

## Effect of interstitial hydrogen and nitrogen on the magnetocrystalline anisotropy of $R_2Fe_{17}$ ( $R=Tb,Dy,Ho,Er$ )

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### Abstract

The magnetocrystalline anisotropies of  $R_2Fe_{17}$  ( $R=Tb,Dy,Ho$  and  $Er$ ) and of the nitrides and hydrides of these compounds are studied by analysing the hard and the easy magnetization curves of magnetically aligned samples in the temperature range 80–300 K. The effects of the hydrogen and the nitrogen atoms on the rare earth sublattice anisotropy are found to be opposite. It is observed that, in contrast to nitrogenation, hydrogenation leads to an easy axis type R sublattice anisotropy for R ions with negative Stevens factor  $\alpha_2$  ( $Tb, Dy$  and  $Ho$ ). An easy-plane to easy-cone transition is detected for  $Dy_2Fe_{17}H_x$  ( $x=3$  and  $5$ ). The magnetic structures of  $Tb_2Fe_{17}H_x$  ( $x=3$  and  $5$ ) are possibly of the easy-cone type at room temperature. © 1997 Elsevier Science S.A.

**Keywords:** Magnetocrystalline anisotropy; Interstitial; Rare earth compounds

### 1. Introduction

Compounds  $R_2Fe_{17}$  are of particular interest due to their large Fe contents which make them to be good candidates for permanent magnets. These compounds crystallize in two slightly different crystallographic types: the rhombohedral  $Th_2Zn_{17}$  structure for  $R=Ce-Dy$  and the hexagonal  $Th_2Ni_{17}$  for  $R=Gd-Lu$ . The difference consists of different stacking sequences of the hexagonal planes along the c-axis. The magnetic structures are determined by both the Fe-Fe and R-Fe exchange and the later lead to the ferromagnetic structure for the light rare earth elements and to the ferrimagnetic structure for the heavy elements. Helimagnetic structures appear in the cases of  $R=Ce,Tm,Yb,Lu$  [1].

The magnetic properties of the series are well studied [2]. The Curie temperatures are relatively low and even the highest one (for R-Gd) does not exceeded 500 K. Primarily due to the Fe sublattice anisotropy contribution all the compounds are easy plane materials at the room temperature. For some of the compounds containing rare earth ions with a positive Stevens factor  $\alpha_2$  spin reorientation transitions occur at low temperatures.

In recent years important progress has been achieved in augmentation of the Curie point. It was shown that insertions of light elements such as hydrogen and nitrogen in the  $R_2Fe_{17}$  alloys produce drastic changes in the magnetic properties of these compounds [3,4]. Nitrogenation of  $Sm_2Fe_{17}$  leads to an increase of the Curie temperature from 350 K to 700 K and to changes of the easy magnetization direction from the basal-plane to the c axis [5]. The rise of the ordering temperature may be ascribed to the increase in Fe-Fe interaction caused by the cell volume increase. The behaviour of the magnetocrystalline anisotropy (MCA) needs further investigation. The purpose of our work is to study the effect of interstitial H and N on MCA of these compounds.

For hexagonal symmetry the MCA can be expressed in the form:

$$E_a = K_1 \sin^2(\theta) + K_2 \sin^4(\theta) + K_3 \sin^6(\theta) + K_4 \sin^6(\theta) \cos(6\varphi), \quad (1)$$

where  $\theta$  and  $\varphi$  are the planar and azimuthal angles of the direction of the magnetization with respect to the c- and a-axis. The values of  $K_1, K_2, K_3$  control in particular the easy magnetization direction of the compound (EMD). When the EMD lie in the basal plane it is appropriate to use the conjugated parameters  $R_1 = -K_1 - 2K_2 - 3K_3, R_2 =$

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$K_2 + 3K_3$ ,  $R_3 = -K_3$  which correspond to the transformation  $\theta' = \theta + \pi/2$  [6].

The values of these parameters can be evaluated from single crystal magnetization curves along the principal directions. In the case of  $R_2Fe_{17}$  compounds this procedure is often complicated since the values of the high order parameters are large and the R-Fe interaction (mutual turning of the sublattice in the external magnetic field) must be taken into account [7]. Therefore different methods applied for the determination of the parameters may give different values, as was reported previously for many other intermetallic systems [8]. Consequently an explicit description of the evaluation method we use becomes important.

In our studies of the effect of the hydrogenation and the nitrogenation on MCA of our compounds we determined in a uniform manner the effective anisotropy constants for the easy plane materials ( $R_1$ ). We report here on the behaviour of  $R_1$  for  $R_2Fe_{17}$  ( $R = Tb, Dy, Ho, Er$ ) and their hydrides and nitrides.

## 2. Experimental details

The  $R_2Fe_{17}$  alloys we started with were produced by arc melting of the elemental components followed by a heat treatment at 1150 °C for 24 h. The nitrides were produced near 450 °C in a  $N_2$  gas atmosphere under the 10 bar pressure. The hydrides were produced in the temperature range 150–300 °C under 5 bar pressure. X-ray diffraction indicated that for all compositions only the  $Th_2Ni_{17}$  crystal structure is observed.

The magnetic measurements were made for aligned and free powder samples in the temperature range 80–300 K and in magnetic fields up to 1.2 T by using a pendulum magnetometer. Since our samples are easy-plane materials we made the alignment in a 0.7 T rotating magnetic field [9]. Effective anisotropy constants were calculated from the slopes of the linear part of the hard magnetization curves (usually the part in fields higher than 0.5 T) and from the values of the saturation magnetization determined from the easy magnetization curves and from the free powder magnetization curves. For some samples the magnetic measurements were made in pulsed fields up to 15 T at 80 K. The anisotropy constants determined from the high field magnetization curves are in a good agreement with those determined from the low field magnetization curves.

## 3. Results

### 3.1. $Er_2Fe_{17}(H,N)_x$

The nitride with  $x=2$  and the hydride with  $x=2$  were studied. For  $Er_2Fe_{17}N_2$  there is a spontaneous magnetic

moment along the c axis at temperatures below 150 K. This testifies the occurrence of an easy-plane to easy-cone spin reorientation transition near this temperature. In the hard magnetization curves, at 80 K, a first order magnetization process (FOMP) takes place in fields near 4 T (see Fig. 1). An analogous behaviour was previously detected and analyzed for  $Er_2Fe_{17}C_x$  [10]. From our point of view the existence of FOMP in the hard magnetization curve of  $Er_2Fe_{17}N_2$  may reflect the presence of a small amount of uncharged  $Er_2Fe_{17}$  that was not detected by X-ray investigation. It is known [11] that because of a limited penetration depth, a single phase X-ray pattern does not guarantee that the nitrogenation process has reached completion.

Hydrogenation of  $Er_2Fe_{17}$ , in contrast to nitrogenation, leads to an increase of the value of  $R_1$  (see Table 1.)

### 3.2. $Ho_2Fe_{17}(N,H)_x$

The temperature dependencies of  $R_1$  and the rare earth part of  $R_1$  versus reduced temperature for the samples  $Ho_2Fe_{17}N_2$ ,  $Ho_2Fe_{17}H_2$  and  $Ho_2Fe_{17}H_5$  are plotted in Fig. 2 and Fig. 3 respectively. The rare earth parts were calculated by subtracting the Fe parts obtained from the data of the  $Y_2Fe_{17}$  hydrides and nitrides [12]. For  $Ho_2Fe_{17}$  there is a pronounced decrease of the  $K_1$  under hydrogenation and an increase under nitrogenation. Our calculations of the changes of the second order CF parameter  $A_2^0$  under nitrogenation and hydrogenation (hydride with  $x=2$ ) give values of  $25 K_{a_0}^{-2}$  per hydrogen atom and  $-60 K_{a_0}^{-2}$  per nitrogen atom. The rare earth part of  $R_1$  for  $Ho_2Fe_{17}H_5$  is nearly the same as for  $Ho_2Fe_{17}$ . From the high field investigation at 80 K we derived values of the anisotropy field near 15 T for  $Ho_2Fe_{17}$  and between 2.8 and 3 T for  $Ho_2Fe_{17}H_2$  and  $Ho_2Fe_{17}H_5$ .

### 3.3. $Dy_2Fe_{17}(N,H)_x$

Easy-plane to easy-cone spin reorientation transitions are found at temperatures near 250 and 200 K for hydrides

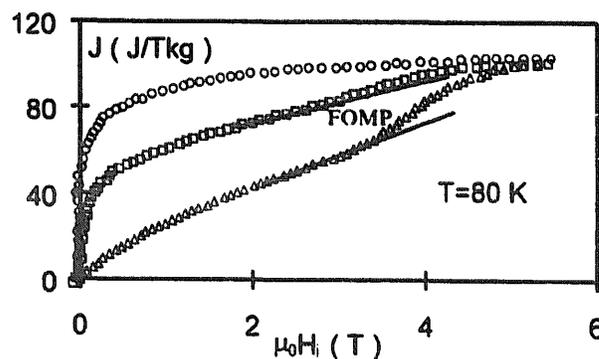


Fig. 1. The hard (squares) and the easy (circles) magnetization curves for  $Er_2Fe_{17}N_2$ , the easy magnetization curve (triangles) for  $Er_2Fe_{17}$ .

Table 1

The magnetic properties of the studied samples. The values of the effective anisotropy constants for the easy plane materials ( $R_1$ ) were deduced from the hard and the easy magnetization curves of textured samples measured in the low fields (up to 1.2 T). The saturation magnetization ( $J_s$ ) are the values of magnetization of the fine free powder in the field of 1.2 T. The anisotropy fields ( $\mu_0 H_a$ ) were determined as the fields of saturation along the hard directions in the pulsed fields (up to 15 T)

Compound	$R_1$ (MJ m <sup>-3</sup> ) ( $T=80$ K)	$\mu_0 H_a$ (T) ( $T=80$ K)	$J_s$ (JT <sup>-1</sup> kg <sup>-1</sup> ) ( $T=80$ K)	$J_s$ (JT <sup>-1</sup> kg <sup>-1</sup> ) ( $T=300$ K)
Dy <sub>2</sub> Fe <sub>17</sub>	1.5	>15	65	58.5
Dy <sub>2</sub> Fe <sub>17</sub> H <sub>3</sub>	cone	>15	80	95.2
Dy <sub>2</sub> Fe <sub>17</sub> H <sub>5</sub>	cone	>15	76.5	91
Dy <sub>2</sub> Fe <sub>17</sub> N <sub>2</sub>	2.9	–	82	90
Ho <sub>2</sub> Fe <sub>17</sub>	2	≈15	66.4	58.5
Ho <sub>2</sub> Fe <sub>17</sub> H <sub>2</sub>	0.6	2.8	78	115
Ho <sub>2</sub> Fe <sub>17</sub> H <sub>3</sub>	0.8	3.0	72.3	93
Ho <sub>2</sub> Fe <sub>17</sub> N <sub>2</sub>	4.5	≈15	80	95
Er <sub>2</sub> Fe <sub>17</sub>	1.5	4.5 (FOMP)	83.5	60
Er <sub>2</sub> Fe <sub>17</sub> H <sub>2</sub>	2	8.0	85	95
Er <sub>2</sub> Fe <sub>17</sub> N <sub>2</sub>	cone	4.3 (FOMP?)	84.5	88.5

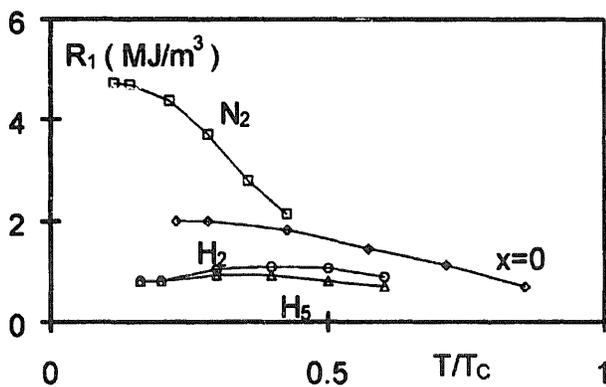


Fig. 2. The second order anisotropy constants of the easy plane materials ( $R_1$ ) versus reduced temperature for Ho<sub>2</sub>Fe<sub>17</sub> (rhombus), Ho<sub>2</sub>Fe<sub>17</sub>N<sub>2</sub> (squares), Ho<sub>2</sub>Fe<sub>17</sub>H<sub>2</sub> (circles) and Ho<sub>2</sub>Fe<sub>17</sub>H<sub>3</sub> (triangles).

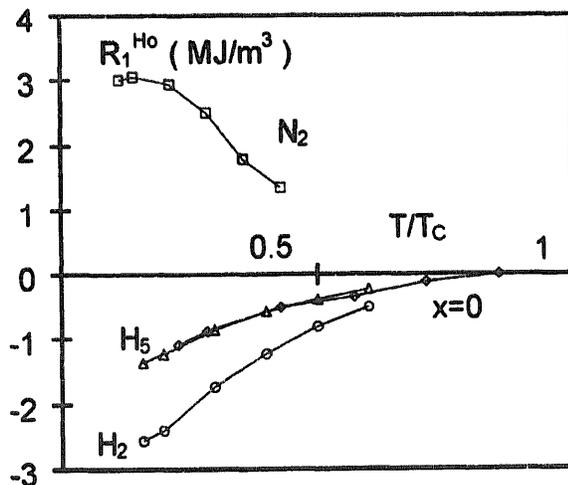


Fig. 3. The rare earth part of  $R_1$  versus reduced temperature for Ho<sub>2</sub>Fe<sub>17</sub> (rhombus), Ho<sub>2</sub>Fe<sub>17</sub>N<sub>2</sub> (squares), Ho<sub>2</sub>Fe<sub>17</sub>H<sub>2</sub> (circles) and Ho<sub>2</sub>Fe<sub>17</sub>H<sub>3</sub> (triangles).

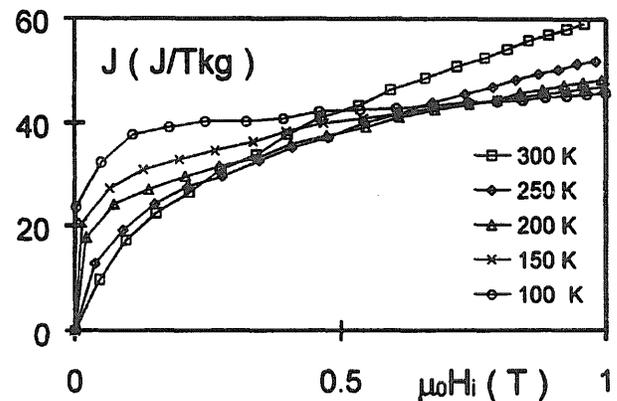


Fig. 4. The hard magnetization curves for Dy<sub>2</sub>Fe<sub>17</sub>H<sub>3</sub>. Imperfect texture is due to the low value of anisotropy at room temperature.

with  $x=3$  and 5, respectively. The hard magnetization curves for Dy<sub>2</sub>Fe<sub>17</sub>H<sub>3</sub> are plotted in Fig. 4. Unfortunately the low value of the anisotropy at room temperature does not allow to produce well aligned samples of these compounds.

#### 3.4. Tb<sub>2</sub>Fe<sub>17</sub>H<sub>x</sub>

Application of rotating and static magnetic fields does not lead to aligned samples for hydrides with  $x=3$  and 5. Two possible origins of this behaviour are: (i) an easy cone structure at the room temperature, (ii) a too high value of the anisotropy in the basal plane. Taking into account that there is a spin reorientation transitions in the Dy<sub>2</sub>Fe<sub>17</sub> hydrides at relatively high temperatures we consider the first cause as the more likely one.

#### 4. Discussion

The data obtained are summarized as follows:

1. The effects of H and N on the values of  $R_1$  are in agreement with the sign of the Stevens factor. In other words the MCA of elements with different signs of the Stevens factors are changed in different directions. From this fact we conclude that the effect can be explained in the framework of the single ion anisotropy theory and ascribed mainly to changes in values of the second order CF parameters.
2. The effects of hydrogen and the nitrogen on MCA are opposite and apparently the signs of the second order CF parameters in the hydrides and nitrides are opposite.
3. The effect on the rare earth part of  $R_1$  for hydrides is highest for concentration near 3 and is dropping in the direction of the highest concentration.

To discuss the difference in influence of the hydrogen and nitrogen on the second order CF parameters it is appropriate to separate 'the lattice contribution' from 'the valence electron contribution'. The first one is due to charges on the neighbouring sites and the second one is due to the valence electron (s, p and d) of the rare earth. If we consider 'the lattice contribution' in the framework of the point charge approximation the changes in the crystal field parameters may be ascribed to two principal factors. The first of these is the lattice expansion. From the general consideration in this case the anisotropy should be determined by the  $c/a$  ratio [13]. Comparing the data as to their behaviour of  $c$  and  $a$  axis parameters under nitrogenation [14] and hydrogenation [15] one may see that  $c/a$  ratio in both cases is insignificantly decreasing for concentrations below  $x=3$ . So this factor cannot adequately explain the behaviour of the anisotropy. The second factor is the direct effect of the interstitial ion on the crystal field parameters. Consideration of this effect can qualitatively explain the difference in MCA changes for  $R_2Fe_{17}$  and  $RFe_{11}Ti$  compounds under nitrogenation but calculated values of the second order CF parameters are nearly two orders higher than the experimental values [16]. If we believe that the nitrogen atoms and hydrogen atoms are both preferably located in the octahedral positions and that their ionic charges are both negative, then the point charge speculation must give the same sign for this part of the second order CF parameter. Therefore 'the lattice contribution' cannot explain the behaviour of the CF in  $R_2Fe_{17}$  under hydrogenation and nitrogenation and 'the valence electron contribution' must be considered. This conclusion is in agreement with the known facts that for metallic systems the CF part acting on the quadruple moments of

the nucleus [17] and the 4f orbital [18] mainly originates from the valence electrons contribution. The main result of this discussion is that the MCA change produced by the interstitial atoms is not determined by the value of their electronegativity. Probably their ability to change the shape of 6p and 5d shells must be considered.

Comparing  $RFe_{11}Ti$  and  $R_2Fe_{17}$  compounds we observe that hydrogenation of  $R_2Fe_{17}$  as well as nitrogenation of  $RFe_{11}T$  lead to a change in sign of the second order anisotropy constant for the rare earth sublattice. Therefore the direction of the changes in the rare earth anisotropy may not only be determined by the positions of the interstitial atoms with respect to the rare earth atom but also may depend on the type of interstitial atoms.

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