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Magnetic properties of a new series of rare-earth iron nitrides $R_3(\text{Fe, Mo})_{29}\text{N}_x$ ($R = \text{Ce, Nd, Sm, Gd, Tb, Dy or Y}$)

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Abstract. A series of interstitial nitrides $R_3(\text{Fe, Mo})_{29}\text{N}_x$ with $3.7 \leq x \leq 4.0$ has been prepared for $R = \text{Ce, Nd, Sm, Gd, Tb, Dy or Y}$. The nitrides have structures related to $\text{Nd}_3(\text{Fe, Ti})_{29}$, but the unit-cell volumes are 4.7–6.6% greater and the magnetic ordering temperatures some 224–361 K higher than those of the $R_3(\text{Fe, Mo})_{29}$ parent compounds, and the saturation magnetizations M_S are also higher than those of the corresponding parent compounds. All compounds investigated exhibit easy-plane anisotropy at room temperature, except for $\text{Sm}_3(\text{Fe, Mo})_{29}\text{N}_x$ which is of an easy-axis nature.

1. Introduction

The $R_3(\text{Fe, M})_{29}$ ($R = \text{rare earth; M = Ti, V, Mn, etc}$) compounds are the most iron rich of all rare-earth iron intermetallics. They exist across almost the whole lanthanide series and crystallize in the monoclinic $\text{Nd}_3(\text{Fe, Ti})_{29}$ -type structure [1]. The magnetic properties of a series of $R_3(\text{Fe, M})_{29}$ ($R = \text{Ce, Nd, Sm, Gd, Tb, Dy or Y; M = Ti, V, Mn, Cr or Mo}$) compounds have been studied in great detail [1–21]. The magnetic ordering temperatures T_C are extremely low. Taking $R_3(\text{Fe, Mo})_{29}$ as an example, the Curie temperatures T_C range from as little as 300 K for $R = \text{Ce}$ to 494 K for $R = \text{Gd}$ [18]. The saturation magnetizations M_S are also lower than those of the corresponding 2:17 compounds. In 1990, Coey and Sun [22] reported that considerable improvements with respect to Curie temperatures and saturation magnetizations of $R_2\text{Fe}_{17}$ were reached by gas-phase interstitial modification. In this paper, we gave the first report of the intrinsic properties of $R_3(\text{Fe, Mo})_{29}\text{N}_x$ nitrides.

2. Experimental details

The 3:29 compounds were first prepared by arc melting the rare-earth elements with Fe and Mo (all 99.9% pure), followed by an anneal in vacuum at 1313–1453 K for 48–72 h and then a quench in water. The conditions of preparation of the single-phase $R_3(\text{Fe, Mo})_{29}$ are listed in table 1. In order to prepare nitrides the ingots were pulverized into fine powders with an average size of 10–15 μm , and then nitrogenation of the samples was performed by heating the fine powder in nitrogen at 1 atm at temperatures of 800–900 K for about 2–2.5 h. The nitrogen contents were determined from the difference between the masses before and after nitrogenation.

Table 1. The conditions of preparation of the single phase $R_3(\text{Fe}, \text{Mo})_{29}$ ($R = \text{Ce}, \text{Nd}, \text{Sm}, \text{Gd}, \text{Tb}, \text{Dy}$ or Y).

Composition details		Annealing conditions	
Compound	x	T_A (K)	t_A (h)
$\text{Ce}_3(\text{Fe}_{1-x}\text{Mo}_x)_{29}$	0.039	1313	24
$\text{Nd}_3(\text{Fe}_{1-x}\text{Mo}_x)_{29}$	0.044	1453	24
$\text{Sm}_3(\text{Fe}_{1-x}\text{Mo}_x)_{29}$	0.034	1453	24
$\text{Gd}_3(\text{Fe}_{1-x}\text{Mo}_x)_{29}$	0.026	1453	24
$\text{Tb}_3(\text{Fe}_{1-x}\text{Mo}_x)_{29}$	0.024	1323	72
$\text{Dy}_3(\text{Fe}_{1-x}\text{Mo}_x)_{29}$	0.016	1253	72
$\text{Y}_3(\text{Fe}_{1-x}\text{Mo}_x)_{29}$	0.031	1353	72

X-ray diffraction with $\text{Cu K}\alpha$ radiation was used to identify the phases of the compounds and to determine the lattice parameters. The thermomagnetic analysis was performed in a low field of about 0.04 T in the temperature range from 300 K to above the Curie temperature. The Curie temperatures T_C were determined from σ^2 - T plots by extrapolating σ^2 to zero. The magnetization curves were measured using an extracting-sample magnetometer with a superconducting magnet with a maximum magnetic field up to 7 T. The saturation magnetizations M_S were derived from M - $1/B$ plots based on the magnetization curves. The anisotropy fields B_a were determined from the intersection point of two magnetization curves measured in the magnetic field applied parallel or perpendicular, respectively, to the alignment direction of the cylinder samples.

3. Results and discussion

The lattice parameters and unit-cell volumes of the $R_3(\text{Fe}, \text{Mo})_{29}\text{N}_x$ nitrides are listed in table 2 and the lattice parameters and unit-cell volumes of the corresponding parent compounds are also included in parentheses. The lattice parameters a , b and c and unit-cell volumes V decrease with an increase in atomic number of rare-earth elements which reflects the lanthanide contraction, but those of the cerium compound are anomalously low, suggesting a $4f^0$ configuration for the rare earth. The same trends are evident as for the parent compounds. Nitrogenation increases the unit-cell volume by 4.6–5.9%. The volume of the cerium compound increases by 6.6% on nitrogenation and it is possible that there is an intermediate $4f^n$, $0 < n < 1$, configuration in the nitride. The expansion rates of the unit-cell volumes V of the $R_3(\text{Fe}, \text{Mo})_{29}$ compounds after nitrogenation is greater than those of the 1:12 compounds, about 3–4% [23], but smaller than those of the 2:17 compounds, about 6–7% [24].

The intrinsic magnetic properties, including the Curie temperatures T_C , saturation magnetizations M_S and anisotropy fields B_a are summarized in table 3. For comparison, the magnetic properties of the corresponding parent compounds are also included in parentheses. The Curie temperatures and saturation magnetizations, similar to those of 2:17 and 1:12 compounds, increase markedly after nitrogenation. The average increase in Curie temperature T_C and saturation magnetization M_S produced by nitrogenation across the series is 279 K or 71%, and 17.6 A m² kg⁻¹ or 24%, respectively. The increase in M_S is attributed to the increase in average Fe moments after nitrogenation [25]. The strong increase in Curie temperature T_C upon nitrogenation may partly be explained in terms of lattice expansion of the nitride which leads to an increase in the average nearest-neighbour Fe-Fe exchange

Table 2. The lattice parameters and unit-cell volumes of the $R_3(Fe, Mo)_{29}N_x$ nitrides (R = Ce, Nd, Sm, Gd, Tb, Dy or Y).

Compound	a (Å)	b (Å)	c (Å)	β (deg)	V (Å ³)	$\Delta V/V$ (%)
Ce ₃ (Fe, Mo) ₂₉ N _x	10.791 (10.555)	8.701 (8.512)	9.887 (9.686)	96.92 (96.78)	921.57 (864.19)	6.6
Nd ₃ (Fe, Mo) ₂₉ N _x	10.856 (10.638)	8.753 (8.582)	9.924 (9.748)	96.72 (96.86)	936.44 (884.00)	5.9
Sm ₃ (Fe, Mo) ₂₉ N _x	10.805 (10.622)	8.703 (8.568)	9.870 (9.738)	97.07 (96.83)	921.09 (879.92)	4.7
Gd ₃ (Fe, Mo) ₂₉ N _x	10.778 (10.585)	8.687 (8.531)	9.869 (9.696)	96.70 (96.85)	917.35 (869.33)	5.5
Tb ₃ (Fe, Mo) ₂₉ N _x	10.746 (10.582)	8.670 (8.519)	9.846 (9.675)	96.70 (96.88)	910.92 (863.12)	5.5
DY ₃ (Fe, Mo) ₂₉ N _x	10.728 (10.574)	8.655 (8.492)	9.843 (9.670)	96.75 (96.96)	907.60 (867.68)	4.6
Y ₃ (Fe, Mo) ₂₉ N _x	10.713 (10.568)	8.666 (8.505)	9.839 (9.672)	96.57 (96.89)	907.40 (861.86)	5.3

Table 3. The magnetic properties of the $R_3(Fe, Mo)_{29}N_x$ nitrides (R = Ce, Nd, Sm, Gd, Tb, Dy or Y).

Compound	T_c (K)	ΔT (K)	M_s (A m ² kg ⁻¹)		B_a (T)	
			4.2 K	300 K	4.2 K	300 K
Ce ₃ (Fe, Mo) ₂₉ N _x	661.0 (300.0)	361.0	155.4 (129.0)	139.2 (81.0)	—	—
Nd ₃ (Fe, Mo) ₂₉ N _x	675.0 (395.0)	280.0	161.0 (151.0)	143.5 (116.0)	—	—
Sm ₃ (Fe, Mo) ₂₉ N _x	704.0 (445.0)	259.0	152.0 (135.0)	137.0 (107.0)	20.5	14.6
Gd ₃ (Fe, Mo) ₂₉ N _x	718.0 (494.0)	224.0	110.9 (94.0)	100.5 (81.0)	—	—
Y ₃ (Fe, Mo) ₂₉ N _x	659.0 (376.0)	283.0	162.1 (147.0)	143.3 (106.5)	—	—
Tb ₃ (Fe, Mo) ₂₉ N _x	690.0 (437.0)	262.0	94.5 (77.5)	90.0 (70.4)	—	—
DY ₃ (Fe, Mo) ₂₉ N _x	675.0 (408.0)	285.0 (74.5)	92.0 (65.2)	87.0	—	—

interaction. A theoretical analysis shows that the increase in Curie temperature T_C may also be ascribed to the increase in magnetization upon nitrogenation and the decrease in the spin-up density of states at the Fermi level E_F associated with narrowing of the 3d band [26].

There are three types of interaction in the $R_3(Fe, Mo)_{29}$ compounds and their nitrides, namely the R–R interactions between the magnetic moments within the R sublattice, the T–T exchange interactions between the magnetic moments of the T sublattice, and the R–T intersublattice exchange interactions. Among them, the T–T exchange interaction is the strongest while the R–R interaction is the weakest and is usually neglected. According to the mean-field analysis of the Curie temperature, J_{RFe} and J_{FeFe} can be expressed as [27]

$$J_{RFe} = g_R g_{Fe} \mu_B^2 N_{Fe} N_{RFe} / 2 Z_{RFe} (g_R - 1) (g_{Fe} - 1) \quad (1)$$

$$3kT_C = a_{FeFe} + (a_{FeFe}^2 + 4a_{RFe} a_{FeR})^{1/2} \quad (2)$$

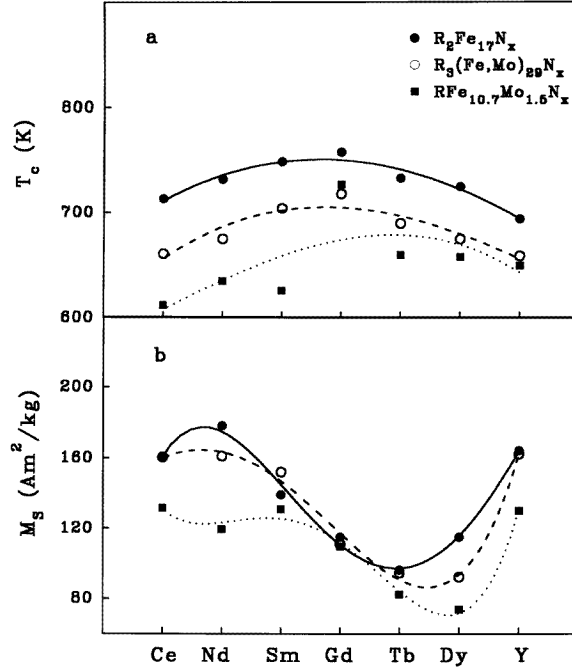


Figure 1. Comparison of the magnetic properties of the $R_3(Fe, Mo)_{29}N_x$ nitrides with those of the $R_2Fe_{17}N_x$ and $RFe_{10.5}Mo_{1.5}N_x$ nitrides, where T_A is the annealing temperature and t_a the annealing time.

where

$$a_{FeFe} = Z_{FeFe} J_{FeFe} S_{Fe} (S_{Fe} + 1) \quad (3)$$

$$a_{RFe} a_{FeR} = Z_{RFe} Z_{FeR} S_{Fe} (S_{Fe} + 1) (gJ - 1)^2 J(J + 1) J_{RFe}^2 \quad (4)$$

and

$$J_{FeFe} = a_{FeFe} / Z_{FeFe} S_{Fe} (S_{Fe} + 1) \quad (5)$$

where a_{ij} represents the magnetic interaction energy between the i and j spins, J_{ij} is the i - j exchange constant, Z_{ij} is the number of j atoms which are nearest neighbour to i atoms. For $R_3(Fe_{1-x}M_x)_{29}$ compounds and their nitrides, each R atom has an average number of $Z_{RFe} = 18(1-x)$ Fe nearest neighbours, while each Fe atom has an average number of $Z_{FeR} = 2$ R nearest neighbours and an average number of $Z_{FeFe} = 10(1-x)$ Fe neighbours [28]. In order to calculate the intersublattice molecular field coupling in the Fe sublattice, we used a value of T_C when R is non-magnetic yttrium. In this calculation, according to our experimental results, the values of the iron spins $S_{Fe} = 0.9$ for the parent compound and $S_{Fe} = 1.0$ for its nitride, have been used, which were obtained from the saturation magnetization of the $Y_3(Fe, Mo)_{29}$ compound and its nitride at 4.5 K. The calculated exchange constants J_{RFe} and J_{FeFe} of the $R_3(Fe, Mo)_{29}$ compounds and their nitrides are listed in table 4. It can be seen that J_{RFe} decreases with increasing atomic number of R in the $R_3(Fe, Mo)_{29}$ compounds and their nitrides. This is associated with the lanthanide contraction. The decrease in the radius of the 4f shell with increasing atomic number of R leads to a smaller overlap of the 4f and 5d shells. Therefore, the 4f-5d

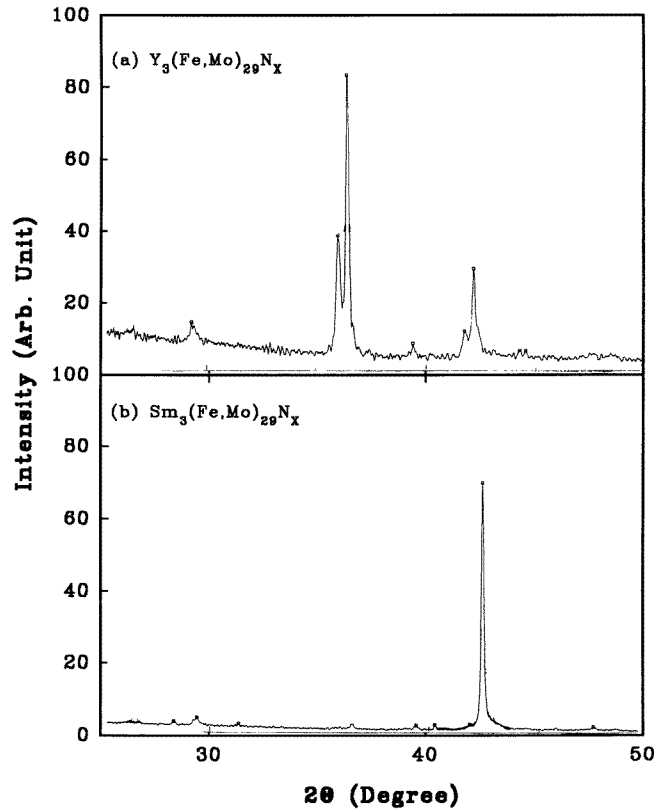


Figure 2. The x-ray diffraction patterns of magnetically aligned samples of (a) $Y_3(Fe, Mo)_{29}N_x$ and (b) $Sm_3(Fe, Mo)_{29}N_x$.

Table 4. Calculated exchange constants J_{FeFe} and J_{RFe} for the $R_3(Fe, Mo)_{29}$ compounds and their nitrides.

R	J_{RFe} (10^{-22} J)		J_{FeFe} (10^{-22} J)	
	Parents	Nitrides	Parents	Nitrides
Sm	2.2	2.0	9.3	13.6
Gd	-1.6	-1.3	9.3	13.6
Tb	-1.4	-1.1	9.3	13.6
Dy	-1.1	-0.9	9.3	13.6
Y			9.3	13.6

hybridization decrease leads to a reduction in the R–Fe interaction. For the same rare earth R, the R–Fe interactions in nitride are slightly weaker than those of corresponding parent compounds, whereas the Fe–Fe interactions in nitrides are stronger than those in the parent compounds.

Figures 1(a) and 1(b) show the comparisons of the Curie temperatures T_C and the saturation magnetization M_S , respectively, of the $R_3(Fe, Mo)_{29}N_x$ nitrides with

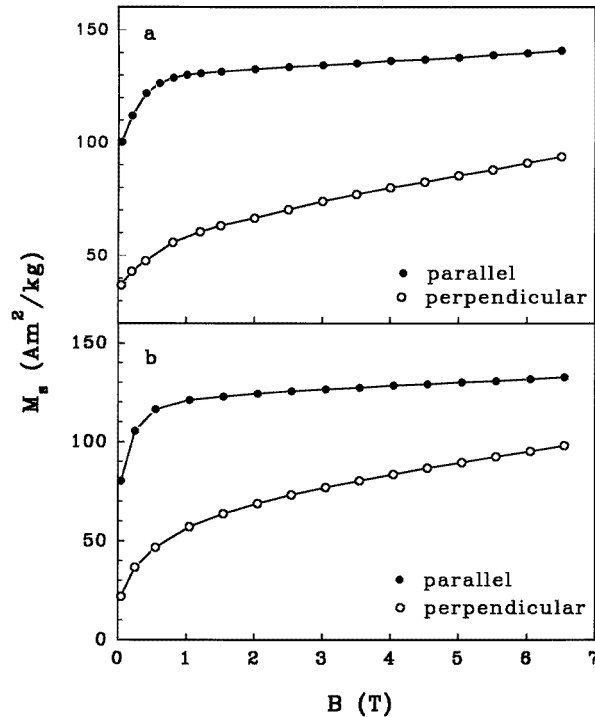


Figure 3. The magnetization curves for the aligned powder sample of the $\text{Sm}_3(\text{Fe, Mo})_{29}\text{N}_x$ in different applied fields at (a) 4.2 K and (b) 300 K.

those of the $\text{R}_2\text{Fe}_{17}\text{N}_x$ and $\text{RFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ nitrides. The Curie temperatures T_C and saturation magnetizations M_S of the $\text{R}_3(\text{Fe, Mo})_{29}\text{N}_x$ nitrides are higher than those of the $\text{RFe}_{10.5}\text{Mo}_{1.5}\text{N}_x$ nitrides [23] but lower than those of the $\text{R}_2\text{Fe}_{17}\text{N}_x$ nitrides [24].

All the compounds investigated exhibit easy-plane anisotropy at room temperature, except for $\text{Sm}_3(\text{Fe, Mo})_{29}\text{N}_x$ which is of an easy-axis nature. Figure 2(a) and 2(b) show the x-ray diffraction patterns of magnetically aligned samples of $\text{Y}_3(\text{Fe, Mo})_{29}\text{N}_x$ and $\text{Sm}_3(\text{Fe, Mo})_{29}\text{N}_x$, respectively. They indicate that the Fe sublattice possesses planar anisotropy in the $\text{R}_3(\text{Fe, Mo})_{29}\text{N}_x$ nitrides and the easy magnetization direction of $\text{Sm}_3(\text{Fe, Mo})_{29}\text{N}_x$ is along [102], which corresponds to the [001] direction in the structure of CaCu_5 . So the introduction of nitrogen leads to the occurrence of uniaxial anisotropy in the nitrides. The magnetization curves for the aligned powder sample of $\text{Sm}_3(\text{Fe, Mo})_{29}\text{N}_x$ nitride in different applied fields at 4.2 and 300 K are presented in figure 3. It can be seen, from table 3 and figure 3, that the high Curie temperature T_C , large saturation magnetization M_S and strong uniaxial anisotropy of $\text{Sm}_3(\text{Fe, Mo})_{29}\text{N}_x$ make it a new candidate for permanent magnet application.

4. Conclusions

In this paper, the structural characteristics and intrinsic magnetic properties of new interstitial nitrides $\text{R}_3(\text{Fe, Mo})_{29}\text{N}_x$ ($\text{R} = \text{Ce, Nd, Sm, Gd, Tb, Dy}$ or Y) with $3.7 \leq x \leq 4.0$ have been reported. The structures of the nitrides are related to the 3:29 parent compounds but

the unit-cell volumes increase by 4.6–5.9% (6.6% for Ce). The R–Fe interactions in the nitride are slightly weaker than those in the corresponding parent compounds, whereas the Fe–Fe interactions in nitrides are stronger than those in the parent compounds. Introduction of nitrogen leads to the occurrence of uniaxial anisotropy in $\text{Sm}_3(\text{Fe}, \text{Mo})_{29}\text{N}_x$. The high Curie temperature T_C , large saturation magnetization M_S and strong uniaxial anisotropy of the $\text{Sm}_3(\text{Fe}, \text{Mo})_{29}\text{N}_x$ make it a new candidate for permanent magnet application.

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