

Magnetic moment, exchange interactions, and anisotropy of the Fe and Gd sublattices in $Y_2Fe_{14}BH_{3.4}$ and $Gd_2Fe_{14}BH_{3.4}$ hydrides

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An investigation was made of the influence of hydrogen on the magnetic properties and crystal structure of single crystals of intermetallic $R_2Fe_{14}BH_x$ compounds ($R = Y, Gd$) with the hydrogen concentration $x = 3.4$. The absorption of hydrogen was accompanied by an anisotropic expansion of the crystal lattice, a considerable change in the thermal expansion coefficient, an increase in the Curie temperature and the magnetic moment of the Fe sublattice, and a considerable weakening of the intersublattice Gd–Fe exchange interaction. Hydrogenation reduced considerably the uniaxial anisotropy of the Fe sublattice but had practically no effect on the planar anisotropy of the Gd sublattice, giving rise to a spin-orientation phase transition in $Gd_2Fe_{14}BH_{3.4}$ at temperatures 280–315 K.

INTRODUCTION

Absorption of hydrogen by intermetallic compounds of rare-earth metals (R) with 3d transition metals (T) can alter radically the crystal structure, as well as the magnetic and electrical properties of these compounds.^{1,2} Compounds with the general formula $R_2Fe_{14}B$, which are used as permanent magnets with record magnetic characteristics,³ readily absorb hydrogen at room temperature and low pressures forming $R_2Fe_{14}BH_x$ hydrides with compositions in the range $0 < x < 5$, which are stable at normal temperatures.^{4,5} Hydrogenation of these R–T intermetallics is accompanied by a considerable increase in the volume of an ingot, eventually breaking up the ingot and transforming it into a powder. Therefore, physical properties of hydrides of these compounds are usually investigated employing powder samples. Since both such R–T intermetallics and their hydrides are highly anisotropic magnetic materials, the results obtained for powders can only be approximate, which makes it difficult to interpret the changes in the magnetic moment, magnetocrystalline anisotropy, and other physical characteristics which occur as a result of hydrogenation. For example, it is reported in several papers that hydrogenation of the intermetallics $Y_2Fe_{14}B$ (Ref. 4) and $Gd_2Fe_{14}B$ (Refs. 6 and 7) alters the nature of the magnetocrystalline anisotropy from uniaxial to planar, although such a change was not found in other investigations.^{8,9} A comparison of the physical properties of $R_2Fe_{14}BH_x$ hydrides of different elements R has been made for samples with different hydrogen concentrations, which is incorrect because these properties depend strongly on the value of x .

We shall report the results of the first investigation of the crystal structure and magnetic properties of single crystals of $Y_2Fe_{14}BH_x$ and $Gd_2Fe_{14}BH_x$ hydrides with the same hydrogen concentration $x = 3.4$.

EXPERIMENTAL METHOD

We prepared $R_2Fe_{14}B$ alloys, where $R = Y$ or Gd (of 99.9, 99.99, and 99% purity for R, Fe, and B, respectively), by melting in an induction furnace filled with helium. We grew single crystals using a variant of the Bridgman method: ingots were remelted in a resistance furnace where a large temperature gradient was established. In this way it was possible to reach grain sizes amounting to several millimeters.

Large ingot grains were used to form single-crystal disks ≈ 2 mm in diameter and 1.5 mm high. The subgrain misorientation angle in the investigated single crystals was less than 3° . The concentration of secondary phases deduced from metallographic, x-ray diffraction, and thermomagnetic analyses was less than 3%.

Before hydrogenation we outgassed $R_2Fe_{14}B$ single crystals in an aluminum container where a vacuum of 0.1 Pa was established; this treatment took place at 470 K and it lasted 1 h. Hydrogenation took place at room temperature at a hydrogen pressure of 10^6 Pa for $Gd_2Fe_{14}B$ and 9×10^5 Pa for $Y_2Fe_{14}B$, which resulted in the formation of stable hydrides with hydrogen content $x = 3.4$. The hydrogen concentration was determined from the change in the mass of a sample and the error in x was ± 0.06 . The thermal expansion was investigated by x-ray diffraction in a diffractometer using chromium radiation; this was done in the temperature range 5–900 K (for the original compounds). Samples were in 0.1 Pa vacuum and under these conditions the hydrogen began to escape from the hydrides, so that single crystals of the hydrides were investigated at temperatures 5–340 K. The lattice parameter a was determined using the β -820 line (diffraction angle $2\theta = 160^\circ$), whereas the parameter c was deduced using the α -00.10 line ($2\theta = 140^\circ$); the error in these measurements was 0.01%.

The magnetic characteristics were determined with a vibrating-sample magnetometer in an electromagnet using static fields up to 20 kOe and pulsed fields up to 100 kOe. Since in these magnetometer measurements the sample was in a helium atmosphere, the release of hydrogen from the hydrides began at a higher temperature than in the study of the thermal expansion, so that the magnetic measurements on hydride single crystals could be carried out in the range 4.2–700 K. The error in the determination of the magnetization was 3% in static fields and 5% in pulsed fields. The magnetocrystalline anisotropy constants were determined by the Sucksmith–Thompson method¹⁰ using the magnetization curves recorded along the a and c axes.

CRYSTAL STRUCTURE

Intermetallic $R_2Fe_{14}B$ compounds have the tetragonal crystal structure of the $Nd_2Fe_{14}B$ type with the space group $P4_2/mnm$ characterized by two crystallographically inequi-

TABLE I. Crystal lattice parameters and magnetic characteristics of $Y_2Fe_{14}B$ and $Gd_2Fe_{14}B$ compounds and their hydrides.

compound	$T=300\text{ K}$		$T=4.2\text{ K}$				$T_c, \text{ K}$	$\xi, \text{ K}$
	$a, \text{ nm}$	$c, \text{ nm}$	μ_s, μ_B	μ_{Fe}, μ_B	$10^5 K_1, \text{ J/m}^3$	$10^5 K_2, \text{ J/m}^3$		
$Y_2Fe_{14}B$	0.87540	1.2040	29.46	2.10	7.8	0	575	—
$Y_2Fe_{14}BH_{3.4}$	0.88469	1.2142	31.6	2.26	0	0.15	614	—
$Gd_2Fe_{14}B$	0.87857	1.2072	17.56	2.25	5.4	0	664	1070
$Gd_2Fe_{14}BH_{3.4}$	0.88495	1.2207	18.74	2.34	-2.6	0.6	682	690

valent positions of the R ions, six Fe positions, and one B position.¹¹ Hydrogenation does not alter the type of the crystal lattice, but simply expands it anisotropically (the lattice parameters of the original compounds and hydrides are listed in Table I). Figure 1 shows the temperature dependence of the lattice parameters a and c of the compounds $Y_2Fe_{14}B$ and $Gd_2Fe_{14}B$, and of their hydrides with $x = 3.4$. Clearly, the absorption of hydrogen had practically no effect on the nature of the thermal expansion along the c axis (curves 1'-4'). Hydrogen had the greatest influence on $a(T)$: the thermal expansion coefficient of the basal plane was considerably greater for the hydrides than for the original compounds and, moreover, the hydrides did not exhibit the Invar anomaly typical of $R_2Fe_{14}B$ compounds and due to the very high exchange magnetostriction in combination with a relatively low Curie temperature. The temperature dependences of the ratio c/a of the original compounds and hydrides were qualitatively quite different: c/a increased with temperature for $x = 0$, but fell for $x = 3.4$.

The dependence $c(T)$ of $Gd_2Fe_{14}BH_{3.4}$ recorded at $T = 315\text{ K}$ had a kink (curve 4' in Fig. 1a). A spin-orientation phase transition took place in the hydride at this temperature (see below).

MAGNETIC MOMENT AND EXCHANGE INTERACTIONS

The spontaneous molecular magnetic moment μ_s and the Curie temperature T_c , deduced from the magnetization curves recorded along the easy axes of the investigated crystals at various temperatures, are listed in Table I. Clearly, the absorption of hydrogen was accompanied by an increase in μ_s and T_c . Since the atoms of yttrium do not have a magnetic moment, compounds with the formula $Y_2Fe_{14}BH_x$ and different values of x could be used to study the influence of hydrogen on the magnetic moment and on the exchange interactions in the iron sublattice. The results obtained demonstrated that introduction of hydrogen into the lattice of a $R_2Fe_{14}B$ compound increased the average magnetic moment μ_{Fe} of the iron atoms and enhanced the Fe-Fe exchange interaction. We assumed that the magnetic moment of gadolinium μ_{Gd} in $Gd_2Fe_{14}B$ and its hydride was $gJ = 7\mu_B$ at $T = 4.2\text{ K}$ (g is the Landé factor and J is the inner quantum number) and that the magnetic structure was collinear ferrimagnetic, and we calculated the average magnetic moments of the iron atoms in these compounds (Table I).

The energy of the intersublattice (Gd-Fe) exchange interaction in $R_2Fe_{14}B$ compounds was considerably less than the energy of the Fe-Fe interaction, as deduced from a comparison of the Curie temperatures of the compounds with $R = Gd$ and Y . Ignoring the weakest exchange interaction (R-R), we calculated the intersublattice exchange interaction parameter ξ using the temperature dependence of the magnetic moment of the rare-earth sublattice approximated by the Brillouin function¹²

$$\mu_R(T) = \mu_R(0) B_J \{ \xi \mu_{Fe}(T) / T \mu_{Fe}(0) \}, \quad (1)$$

where $\mu_R(0)$ and $\mu_{Fe}(0)$ are the magnetic moments of the R and Fe sublattices at $T = 0\text{ K}$ and $B_J\{x\}$ is the Brillouin function. The $\mu_{Gd}(T)$ dependence was obtained by subtracting $\mu_s(T)$ of the compounds with yttrium from $\mu_s(T)$ of the compounds with gadolinium containing the same amount of hydrogen. The values of ξ ensuring the best agreement between the experimental dependence $\mu_{Gd}(T)$ and that calculated in Eq. (1) are given in Table I. Clearly, absorption of hydrogen by the intermetallic $Gd_2Fe_{14}B$ reduced considerably the intersublattice exchange interaction.

MAGNETIC ANISOTROPY

The original compounds are highly anisotropic uniaxial magnetic materials throughout the temperature range of existence of the magnetically ordered state (anisotropy constants $K_1 > 0$ and $K_2 = 0$). The considerable uniaxial anisotropy of the iron sublattice, which is the reason for the use of

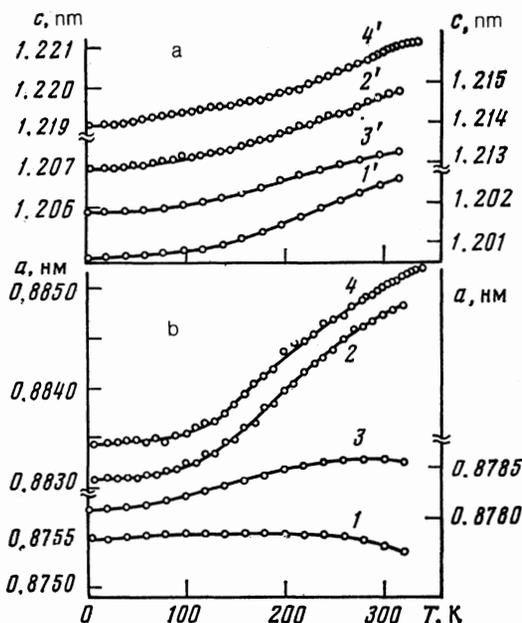


FIG. 1. Temperature dependences of the crystal lattice parameters c (a) and a (b) of the compounds $Y_2Fe_{14}BH_x$ with $x = 0$ (1, 1') and $x = 3.4$ (2, 2') and $Gd_2Fe_{14}BH_x$ with $x = 0$ (3, 3') and $x = 3.4$ (4, 4').

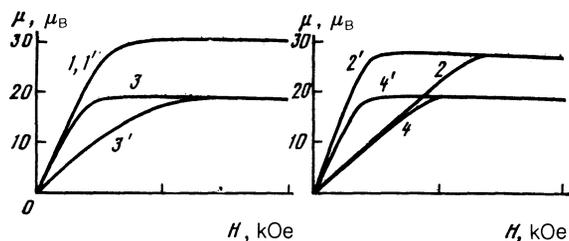


FIG. 2. Magnetization curves plotted along different crystallographic axes of $Y_2Fe_{14}BH_{3.4}$ single crystals at $T = 4.2$ K (curves 1 and 1' represent the parameters a and c) and $T = 400$ K (curves 2 and 2' represent the parameters a and c) and of $Gd_2Fe_{14}BH_{3.4}$ at $T = 4.2$ K (curves 3 and 3' represent the parameters a and c) and $T = 300$ K (curves 4 and 4' represent the parameters a and c). The scale divisions on the abscissa represent 10 and 20, respectively.

$R_2Fe_{14}B$ compounds in permanent magnets of high energy capacity, is associated with "unfreezing" of the orbital magnetic moment of the Fe ions.¹³ Figure 2 shows the magnetization curves of the hydride single crystals obtained at various temperatures. Clearly, these hydrides also exhibit a significant anisotropy, which is however less than for the original compounds.

The temperature dependences of K_1 obtained for $Y_2Fe_{14}B$ and $Gd_2Fe_{14}B$ and shown in Fig. 3 (they agree well with those obtained earlier in Ref. 14) are anomalous: the anisotropy constant K_1 increases with temperature up to $T = 0.55T_c$ and falls only above this temperature. The main contribution to K_1 comes from the Fe sublattice, as demonstrated by a comparison of K_1 for the compounds with $R = Y$ or Gd . We know that K_1 is less for the compound with Gd than for the nonmagnetic Y and, therefore, we can assume that the gadolinium ions make a negative contribution to K_1 . Since the orbital momentum of the Gd^{3+} ion is $L = 0$, so that there is no single-ion anisotropy because of the interaction of the orbital magnetic moment with the crystal field and the most probable mechanism which can account for the anisotropy of the Gd sublattice is the dipole-dipole interaction (of the Gd - Gd or Fd - Fe type).

Introduction of hydrogen significantly lowers the anisotropy of the Fe sublattice: in the case of the $Y_2Fe_{14}B$ hydride we have $K_1 = 0$ at temperatures in the range

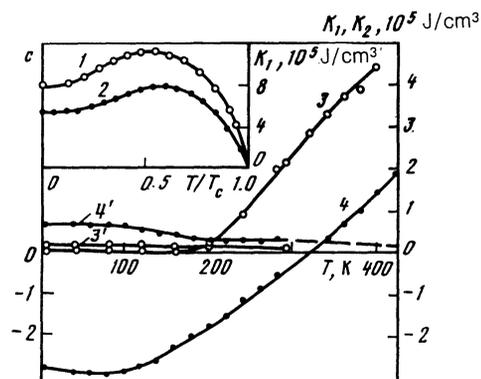


FIG. 3. Temperature dependences of the anisotropy constants K_1 and K_2 of the compounds $Y_2Fe_{14}B$ (curve 1 represents K_1), $Gd_2Fe_{14}B$ (curve 2 represents K_1), and their hydrides $Y_2Fe_{14}BH_{3.4}$ (curves 3 and 3' represent K_1 and K_2) and $Gd_2Fe_{14}BH_{3.4}$ (curves 4 and 4' represent K_1 and K_2).

$4.2 < t < 160$ K. This is followed by a rise of K_1 with temperature, i.e., the dependence $K_1(T)$ is anomalous for the hydride. The nonmonotonic dependence $K_1(T)$ obtained for the iron sublattice in the original $R_2Fe_{14}B$ compounds is explained in Ref. 15 allowing for the change in the ratio c/a with temperature:

$$K_1(T)/K_1(0) = [\mu_{Fe}(T)/\mu_{Fe}(0)]^2 [1 - \alpha(c/a)^2], \quad (2)$$

where α is a numerical coefficient, but our investigations of the thermal expansion showed that the temperature dependences of c/a in the original compound and the hydride are opposite and the region of rise of K_1 with T is observed in the dependences $K_1(T)$ obtained for both cases. Therefore, the explanation proposed in Ref. 15 is not self-consistent.

The anomalous behavior $K_1(T)$ of the iron sublattice can be due to two factors. Firstly, it may be due to different temperature dependence of the magnetic moment of the iron ions occupying crystallographically inequivalent positions and characterized by opposite signs of the local anisotropy constant K_{1Fe} . It follows from Mössbauer investigations of the temperature dependence of the hyperfine magnetic fields B_{hf} of the ^{57}Fe nuclei at the six crystallographically inequivalent positions of the iron ions in $R_2Fe_{14}B$ compounds¹⁶ that the strongest reduction in the B_{hf} with increasing temperature is observed at the $16k_2$, $4e$, and $4c$ positions, whereas at the $8j_2$, $16k_1$, and $8j_1$ positions the dependence $B_{hf}(T)$ exhibits a less steep fall. Therefore, if we assume $B_{hf} \propto \mu_{Fe}$ and that the anisotropy constant at a given position of the Fe ion is governed by the second-order crystal field parameters,¹⁵ i.e., if we assume $K_{1Fe} \propto \mu_{Fe}^3$ and that the constants K_{1Fe} have opposite signs at the inequivalent positions, we find that the temperature dependence of the combined anisotropy constant K_1 may be nonmonotonic. Secondly, allowance for the influence of the temperature dependence of the interatomic distances (noting that the temperature dependence of the parameter a has an Invar anomaly¹⁷ in the magnetically ordered range of temperatures of the original compounds) on the single-ion anisotropy constant of the Fe sublattice $K_1(T)$, i.e., allowance for the change in the crystal field parameters as a result of thermal expansion, can also give rise to an anomalous $K_1(T)$ dependence.

Hydrogenation of $R_2Fe_{14}B$ intermetallics results in the localization of the hydrogen at interstices (as deduced from neutron-diffraction investigations reported in Ref. 18) located mainly near the iron atoms at the $8j_2$ and $16k_2$ positions. The atoms of iron at the $8j_2$ positions had the largest orbital magnetic moment,¹³ i.e., they have the strongest anisotropy. Consequently, when $R_2Fe_{14}B$ is hydrogenated, the hydrogen influences the most anisotropic Fe ion at the $8j_2$ position and we should bear in mind that the temperature dependence of the magnetic moment at this position is different from that exhibited by the Fe ion at the $16k_2$ position. Therefore, vanishing of the combined anisotropy constant K_1 of the iron sublattice in the hydride of $Y_2Fe_{14}B$ observed at low temperatures may be a consequence of changes to contributions made by the competing Fe sublattices with different signs of the local K_{1Fe} constants.

The considerable change in the nature of the thermal expansion as a result of hydrogenation of $R_2Fe_{14}B$ should alter the $K_1(T)$ dependence in the hydrides compared with

the original compounds. Separation of the contributions responsible for the anomalous behavior of $K_1(T)$ [i.e., the competition between the anisotropy constants of the individual Fe sublattices and the influence of the thermal expansion on the $K_1(T)$ dependence] cannot be carried out on the basis of the reported results. Separation of these contributions requires, for example, investigating how the magnitude and the temperature dependence of the anisotropy constant of the 3d sublattice are affected by replacement of the iron ions with the cobalt ions, which occurs with unequal probabilities at the six different positions, and by making neutron-diffraction and Mössbauer studies of these intermetallics.

At low temperatures the anisotropy of the hydride $Gd_2Fe_{14}BH_{3.4}$ is of the easy-plane type. In the temperature range 280–315 K there is a cone of the easy axes which collapses above 315 K to form a single easy axis. No anisotropy has been found in the basal plane. Since the iron sublattice of the hydride with $x = 3.4$ does not exhibit a low-temperature anisotropy, the overall anisotropy of the hydride with $R = Gd$ with this concentration of hydrogen can be attributed to the Gd sublattice. Spin reorientation is a consequence of the competition between the planar anisotropy of Gd and the uniaxial contribution of the iron sublattice which appears above 160 K. The value of K_1 for the hydride $Gd_2Fe_{14}BH_{3.4}$, amounting to -0.26 MJ/m^3 , is practically equal to the difference between the anisotropy constants K_1 of the compounds $Gd_2Fe_{14}B$ and $Y_2Fe_{14}B$, which amounts to -0.24 MJ/m^3 , i.e., the absorbed hydrogen does not influence the anisotropy of the Gd sublattice, in contrast to the anisotropy of the Fe sublattice which is very sensitive to hydrogen.

The results of our investigation of the thermal expansion can be used to estimate the anisotropic magnetostriction constant of $Gd_2Fe_{14}BH_{3.4}$. The anomaly of $c(T)$ as a result of spin orientation can be used to find the reorientation constant $\lambda_2^{\alpha,2}$, which is less than 1×10^{-4} . In the planar anisotropy region there are no orthorhombic distortions of the crystal, which are governed by the magnetostriction constant $\lambda^{\gamma,2}$; therefore, the upper limit of $\lambda^{\gamma,2}$ can be estimated to be 5×10^{-5} (these magnetostriction constants are designated in accordance with Ref. 19).

CONCLUSIONS

1. Single crystals of hydrides of the compounds $R_2Fe_{14}B$, with $R = Y, Gd$, were obtained for the first time with the same hydrogen concentration, so that a proper comparison of the magnetic properties of the hydrides con-

taining nonmagnetic and magnetic R ions could be made.

2. The absorption of hydrogen increased anisotropically the dimensions of a crystal and altered strongly the thermal expansion coefficients in the basal plane. An increase in the ratio c/a with temperature, observed for the original compounds, changed to a reduction in the case of the hydrides.

3. The absorption of hydrogen enhanced the Fe–Fe exchange interaction, but it weakened considerably the inter-sublattice Gd–Fe exchange interaction.

4. The uniaxial anisotropy of the Fe sublattice was reduced greatly by hydrogenation whereas the planar anisotropy of the Gd sublattice was practically unaffected, which gave rise to a spin-orientation phase transition in the hydride $Gd_2Fe_{14}BH_{3.4}$.

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