given in Table I represents a lower limit, the value obtained on re-cooling was typically 100 K lower, reflecting a significant loss of hydrogen. The room temperature Mössbauer spectrum (Fig. 1) exhibits a substantially increased average hyperfine field; however, the measurement at 12 K (Fig. 2) shows this to be almost entirely due to the higher ordering temperature. The measured lattice expansion is ~2%, giving an effective volume change per hydrogen atom of ~2.0 Å^3, close to values typical of intermetallic hydrides.[7]

Nitrogen also reacts easily with this alloy. Annealing for 70 h in 1.6 bar of N_2 at 400 °C takes the reaction close to completion and yields nitrogen contents of ~4.5 N/f.u. Higher apparent concentrations (~5.8 N/f.u.) can be achieved by annealing at higher temperatures (e.g., 500 °C); however, the observed ordering temperature does not increase, and there is evidence of α-Fe precipitation. The 6.5% volume expansion corresponds to a volume change of ~7 Å^3/N atom, as found in the R_2Fe_{17} nitrides.[1] The Mössbauer spectra show a substantial increase in the hyperfine field both at room temperature and 12 K. Values listed in Table I are in close agreement with those reported earlier.[5] As in the 2-17 and 1-12 alloys, nitriding leads to an increase both in T_c and in the average Fe moment.

TABLE I. Summary of magnetic and structural changes resulting from the addition of H, C, or N to $Nd_3(Fe,Ti)_{29}$.

Sample	T_c (K)	$\langle B_{hf} \rangle$ (T) 12 K	RT	$\Delta V/V$ (%)
$Nd_3(FeTi)_{29}$	426	29.0	21.0	⋯
$Nd_3(FeTi)_{29}H_{6.1}$	>548	30.2	26.4	2.2±0.5
$Nd_3(FeTi)_{29}C_y$	~660	⋯	⋯	⋯
$Nd_3(FeTi)_{29}N_{4.5}$	723	33.4	31.0	6.5±0.7

TABLE II. The four largest voids in the $Nd_3(Fe,Ti)_{29}$ alloy system, derived from an analysis of the crystal structure. The $4e_3$ is assumed to be unoccupied as it is too small for nitrogen, and only coordinated by Fe atoms.

Site	Location x	y	z	Radius (Å)	Coordination	Occupied by
$4e_1$	0.49	0.75	0.23	0.64	2-Nd 4-Fe	HCN
$4e_2$	0.20	0.50	0.40	0.59	2-Nd 4-Fe	HCN
$4e_3$	0.10	0.51	0.95	0.45	4-Fe	empty(?)
$4e_4$	0.44	0.23	0.92	0.42	1-Nd 3-Fe	H

The carbide does not form easily. Conditions appropriate for 1-12 or 2-17 alloys tend to lead to a disproportionation reaction, with the principal magnetic phases being Fe_3C (possibly containing some of the Ti) and α-Fe. Even short duration (~30 min) anneals at temperatures between 350 and 500 °C led to partially decomposed samples. It therefore appears that in this phase, the competition from the disproportionation reaction is too strong, and the carbide tends not to form in significant amounts. A magnetic event at ~660 K is tentatively associated with a $Nd_3(Fe,Ti)_{29}C_y$ phase; however, the actual carbon content is unknown. Given the mixture of magnetic phases present, no attempt was made to extract Mössbauer parameters.

An analysis of the 3-29 structure yields only a very limited number of holes large enough to accommodate interstitial atoms (see Table II), and all of them are $4e$ sites (the $2a$ and $2d$ sites are occupied by Nd and Fe, respectively, and both the $2b$ and $2c$ sites lie inside other atoms). The two largest voids have radii of 0.64 and 0.59 Å, and could hold either carbon or nitrogen atoms. Full occupancy of these sites by nitrogen would yield a composition of $Nd_3(Fe,Ti)_{29}N_4$. This composition is also consistent with the 3-29 structure being derived from alternate stacking of 1-12 and 2-17 units, which can hold 1 and 3 nitrogen atoms, respectively. Our measured nitrogen content of 4.5 N/f.u. probably results from a partial decomposition of the material, with the excess nitrogen in the form of neodymium nitride. The next hole is only 0.45 Å in radius, far too small to accept either nitrogen or carbon. While this site is large enough to take a hydrogen atom,[7] the coordination solely by Fe atoms may make the environment energetically unattractive. The next largest site with one Nd neighbor has a radius of 0.42 Å and is more likely to be the hydrogen location. Occupation of the three largest rare-earth coordinated holes by hydrogen gives the composition $Nd_3(Fe,Ti)_{29}H_6$, as observed.

In conclusion, adding hydrogen leads to a significant increase in T_c, but essentially no change in the iron moment, whereas nitrogen leads to an increase in both parameters. These results are similar to those found in the 1-12 and 2-17 rare-earth iron alloys. Attempts to make the carbide were unsuccessful due to a rapid disproportionation of the material. An examination of the crystal structure shows that the hydrogen and nitrogen concentrations achieved are the maximum values allowed.

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