Nitrogen atom location in rhombohedral and hexagonal $RE_2Fe_{17}N_x$ compounds

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Abstract. High resolution neutron powder diffraction studies were performed on $\mathrm{Nd_2Fe_{17}N_x}$ and $\mathrm{Y_2Fe_{17}N_x}$. A strong preferential site occupation of the N atoms on the 9e position of the rhombohedral compound $\mathrm{Nd_2Fe_{17}N_x}$ was observed. In the hexagonal compound $\mathrm{Y_2Fe_{17}N_x}$ the N atoms occupy primarily the 6h sites (82%) and only a small fraction goes into the 12i site (12%). The refined nitrogen occupation numbers correspond to the formula compositions $\mathrm{Nd_2Fe_{17}N_{2.6}}$ and $\mathrm{Y_2Fe_{17}N_{2.9}}$.

1. Introduction

The intermetallic rare earth iron compounds of the type $\mathrm{RE_2Fe_{17}}$ (RE = rare earth) appear to be very amenable to the interstitial solution of smaller types of atoms such as H, N and C (Isnard *et al* 1990, Hong Sun *et al* 1990, Haije *et al* 1990). This interstitial solution is accompanied by drastic changes in some of the magnetic properties. All three types of interstitial solutions give rise to a strong increase of the Curie temperature. This effect is particularly pronounced for the nitrides where enhancements of T_c of about 400 K have been observed (Hong Sun *et al* 1990, Buschow *et al* 1990). For the carbides and nitrides one has the additional effect of a strong enhancement of the rare earth sublattice anisotropy (Gubbens *et al* 1989, Coey and Hong Sun 1990). This has consequences for the technological application of some of these materials as permanent magnets.

Neutron diffraction measurements made on various compounds of the type $\mathrm{RE_2Fe_{17}C_x}$ have revealed that the C atoms occupy interstitial hole positions next to the RE atoms (Haije *et al* 1990, Helmholdt and Buschow 1989). It is this close proximity of the C atoms to the RE atoms that is generally held responsible for strong changes in the crystal field seen by the 4f electrons and the concomitant changes in the RE sublattice anisotropy (Gubbens *et al* 1989, Dirken *et al* 1989).

There are strong indications that the changes in RE sublattice anisotropy in the nitrides $\mathrm{RE_2Fe_{17}N_x}$ are even stronger than in the carbides $\mathrm{RE_2Fe_{17}C_x}$. This may in part be due to the higher x values reached in the former. However, it is equally possible that the effect of N atoms on the crystal field experienced by the 4f electrons is larger than

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that of C atoms. Before a meaningful answer to this question can be given, it seems imperative to have experimental information of the crystallographic position of the N atoms in $RE_2Fe_{17}N_x$ and to have an accurate estimate of the nitrogen content, x, reached when charging the RE_2Fe_{17} compounds with N_2 gas. In order to supply the information regarding position and concentration of N atoms in $RE_2Fe_{17}N_x$, we have studied two representative nitrides by means of high resolution neutron powder diffraction. Neutrons are an ideal probe for such investigations since the neutron scattering length for N is comparable to that of Fe and hence the determination of the N location is a far easier task with neutron diffraction than with x-ray diffraction.

2. Experiment

Samples of $Nd_2Fe_{17}N_x$ and $Y_2Fe_{17}N_x$ were prepared by arc melting using Nd(Y) and Fe of at least 99.9% purity. After arc melting these samples were vacuum annealed at temperatures of about 1100 °C for about 10 days. X-ray diffraction showed these samples to be approximately single phase. The annealed samples were pulverized and heated in an atmosphere of purified N_2 gas for about 3 h at 500 °C. After this treatment the samples were investigated by x-ray diffraction and magnetic measurements.

From the x-ray diagrams it followed that the nitriding process had reached completion, the diffraction peaks of the ternary nitrides being shifted considerably to lower diffraction angles than those of the original RE_2Fe_{17} compounds. Apart from the diffraction peaks of the ternary nitrides, there were broadened peaks of low intensity which were attributed to α-Fe in which small amounts of nitrogen had dissolved. The lattice constants of the ternary nitrides was derived from the diffraction patterns, and when compared with the lattice constants of the original compounds, had increased considerably. The nitride of Nd_2Fe_{17} has the rhombohedral Th_2Zn_{17} type structure ($R\bar{3}m$), the nitride of Y_2Fe_{17} has the hexagonal Th_2Ni_{17} structure ($P6_3/mmc$).

Magnetic measurements made in low fields (1 kA cm^{-1}) showed that the charging with nitrogen gas had increased the Curie temperature from 327 K to 740 K ($Nd_2Fe_{17}N_x$) and from 324 K to 690 K ($Y_2Fe_{17}N_x$).

The neutron powder diffraction experiments were performed on the High Resolution Powder Diffractometer (HRPD) at the ISIS spallation neutron source, Rutherford Appleton Laboratory, UK (David *et al* 1988). Data were recorded in backscattering ($2\theta_{ave} = 168°$) over a time-of-flight region of 12–112 ms, providing a d-spacing range of ~0.24–2.24 Å. The instrumental resolution, $\Delta d/d \sim 8 \times 10^{-4}$, is constant for all d-spacings. The diffraction data were collected at room temperature at which nuclear as well as magnetic reflections are expected since magnetic ordering of these compounds occurs at fairly high temperatures. Approximately 600 mm^3 of each sample, contained in a thin walled cylindrical vanadium container of diameter 5 mm and height 30 mm, was used to obtain a complete data set. Data collection times were typically less than 6 h. Results obtained for these compounds are shown in figure 1. In both cases the diffraction patterns show a significant although very small anisotropic intrinsic line broadening. A marked line broadening of the impurity phase (α-Fe), as was found in the corresponding x-ray diffraction patterns, is also clearly seen.

3. Results of the structure determination

The diffraction data collected on the HRPD instrument were analysed by the Rietveld technique (Rietveld 1969) using program TF12LS based upon the Cambridge Crystallography Subroutine Library (CCSL) as described by Brown and Matthewman (1985).
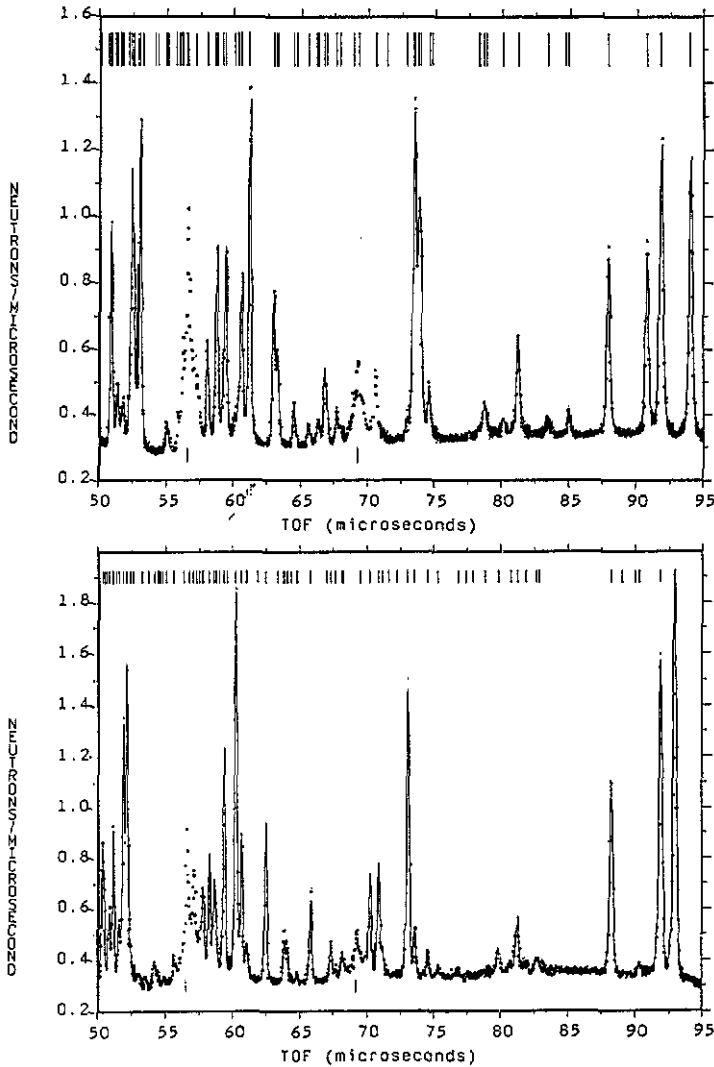
Figure 1. Calculated (full curves) and observed data (points) neutron diffraction patterns of $Nd_2Fe_{17}N_{2.8}$ (top) and $Y_2Fe_{17}N_{2.8}$ (bottom) at 293 K. The neutron time of flight is given in thousands of microseconds. Calculated positions are indicated at the top of each pattern, whilst the impurity Fe phase reflections are indicated at the bottom of each pattern.

TF12LS is a program for the least squares refinement of time-of-flight powder diffraction data using a peak-shape function that is the convolution of a modified Ikeda–Carpenter lineshape and Voigt function (David *et al* 1988). The rhombohedral Th_2Zn_{17} structure for $Nd_2Fe_{17}N_x$ and the hexagonal Th_2Ni_{17} structure for $Y_2Fe_{17}N_x$ were taken as starting models. The N atoms were accommodated statistically at the interstitial sites 9e and 18g for the rhombohedral $Nd_2Fe_{17}N_x$ compound and the sites 6h and 12i for the hexagonal $Y_2Fe_{17}N_x$ component. Furthermore, for the hexagonal compound, the starting model also included the partial disorder observed previously for Lu_2Fe_{17} (Givord *et al* 1972)

and Ho_2Fe_{17} (Christensen and Hazell 1980). This partial disorder consists of the replacement of some of the RE atoms at site 2b by a pair of Fe atoms (4e).

In each case some care was taken in order to account for the magnetic scattering from the Nd and Fe sublattices. Heating the samples to above their Curie points (>700 °K) could have proven disadvantageous, resulting in possible decomposition of the nitride. However a full profile refinement structural analysis is further complicated by the presence of magnetic scattering.

A reliable structural refinement from powder diffraction data, neglecting the magnetic scattering may be obtained by using only short d-spacing data, where, because of the very rapid fall off in the magnetic form factor, the magnetic scattering is effectively zero. HRPD with both high resolution and an epithermal neutron flux is an ideal instrument for obtaining such diffraction data, enabling a structural study to be performed neglecting the contribution from magnetic scattering. The rapid fall off in the magnetic form factor was confirmed by calculation of the expected magnetic scattering for both the rhombohedral and hexagonal phases.

For a powder the magnetic scattering intensity is given by (Shirane 1959):

$$I = \sum_{hkl} j_{hkl} \langle q^2 \rangle |F_m(hkl)|^2$$

where $F_m(hkl) = \Sigma p_i \exp 2\pi i(hx_i + ky_i + lz_i)$ is the magnetic structure factor for a reflection with Miller indices (hkl). The magnetic scattering length p_i is given by $p_i = (e^2\gamma/2mc^2)\mu_i f_i(hkl)$, with μ_i the magnetic moment in Bohr magnetons at site i and $f_i(hkl)$ the magnetic form factor for atom i. The term $\langle q^2 \rangle$ is the orientation average of the sine of the angle between the moment direction and the neutron scattering vector, and j_{hkl} is the multiplicity of $F_m(hkl)$. The standard hexagonal Miller indices $(hkil)$ can be expressed in terms of the indices (hkl) with the condition $h + k + i = 0$. Thus for hexagonal symmetry:

$$\langle q^2_{hkl} \rangle = 1 - [\tfrac{1}{2}(h^2 + k^2 + hk) 4 \sin^2\varphi/3a^2 + l^2 \cos^2\varphi/c^2] d^2$$

and for rhombohedral symmetry

$$\langle q^2_{hkl} \rangle = 1 - [(h^2 + k^2 + l^2 - hk - kl - lh)(1 - \cos a^*) \sin^2\varphi$$
$$+ (h^2 + k^2 + l^2 + 2hk + 2kl + 2lh)(1 + 2\cos a^*) \cos^2\varphi] d^2/3a^2$$

where φ is the angle between the magnetic moment direction and the unique axis. The terms a, c and d are the lattice parameters and d-spacing respectively. For rhombohedral symmetry, α^* is the reciprocal lattice equivalent of the angle between polar edges. Some typical magnetic moment values for the Nd and Fe sublattices were taken from previous neutron investigations of $RE_2Fe_{17}H_x(D_a)$ compounds (Isnard *et al* 1990). Analytic approximations for the Nd^{3+} and metallic Fe form factors were also employed in the calculation (Lisher and Forsyth 1971).

Typical calculated magnetic scattering lengths for Fe are about 0.6×10^{-12} cm. By contrast, the neutron–nuclear scattering length for Fe is $b_{Fe} = 0.954 \times 10^{-12}$ cm. Neutron–nuclear scattering lengths for the other constituent atoms were taken to be $b_Y = 0.775 \times 10^{-12}$ cm, $b_{Nd} = 0.78 \times 10^{-12}$ cm and $b_N = 0.930 \times 10^{-12}$ cm. In each case the magnetic scattering contributions for d-spacings less than 1.9 Å were found to be entirely negligible in comparison with the nuclear scattering. For this reason the structural refinement was carried out neglecting the magnetic contribution.

Table 1. Refined parameters of Nd$_2$Fe$_{17}$N$_{2.6}$. Space group: rhombohedral (Th$_2$Zn$_{17}$-type); $R\bar{3}m$ (No 166). $a = 8.7760(1)$ Å and $c = 12.6366(8)$ Å.

Atom position		x/a	y/b	z/c	B	n
Nd	6b	0.0000	0.0000	0.3418(8)	0.31	1.00
Fe(1)	6c	0.0000	0.0000	0.0938(8)	0.34	1.00
Fe(2)	9d	0.5000	0.0000	0.5000	0.34	1.00
Fe(3)	18f	0.2825(3)	0.0000	0.0000	0.34	1.00
Fe(4)	18h	0.5038(3)	0.4962(3)	0.1522(3)	0.34	1.00
N	9e	0.5000	0.0000	0.0000	0.52	0.86(2)

B (Å^2) is the isotropic temperature factor and n the site occupancy.
$R_p = 5.61\%$, $R_c = 5.81\%$; $\chi^2 = 1.36$.

Table 2. Refined parameters of Y$_2$Fe$_{16.5}$N$_{2.9}$. Space group: hexagonal (Th$_2$Ni$_{17}$-type); $P6_3/mmc$ (No 194). $a = 8.6393(1)$ Å and $c = 8.4749(2)$ Å.

Atom position		x/a	y/b	z/c	B	n
Y(1)	2b	0.0000	0.0000	0.2500	0.31	0.36(3)
Y(2)	2d	0.3333	0.6667	0.7500	0.31	1.00
Y(3)	2c	0.3333	0.6667	0.2500	0.31	0.63(2)
Fe(1)	4e	0.0000	0.0000	0.0933(20)	0.34	0.35(2)
Fe(2)	4f	0.3333	0.6667	0.1102(5)	0.34	1.00
Fe(3)	6g	0.5000	0.0000	0.0000	0.34	1.00
Fe(4)	12k	0.1660(3)	2x	0.9820(3)	0.34	1.00
Fe(5)	12j	0.3276(6)	0.9489(4)	0.2500	0.34	0.80(1)
N(1)	6h	0.8329(5)	2x	0.2500	0.52	0.77(1)
N(2)	12i	0.1465(19)	0.0000	0.0000	0.52	0.10(1)

B (Å^2) is the isotropic temperature factor and n the site occupancy.
$R_p = 7.22\%$, $R_c = 7.04\%$; $\chi^2 = 1.70$.

The parameters considered in the refinement included atomic coordinates of the rhombohedral and hexagonal unit cells, the corresponding unit cell constants and iso-tropic temperature factors. For the N atoms the refinement also included the populations of the sites mentioned above. The refined parameters are listed in tables 1 and 2, together with the corresponding reliability factors. The exclusion from the refinement of diffraction lines from the α-Fe impurity phase and concomitant loss of information caused difficulties in de-correlating temperature factor and site occupancy information. For this reason values for isotropic temperature factors and Y site occupancies in the hexagonal structure were fixed during the final refinement.

4. Discussion

The most important result derived from the structural refinement is that the nitrogen atoms occupy primarily the interstitial hole sites close to the rare earth atoms (9e for Nd$_2$Fe$_{17}$N$_x$ and 6h for Y$_2$Fe$_{17}$N$_x$) and in this respect show a behaviour quite similar to that observed for the carbides (Haije *et al* 1990). We consider the results obtained in the

present neutron experiments as quite conclusive since the N atoms have a scattering power of about the same size at the Fe atoms.

Of equal importance is the result that the nitrogen concentration in both ternary nitrides approaches the $RE_2Fe_{17}N_3$ expected for a full occupation of the interstitial hole sites mentioned. Our N concentrations are slightly higher than those of Coey and Hong Sun (1990), who found a nitrogen content corresponding to $x = 2.3$ by means of gravimetric measurements.

Furthermore, the neutron diffraction data obtained in the course of the present investigation confirm earlier results obtained by x-ray diffraction (Buschow *et al* 1990) that charging with nitrogen does not lead to changes in the basic crystal structure, as was found for the corresponding carbides and hydrides.

The nitrogen absorption reaction can formally be written as

$$2RE_2Fe_{17} + zN_2 \leftrightarrows 2RE_2Fe_{17}N_z. \tag{1}$$

The absorption isotherm which describes the concentration dependence of the gas pressure at a given temperature above the gas–solid equilibrium ideally has a flat portion, the so-called plateau pressure, i.e. the concentration dependence of the pressure remains virtually independent of z up to the concentration of the ternary phase, which is fixed. The constancy of the pressure reflects the fact that only the relative amounts of the binary and ternary phase change, but not their compositions.

The temperature dependence of the equilibrium plateau pressure can generally be obtained from the Van 't Hoff equation, leading to

$$\ln p_{N_2} = 2\Delta H_f/xRT - 2\Delta S_f/xR \tag{2}$$

where x is the composition of the ternary nitride $RE_2Fe_{17}N_x$ and $\Delta H_f (\Delta S_f)$ are the enthalpy (entropy) of formation according to reaction (1). The main contribution to ΔS_f is the entropy of the nitrogen gas, which is last to be involved in the formation of the ternary nitride, so that it is primarily the value of ΔH_f which determines the equilibrium pressure.

Using the same semi-empirical model as derived earlier for the formation of ternary hydrides (Buschow *et al* 1982) one finds that ΔH_f is much more negative for ternary nitrides than for ternary hydrides. Even at 500 °C the equilibrium plateau pressure when calculated by means of equation (2) is considerably below 1 atm, explaining why formation of the ternary nitride could proceed under the experimental circumstances used in the present investigation. Using the same arguments as presented before for ternary hydrides, one may expect that at still higher temperatures the ternary nitrides will decompose into REN and α-Fe (Buschow 1977; Buschow *et al* 1982).

The concentration x of the ternary nitride phase does not necessarily correspond exactly to the number of a given type of interstitial sites. This may be illustrated by comparing it again with results obtained earlier for ternary hydrides. In the two isotopic compounds $LaCo_5$ and $NaNi_5$, the first ternary hydride phases have dissimilar compositions, the approximate formula compositions being $LaCo_5H_4$ and $LaNi_5H_6$, respectively. The reason for this is that two types of interstitial sites (3c and 6d) are filled simultaneously upon hydriding. Note that in both compounds the composition of the first ternary hydride ($x = 4$ and 6, respectively) remains substantially below the composition at which the two types of interstitial holes would have been filled completely ($x = 9$).

When viewed in the light of the discussion given above, our neutron diffraction results obtained on the rhombohedral compound $Nd_2Fe_{17}N_x$ may be interpreted as

follows: the fact that occupation by N atoms is restricted exclusively to one site (the 9e site) suggests that the upper limit of the composition of the first ternary nitride corresponds to $x = 3$. As in the case of the hydrides the ternary interstitial compound may, however, occur at a composition below this upper limit. Furthermore, one has to take into account that the length of the horizontal isotherm defining the equilibrium plateau pressure (terminating at $z = x$) becomes shorter with increasing temperature (see, for instance, the review of Buschow *et al* 1982). This means that even if the composition of the ternary nitride would correspond to $x = 3$ at 0 K it would be of lower N content than $x = 3$ at any gas–solid equilibrium at higher temperatures. The refined value $x = 2.6$ found by us for Nd$_2$Fe$_{17}$N$_x$ is therefore not surprising, since in the present experiment the charging with N$_2$ gas was performed at 500 °C.

Approximately the same considerations apply to Y$_2$Fe$_{17}$N$_x$, although the situation is less clear here, in view of the fact that about 12% of the absorbed nitrogen spills into a second interstitial site. Structural differences between rhombohedral Nd$_2$Fe$_{17}$N$_x$ and hexagonal Y$_2$Fe$_{17}$N$_x$ may be responsible for this.

Finally, we wish to comment on the intrinsic line broadening observed in the neutron powder diffraction patterns. Both the rhombohedral and hexagonal RE$_2$Fe$_{17}$ compounds have been shown to be very susceptible to the occurrence of stacking faults. The occurrence of these stacking faults is related to the structural similarity between the rhombohedral and hexagonal type of layer stacking. Various types of stacking faults were discovered by means of high-energy electron microscopy in the pure RE$_2$Fe$_{17}$ compounds as well as in their carbides (Coene *et al* 1990). It is very likely that they are also present in the nitrides, presumably even before the charging with N$_2$ gas. An *hkl*-dependent line-broadening analysis is currently underway in order to establish the exact nature of the line broadening observed in the neutron powder diffraction patterns obtained in the course of the present investigation. Such an analysis will discriminate between particle size effects (isotropic *hkl*-dependence) and variations in stacking faults (anisotropic *hkl*-dependence).

Acknowledgments

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