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Magnetic properties of $(Y_{1-x}Th_x)_2Fe_{14}B$

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Abstract

The concentration and temperature dependencies of magnetic anisotropy in the quasiternary $(Y_{1-x}Th_x)_2Fe_{14}B$ system have been studied on aligned powders. With increasing Th content, the enhancement of the uniaxial anisotropy at low temperatures (K_1 at 4.2 K increases from 0.8 MJ m^{-3} for $x=0$ to 1.5 MJ m^{-3} for $x=1$) and the change in $K_1(T)$ behaviour from anomalous characteristic for $Y_2Fe_{14}B$ to the monotonous decrease with increasing temperature have been found. © 1997 Elsevier Science S.A.

Keywords: Hard magnetic materials; Rare-earth intermetallics; Magnetic anisotropy; Thermal expansion

1. Introduction

$Th_2Fe_{14}B$ is the only actinide analogue of rare-earth (R) compounds with the tetragonal crystal structure of the $Nd_2Fe_{14}B$ type. The structure has two non-equivalent positions for R atoms, six for Fe and one for B. In $R_2Fe_{14}B$, the Fe sublattice has strong uniaxial magnetic anisotropy, which is one of the main physical reasons for the perfect permanent-magnet properties of this group of magnetic materials (see for review [1]). Concentration dependence of the average Fe magnetic moment μ_{Fe} and the Curie temperature T_C have been studied in solid solutions $(Y_{1-x}Th_x)_2Fe_{14}B$ [2]. Both the Y and Th atoms do not carry a magnetic moment, but Y is trivalent and Th is tetravalent. Both, the considerable reduction of T_C and the small reduction of μ_{Fe} in observed $Th_2Fe_{14}B$ in comparison to $Y_2Fe_{14}B$ are attributed to additional filling of the Fe 3d band in the Th compound. The magnetic anisotropy energy of $Y_2Fe_{14}B$ (described completely by the first anisotropy constant K_1) has anomalous non-monotonous temperature dependence. In contrast to that, the $K_1(T)$ dependence is monotonous in $Th_2Fe_{14}B$. In the present work, the concentration and temperature dependencies of the magnetic anisotropy in the quasiternary $(Y_{1-x}Th_x)_2Fe_{14}B$ system have been studied systematically.

2. Experimental

The alloys were prepared by arc melting the appropriate amounts of the components under helium protective atmosphere with further annealing for a week at 1100°C. The magnetization curves were measured on aligned powders parallel and perpendicular to the axis of alignment in pulsed magnetic fields up to 10 T in the temperature range 4.2–320 K. The anisotropy field was determined by the single-point-

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detection method from hard-direction magnetization curves. Thermal expansion was studied by X-ray dilatometry.

3. Results and discussion

Figure 1 shows magnetization curves measured parallel and perpendicular to the axis of alignment for $Th_2Fe_{14}B$. An imperfect alignment, which is indicated by a non-linearity of the hard-direction curve and by a relatively high (~ 3 T) saturation field in the easy-magnetization direction, is due to the relatively low anisotropy of the compounds and a small amount (2–3%) of an isotropic impurity phase based on α-Fe. Nevertheless, the alignment is strong enough to determine the spontaneous magnetization M_s properly (from the easy-magnetization direction curve) and the anisotropy field B_a (from the hard-magnetization direction curve). B_a determined as a point of minimum of d^2M/dB^2 is shown in Fig. 1 by the arrow. For other compounds studied, the magnetization curves are qualitatively similar.

Figure 2 shows the temperature dependence of the first anisotropy constant $K_1 = (M_s B_a)/2$. A gradual development from anomalous to normal $K_1(T)$ behaviour with increasing Th content is seen in Fig. 2. For the compounds with $x \leq 0.4$, an anomalous growth characteristic for $Y_2Fe_{14}B$ is observed.

The anomalous temperature dependence of K_1 of the Fe sublattice in $R_2Fe_{14}B$ (with a trivalent R ion) is considered to originate from the different temperature dependence of the magnetic moments of the Fe atoms located on crystallographically non-equivalent

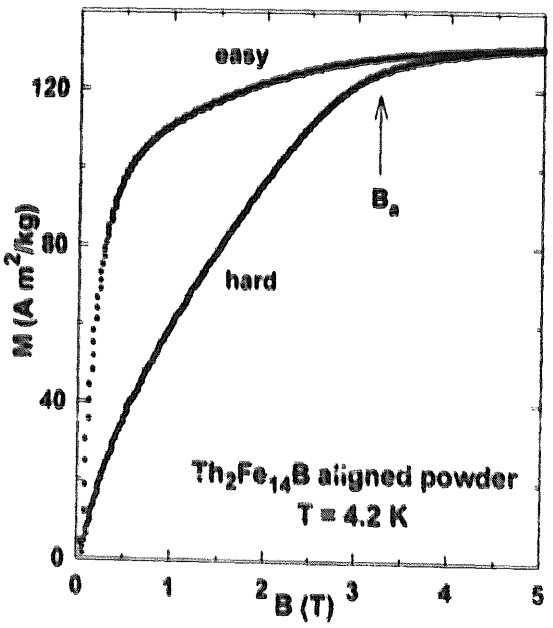

Fig. 1. Magnetization curves of aligned powder of $Th_2Fe_{14}B$ parallel and perpendicular to the axis of alignment at 4.2 K.

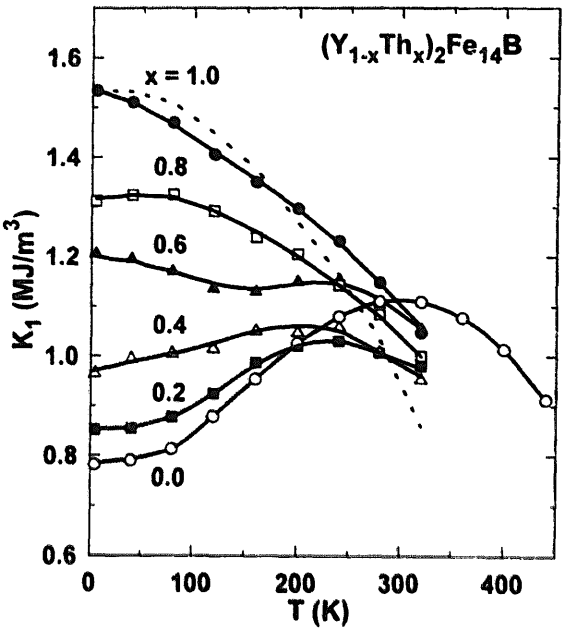

Fig. 2. Temperature dependence of the first anisotropy constant K_1 of $(Y_{1-x}Th_x)_2Fe_{14}B$. The dashed line represents third power of magnetization for $x = 1.0$ matched at 4.2 K. The data for $x = 0$ are taken from the single-crystal measurements [3].

positions. They have different signs of the local anisotropy constant. According to the Mössbauer-effect investigations of the hyperfine magnetic fields H_{hf} on ^{57}Fe nuclei in different non-equivalent positions in $R_2Fe_{14}B$ [4], the most gently sloping $H_{hf}(T)$ dependence is observed for the positions $8j_1$, $8j_2$ and $16k_1$, while in the other positions, 4e, 4c and $16k_2$, the values of $H_{hf}(T)$ (and, consequently, of the Fe magnetic moment M_{Fe}) decrease more steeply with increasing temperature.

According to the single-ion model, the local second-order anisotropy constant K_1^i (for ith position) is proportional at low temperatures to M_{Fe}^3. Therefore, the observed non-monotonous temperature dependence of the total constant

$$K_1 = \sum_{i=1}^{6} K_1^i \qquad (1)$$

can be explained assuming negative K_1^i for Fe atoms located on positions with steep temperature decrease of M_{Fe}. It should be noted, that using the $K_1(T) \propto M_s^3(T)$ relation for macroscopic values of K_1 and M_s leads to confusion. For $Th_2Fe_{14}B$, the fit $K_1(T) \propto M_s^3(T)$ is shown in Fig. 2 (matched at 4.2 K). $K_1(T)$ scales rather poorly with the third power of $\mu_{Fe}(T)$. In the remaining compounds, it does not scale at all, since the temperature dependence of spontaneous magnetization is monotonous for all compounds. Therefore $K_1(T)$ cannot be described using the tem-

perature dependence of the average Fe magnetic moment. The consideration of several Fe sublattices is a principal point in the explanation of the observed anomaly.

The enhancement of the uniaxial anisotropy at low temperatures as well as the change of the temperature dependence in the $(Y_{1-x}Th_x)_2Fe_{14}B$ system with increasing Th content can be explained by the influence of the effective valence of the R ion on the magnetocrystalline anisotropy of the Fe sublattice. Assuming the point charge model, K_1^i depends on the effective charge of R ligands around ith Fe atom [5]:

$$K_1^i \propto A_{20}^i = Z_R \lambda_R^i + Z_{Fe} \lambda_{Fe}^i \quad (2)$$

where A_{20}^i is the second-order crystal field parameter, Z_R and Z_{Fe} are the effective charges of the R and Fe ions, λ_R^i and λ_{Fe}^i are the lattice sums. The effective charges of the ions are usually assumed to be $Z_R = 3|e|$ for the trivalent R, $Z_R = 4|e|$ for the tetravalent R and $Z_{Fe} \approx 0.5|e|$ [5]. Since the lattice sums λ_R^i and λ_{Fe}^i are comparable [6], the change of the valence from 3 + (Y) to 4 + (Th) should result in a large change in K_1^i.

Concentration dependencies of magnetization and magnetic anisotropy are presented in Fig. 3. Although the spontaneous specific magnetization M_s at 4.2 K exhibits a strong decrease with increasing Th content, the corresponding increase in μ_{Fe} is very small. K_1 at

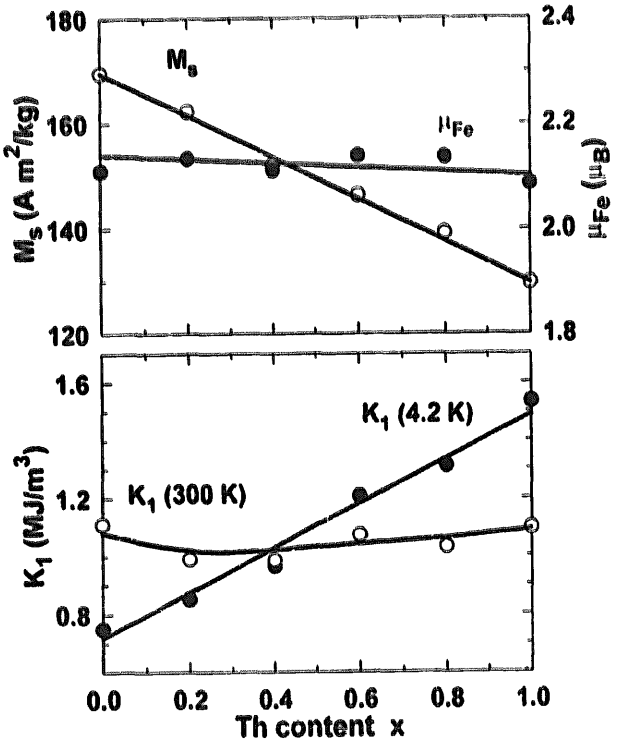

Fig. 3. Concentration dependences of spontaneous specific magnetization M_s, average spontaneous magnetic moment per Fe atom μ_{Fe} (top) and first anisotropy constant K_1 at 4.2 and 300 K (bottom).

4.2 K increases practically linearly with increasing Th content. Different temperature dependence leads to almost the same K_1 values (1 MJ m^{-3}) for all the compounds at room temperature. The Curie temperature decreases with x somewhat non-linearly from 572 to 487 K.

Besides the anomaly in magnetic anisotropy discussed above, there is another specific feature of the $R_2Fe_{14}B$ compounds. They have Invar-type thermal expansion behaviour below T_C due to very large spontaneous magnetostriction, and the volume effects ω_s reaches 2% at low temperatures [7]. This Invar effect was considered as the origin of the non-monotonous $K_1(T)$ behaviour [8]. We have found, however, that there is no principal difference in thermal expansion between compounds with 'normal' and 'anomalous' $K_1(T)$ dependence in the $Y_2(Fe_{1-x}Co_x)_{14}B$ system [9]. Thermal expansion of $Y_2Fe_{14}B$ and $Th_2Fe_{14}B$ measured on small single crystals is shown in Fig. 4. The lines represent the extrapolation of paramagnetic behaviour onto the ordered range (the Debye temperature value $T_D = 450$ K was used for the extrapolation). The related differences between measured and extrapolated values of lattice parameters correspond to the linear λ_a (in the basal plane) and λ_c (along the c axis) spontaneous magnetostrictions. Both terminal compounds have rather similar thermal expansion. At 5 K, they have nearly the same $\lambda_a = 9 \times 10^{-3}$. The difference is in the λ_c values (2.5×10^{-3} and 5×10^{-3} in $Y_2Fe_{14}B$ and $Th_2Fe_{14}B$, respectively). However, this difference could not influence magnetic anisotropy, as follows from data on $(Y_{0.8}Th_{0.2})_2Fe_{14}B$ (Fig. 4). This compound has already λ_c as in $Th_2Fe_{14}B$, but still has non-monotonous $K_1(T)$ (Fig. 2). The volume effect $\omega_s = 2\lambda_a + \lambda_c$ increases slightly from 20×10^{-3} to 23.5×10^{-3} with increasing Th content. This shows no correlation between the huge Invar effect in $R_2Fe_{14}B$ and the anomalous behaviour of magnetic anisotropy of the Fe sublattice.

We can also mention in this respect that the difference in lattice parameters between $La_2Fe_{14}B$ and $Lu_2Fe_{14}B$ is 1.4% (a) and 4.1% (c) [10]. The c/a ratio differs by 2.7%. However, these large variations do not affect the character of the $K_1(T)$ curve. For both compounds, $K_1(T)$ is non-monotonous and very similar in both cases. The influence of the thermal expansion on the interatomic distances is much weaker, all changes in a, c and c/a do not exceed 0.5% below T_C. The point-charge-model calculation shows that the change in K_1 in $Y_2Fe_{14}B$ owing to the thermal expansion would be less than 1% in the temperature interval 0–0.5 T_C where non-monotonous behaviour of K_1 is observed [5]. Extrapolation of the high-temperature $K_1(T)$ curve to 0 K gives a much larger difference (approx. 40%) with respect to

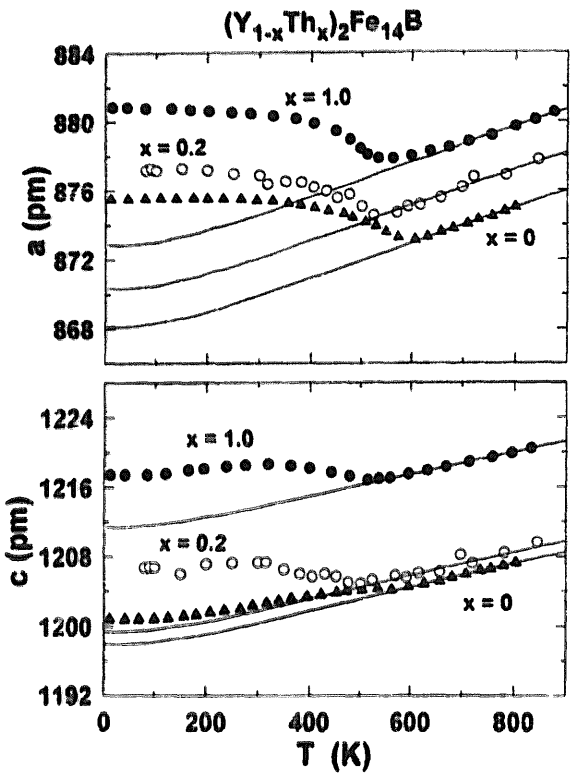

Fig. 4. Temperature dependences of the lattice parameters a and c for some of the $(Y_{1-x}Th_x)_2Fe_{14}B$ compounds. The lines are the extrapolations from the paramagnetic to the ordered range.

the actual K_1(4.2 K) value, which cannot be explained by a possible influence of the thermal expansion.

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