

Effect of hydrogen on magnetic properties of $\text{Lu}_2\text{Fe}_{14}\text{B}$ single crystal

I.S. Tereshina^{a,b,*}, A.V. Andreev^c, H. Drulis^d, E.A. Tereshina^e

^a Baikov Institute of Metallurgy and Materials Science RAS, 119991 Moscow, Russia

^b International Laboratory of High Magnetic Fields and Low Temperatures, 95 Gajowicka Str., 53-421 Wrocław, Poland

^c Institute of Physics ASCR, 18221 Prague, Czech Republic

^d Polish Academy of Sciences, Trzebiatowski Institute of Low Temperature and Structure Research, P.O. Box 1410, 50-950 Wrocław 2, Poland

^e Faculty of Physics, Moscow State University, 119992 Moscow, Russia

Received 7 June 2004; received in revised form 25 February 2005; accepted 3 March 2005

Available online 11 July 2005

Abstract

Effect of hydrogen on the magnetic properties of $\text{Lu}_2\text{Fe}_{14}\text{B}$ is studied on single crystal samples of the compound and the hydride $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$. The Curie temperature T_C and the average Fe magnetic moment M_{Fe} increase upon hydrogenation whereas the first anisotropy constant K_1 decreases. In both the hydride and the parent compound, $K_1(T)$ exhibits a characteristic non-monotonous behavior.

© 2005 Elsevier B.V. All rights reserved.

Keywords: $\text{R}_2\text{Fe}_{14}\text{B}$; Hydrides; Ferromagnetism; Magnetic anisotropy

1. Introduction

Magnetic properties of iron-rich rare-earth containing intermetallics $\text{R}_2\text{Fe}_{14}\text{B}$ (R is a rare earth atom) have attracted much attention as the basic compounds of the best permanent-magnet materials [1,2]. Among other interesting properties, they are known to absorb some amounts of hydrogen and to form stable hydrides $\text{R}_2\text{Fe}_{14}\text{BH}_x$ with $x \leq 5$. The introduction of hydrogen into $\text{R}_2\text{Fe}_{14}\text{B}$ leads to an expansion of the tetragonal ($P4_2/mnm$ space group) crystal lattice without change of its symmetry. The increase of Fe–Fe distances and the additional electrons donated from hydrogen atom into conduction band modify the electronic structure and, therefore, the exchange and anisotropic interactions in these metallic systems. This results in changes of bulk magnetic characteristics of the compounds such as the Curie temperature T_C , the spontaneous magnetic moment M_s and the magnetic anisotropy energy E_a [1–8]. Contribution to the magnetism from the Fe sublattice is very important in $\text{R}_2\text{Fe}_{14}\text{B}$ because it is origin of the high T_C and M_s values. Particularly, the large uniaxial magnetic anisotropy of the Fe sublattice is the impor-

tant factor for their excellent permanent-magnet properties. The Fe sublattice magnetic contribution could be investigated on compounds with a non-magnetic $R = \text{La, Y, Th}$ and Lu [9].

Since the $\text{R}_2\text{Fe}_{14}\text{B}$ compounds exhibit a clear magnetic anisotropy, the single crystal samples are strongly desirable for the study. The magnetic properties of $\text{Lu}_2\text{Fe}_{14}\text{B}$ [1,2,9,10] and its hydride [11] have been previously investigated on polycrystalline samples. Until now no data on the preparation of $\text{Lu}_2\text{Fe}_{14}\text{B}$ single crystals and, moreover, of its hydride have been reported. The hydrogenation of intermetallic compounds leads usually to the crumbling of ingots into fine powders. This is due to the lattice expansion which exceeds the elastic limits of strains in these brittle materials [12]. Nevertheless, under certain conditions, it is possible to avoid the crumbling and to prepare and study the single crystals of some $\text{R}_2\text{Fe}_{14}\text{B}$ hydrides [6,7]. In this work we present the results of study of magnetization and magnetic anisotropy performed for the first time on single crystals of $\text{Lu}_2\text{Fe}_{14}\text{B}$ and its hydride $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$.

2. Experimental

To prepare the $\text{Lu}_2\text{Fe}_{14}\text{B}$ sample, a large (100 g) ingot of the alloy-precursor Fe_{14}B (Fe 99.9% purity, B 99.6%)

* Corresponding author. Tel.: +7 95 1359615; fax: +7 95 1354438.

E-mail address: teresh@ultra.imet.ac.ru (I.S. Tereshina).

was melted out in an induction furnace under a protective argon atmosphere. Then the stoichiometric mixture (7 g) of Lu (99.9%) and alloy-precursor was melted in a tri-arc furnace on a rotated water-cooled copper crucible under the argon atmosphere. The alloy button was turned several times and then kept in molten state for about 1 h in order to ensure a good homogeneity. The ingot was pulled out at 10 mm/h pulling speed by Czochralski method using a tungsten wire as a seed. The resulting product was found to be a polycrystal with a well-aligned structure rather than a single crystal. Single-crystalline grains of 1–2 mm size have been extracted from the ingot and used for the study. Conventional back Laue patterns were used to check the single-crystal state and to orient the samples.

To prepare the hydride, a portion of the ingot was exposed for 15 h to a hydrogen atmosphere under a pressure of 0.1 MPa at a temperature of 150 °C. The slow hydrogenation process allowed us to avoid the destruction of grains and to prepare single crystals of the hydrogen-containing compound $\text{Lu}_2\text{Fe}_{14}\text{BH}_x$. The content of the absorbed hydrogen $x = 2.5$ atoms per formula unit was estimated by a volumetric method. The phase purity and the lattice parameters of the initial compound and the hydride were determined by a standard X-ray powder diffraction analysis.

The magnetization measurements were performed in a temperature range of 4.2–300 K in magnetic fields of up to 140 kOe using a capacitance magnetometer. The T_C values were determined from the thermomagnetic scans in a 500 Oe field applied along the easy-magnetization axis. The magnetic anisotropy energy, determined from the magnetization curves along the hard- and the easy-magnetization directions, was also measured by using a torque magnetometer in the temperature range from 77 to 700 K in fields up to 16 kOe.

3. Results and discussion

The crystal lattice expansion caused by the hydrogenation of $\text{Lu}_2\text{Fe}_{14}\text{B}$ is found to be almost isotropic, i.e. the a and c lattice parameters increase by 0.65 and 0.70 Å, respectively; this corresponds to 2% volume expansion. The single-phase state observed for the initial compound also remains in the hydride. The lattice parameter values, both for the initial compound and the hydride, are in a very good agreement with those reported in [11]. The structural and magnetic characteristics of $\text{Lu}_2\text{Fe}_{14}\text{B}$ and $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$ are listed in Table 1.

Fig. 1 shows the high-temperature portion of the temperature dependence of the specific magnetization σ of both compounds. For the initial compound, the T_C value

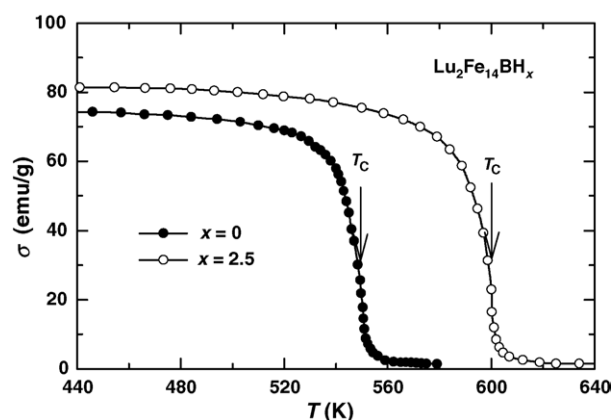


Fig. 1. High-temperature part of thermomagnetic scans of the $\text{Lu}_2\text{Fe}_{14}\text{B}$ and $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$ crystals along the easy magnetization axis in magnetic field of 500 Oe. The arrows indicate the Curie temperature T_C .

determined is slightly higher than that (535 K) given in [1]. It is seen that the hydrogenation leads to a substantial enhancement of the exchange interactions, since T_C of the hydride is higher than that of initial compound by $\Delta T_C = 53$ K (see Table 1). $\Delta T_C = 39$ K found in [11] is related to a lower hydrogen content ($x = 2.3$). The increase of T_C upon hydrogenation in Lu-containing compounds is larger than for Y-containing compounds (for example, ΔT_C for $\text{Y}_2\text{Fe}_{14}\text{BH}_{3.4}$ single crystal is 39 K [7], despite of the considerably lower hydrogen content in the case of Lu-containing compounds). On the other hand, even larger increase of T_C was observed in $\text{Th}_2\text{Fe}_{14}\text{BH}_4$ [8]. In this compound, the lattice parameters are larger than in the case of Lu but T_C of initial compound is considerably lower due to the tetravalent state of Th. However, in this viewpoint it is not clear what is the reason of very large increase of T_C in $\text{La}_2\text{Fe}_{14}\text{BH}_x$ [13].

Magnetization curves measured for $\text{Lu}_2\text{Fe}_{14}\text{BH}_x$ ($x = 0$; 2.5) at 4.2 K in the magnetic field applied parallel and perpendicular to the c -axis are shown in Fig. 2. Note, that the applied magnetic field was corrected for the demagnetizing factor; therefore the horizontal scale in Fig. 2 represents the internal field. It is seen that both compounds exhibit a uniaxial magnetic anisotropy, i.e. the c -axis is the easy-magnetization direction. The average Fe magnetic moment $M_{\text{Fe}} = 2.03\mu_B$ of $\text{Lu}_2\text{Fe}_{14}\text{B}$ determined from the c -axis magnetization curve agrees well with polycrystalline result [1] and is equal to that in many other high-Fe-content intermetallics. The hydrogen absorption causes a $\sim 6\%$ increase in the spontaneous magnetization σ_s and, consequently, in M_{Fe} (see Table 1). This is a general feature of hydrides of the R–Fe intermetallics, which is caused by the narrowing 3d band upon the volume expansion [2,3].

Table 1
Structural and magnetic properties of the $\text{Lu}_2\text{Fe}_{14}\text{BH}_x$ single crystals

x	a (Å)	c (Å)	c/a	V (Å ³)	T_C (K)	σ_s (4.2 K) (emu/g)	M_{Fe} (4.2 K) (μ_B)	K_1 (4.2 K) (Merg/cm ³)
0	8.710	11.878	1.364	901.1	549	139.2	2.03	9.4
2.5	8.766	11.962	1.365	919.2	602	147.5	2.16	6.7

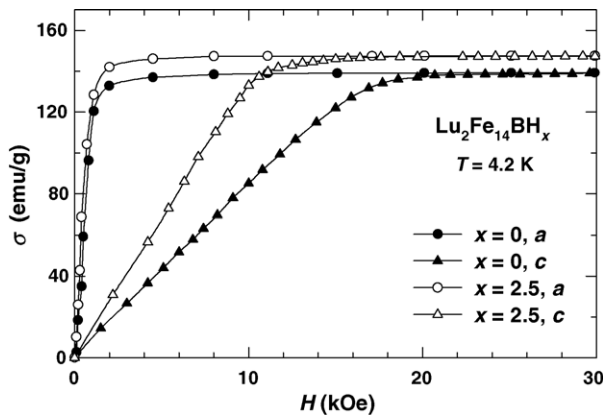


Fig. 2. Magnetization curves parallel and perpendicular to the c -axis of the $\text{Lu}_2\text{Fe}_{14}\text{B}$ and $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$ single crystals at 4.2 K.

The magnetic anisotropy energy $E_a = K_1 \sin^2 \Theta + K_2 \sin^4 \Theta$, where K_1 and K_2 are the first and the second anisotropy constants and Θ is the angle between the c -axis and the magnetization direction, was determined using the Sucksmith–Thompson method [14]. The linearity of the hard-direction magnetization curves (Fig. 2) indicates the negligible magnitude of K_2 the same as in $\text{Y}_2\text{Fe}_{14}\text{B}$ [15]. Indeed, if K_1 of $\text{Lu}_2\text{Fe}_{14}\text{B}$ reaches 9.4 Merg/cm^3 at 4.2 K, K_2 is only 1.1 Merg/cm^3 . The relation $K_1 \gg K_2$ is valid also for the hydride. The negligible magnitude of K_2 in comparison with K_1 is a common feature of the R–Fe intermetallics with a non-magnetic R. We will discuss below only K_1 . The magnetic anisotropy of $\text{Lu}_2\text{Fe}_{14}\text{B}$ has been studied on polycrystals using a singular-point detection method [16]. K_1 was estimated to be by 20% larger than that obtained in our study. In our opinion, the main reason of discrepancy is a difficulty to make a proper correction to demagnetization field, which in these compounds is comparable with the anisotropy field. The other reason could be the fact that we have taken into account the small, but non-zero K_2 .

Similar to other $\text{R}_2\text{Fe}_{14}\text{B}$, the hydrogenation of $\text{Lu}_2\text{Fe}_{14}\text{B}$ causes the considerable (30%) decrease in K_1 (see Table 1). Nevertheless, it does not lead to the virtually zero ($\text{R} = \text{Y}$) or even negative ($\text{R} = \text{Gd}$) K_1 value as it was observed for their hydrides with $x \geq 3$ [4,5,7]. (We remind that Gd is magnetic, however, it is isotropic ion and the anisotropy of $\text{Gd}_2\text{Fe}_{14}\text{BH}_x$ is also determined by the Fe sublattice.) The magnetization measurements were performed in our work only up to room temperature. In order to determine the $K_1(T)$ dependence up to T_C , we applied torque measurements. In the case when the applied field is lower than the anisotropy field, the magnetization vector does not coincide with field direction and a correction of the experimental torque curves is needed. The magnetic anisotropy constants were calculated from the corrected torque curves by determining successive harmonics using a least squares method [17]. Fig. 3 illustrates the angle dependence of torque $L(\Theta)$ for the $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$ disk within the a – c -plane. The analysis of these curves shows that in whole temperature range under study the easy magnetiza-

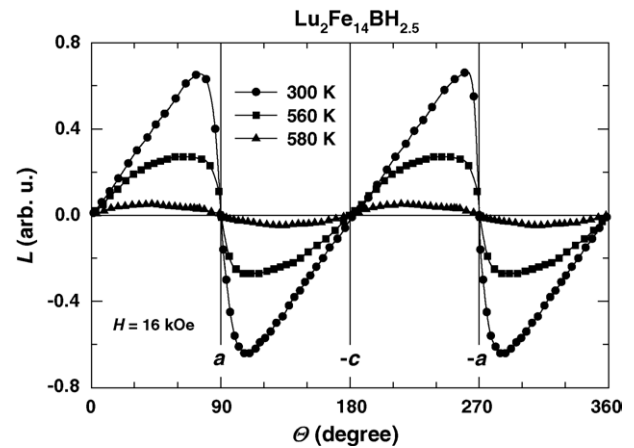


Fig. 3. The torque measured at several temperatures on a disk of $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$ (with the c -axis in the plane of the disk). Zero angle Θ corresponds to the c -axis.

tion direction coincides with the c -axis. The torque vanishes as the temperature approaches T_C .

The $K_1(T)$ dependence is represented in Fig. 4. For both compound and hydride the $K_1(T)$ curve exhibits a non-monotonous shape characteristic for $\text{R}_2\text{Fe}_{14}\text{B}$ with non-magnetic R or isotropic Gd [1,2]. This anomaly is well explained in terms of the individual site anisotropy model that is related to the complex crystal structure of these compounds. There are six Fe sublattices with different symmetry leading to different magnetic characteristics. In particular, the Fe atoms on different sites have different magnetic anisotropy, either negative or positive, and different temperature behavior. The absolute value of positive contributions is larger which determines the uniaxial anisotropy. The negative contributions decrease with temperature faster than the positive ones, which lead to the observed non-monotonous changes. It is worth to mention, that in $\text{Th}_2\text{Fe}_{14}\text{B}$ $K_1(T)$ is monotonous [8,18]. The hydrogen weakens the anisotropy

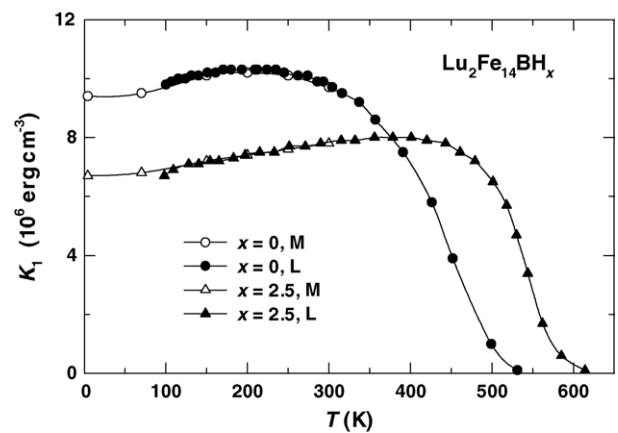


Fig. 4. Temperature dependence of the first anisotropy constant K_1 of $\text{Lu}_2\text{Fe}_{14}\text{B}$ and $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$ single crystals. In the legend: index M corresponds to the data from the magnetization curves, L from the torque measurements.

first of all of the Fe atoms with positive local anisotropy, which leads to the reduction of total anisotropy. This effect may result even in the change of the total anisotropy at low temperatures, i.e., lead to the easy-plane anisotropy type. Since at the elevated temperature the positive anisotropy dominates, a spin-reorientation may take place as was observed in $\text{Gd}_2\text{Fe}_{14}\text{BH}_{3.4}$ [7]. We think that this change of the anisotropy type can be also observed in $\text{Lu}_2\text{Fe}_{14}\text{BH}_x$ with x higher than 2.3–2.5 reached in [11] and in the present work. The efforts to prepare such hydrides are in progress.

4. Conclusion

Single crystals of $\text{Lu}_2\text{Fe}_{14}\text{B}$ and its hydride $\text{Lu}_2\text{Fe}_{14}\text{BH}_{2.5}$ have been prepared for the first time. Hydrogen absorption leads to a 2% volume expansion isotropically distributed over the principal axes. The Curie temperature and the average Fe magnetic moment increase upon hydrogenation whereas the first anisotropy constant decreases. In both the hydride and the parent compound, temperature dependence of the first anisotropy constant exhibits a characteristic non-monotonous behavior.

Acknowledgments

The authors thank I.V. Telegina for the control of the single crystals. The work has been supported by Department of Chemistry and materials science RAS program 8, grants RFBR 05-02-16361, and GACR 202/03/0550.

References

- [1] J.F. Herbst, Rev. Mod. Phys. 63 (1991) 819.
- [2] K.H.J. Buschow, Handbook of Magnetic Materials, vol. 10, Elsevier, Amsterdam, 1997, p. 463.
- [3] G. Wiesinger, G. Hilscher, Handbook of Magnetic Materials, vol. 6, Elsevier, Amsterdam, 1991, p. 511.
- [4] L.Y. Zhang, F. Pourarian, W.E. Wallace, J. Magn. Magn. Mater. 71 (1988) 203.
- [5] M.D. Kuz'min, L.M. Garcia, I. Plaza, J. Bartolome, D. Fruchart, K.H.J. Buschow, J. Magn. Magn. Mater. 146 (1995) 77.
- [6] A.V. Andreev, A.V. Deryagin, N.V. Kudrevatykh, N.V. Mushnikov, V.A. Reimer, S.V. Terent'ev, JETP 63 (1986) 608.
- [7] M.I. Bartashevich, A.V. Andreev, Physica B 162 (1990) 52.
- [8] A.V. Andreev, M.I. Bartashevich, J. Less-Common Met. 167 (1990) 107.
- [9] F. Bolzoni, J.P. Cavigan, D. Givord, H.S. Li, O. Moze, L. Pareti, J. Magn. Magn. Mater. 66 (1987) 158.
- [10] A.V. Andreev, M.I. Bartashevich, A.V. Deryagin, S.M. Zadvorkin, E.N. Tarasov, S.V. Terent'ev, Sov. Phys. Dokl. 30 (1985) 720.
- [11] P. L'Heritier, R. Fruchart, J. de Phys., 46 (1985) 319.
- [12] D. Fruchart, S. Miraglia, P. de Rando, P. Wolfers, J. Alloys Compd. 383 (2004) 17.
- [13] J. Bartolome, M.D. Kuz'min, Cz. Kapusta, P.C. Riedi, M. Ellouze, Ph. l'Heritier, Solid State Commun. 129 (2004) 331.
- [14] W. Sucksmith, J.E. Thompson, Proc. R. Soc. (London) 225 (1954) 362.
- [15] J.M.D. Coey, J. Magn. Magn. Mater. 80 (1989) 9.
- [16] R. Grössinger, X.K. Sun, R. Eibler, K.H.J. Buschow, H.R. Kirchmayer, J. Magn. Magn. Mater. 58 (1986) 55.
- [17] F. Ono, Y. Ohtsu, O. Yamada, J. Magn. Magn. Mater. 70 (1987) 319.
- [18] A.V. Andreev, M.I. Bartashevich, T. Goto, S.M. Zadvorkin, J. Alloys Compd. 262/263 (1997) 467.