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Structural and magnetic properties of $Dy_2Fe_{17}H_x$ ($x = 0$ and 3) single crystals

I. Tereshina[a,b], S. Nikitin[a,c,*], W. Suski[b,d], J. Stepien-Damm[d], W. Iwasieczko[d], H. Drulis[d], K. Skokov[b,e]

[a] Baikov Institute of Metallurgy and Materials Science RAS, Leninski pr., 49, Moscow 119991, Russia
[b] International Laboratory for High Magnetic Fields and Low Temperatures, 95 Gajowicka Str., 53-421 Wroclaw, Poland
[c] Department of Physics, Lomonosov Moscow State University, 119992 Leninski Gory, Moscow, Russia
[d] Trzebiatowski Institute of Low Temperature and Structure Research, P.O. Box 1410, 50-950, Wroclaw 2, Poland
[e] Department of Physics, Tver State University, 170002, Zheljabova Str. 33, Tver, Russia

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Abstract

The effect of hydrogen on structural and magnetic properties of the $Dy_2Fe_{17}H_x$ single crystal was investigated. The host alloys symmetry is retained upon hydrogenation. It was found that the magnetic characteristics (such as the Curie temperature and magnetocrystalline anisotropy) are highly sensitive to the presence of hydrogen and exhibit dramatic changes with changing of H content. The results are discussed in terms of a model considering the interaction of the quadrupole and 4f electron magnetic moments of the rare-earth ion with the interstitial hydrogen atoms.
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1. Introduction

The iron-rich rare-earth intermetallic compounds R_2Fe_{17} have a large magnetic moment originating from the 3d-sublattice and magnetocrystalline anisotropy from the rare-earth sublattice. All compounds have easy plane magnetic anisotropy at room temperatures and rather low Curie temperature compared to that of metallic Fe [1,2]. As materials for permanent magnets, R_2Fe_{17} compounds have attracted considerable attention because of their ability to form interstitial solid solutions with nitrogen and carbon atoms, the anisotropy of which may be uniaxial and Curie temperature – rather high [3]. These compounds have been shown also to absorb a considerable amount of hydrogen, leading to stable hydrides [4].

To gain greater insight into the influence of interstitial hydrogen on structure and magnetic properties (in particular magnetocrystalline anisotropy (MCA)) of the R_2Fe_{17}, it is primarily necessary to obtain hydride single crystals of high quality. The intrinsic magnetic properties of the $R_2Fe_{17}H_x$ ($R = Y$, Gd, Tb, Ho and Er; $x = 0$; 3) single crystals have been previously investigated [5]. The purpose of the present work was to investigate structural and magnetic properties of $Dy_2Fe_{17}H_x$ single crystals.

2. Experimental details

Polycrystalline ingots of Dy_2Fe_{17} compounds were prepared by induction melting of appropriate amounts of the constituent metals having a purity better than 99.95 wt.%. The ingots were remelted in an electric resistance furnace with high temperature gradient and cooled slowly through the melting point in order to increase the grain size. The single crystals Dy_2Fe_{17} were extracted from the solidified ingots. Hydrogenation was performed in stainless steel autoclave under hydrogen gas pressures of 1 MPa at 150 °C

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* Corresponding author. Fax: +7 95 9328820.
E-mail address: nikitin@phys.msu.ru (S. Nikitin).

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and it led to stable hydrides. The hydrogen uptake was determined by volumetric method with an accuracy of 0.1 hydrogen atom per formula unit. The crystal structure of Dy_2Fe_{17} and its hydrides were investigated in a CrysAlis-Oxford Diffraction four-circle diffractometer equipped with CCD camera using graphite-monochromatized Mo $K\alpha_a$ radiation ($\lambda = 0.71073$ Å). The intensities of reflections were corrected for Lorentz and polarization effects. Analytical absorption correction was applied [6]. Magnetization measurements along the main crystallographic directions of the hexagonal structure were performed on $Dy_2Fe_{17}H_x$ ($x = 0$; 3) single crystals at high applied magnetic fields up to 140 kOe in the temperature range 4.2–300 K. The Curie temperatures were determined from thermomagnetic scans using a pendulum magnetometer in an applied magnetic field of 500 Oe.

3. Results and discussion

The crystal structure of Dy_2Fe_{17} and $Dy_2Fe_{17}H_x$ ($x = 0$; 3) was solved on 8017 ($R_{nt} = 0.081$) and 8970 ($R_{int} = 0.053$) reflections by Patterson method [7] and refined by the full matrix least squares method using SHELX-97 program [8] with discrepancy factors R1 = 0.0354, and R1 = 0.0339, respectively. Positional parameters of hydrogen atoms have not been refined. The same small deviations from 2:17 stoichiometry with iron excess have been observed in both, as cast and hydrogenated crystals. Both, $Dy_{1.85}Fe_{17.30}$ ($a = 8.460(1)$ Å, $c = 8.325(2)$ Å) and $Dy_{1.85}Fe_{17.34}H_3$ ($x = 0$; 3) ($a = 8.546(1)$ Å, $c = 8.343(2)$ Å) are isostructural with $Y_2Fe_{17.3}$ [9], disordered variant of hexagonal Th_2Ni_{17} type of structure (sp. gr. $P6_3/mmc$, $Z = 2$) [10]. The final atomic positional parameters and isotropic displacement coefficients are given in Table 1 (data for hydride – in italic). The arrangement Fe1 and Fe2 dumbbells as well as Fe41 and Fe42 splitting are similar to those in $Lu_{1.86}Fe_{17.46}$ crystal [11]. Hydrogenation of $Dy_{1.85}Fe_{17.34}$ sample causes a small changes of interatomic distances and the increasing of unit cell volume but does not introduce changes in the crystal structure. The list of selected average interatomic distances is given in Table 2.

In this work the effect of hydrogen on the Curie temperature, magnetization and magnetocrystalline anisotropy of Dy_2Fe_{17} single crystal was also investigated. The $T_C =$ 370 K for Dy_2Fe_{17} and an extremely high magnetic ordering temperature $T_C = 518$ K for $Dy_2Fe_{17}H_3$ trihydride have been observed. Fig. 1 shows the magnetization curves versus magnetic field measured on Dy_2Fe_{17} (top) and its hydride (bottom) at $T = 4.2$ K. The magnetic field is applied along [0 0 1], [1 0 0] and [1 2 0] crystalline axes. As appears from Fig. 1 the easy magnetization direction (EMD) for the Dy_2Fe_{17} single crystal is along the [1 0 0] axis within the basal plane of the hexagonal structure. The spontaneous magnetization measured at 4.2 K along such direction is 74 emu/g (Fig. 1a). The anisotropy field measured is larger than 140 kOe and larger than in the compounds with non-magnetic Y and Lu elements, indicating that the Dy sublattice is mainly responsible for the anisotropy in these compounds. Drastic changes in the magnetization are observed when the interstitial H atoms appear in the $Dy_2Fe_{17}H_3$ hydride crystal lattice. It probably reflects the complex cone magnetic structure presence in hydride phase (see Fig. 1b). The spontaneous magnetization remains practically unaffected for $Dy_2Fe_{17}H_3$ (74.7 emu/g at 4.2 K).

The hydrogenation of the Dy_2Fe_{17} compound causes also the change in the type of magnetic anisotropy, The magnetic anisotropy constant of the rare-earth sublattice K_{1Dy} changes

Table 1
Atomic coordinates and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for $Dy_{1.85}Fe_{17.30}$ and $Dy_{1.85}Fe_{17.34}H_3^*$

Atom	Site	Occupancy	X/a	Y/b	Z/c	U_{eq}
Dy1	2b	0.732(4)	0	0	1/4	11(1)
		0.734(3)				*10(1)*
Dy2	2c	0.132(5)	1/3	2/3	1/4	10(2)
		0145(3)				*9(1)*
Dy3	2d	1	1/3	2/3	3/4	8(1)
		1				*7(1)*
Fe1	4e	0.268(7)	0	0	0.3938(7)	12(2)
		0.275(5)			*0.3935(5)*	*4(2)*
Fe2	4f	0.882(9)	1/3	2 /3	0.1072(2)	9(1)
		0.887(7)			*0.1064(1)*	*8(1)*
Fe3	6g	1	1/2	0	0	9(1)
		1				*8(1)*
Fe41	12j	0.74	0.3324(3)	0.3748(2)	1/4	9(1)
		0.74	*0.3310(1)*	*0.3785(1)*		*11(1)*
Fe42	12j	0.26	0.2968(9)	0.3079(7)	1/4	16(1)
		0.26	*0.2857(5)*	*0.2883(6)*	1/4	*6(1)*
Fe5	12k	1	0.1663(1)	0.3326(1)	0.5136(1)	9(1)
		1	*0.1667(1)*	*0.3334(1)*	*0.5133(1)*	*8(1)*
H	6h					
			0.823(19)	*0.650(30)*	1/4	*98(9)*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

its sign due to the H atoms presence at octahedral positions. Using the theory of magnetocrystalline anisotropy of 3d–4f intermetallics [12,13], the crystal field parameters A_2^0 was calculated from $K_{1R}(T)$. The calculated A_2^0 values were of -25 and $56K/a_0^2$ for Dy_2Fe_{17} and $Dy_2Fe_{17}H_3$, respectively. It is seen that, upon hydrogenation, the crystal field parameter changes both the magnitude and the sign. The change of the second-order crystal-field A_2^0 term of the electrical potential acting on the 4f shell after hydrogenation can be understood by using a scheme of the quadrupolar and magnetic moment interactions of the 4f electron sphere with the interstitial hydrogen atoms as shown in [5,14] [see Fig. 3].

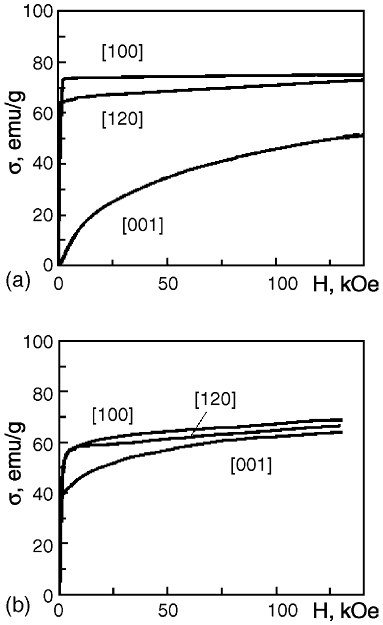

Fig. 1. (a) Field magnetization curves of Dy_2Fe_{17} and (b) $Dy_2Fe_{17}H_3$ hydride single crystals measured at $T = 4.2\,K$ in the magnetic field applied along [0 0 1], [1 0 0] and [1 2 0] directions.

Table 2
Selected interatomic distances (Å ^{2}) in $Dy_{1.85}Fe_{17.30}$ and $Dy_{1.85}Fe_{17.34}H_3^*$ (*in italic)

Dy1	Fe1	1.197(5)	*1.198(4)*
	Fe42	2.559(6)	*2.453(4)*
	Fe1	2.965(5)	*2.974(4)*
	Fe41	3.0075(16)	*3.0518(10)*
Dy2	Fe2	1.1884(17)	*1.9791(12)*
	Fe41	2.4648(18)	*2.4532(10)*
	Fe42	2.893(5)	*3.050(4)*
Dy3	Fe2	2.9741(18)	*2.9736(14)*
	Fe41	3.019(2)	*3.0795(9)*
	Fe42	3.027(6)	*3.082(4)*
Fe1	Fe1	1.768(11)	*1.776(8)*
	Fe1	2.395(11)	*2.395(8)*
	Fe5	2.5561(18)	*2.5871(14)*
	Fe5	2.633(2)	*2.6622(16*
	Fe42	2.825(6)	*2.729(4)*
Fe2	Fe2	2.377(3)	*2.396(2)*
	Fe3	2.6003(6)	*2.219(5)*
	Fe5	2.6460(10)	*2.6611(8)*
	Fe41	2.7363(17)	*2.7300(10)*
Fe3	Fe41	2.4418(10)	*2.4526(6)*
	Fe5	2.4474(5)	*2.4692(4)*
	Fe42	2.671(4)	2.769(3)
Fe41	Fe41	2.452(4)	*2.4233(16)*
	Fe42	2.483(5)	2.511(3)
	Fe5	2.5324(13)	*2.5308(8)*
	Fe5	2.6440(13)	26855(8)
Fe42	Fe5	2.401(3)	2360(2)
	Fe42	2.417(13)	2419(7)
	Fe5	2.511(3)	*2.5298(19)*
	Fe42	2.699(11)	2.486(8)
Fe5	Fe5	2.4474(8)	*2.4775(6)*

4. Conclusion

X-ray diffraction and bulk magnetic measurements were applied in order to elucidate the influence of hydrogen on the structural and magnetic properties of the ternary hydride $Dy_2Fe_{17}H_x$ ($x = 0$; 3). The hydrogenation results in the expansion of the crystal lattice and in the modification of the exchange and magnetocrystalline interactions. The expansion of crystal lattice is not isotropic. The hydrogenation increases the magnetic transition temperature and changes the type of MCA in the Dy_2Fe_{17} intermetallic compound.

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