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Temperature dependence of the magneto-crystalline anisotropy in R_2Fe_{17} (R=Y, Gd, Tb, Dy, Er)

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Abstract

We measured the temperature dependence of the magneto-crystalline anisotropy constants K_1 and K_2 in R_2Fe_{17}, where R=Gd, Tb, Dy, Er and Y. Relatively large single crystals were grown by the Bridgman method under 1.2 atm argon atmosphere. The starting materials were polycrystalline alloys prepared in an arc-melting furnace. The anisotropy constants K_1 and K_2 were derived by a Sucksmith and Thompson analysis from the magnetization curves of each single crystal which were measured from room temperature to 4.2 K. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Bridgman method; Magneto-crystalline anisotropy; R_2Fe_{17}; Sucksmith and Thompson analysis

1. Introduction

Intermetallic compounds in the rare-earth–iron system are RFe_2, RFe_3, R_6Fe_{23} and R_2Fe_{17}. Each phase shows characteristic magnetic properties. R_2Fe_{17} is the most Fe-rich (89.5 at% Fe) compound among R_mFe_n phases. Several R_2Fe_{17} compounds are not simply ferro- or ferrimagnetic but have a non-collinear magnetic structure [1]. The Fe moments in this system are almost as large as those in iron metal, while the Curie temperature (the magnetic ordering temperature) is rather low compared with other R_mFe_n and R_2Co_{17} compounds. The R_2Fe_{17} intermetallics show large spontaneous volume magnetostriction which causes a negative thermal expansion anomaly [2,3]. Most R_2Fe_{17} compounds have easy plane magnetic anisotropy.

Of the materials for permanent magnets, R_2Fe_{17} compounds have attracted considerable attention because of their ability to form interstitial solid solutions with C and N atoms, the anisotropies of which may be uniaxial [4,5].

All these interesting magnetic properties of the intermetallics are believed to be related to competition between the positive and negative interaction associated with the substitutional pairs of iron atoms having a higher degree of localization character than cobalt or nickel [6]. The large magneto-crystalline anisotropy makes it necessary to perform magnetization measurements on single crystals in order to be able to extract the 3d–4f interaction in a proper way from the experimental results [7]. Therefore, a systematic investigation of the R_2Fe_{17} system has been undertaken on the basis of measurements on large single crystalline specimens.

In the present paper, the structural and magnetic parameters and temperature dependencies of the magneto-crystalline anisotropy constants K_1 and K_2 obtained for some R_2Fe_{17} single crystals are reported.

2. Single crystal preparation

Polycrystalline alloy ingots were prepared by argon arc-melting from starting materials of 99.9% purity with 10–15 wt.% excess of rare earth. The Bridgman method was used to grow relatively large single crystals from the alloy grains made by crushing the ingots. A recrystallized alumina crucible having a conical bottom was filled with the grains to about 15 g and heated in an rf induction furnace. Electric power was supplied to the furnace by an rf generator of 4 kW at 350 kHz frequency. The inside of the crucible was glazed with boron nitride to prevent interaction with the crucible, and the crucible was surrounded by a tantalum tube to improve the temperature uniformity. A crucible dropping rate varying from 5 to 7 mm h^{-1} was used under an argon atmosphere of 1.2 atm.

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As an example, the as-grown ingot of Gd_2Fe_{17} was about 30 mm in length and 10 mm in diameter and two-thirds of the ingot (underpart) was a single crystal.

3. Characterization

It was confirmed using a Laue back-scattering technique that the lower part of the as-grown ingot was a single crystal. The lattice constants *a* and *c*, and the density were determined by X-ray diffraction analysis. The powder specimens were oriented and fixed with resin in a magnetic field of 0.9 T. The direction of easy magnetization of each crystal was determined by the X-ray diffraction pattern for the oriented powder specimens. Magnetization measurements were performed in a vibrating sample magnetometer capable of up to 1.7 T in the temperature range from 4.2 K to the Curie temperature. For magnetization experiments a sphere with a diameter of 2–3 mm was taken from each single crystalline batch, which was oriented with the applied field along the principal crystallographic directions. The Curie temperatures were determined from the curves of the square of the magnetization versus temperature using the Arrott plot technique. The magneto-crystalline anisotropy constants K_1 and K_2 were derived from a Sucksmith and Thompson analysis of the magnetization data in fields up to 1.7 T. The temperature dependencies of K_1 and K_2 were obtained in the range from room temperature to 4.2 K.

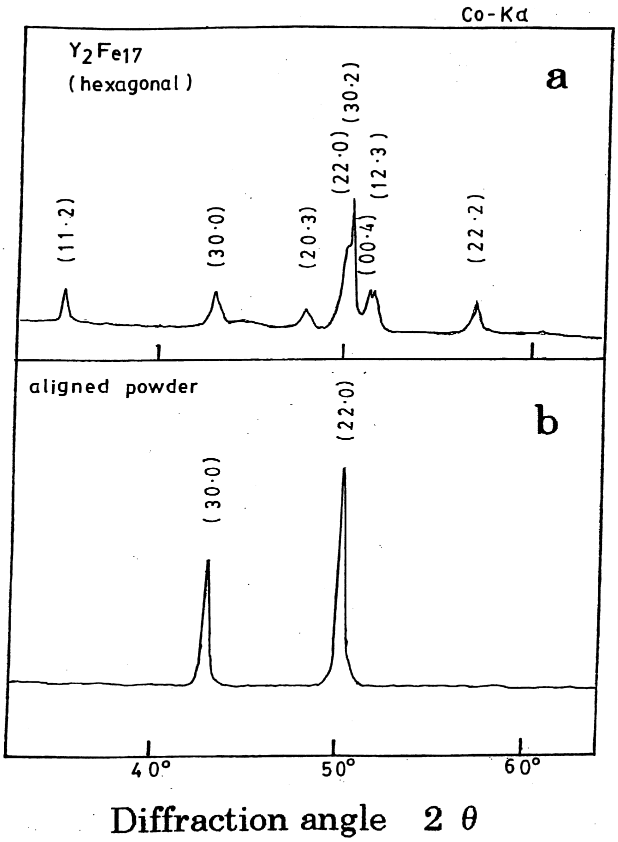

Fig. 1. X-ray diffraction pattern traces: (a) for the randomly oriented powder specimen of hexagonal Y_2Fe_{17} (Th_2Ni_{17}-type); (b) for the oriented powder specimen's surface perpendicular to the magnetizing field.

4. Results and discussion

4.1. Structural features

4.1.1. Y_2Fe_{17}

The grown single crystal of Y_2Fe_{17} was homogenized at 1100°C for 5 h in a pure argon atmosphere, and cooled to room temperature at a rate of $1°C\,min^{-1}$. It was found using a Laue back-scattering technique that the Y_2Fe_{17} single crystal had the preferred crystal growth direction parallel to the [00·1] axis (*c*-axis). The X-ray diffraction powder pattern of the Y_2Fe_{17} single crystal is shown in Fig. 1a. All the diffraction pattern peaks can be indexed as the Th_2Ni_{17}-type structure (hexagonal) with a=844.4 pm and c=825.2 pm. Fig. 1b shows the X-ray diffraction pattern of magnetically aligned Y_2Fe_{17} powder bonded with resin, the strong $(h\,k \cdot 0)$ reflection of which reveals that the easy magnetization direction of the crystal lies in the basal *c*-plane.

4.1.2. Gd_2Fe_{17}

The single crystal of Gd_2Fe_{17} was confirmed by means of X-ray diffraction analysis to have Th_2Zn_{17}-type structure (rhombohedral). It was found that Gd_2Fe_{17} showed growth perpendicular to the *c*-axis. The lattice constants of the crystal are a=856.9 pm and c=1252.2 pm. The X-ray diffraction pattern recorded for a powder specimen of Gd_2Fe_{17} is shown in Fig. 2a. Fig. 2b is a powder diffraction pattern recorded for the magnetically aligned powder specimen's surface perpendicular to the magnetizing field. These data show that the Gd_2Fe_{17} single crystal has the easy magnetization in the *c*-plane owing to the same reason described above.

4.1.3. Tb_2Fe_{17}

It was confirmed by means of X-ray diffraction analysis that the as-grown Tb_2Fe_{17} single crystal has Th_2Ni_{17}-type structure. It was found that the single crystal had its preferred crystal growth direction parallel to the *c*-axis. All the diffraction peaks which appeared in an ordinary X-ray powder diffraction pattern can be indexed as hexagonal with a=849.0 pm and c=835.7 pm. The X-ray diffraction data of the magnetically aligned powder specimen suggest that the single crystal has the easy magnetization in the *c*-plane because all the diffraction peaks are diffracted by crystal planes such as (11·0), (30·0) and (22·0) which are perpendicular to the basal *c*-plane.

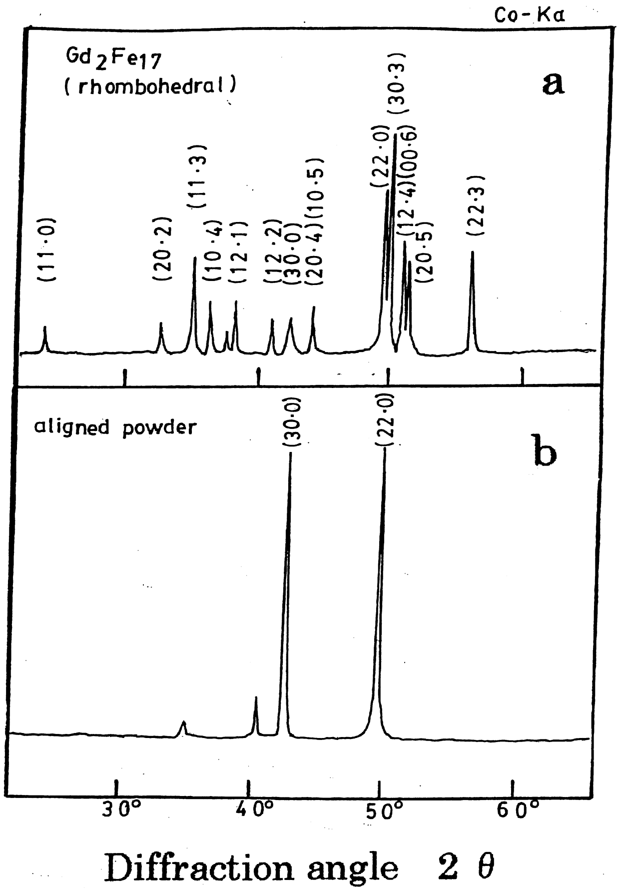

Fig. 2. X-ray diffraction pattern traces: (a) for the randomly oriented powder specimen of rhombohedral Gd_2Fe_{17} (Th_2Zn_{17}-type); (b) for the oriented powder specimen's surface perpendicular to the magnetizing field.

4.1.4. Dy_2Fe_{17}

The as-grown Dy_2Fe_{17} single crystal was confirmed by means of X-ray diffraction analysis to have the Th_2Ni_{17}-type structure. The preferred crystal growth direction of this single crystal is parallel to the *c*-axis. All the diffraction peaks in the conventional powder diffraction pattern can be indexed as hexagonal with $a=848.3$ pm and $c=833.6$ pm. The diffraction pattern of a magnetically aligned powder specimen suggests that the Dy_2Fe_{17} single crystal has the easy magnetization within the *c*-plane, because all the diffraction planes appeared, such as (30·0) and (22·0), which are perpendicular to the basal *c*-plane.

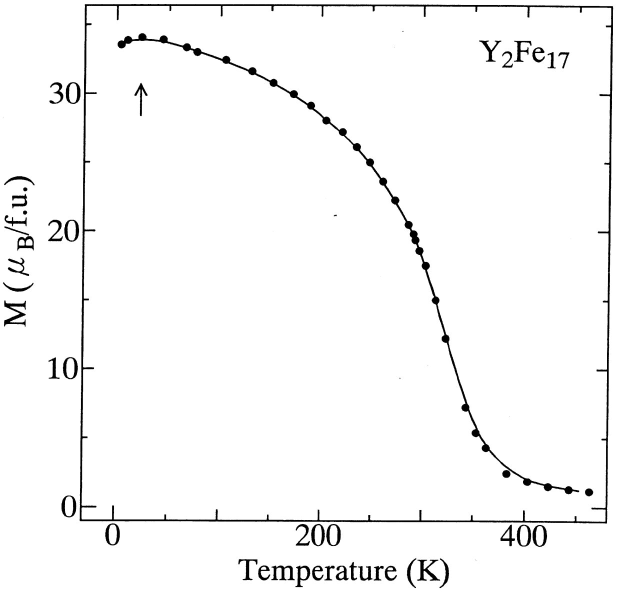

Fig. 3. Temperature dependence of M_s for the Y_2Fe_{17} single crystal.

4.1.5. Er_2Fe_{17}

The as-grown single crystal of Er_2Fe_{17} was found by means of X-ray diffraction analysis to have the Th_2Ni_{17}-type structure. All the diffraction peaks in the ordinary X-ray powder diffraction pattern can be indexed as hexagonal with $a=843.4$ pm and $c=829.8$ pm. The diffraction pattern recorded for the magnetically aligned powder specimen suggests that the easy magnetization of Er_2Fe_{17} lies in the basal *c*-plane, since all the diffraction peaks are perpendicular to the basal *c*-plane.

In summary, R_2Fe_{17}, with R=Y, Tb, Dy and Er, were found to have the hexagonal Th_2Ni_{17}-type structure, but Gd_2Fe_{17} crystallized in the rhombohedral Th_2Zn_{17}-type structure. Table 1 summarizes the cell parameter values of single crystalline R_2Fe_{17}. The directions of preferential crystal growth are also shown.

Table 1
Crystallographic data for R_2Fe_{17} single crystals

	Y_2Fe_{17}	Gd_2Fe_{17}	Tb_2Fe_{17}	Dy_2Fe_{17}	Er_2Fe_{17}
Treatment	Annealed	As-grown	As-grown	As-grown	As-grown
Crystal structure	Hexagonal	Rhombohedral	Hexagonal	Hexagonal	Hexagonal
Direction of crystal growth	∥ *c*-axis	⊥ *c*-axis	∥ *c*-axis	∥ *c*-axis	Not clear
a (pm)	844.4	856.9	849.0	848.3	843.4
c (pm)	825.2	1252.2	835.7	833.6	829.8
V (nm^3)	0.5095	0.7963	0.5218	0.5195	0.5112
ρ ($\times 10^3$ kg m^{-3})	7.35	7.91	8.07	8.15	8.35

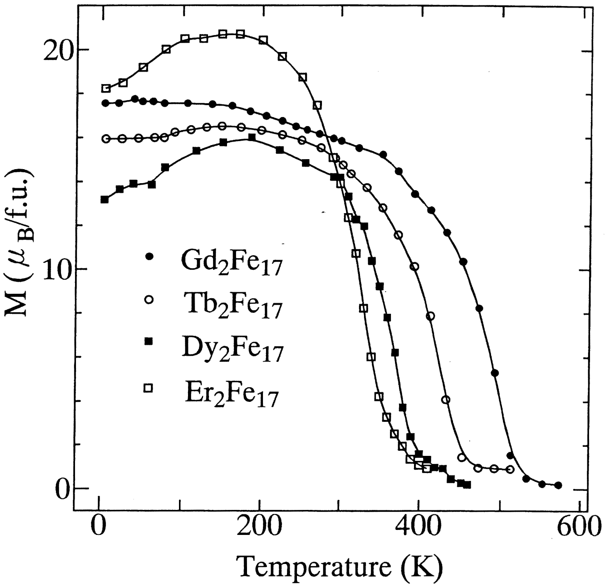

Fig. 4. Temperature dependencies of M_s for Gd_2Fe_{17}, Tb_2Fe_{17}, Dy_2Fe_{17} and Er_2Fe_{17} single crystals.

4.2. Magnetic properties

Fig. 3 shows the temperature dependence of M_s for a Y_2Fe_{17} single crystal. This curve shows a slight peak in the vicinity of 25 K. R_2Fe_{17} compounds with a heavy rare earth tend to form a peak in the curve of the temperature dependence of M_s because of their ferri-magnetic behavior. Y_2Fe_{17} is ferro-magnetic since yttrium is nonmagnetic. Therefore, this peak in Y_2Fe_{17} may be due to spin reorientation. For the mechanism, we propose the following two possibilities: one is the competition between the anisotropy of different Fe sites similar to the case of YCo_4B [8]; the other is the competition between local anisotropies originating from the local crystal environment. That is, if there was a small excess of yttrium in Y_2Fe_{17}, it should be replaced by the dumbbell Fe sites in the crystal structure. Such a replacement results in a change of the crystal environment locally and induces remarkable changes in magnetic behavior. Such an anisotropy change was indeed observed for Gd_2Co_{17} [9]. The temperature dependencies of M_s for Gd_2Fe_{17}, Tb_2Fe_{17}, Dy_2Fe_{17} and Er_2Fe_{17} are shown in Fig. 4. Their Curie temperatures were determined by the Arrott plot technique on the M_s–T curves. The values of T_C are little different from previously reported data. The differences among authors may originate from the slight deviations of their specimens from stoichiometry. The saturation magnetization at a constant temperature was accurately determined by the isothermal magnetization measurements. However, the external field of 1.7 T may not have been sufficient to saturate the magnetization of single crystalline Tb_2Fe_{17} [10]. The spontaneous magnetic moment σ_s of single crystalline Y_2Fe_{17} amounts to 33.5 μ_B/f.u. (166.0 A m^2 kg^{-1}). Since yttrium is nonmagnetic, the iron sublattice magnetic moment per formula unit M_{Fe} corresponds to 33.5 μ_B/f.u. Therefore, an average iron moment μ_{Fe} of 1.97 μ_B is deduced. The spontaneous magnetic moments of single crystalline Gd_2Fe_{17}, Tb_2Fe_{17}, Dy_2Fe_{17} and Er_2Fe_{17} amount to 17.6, 16.0, 13.2 and 18.2 μ_B/f.u., respectively. Each iron sublattice magnetic moment per formula unit M_{Fe} was calculated by taking the trivalent ion values of 7.63, 9.33, 10.3 and 9.0 μ_B for the gadolinium, terbium, dysprosium and erbium magnetic moments [11]. The average iron moments μ_{Fe} are listed in Table 2. We also obtained the anisotropy field H_a of the phases, except Dy_2Fe_{17}, from the isothermal magnetization measurements at 4.2 K. It is defined as the extrapolated field which is necessary to saturate the magnetization in the hard direction and is related to the anisotropy constants and the saturation magnetization M_s as

$$\mu_0 H_a = -(2K_1/M_s)(1 + 2K_2/K_1) \text{ for an easy } c\text{-plane.}$$

The calculated values of the anisotropy field $\mu_0 H_a$ are 5.01, 7.01, 15.8, 4.65 and 9.20 T for single crystalline Y_2Fe_{17}, Gd_2Fe_{17}, Tb_2Fe_{17}, Dy_2Fe_{17} and Er_2Fe_{17}, respectively. Fig. 5 shows the temperature dependencies of the magneto-crystalline constants K_1 and K_2 for R_2Fe_{17} single crystals. The values of K_1 and K_2 for Y_2Fe_{17} at 4.2 K are

Table 2
Magnetic parameters for R_2Fe_{17} single crystals

	Y_2Fe_{17}	Gd_2Fe_{17}	Tb_2Fe_{17}	Dy_2Fe_{17}	Er_2Fe_{17}
Easy axis	In c-plane	In c-plane	In c-plane	In c-plane	In c-plane
T_C (K)	341	506	440	383	344
M_s (μ_B/f.u.) 4.2 K	33.5	17.6	16.0	13.2	18.2
M_s (μ_B/f.u.) room temp.	18.2	15.9	14.8	13.8	13.9
μ_{Fe} (μ_B)	1.97	1.95	2.09	2.01	2.20
K_1 (K/f.u.) 4.2 K	−66.2	−78.7	−708	−138	−386
K_2 (K/f.u.) 4.2 K	5.3	18.0	313	58.8	165
K_1 (K/f.u.) room temp.	−11.9	−21.1	−9.3	−23.3	−7.7
K_2 (K/f.u.) room temp.	2.9	0.75	−5.9	3.2	2.8
$\mu_0 H_a$ (T) 4.2 K	5.14	7.68	17.3		9.82
$\mu_0 H_{a\ calc.}$ (T) 4.2 K	5.01	7.01	15.8	4.65	9.20

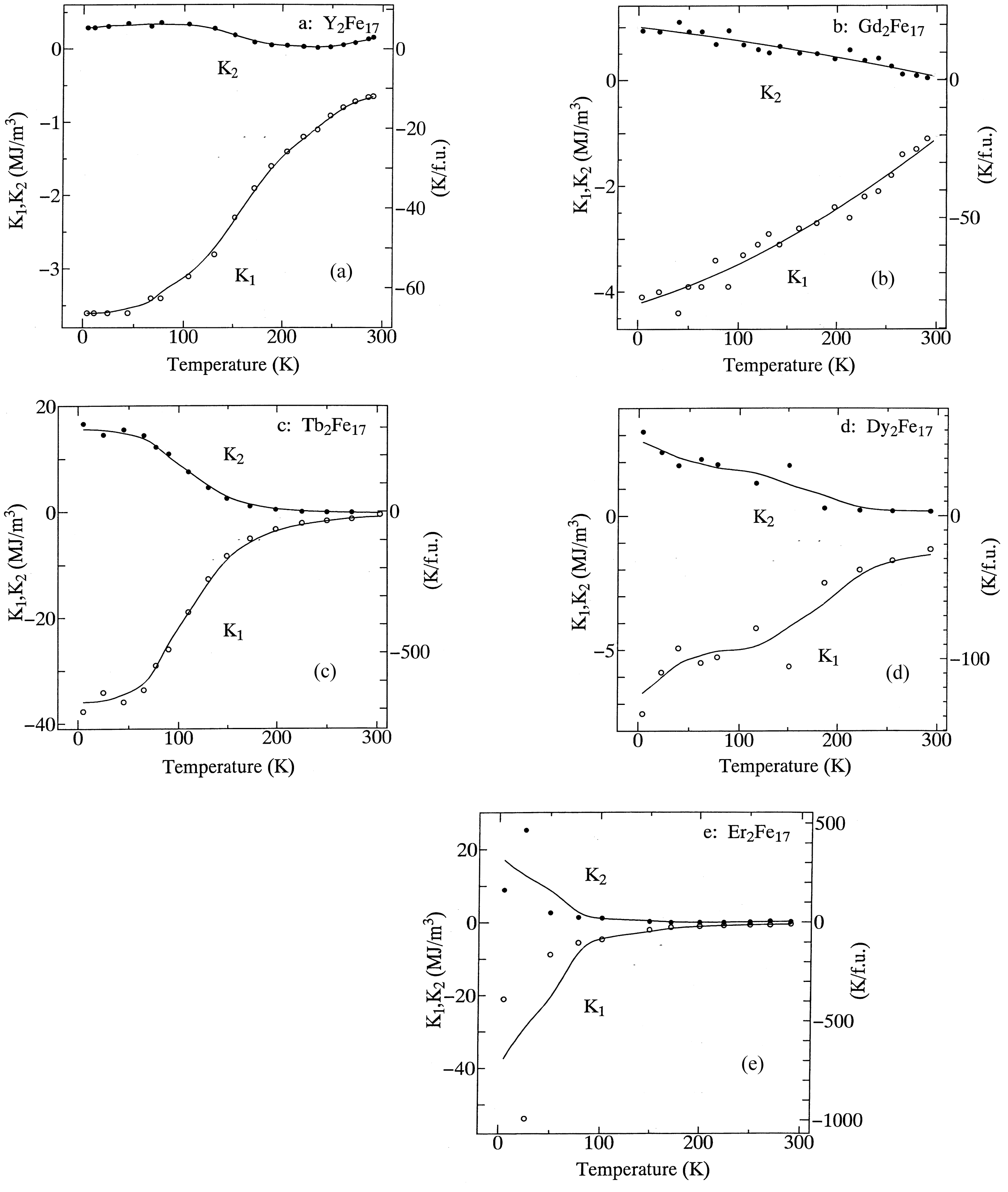

Fig. 5. Temperature dependencies of K_1 and K_2 for: (a) Y_2Fe_{17}, (b) Gd_2Fe_{17}, (c) Tb_2Fe_{17}, (d) Dy_2Fe_{17}, (e) Er_2Fe_{17}.

−66.2 and +5.3 K/f.u., respectively. For example, the values in the study of Galcia-Landa et al. are $K_1 = -50.4$ and $K_2 = -0.85$ K/f.u. This difference reveals the large effect of nonstoichiometry on the anisotropy constants [12]. We also believe that this is due to a stoichiometry difference. If a Y_2Fe_{17} single crystal had a small excess of yttrium as compared with the stoichiometric composition, the saturation magnetization should be a little lower and the anisotropy should be changed from that of the stoichiometric composition. Table 2 summarizes the magnetic parameters obtained from the single crystalline specimens. The anisotropy fields $\mu_0 H_a$ are also listed.

5. Conclusion

There are few previous data on the temperature dependence of the magneto-crystalline anisotropy constants K_1 and K_2 in R_2Fe_{17}. We have measured them in external fields up to 1.7 T. The linearity of the isotherms showed the goodness of the single crystallinity. For example, the values of K_1 and K_2 of Y_2Fe_{17} are -66.2 K/f.u. ($=-489$ J kg^{-1}) and 5.3 K/f.u. ($=39.5$ J kg^{-1}), respectively, at 4.2 K. These values are comparable to the results of magnetization measurements performed on Y_2Fe_{17} in fields up to 6 T [13].

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