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Electronic and Magnetic Structures of the Rare-Earth Compounds: $R_2Fe_{17}N_\xi$

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Structural and magnetic properties of the rare-earth compounds $R_2Fe_{17}N_\xi$ have been studied with neutron-diffraction measurements and self-consistent spin-polarized electronic-structure calculations. The diffraction results indicate for the Nd compound that N goes into two sites in two or more phases of varying fractional N occupations. For the Y compound, N occupies only one site. Electronic-structure calculations for Y_2Fe_{17} and $Y_2Fe_{17}N_3$ give excellent results for site-dependent Fe moments, and, with spin-fluctuation theory, explain the large change in the Curie temperature on nitrogenation.

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One of the most important recent developments in the field of magnetism and magnetic materials has been the realization that great improvements in properties can be achieved by expanding one's vision from binary to ternary intermetallic compounds. This is particularly true for permanent magnet materials, which require large values of magnetization, uniaxial anisotropy, Curie temperature T_c, and coercivity. The best known example of this is the discovery of the class of rare-earth (R) compounds, $R_2Fe_{14}B$, especially for $R=$Nd [1]. While compounds of the R_2Fe_{17} class have large magnetization values, they also have rather low ordering temperatures and anisotropy constants. However, recently Coey and co-workers [2] found that the absorption of N_2 by Sm_2Fe_{17} and Y_2Fe_{17} roughly doubles their T_c values and changes the anisotropy of the former from planar to uniaxial. $R_2Fe_{17}N_\xi$ compounds can be prepared with ξ values typically up to 2.6 and generally having the hexagonal Th_2Ni_{17} structure for the heavy rare earths, and the rhombohedral Th_2Zn_{17} structure for the light rare earths. Schnitzke *et al.* [3] recently were able to produce microcrystalline $Sm_2Fe_{17}N_\xi$ samples with coercivities as high as 30 kOe. These developments suggest that the $R_2Fe_{17}N_\xi$ compounds have exciting prospects as permanent magnet materials.

In this work we have investigated two fundamental aspects of the nitrogenated materials. These are (1) detailed aspects of the occupancy of interstitial sites by N atoms, and (2) the spin-polarized electronic structure and its relationship to the site-dependent magnetic moments and increase in the Curie temperature. Both of these aspects are important for understanding how nitrogen, or other added elements, enhance the permanent-magnet characteristics of these newly discovered materials.

Samples of R_2Fe_{17} with $R=$Y, Nd, and Sm were prepared by arc melting appropriate quantities of the elements. Because the 2:17 phase cannot be formed from the melt, a heat treatment at 1050 °C for periods ranging from several hours to two days was required to obtain a single phase. Powders were prepared by crushing, grinding, and sieving in a glove box under an argon atmosphere. Finally, the nitrides were produced by heating the powders of R_2Fe_{17} alloys in approximately 100 kPa of N_2 gas for about 2 h at 500 °C.

Since neutron-diffraction measurements on the Sm compound are not feasible because of the large absorption cross section of its most abundant isotope, data were collected on the Nd and Y compounds at room temperature with a high-resolution powder diffractometer with $\lambda=1.547$ Å. Data were analyzed using GSAS, a modified Rietveld code capable of refining several phases simultaneously. This version does not include magnetic scattering, but the total magnetic contribution to the diagram is small in Nd_2Fe_{17} and the nitride, and reliable structural parameters may be extracted while neglecting the magnetic effects.

Initial refinement of $Nd_2Fe_{17}N_\xi$ using the cell parameters reported by Otani *et al.* [4] left a difference pattern similar to the original diagram, but shifted to lower angle, and it was realized that the sample consists of particles in which the nitrogen content varies. In order to treat this, the data were refined as a two-phase sample

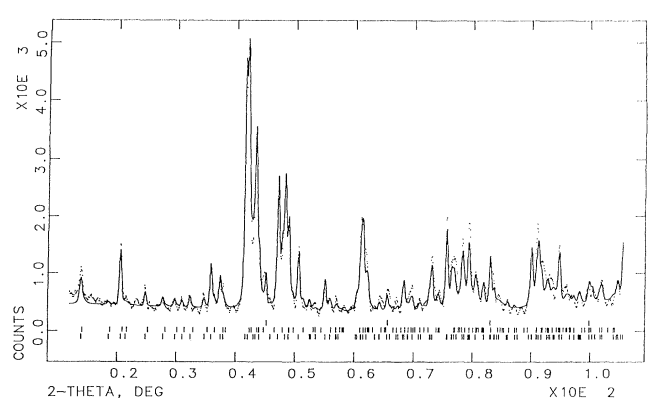

FIG. 1. Powder diffraction patterns for $Nd_2Fe_{17}N_\xi$. Observed (calculated) profiles are given by the dotted (solid) curves and calculated positions are indicated at the bottom, including a minor α-Fe contaminant.

with two different nitrogen contents (and differing cell parameters, etc.). While this leads to a reasonable fit as shown in Fig. 1, it appears that there is actually a range of compositions present, with the two refined compositions corresponding roughly with the lower and upper limits of nitrogen uptake. No evidence for untransformed Nd_2Fe_{17} was seen. The results of the refinement are given in Table I, along with the parameters refined for Nd_2Fe_{17} [5].

These results suggest that nitrogen occupies two sites in the Nd_2Fe_{17} structure as shown in Fig. 2: the *e* site, as has previously been reported [6], and the *g* site, which was also found to contain hydrogen in $Nd_2Fe_{17}H_\xi(D_\xi)$ [7]. It appears, somewhat surprisingly, however, that the nitrogen fills the *g* site first, to its limit ($\sim\frac{1}{6}$) and then fills the *e* site to its limit ($\sim\frac{2}{3}$). If both sites fill to these limits, the composition would reach $Nd_2Fe_{17}N_3$, but in the present case, the two phases correspond to $Nd_2Fe_{17}N_{2.5}$ and $Nd_2Fe_{17}N_{1.3}$. The volume increases approximately linearly with the *e* site contents, but not with total N content. In the present sample, ~80% of the intensity can be attributed to the $N_{2.5}$ composition which has the same cell parameters as reported by Otani *et al.* [4] and others.

Refinement of the $Y_2Fe_{17}N_\xi$ structure presented a different problem. The hexagonal compounds show considerable compositional variation as well as disorder associated with less than complete dumbbell substitution on one-third of the rare-earth sites. Therefore, we measured and refined the pure (nominal) Y_2Fe_{17} material, allowing partial dumbbell occupancy of both Y sites (at $\frac{1}{3},\frac{2}{3},\frac{1}{4}$ and $\frac{1}{3},\frac{2}{3},\frac{3}{4}$) to account for the disorder. A satisfactory fit was obtained with a stoichiometry of about Y_2Fe_{18} and partial occupancies of these positions. The refinement of the nitrided sample found the nitrogen on the 6*h* sites $(x,2x,\frac{1}{4})$ with $x=-0.1681$. The occupancy of this site refined to $\frac{2}{3}$ within statistical error (±0.02) suggesting, as in the rhombohedral compound, that the Fe atoms can move to accommodate two N atoms but are then too close

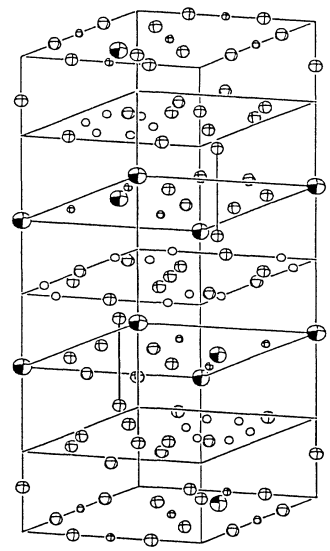

FIG. 2. Unit cell of $R_2Fe_{17}N_\xi$ in the rhombohedral (Th_2Zn_{17}) structure. Largest balls (partially darkened) represent *R* sites, the intermediate-sized balls represent Fe sites, and the small balls represent the N sites. The open (circled) N sites denote 18*g* (9*e*) positions.

TABLE I. Structural parameters for Nd_2Fe_{17} and $Nd_2Fe_{17}N_\xi$ compounds. n.r. denotes not refined; *n* is the fractional site occupancy; and *m* denotes multiplicity, referred to hexagonal cell with three formula units. Values in parentheses indicate uncertainties in least significant digits.

Atom, *m*	$Nd_2Fe_{17}N_{max}$	$Nd_2Fe_{17}N_{min}$	Nd_2Fe_{17}
Nd(*b*), 6	$z=0.344(1)$	$z=0.337(4)$	$z=0.343(1)$
$(x=y=0,n=1)$			
Fe(*b*), 6	$z=0.092(1)$	$z=0.100(3)$	$z=0.096(1)$
$(x=y=0,n=1)$			
Fe(*d*), 9			
$(x=\frac{1}{2},y=0,z=\frac{1}{2},n=1)$			
Fe(*f*), 18	$x=0.288(1)$	$x=0.280(2)$	$x=0.288(1)$
$(y=0,z=0,n=1)$			
Fe(*h*), 18	$x=-y=0.1734(4)$	$x=-y=0.175(1)$	$x=-y=0.168(1)$
$(n=1)$	$z=0.4872(6)$	$z=0.490(2)$	$z=0.489(1)$
Ne(*e*), 9	$n=0.60(2)$	$n=0.14(5)$	
$(x=\frac{1}{2},y=0,z=0)$			
N(*g*), 18	$x=0.806(6)$	$x=0.805$(n.r.)	
$(y=0,z=\frac{1}{2})$	$n=0.12(1)$	$n=0.14(5)$	
a (Å)	8.763(1)	8.629(1)	8.567(5)
c (Å)	12.644(2)	12.512(2)	12.443(5)
Vol. (Å^3)	840.86(25)	806.89(27)	790.88
Intensity	7200(80)	1756(54)	

for further substitution. No other sites appear to contain N atoms. The refined composition is then about $Y_2Fe_{18}N_2$. Details of these results will be published elsewhere.

The electronic structures of the R_2Fe_{17} and $R_2Fe_{17}N_\xi$ compounds were investigated by focusing on Y_2Fe_{17} and $Y_2Fe_{17}N_3$ in the experimentally observed hexagonal Th_2Ni_{17} structure. The choice of Y was made based on our earlier results [8] in the $R_2Fe_{14}B$ class wherein the electronic structure and Fe magnetic moments are independent of R—save for the presence of localized occupied $4f$ levels below the Fermi level, which lead to localized magnetic moments on the R atoms. In both classes of materials the replacement of R by Y avoids the difficult problem of handling the $4f$ states without any loss of understanding of the electronic and magnetic structure of the Fe magnetic subnetwork. The self-consistent spin-polarized calculations are based on the linear-muffin-tin-orbitals (LMTO) method in the scalar-relativistic approximation [9]. To study the effect of nitrogenation the compounds Y_2Fe_{17} and $Y_2Fe_{17}N_3$ were studied, with 38 and 44 atoms per primitive cell, respectively. The N atoms are placed at the experimentally found h sites in the hexagonal structure which are equivalent to the sites occupied by the majority of the N atoms in the rhombohedral structure.

The spin-polarized densities of states (DOS) for Y_2Fe_{17} and $Y_2Fe_{17}N_3$ are shown in Fig. 3. As expected, the DOS are dominated by the Fe d bands near the Fermi level. The structure around 6 eV in $Y_2Fe_{17}N_3$ is due to the N $2p$ states. The structure due to the Fe d bands in $Y_2Fe_{17}N_3$ DOS is shifted to higher binding energy due to the reduction in overlap upon nitrogenation. This leads to a decrease in the values of both the up- and down-spin DOS values at the Fermi level.

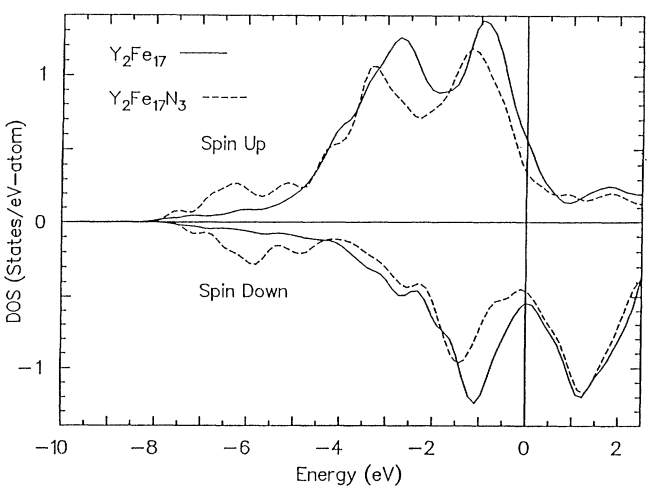

FIG. 3. Spin-polarized density of states for Y_2Fe_{17} (solid line) and $Y_2Fe_{17}N_3$ (dashed line). The zero of energy represents the Fermi energy.

The calculated magnetic moments for the different atomic sites in the two compounds are given in Table II. It should be noticed that small negative moments develop on the Y sites. The total moments per formula unit (fu) are 35.40 μ_B/fu and 39.60 μ_B/fu for Y_2Fe_{17} and $Y_2Fe_{17}N_3$, respectively. The former value is very similar to that calculated by Coehoorn (35.02 μ_B/fu) by the augmented-spherical-wave method for the rhombohedral structure [10]. These results are also in excellent agreement with the 4.2-K magnetization measurements of 34.7 μ_B/fu and 40.3 μ_B/fu for Y_2Fe_{17} and $Y_2Fe_{17}N_{2.6}$, respectively [11].

Table II also lists site-dependent Fe moments for Lu_2Fe_{17} and $Lu_2Fe_{17}N_\xi$ compounds as calculated from the 4.2-K Mössbauer hyperfine-field measurements of Zouganelis, Anagnostou, and Niarchos [12]. The individual hyperfine fields for Y_2Fe_{17} have not been determined to our knowledge, but existing data of Gubbens *et al.* [13] and Zouganelis, Anagnostou, and Niarchos [12] indicate that there is little difference among most of the different R_2Fe_{17} (and $R_2Fe_{17}N_\xi$) compounds. The other assumption in the calculation of the LuFe-site moments is the often-used proportionality of hyperfine field to Fe $3d$ magnetic moment (149 kOe/μ_B). With one exception, to be discussed below, there is a reasonable correspondence between the theoretical and experimental values.

The magnetic moments for the different atomic sites in the two compounds are compared in Table II. The expansion of the lattice due to N lowers the overlap among the $6g$ and $12k$ Fe atoms in the Fe-only planes ($z=0, \frac{1}{2}$) and hence their magnetic moments go up by about 30%. Since the $12j$ Fe atoms now have overlaps with the N atoms, their moments go down by about 12%. The $4f$ Fe moment is the least affected, with only a small increase in its value. The exception mentioned above, the reversal in the magnitude of the $12j$ and $12k$ moments between experiment and theory, may be the result of the wrong association of the larger hyperfine field in the nitrogenated compounds with the $12j$ sites; the local N environments of the $12j$ and $12k$ sites are consistent with the relative sizes of the $12j$ and $12k$ magnetic moments as obtained in the calculations.

TABLE II. Magnetic moments (in μ_B) for different sites in R_2Fe_{17} and $R_2Fe_{17}N_\xi$ compounds.

	Calculated values		Experimental values[a]	
Site	Y_2Fe_{17}	$Y_2Fe_{17}N_3$	Lu_2Fe_{17}	$Lu_2Fe_{17}N_\xi$
$R(2b)$	−0.47	−0.20	···	···
$R(2d)$	−0.45	−0.45	···	···
Fe($4f$)	2.53	2.65	2.47	2.69
Fe($6g$)	1.92	2.53	2.23	2.51
Fe($12j$)	2.25	2.01	2.07	2.35
Fe($12k$)	2.00	2.57	1.87	2.17
N($6h$)	···	−0.04	···	···

[a]From Mössbauer results of Ref. [12] (see text).

It is natural to ask if the increase in T_c upon nitrogenation can be understood theoretically. According to the spin-fluctuation theory of Mohn and Wohlfarth [14], the Curie temperature T_c is given by

$$T_c \propto M_0^2/\chi_0 ,$$

where M_0 is the zero-temperature magnetic moment per atom and the enhanced susceptibility χ_0 is given by

$$\chi_0^{-1} = [1/2N_\uparrow(E_F) + 1/2N_\downarrow(E_F) - I]/2\mu_B^2 .$$

$N_\uparrow(E_F)$ and $N_\downarrow(E_F)$ are the up- and down-spin DOS at the Fermi level and I is the Stoner parameter. These parameters as obtained from the band-structure results are listed in Table III, and they give $R \equiv T_c(Y_2Fe_{17}N_3)/T_c(Y_2Fe_{17}) = 2.34$. The experimental data for $\xi = 2.6$ give $R = 694/325 = 2.14$ [2]. An increase in M_0 and a substantial decrease in $N_\uparrow(E_F)$ upon nitrogenation are responsible for almost doubling T_c. These changes are due to the overall narrowing of the Fe d band caused by the reduction in overlap upon lattice expansion. This good agreement between experiment and theory concerning the increase of T_c indicates that the spin-fluctuation theory is a reasonable model for the magnetism of this class of compounds.

In summary, our work has shown that there are rather subtle structural effects concerning the site occupations of the N atoms in the R_2Fe_{17} structures. Although we find that the e site is primary, in agreement with recent neutron-diffraction studies by Ibberson *et al.* [15], we report a second (low occupancy) site in Nd_2Fe_{17} which they do not. Unfortunately, neither our data, nor that of Ibberson *et al.*, are ideal, showing significant broadening effects. Efforts to resolve these differences, including variations in nitrogen charging and starting materials, are certainly warranted. The self-consistent spin-polarized electronic structure calculations show (i) a decrease in the Fe moments for those atoms with N nearest neighbors, due to their overlap with the N atoms, (ii) an increase in the Fe moments with no N nearest neighbors, due to a decrease in Fe-Fe overlap caused by the lattice expansion, and (iii) an overall increase in the magnetization upon nitrogenation. The important theoretical conclusion is that the spin-fluctuation theory, in combination with the electronic-structure results, satisfactorily describes the significant increase in T_c on nitrogenation; this is due to both the increase in magnetization and decrease in spin-up density of states.

TABLE III. Band-structure parameters.

	Density of states at E_F [states/(eV Fe-atom)] Up	Down	Magnetic moment (μ_B/Fe-atom)	Stoner parameter (eV)
Y_2Fe_{17}	0.663	0.545	2.11	0.95
$Y_2Fe_{17}N_3$	0.365	0.536	2.34	0.93

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