

ノート

Er₂Fe₁₄Bとその水素化物の磁性

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Magnetic Properties of Er₂Fe₁₄B and Er₂Fe₁₄BH_x

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Abstract

The compound Er₂Fe₁₄B was hydrogenated to Er₂Fe₁₄BH_x up to x=2.2 under a hydrogen pressure of ~0.1atm. The average volume expansion per hydrogen atom was found to be 3.8Å³/H for the Er₂Fe₁₄BH_{1.0} and Er₂Fe₁₄BH_{1.8} compounds. The ¹⁶⁷Er NMR measurements were also done on Er₂Fe₁₄BH_{1.0} by means of spin echo method. The Er hyperfine fields at the f and g sites in the hydride slightly decrease when compared with those in Er₂Fe₁₄B. The electric quadrupole interaction parameters for Er at the f and g sites remain almost constant within the range of accepted uncertainties.

The intermetallic compounds R₂Fe₁₄B (R=rare earth) have the tetragonal structure with the space group P4₂/mmn shown in Fig. 1 (a). There are two inequivalent rare earth sites 4f and 4g and are six Fe sites.^{1, 2)} The wide variety of magnetic properties of R₂Fe₁₄B is mainly due to competition between rare earth and Fe sublattice anisotropies. The easy magnetization direction is characterized by sign of the second-order Stevens coefficient α_2 of R³⁺ ion. The magnetic moment tends to lie in the c-

plane for the ion with positive α_j and to be along the c-axis for the ion with negative α_j . Hydrogenation of $R_2Fe_{14}B$ is known to modify the physical properties of the original compound as well as binary rare earth intermetallics. The magnetic properties of hydrides, especially Fe magnetic moment and spin reorientation temperature, significantly differ from those of the parent compounds³⁾, while the crystal structure of $R_2Fe_{14}BH_x$ remains in the $Nd_2Fe_{14}B$ type structure for the hydrogen content up to $x \sim 5$.

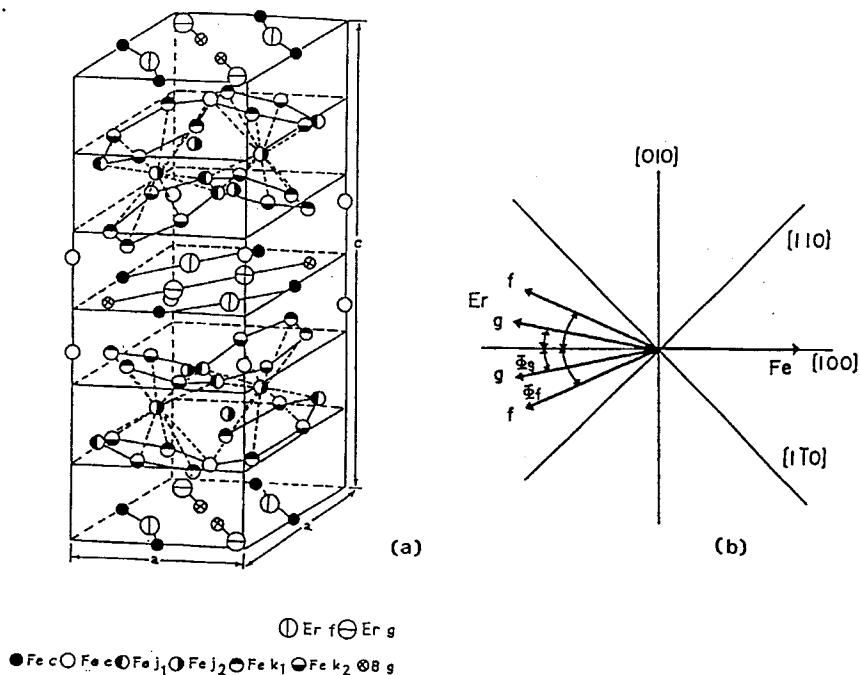


Fig. 1. (a) Crystal structure of $R_2Fe_{14}B$. Site notation is referred to ref. 2.
 (b) Schematic spin structure of $Er_2Fe_{14}B$ at 4.2K.

In $Er_2Fe_{14}B$, the canted magnetic structure in the c-plane which is shown in Fig. 1(b) has been found at low temperatures by the magnetization⁴⁾ and the neutron diffraction measurements.⁵⁾ Although the ^{166}Er Mössbauer effect measurements^{6, 7)} have already been done on $Er_2Fe_{14}B$, the Er hyperfine fields at the 4f and 4g sites have not been distinguished because of the large line width. We have done ^{167}Er NMR measurements on $Er_2Fe_{14}B$ and $Er_2Fe_{14}BH_{1.0}$ by spin echo method in order to clarify the magnetic properties of the compounds from a microscopic point of view. The results for $Er_2Fe_{14}B$ have partly been presented in ref. 8. In this note, we report the sample preparation and the preliminary results of the effect of hydrogen absorption on the lattice parameters and the Er hyperfine field of $Er_2Fe_{14}B$.

The ingot of $Er_2Fe_{14}B$ was prepared by argon arc melting appropriate constituents.

Purity of the raw material is 99.9% for Er, 99.95% for Fe and 99.5% for B. The as-cast ingot was annealed at 900°C for two weeks under a pressure of $\sim 3 \times 10^{-6}$ Torr. Then, some pieces were cut from the ingot for hydrogenation by a diamond cutter. One of them was crushed into powder for x-ray diffraction. X-ray diffraction measurements were done at room temperature with a graphite monochromated Cu-K_α radiation. The sample was confirmed to have a $\text{Nd}_2\text{Fe}_{14}\text{B}$ type structure. Three pieces were prepared for hydrogenation. In usual cases^{9, 10)}, the hydrogenation was done under high hydrogen pressure from 5 ~ 60 atm. In the present case, the hydrogenation was done under hydrogen pressure of ~ 0.1 atm. The hydrogenation procedure is as follows : The plateletlike specimen is placed in quartz cell of 3cm in diameter and 10cm in length. The cell is evacuated at 600°C for ~ 3 h and then is filled with hydrogen ~ 76 Torr at room temperature. In some cases, the heat treatment under high vacuum is done at various temperatures from 200 to 600°C . After vacuum heating, in order to increase the hydrogen absorption rate, hydrogen plasma is generated several times by discharging gas. The operating pressure is in the range from 0.2 to 0.7 Torr. The output power of the apparatus used is about 40W. After plasma discharge, the cell is again filled with hydrogen of ~ 86 Torr and is left for about 40 hours. As shown in Fig. 2 (a), the absorption rate clearly increases by plasma discharge. In Fig. 2 (b), the absorption rate K is plotted against the initial pressure of hydrogen which is the pressure of hydrogen introduced to the cell before product of the plasma discharge. The absorption rate has a peak around 0.3 Torr of hydrogen pressure. Therefore, for other specimens

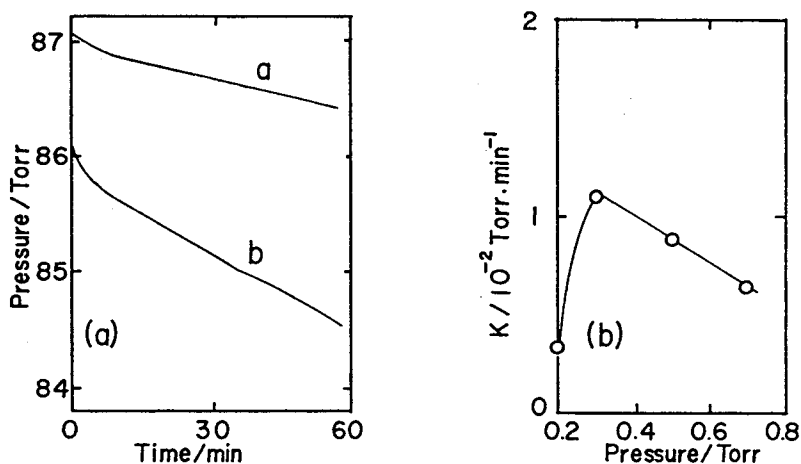


Fig. 2. (a) Hydrogen pressure vs. absorption time : a before plasma discharge and b after plasma discharge.
 (b) Absorption rate K vs. initial hydrogen pressure.
 The solid line is only for eye guide.

the plasma discharges were done under 0.3 Torr hydrogen pressure.

The relation of the absorption rate to the initial hydrogen pressure might depend on the output power of the apparatus. At least the plasma discharge was found to accelerate the absorption rate. The lattice parameters vs. hydrogen concentration x are shown in Fig. 3. The average volume expansion per hydrogen is $3.8 \text{ \AA}^3/\text{H}$ between $\text{Er}_2\text{Fe}_{14}\text{BH}_{1.0}$ and $\text{Er}_2\text{Fe}_{14}\text{BH}_{1.8}$ com-

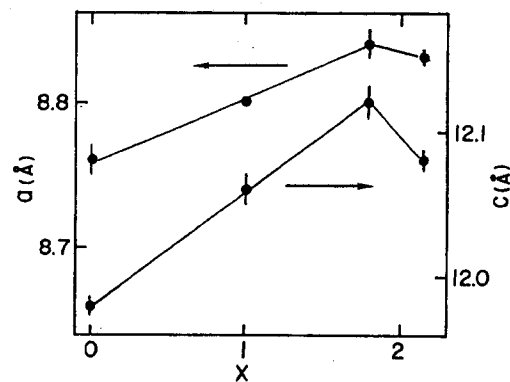


Fig. 3. Lattice parameters a and c vs. hydrogen concentration for $\text{Er}_2\text{Fe}_{14}\text{BH}_x$.

pounds. This value is rather large compared with most of the rare earth hydrides.¹¹⁾ For the $\text{Er}_2\text{Fe}_{14}\text{B}$ as starting material, the lattice parameters a and c are found to be large by an amount of $\sim 0.3\%$ compared to the published data^{9, 10)}. As shown in Fig. 3, both parameters a and c increase linearly with hydrogen concentration up to $x=1.8$. However, the relative increases $\Delta a/a$ and $\Delta c/c$ decrease at $x=2.2$. This anomalous behavior around $x=2$ is inconsistent to the results already reported. The lattice parameters a and c have been found to increase monotonically with^{9, 10)} hydrogen concentration up to $x\sim 5$. In $\text{Er}_2\text{Fe}_{14}\text{B}$, spin reorientation associated to the transition of the easy magnetization between the c -axis and the basal plane occurs at $\sim 323\text{K}$. Then, the lattice parameters might change at the reorientation temperature T_{sr} by the magnetostriction. On hydrogenation the spin reorientation temperature has been found to increase by $\sim 30\text{K}$ ^{9, 10)}. In our case, since x-ray diffraction has been done at lower temperature than T_{sr} , the anomaly of the lattice parameters behavior vs. hydrogen concentration can not be ascribed to the change in the spin reorientation temperature. As seen in the NMR spectrum in Fig. 4, there exist some impurity phases in the $\text{Er}_2\text{Fe}_{14}\text{BH}_{1.0}$, although we are uncertain whether or not such degradation is associated with the hydrogen absorption. The powder x-ray diffraction pattern of $\text{Er}_2\text{Fe}_{14}\text{B}$ is rather complex and consists of reflections with low intensities. Therefore it is difficult to detect the presence of impurity phase. Thus, the lattice parameter anomaly shown in Fig. 3 might be due to mis-indexing because of superposition of the reflections from the impurity phases. At present we do not draw a conclusion for the origin of the anomaly. In Fig. 4, ¹⁶⁷Er NMR spectra for $\text{Er}_2\text{Fe}_{14}\text{B}$ and $\text{Er}_2\text{Fe}_{14}\text{BH}_{1.0}$ are shown for the Zeeman line and the adjacent lines split by electric quadrupole interaction. The extra lines observed in the frequency range from 910 to 950MHz are probably due to impurity phas-

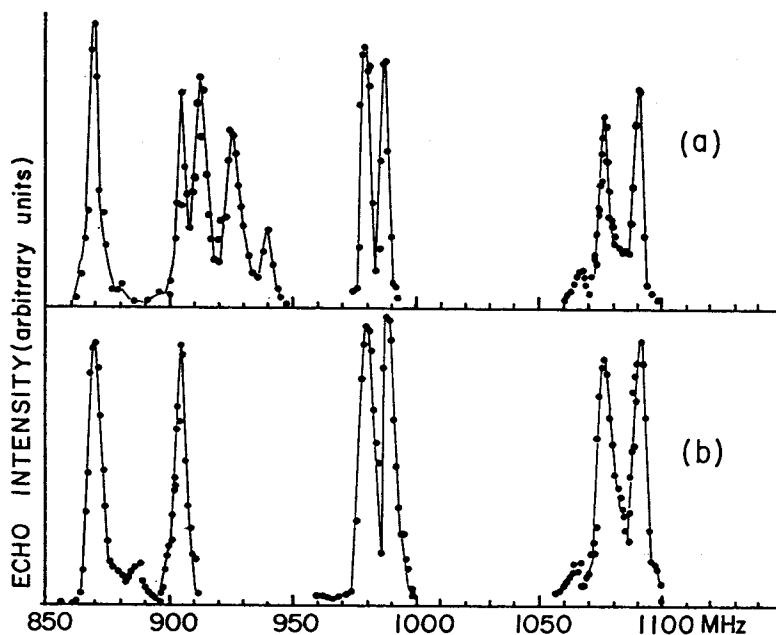


Fig. 4. ^{167}Er NMR spectra taken at 4.2K corresponding to the $-1/2 \leftrightarrow 1/2$ and the adjacent transitions for (a) $\text{Er}_2\text{Fe}_{14}\text{BH}_{1.0}$ and (b) $\text{Er}_2\text{Fe}_{14}\text{B}$.

Table I. Hyperfine field (kOe) and electric quadrupole interaction parameter 2P (MHz) for f and g sites. The values of 2P for Dy and Er compounds correspond to those for ^{161}Dy and ^{167}Er nuclei, respectively.

compound	Hhf		2P		ref.
	f	g	f	g	
$\text{Dy}_2\text{Fe}_{14}\text{B}$	6283 ± 15	6164 ± 15	356 ± 6	360 ± 6	12)
$\text{Dy}_2\text{Fe}_{14}\text{BH}_{3.3}$	6219 ± 15	6097 ± 15	392 ± 6	406 ± 6	
$\text{Er}_2\text{Fe}_{14}\text{B}$	8042 ± 8	7977 ± 8	89 ± 4	111 ± 2	present
$\text{Er}_2\text{Fe}_{14}\text{BH}_{1.0}$	8030 ± 8	7969 ± 8	86 ± 4	111 ± 2	work
$\text{Er}_2\text{Fe}_{14}\text{B}$	8121 ± 50		102 ± 4		6)
$\text{Er}_2\text{Fe}_{14}\text{BH}_{2.6}$	7863 ± 50		106 ± 4		

es which are not yet identified. The magnetic hyperfine field H_{hf} and the electric quadrupole interaction parameter P are shown in Table I. The hyperfine field for the hydride seems to decrease as compared with that of original compound, which is consistent, but a lesser extent, to the Mössbauer results of $\text{Dy}_2\text{Fe}_{14}\text{BH}_{3.3}$ ¹²⁾ and $\text{Er}_2\text{Fe}_{14}\text{BH}_{2.6}$ ⁶⁾. The hyperfine field at Er consists of the intra-ionic contribution

arising from 4f electrons of the parent ion and the extra-ionic contributions: The main contribution among the extra-ionic ones is the transferred hyperfine field from Fe magnetic moment. Since the average Fe moment has been found to increase by a few percent on hydriding¹³⁾, the difference in H_{hf} between the hydride and the original compound may be ascribed to the change in the transferred hyperfine field. The electric quadrupole interaction P of the hydride is almost the same as that of original compound within the uncertainties. In ^{166}Er Mössbauer results⁶⁾ for $\text{Er}_2\text{Fe}_{14}\text{BH}_{2.6}$ and $\text{Er}_2\text{Fe}_{14}\text{B}$, the magnitude of the quadrupole interaction remains almost constant within uncertainties, while that of ^{161}Dy in $\text{Dy}_2\text{Fe}_{14}\text{BH}_x$ ^{12, 14)} increases with hydrogen concentration. The electric field gradient at Er arising from the lattice would be disordered by hydrogen absorption. Then the width of the NMR line split by electric quadrupole interaction is expected to become broad. As shown in Fig. 4, however, the NMR lines seem to be almost the same as those of the original compound. This constancy of the electric quadrupole interaction might be related to the hydrogen localization in $\text{Er}_2\text{Fe}_{14}\text{B}$.

As for the dependence of the hyperfine interaction at Er in $\text{Er}_2\text{Fe}_{14}\text{B}$ on hydrogen absorption, the study on the compound with higher hydrogen concentration is necessary and is in progress.

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