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LETTER TO THE EDITOR

Magnetic properties of a new series of rare-earth iron nitrides: $R_2Fe_{17}N_y$ ($y \sim 2.6$)

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Abstract. A series of interstitial ternary nitrides $R_2Fe_{17}N_y$ with $2.3 < y < 2.9$ has been prepared for $R = Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu$ and Y . The nitrides have structures related to those of Th_2Zn_{17} or Th_2Ni_{17} , but the unit cell volumes are 6–7% greater, and the magnetic ordering temperatures some 400 K higher than for the 2:17 parent compounds. The Fe–Fe exchange interactions are more than doubled by nitrogenation, whereas the R–Fe exchange interactions are little changed. All compounds exhibit easy-plane anisotropy at room temperature, except for $Sm_2Fe_{17}N_y$, which is easy-axis.

The R_2Fe_{17} compounds are the most iron-rich of all binary rare-earth (RE) iron intermetallics. They exist across the whole lanthanide series, except for La itself, crystallising in the rhombohedral Th_2Zn_{17} structure for RES lighter than Gd, and in the hexagonal Th_2Ni_{17} structure for RES heavier than Dy; both structure types may coexist for $R = Gd, Tb$ and Dy . The differences between the two structures are slight, being related to the stacking sequence of hexagonal planes along the c axis [1]. The Th_2Zn_{17} and Th_2Ni_{17} structures are generally indexed on hexagonal cells with $a \sim 0.85$ nm, $c \sim 1.24$ nm and $Z = 3$, or $a \sim 0.85$ nm, $c \sim 0.83$ nm and $Z = 2$ respectively.

The magnetic properties of the series have been studied in great detail [2, 3]. The magnetic ordering temperatures T_C are remarkably low, ranging from as little as 240 K for $R = Ce$ to 480 K for $R = Gd$; corresponding values for the isostructural cobalt series are around 1200 K. Magnetic structures (ferromagnetic for the light RES and ferrimagnetic for the heavy RES) are governed by the predominantly ferromagnetic Fe–Fe exchange coupling, and the R–Fe exchange which tends to align RE and iron spins antiparallel. Exceptions are the $R = Ce, Tm, Yb$ and Lu compounds, which have helimagnetic structures [4].

The magnetic properties of the R_2Fe_{17} intermetallics are very sensitive to composition: many atoms, M, that substitute for iron in $R_2M_xFe_{17-x}$ such as Al, Si, Ni and Co will raise T_C , whether they bear a magnetic moment or not [5, 6, 7]. The interstitial atoms H [8, 9, 10] and C [11, 12] are even more effective at raising T_C in $R_2Fe_{17}M_y$ and in both cases a range of interstitial concentrations are possible. With $M = C$, the solubility limit is close to $y = 1$ and an increase of the Curie temperature of approximately 200 K is achieved [11].

We recently succeeded in preparing the interstitial nitrides $R_2Fe_{17}N_y$ with $y \sim 2.3$ and $R = Y$ and Sm [13]. Here we present the magnetic properties of these compounds for RES ranging from Ce to Lu.

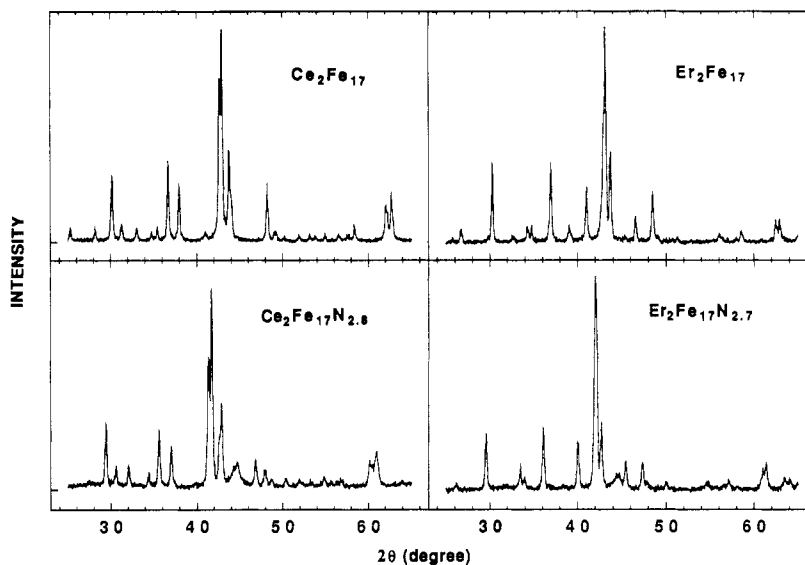


Figure 1. X-ray diffraction patterns of $\text{Ce}_2\text{Fe}_{17}$ and $\text{Er}_2\text{Fe}_{17}$ before and after nitrogenation.

The 2:17 compounds were first prepared by arc melting the RE elements with iron (all 3N pure), followed by an anneal in vacuum at 1000 °C for 50 h for the light REs. The nitrogen absorption characteristic was then determined for each compound by heating a small sample (~ 50 mg) at $10^\circ\text{C min}^{-1}$ in 1 bar of N_2 in a thermopiezic analyser [14]. A suitable temperature for nitrogenation was deduced, which is typically 500 °C. The nitrogen content of the alloy was deduced from the pressure drop observed on cycling up to the maximum temperature and back to room temperature again. The experimental accuracy in y is ± 0.1 atoms/formula.

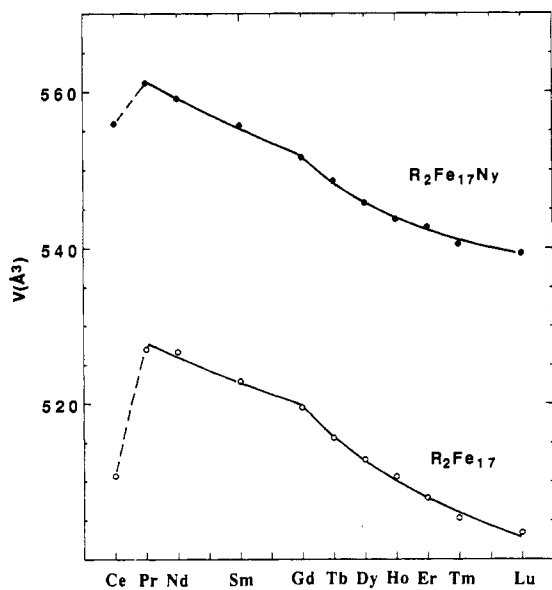
Lattice parameters and cell type were determined from powder diffraction patterns obtained on a Siemens D500 diffractometer, equipped with a graphite monochromator. The anisotropy direction was deduced from diffraction patterns of finely ground powder samples mixed with epoxy which were oriented in a magnetic field of 1 T. Magnetic ordering temperatures were deduced using a vibrating-sample magnetometer from thermomagnetic scans in an applied field of 40 mT. The spontaneous magnetisation σ_s of each sample was measured at room temperature using an 8 T pulsed field on free powder. In cases when T_C was close to room temperature, σ_s was obtained from an Arrott plot.

All samples before nitrogenation were entirely composed of the 2:17 compound (as judged by x-ray diffraction), with the exception of the Pr and Sm alloys, which contained a trace of unreacted αFe . Compounds from Ce to Tb were essentially rhombohedral, whereas those from Dy to Lu were essentially hexagonal. In some cases, notably Gd and Lu, there was an admixture of the other structure type. After nitrogenation, there are traces of some poorly crystallised iron in all the samples (a broad x-ray diffraction peak at $2\theta = 44^\circ$). The primary effect of nitrogen, however, is to expand the unit cell without changing the hexagonal or rhombohedral symmetry of the 2:17 alloy. Some typical x-ray diffraction patterns are shown in figure 1.

Results of all the measurements are collected in table 1. The unit cell volume ($\frac{2}{3}$ of the hexagonal cell volume for the rhombohedral alloys) is plotted in figure 2. The main

Table 1. Structural and magnetic properties of R_2Fe_{17} and $R_2Fe_{17}N_y$.

| | Structure type | a (nm) | c (nm) | T_C (K) | σ_s ($J T^{-1} kg^{-1}$) |
|----------------------|----------------|----------|----------|-----------|-----------------------------------|
| Ce_2Fe_{17} | Th_2Zn_{17} | 0.847 | 1.232 | 241 | 0 |
| $Ce_2Fe_{17}N_{2.8}$ | Th_2Zn_{17} | 0.873 | 1.265 | 713 | 160 |
| Pr_2Fe_{17} | Th_2Zn_{17} | 0.857 | 1.242 | 290 | 82 |
| $Pr_2Fe_{17}N_{2.5}$ | Th_2Zn_{17} | 0.877 | 1.264 | 728 | 167 |
| Nd_2Fe_{17} | Th_2Zn_{17} | 0.856 | 1.244 | 330 | 77 |
| $Nd_2Fe_{17}N_{2.3}$ | Th_2Zn_{17} | 0.876 | 1.263 | 732 | 178 |
| Sm_2Fe_{17} | Th_2Zn_{17} | 0.854 | 1.243 | 389 | 100 |
| $Sm_2Fe_{17}N_{2.3}$ | Th_2Zn_{17} | 0.873 | 1.264 | 749 | 139 |
| Gd_2Fe_{17} | Th_2Zn_{17} | 0.851 | 1.243 | 477 | 46 |
| $Gd_2Fe_{17}N_{2.4}$ | Th_2Zn_{17} | 0.869 | 1.266 | 758 | 115 |
| Tb_2Fe_{17} | Th_2Zn_{17} | 0.845 | 1.241 | 404 | 51 |
| $Tb_2Fe_{17}N_{2.3}$ | Th_2Zn_{17} | 0.866 | 1.266 | 733 | 96 |
| Dy_2Fe_{17} | Th_2Ni_{17} | 0.845 | 0.830 | 367 | 50 |
| $Dy_2Fe_{17}N_{2.8}$ | Th_2Ni_{17} | 0.864 | 0.845 | 725 | 115 |
| Ho_2Fe_{17} | Th_2Ni_{17} | 0.844 | 0.828 | 327 | 49 |
| $Ho_2Fe_{17}N_{3.0}$ | Th_2Ni_{17} | 0.862 | 0.845 | 709 | 115 |
| Er_2Fe_{17} | Th_2Ni_{17} | 0.842 | 0.827 | 296 | 32 |
| $Er_2Fe_{17}N_{2.7}$ | Th_2Ni_{17} | 0.861 | 0.846 | 697 | 134 |
| Tm_2Fe_{17} | Th_2Ni_{17} | 0.840 | 0.828 | 260 | 0 |
| $Tm_2Fe_{17}N_{2.7}$ | Th_2Ni_{17} | 0.858 | 0.847 | 690 | 137 |
| Lu_2Fe_{17} | Th_2Ni_{17} | 0.839 | 0.826 | 255 | 0 |
| $Lu_2Fe_{17}N_{2.7}$ | Th_2Ni_{17} | 0.857 | 0.848 | 678 | 147 |
| Y_2Fe_{17} | Th_2Ni_{17} | 0.848 | 0.826 | 325 | 92 |
| $Y_2Fe_{17}N_{2.6}$ | Th_2Ni_{17} | 0.865 | 0.844 | 694 | 164 |

**Figure 2.** Unit cell volume for the R_2Fe_{17} and $R_2Fe_{17}N_y$ series.

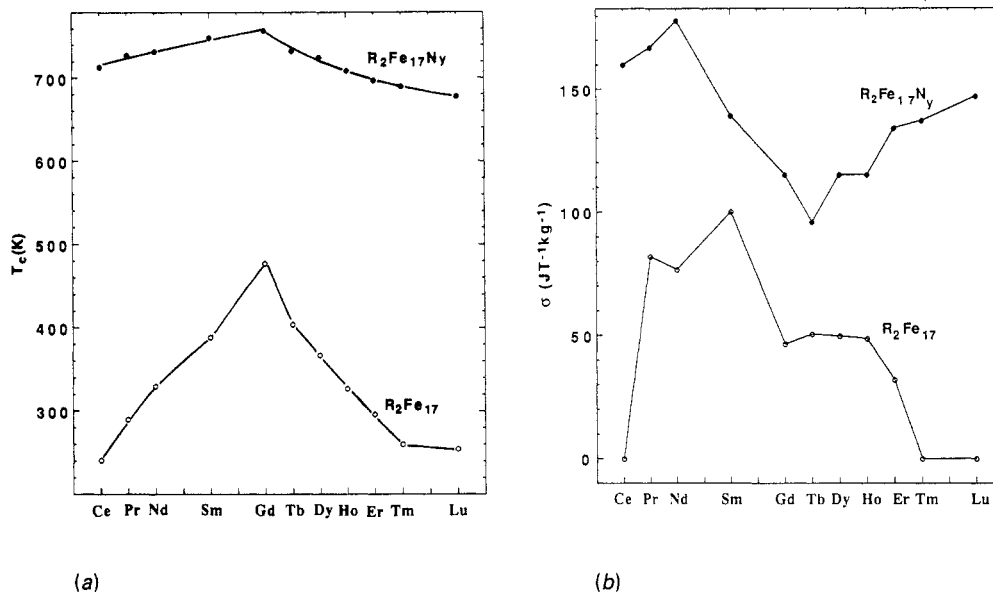


Figure 3. (a) Curie temperature, and (b) magnetisation at room temperature for the R_2Fe_{17} and $R_2Fe_{17}N_y$ series.

trend reflects the lanthanide contraction, but the volume of the cerium compound is anomalously low, suggesting a $4f^0$ configuration for the RE. There is also evidence of a superposed magnetovolume anomaly, with a peak at Gd. Nitrogenation increases the unit cell volume by 6–7%. The same trends are evident as for the parent compounds, except that the position of Ce is much less anomalous. The volume of the Ce compound increases by 9% on nitrogenation, and it is possible that there is an intermediate $4f^n$ configuration in the nitride, with $0 < n < 1$.

The variation of the Curie temperature is shown in figure 3. The usual maximum is observed at $R = Gd$, but the increase in T_C produced by nitrogenation is quite extraordinary. The average increase across the series is 387 K, or 125%. Analysis of the Curie temperatures of the heavy RE compounds in terms of the expression [15]

$$T_C = \frac{1}{2}(T_{Fe} + (T_{Fe}^2 + 4T_{RFe}^2)^{1/2})$$

where

$$T_{Fe} = n_{Fe-Fe} N_{Fe} [4S^*(S^* + 1)\mu_B^2/3k]$$

$$T_{RFe} = n_{R-Fe} |\gamma| (N_{Fe} N_R)^{1/2} \{2g[S^*(S^* + 1)J(J + 1)]^{1/2} \mu_B^2/3k\}.$$

Here N_{Fe} and N_R are the number of atoms per unit volume, γ is $2(g - 1)/g$, where g is the Landé g -factor and J is the RE angular momentum quantum number; n_{Fe-Fe} and n_{R-Fe} are the molecular field coefficients. The effective iron spin S^* ($1.0 \mu_B$) is defined from the average iron moment at 0 K as $2S^* \mu_B$. Values of the molecular field coefficients thus obtained are given in table 2. The effective exchange field (in tesla) acting on the iron and RE sublattices are $(n_{Fe-Fe} M_{Fe} + n_{R-Fe} \gamma M_R)$ and $n_{R-Fe} \gamma M_{Fe}$ respectively; M_{Fe} is approximately $1.16 \times 10^6 J T^{-1} m^{-3}$ for $R_2Fe_{17}N_y$ and $0.67 \times 10^6 J T^{-1} m^{-3}$ for R_2Fe_{17} .

Table 2. Molecular field coefficients (in units of μ_0) for R_2Fe_{17} and $R_2Fe_{17}N_y$.

| | n_{R-Fe} | n_{Fe-Fe} |
|-----------------|------------|-------------|
| R_2Fe_{17} | 225 | 181 |
| $R_2Fe_{17}N_y$ | 208 | 515 |

The n_{R-Fe} coefficient is now known to decrease substantially from the beginning to the end of the RE series, due to the decreasing 4f–5d overlap associated with the lanthanide contraction [16]. However, most of the decrease occurs for the light REs, and the fall from Gd to Lu is only about 20%. The values in table 2 therefore indicate the trends in the exchange interactions for the heavy REs; the Fe–Fe interaction is more than doubled in the nitrides, whereas the R–Fe interaction is slightly weakened.

From the values of magnetisation given in table 1, it appears that the contribution of the iron sublattices at room temperature is approximately $33 \mu_B$, as indicated by the magnetisation of the Y, Lu and Ge compounds. The larger values of magnetisation for the light REs and the smaller ones for the heavy REs suggest the conventional systematic of ferromagnetic spin structures for light RE intermetallics and ferrimagnetic structures for heavy RE intermetallics.

The sign of the magnetic anisotropy at room temperature was deduced from x-ray diffraction patterns of magnetically aligned powders. Some typical data are shown in figure 4. The $Sm_2Fe_{17}N_y$ compound was already shown to exhibit easy-*c* axis anisotropy

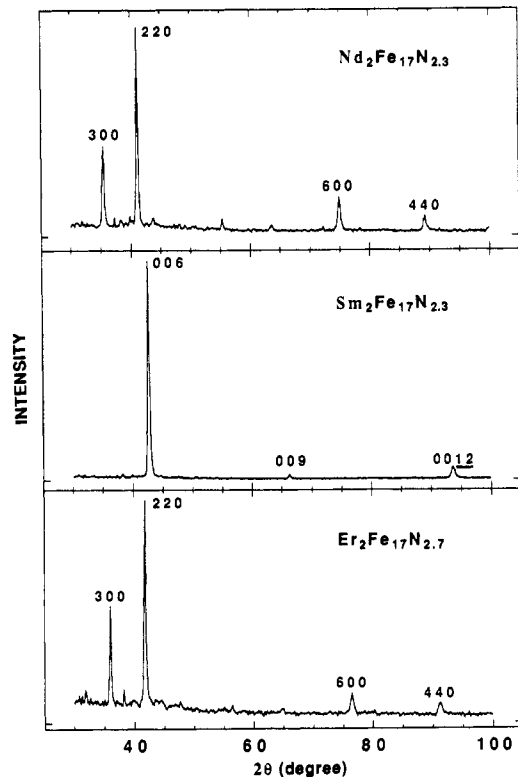


Figure 4. X-ray diffraction patterns of oriented samples of $R_2Fe_{17}N_y$, showing a *c* axis alignment of Sm, and a *c* plane alignment for Nd and Er.

at room temperature [13]. Here we find that it is the only compound in the series to do so. All the others have an easy-axis perpendicular to c , indicating that the easy-plane anisotropy of the iron sublattices in the nitrides outweighs the tendency to easy-axis anisotropy that is expected for Er and Tm, which, like Sm, have a positive sign of the second-order Stevens coefficient α_J .

In conclusion:

(i) a new interstitial nitride phase $R_2Fe_{17}N_y$ with $y \sim 2.6$ exists across the entire RE series.

(ii) The structure of the nitride is related to that of the parent 2:17 compound, but the unit cell volume increases by 6–7% (9% for Ce).

(iii) The enormous increase in Curie temperature in the nitrides is due to more than the doubling of the Fe–Fe exchange interactions, associated with the change in cell volume; R–Fe interactions are little changed.

(iv) Uniaxial anisotropy is found at room temperature only for the Sm compound; all the rest are easy-plane. The negative sign of the iron anisotropy is unchanged after nitrogenation.

(v) The $Sm_2Fe_{17}N_{2.3}$ compound is a promising starting point for the development of new permanent magnets. Although no RE substitution is able to increase the uniaxial anisotropy, it is likely that substitution of Co for Fe or substitution of C [13] or another group V element for N may do so.

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