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Magnetocrystalline anisotropy of non-uniaxial R–T magnetic materials studied by the singular point detection technique: an application to $R_2Fe_{17-x}Ga_x$ compounds (R = Y or Gd and $x = 0$ or 1)

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Abstract. The easy magnetization direction of $R_2Fe_{17-x}Ga_x$ lies within the basal plane over all magnetic ordering temperatures. A spinning-sample magnetic alignment technique was used to align the basal planes of fine single crystallites of $R_2Fe_{17-x}Ga_x$ (R = Y or Gd and $x = 0$ or 1) to be parallel to each other. The degree of magnetic alignment was checked by x-ray diffraction. The magnetocrystalline anisotropy field of $R_2Fe_{17-x}Ga_x$ has been determined by a singularity appearing in the curve of d^2M/dt^2 versus H measured on a magnetically aligned sample when an external field is applied perpendicular to aligned basal planes. The temperature dependence of the anisotropy fields was measured from 4.2 K up to the corresponding Curie temperatures. It was found that the Curie temperatures of R_2Fe_{17} compounds with R = Y or Gd were enhanced upon partial substitution of Fe by Ga. However, the magnetic anisotropy fields of Ga-containing compounds are smaller than those of the corresponding pure R_2Fe_{17} compounds at low temperatures.

1. Introduction

The magnetocrystalline anisotropy field, H_A, is an important property characterizing magnetic materials. A straightforward way to determine H_A experimentally is to measure the magnetization on a single crystal with a magnetic field applied parallel to different crystallographic directions (see for example García-Landa *et al* 1995). The anisotropy field is the minimum field needed to rotate the magnetic moment from the easy magnetization direction (EMD) to the hard direction. However, a single crystal is either not easy to grow or, in some cases, impossible to produce, e.g., interstitial compounds such as nitrides, carbides or hydrides prepared by solid–gas reaction. Considering this point, a quasi-single crystalline sample, in which the EMD of fine-powdered single crystallites is magnetically aligned and fixed, becomes an important alternative. For materials having an EMD parallel to a uniaxial crystallographic direction, e.g., the c-axis, a singularity indicating the anisotropy field H_A is clearly detectable if d^2M/dt^2 is plotted as a function of H when an external field ($> H_A$) is applied perpendicular to the alignment direction. M represents the magnetization, H the applied magnetic field and t the time corresponding to the pulsed field H and magnetization M. This method is well known as the singular point detection (SPD) technique (Asti and

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Rinaldi 1972, 1974, Grössinger 1982). Furthermore, it was found that this singularity is also clearly detectable even when the measurement is performed on an isotropic (non-aligned) sample (Sun 1986, Kou and Grössinger 1991, Grössinger *et al* 1992). The main advantage of the SPD technique is therefore that the anisotropy field can be determined precisely and directly on a polycrystalline sample. However, for polycrystalline materials having an EMD on the basal plane, the anisotropy field cannot be determined directly from magnetic measurements on isotropic samples. No singularity in the d^2M/dt^2 versus H curve is expected at $H = H_A$ when the SPD measurement is performed on isotropic non-uniaxial magnetic materials. The magnetic alignment of non-uniaxial magnetic materials is difficult because the EMD of these materials lies within the basal lanes, which cannot be magnetically aligned parallel to each other simply by applying a static magnetic field. In the present paper, a spinning-sample magnetic alignment method was used to align the basal planes of fine-powdered single crystallites. This method was first introduced by Wang *et al* (1992) and was applied to $Y_2Co_{14}B$ and Er_2Co_{17} compounds and later by Kou *et al* to the $Er_2Fe_{14}B$ compound (Kou *et al* 1995). Some typical materials, i.e., R_2Fe_{17} type, were chosen for the present study due to their well known non-uniaxial anisotropy. A singularity indicating the anisotropy field is clearly detectable at the field $H = H_A$ when an external field is applied perpendicular to the aligned basal planes.

2. Experimental details

Compounds of $R_2Fe_{17-x}Ga_x$ with R = Y or Gd and $x = 0$ or 1 were prepared by induction melting appropriate amounts of the component metals having purities of 99.99 wt%. The as-cast ingot was annealed in each case at 1273 K for 3 weeks under the protection of purified argon gas. An annealing treatment at high temperature for a long time was necessary in order to obtain grains as large as possible in the bulk samples, which makes both powdering and the following magnetic alignment process easier and more successful. X-ray diffraction using Cr Kα radiation was used to check the purity and to determine the crystallographic structure of annealed samples. For the determination of lattice constants, a and c, Ge powder as the calibration sample was mixed with the measured powders. The crystalline cubic Ge shows a reflection line [111] at $2\theta = 41.04^\circ$ and the [220] at $2\theta = 69.83^\circ$ for Cr Kα radiation, which can be used to calibrate the x-ray measurements. It was found that $Y_2Fe_{17-x}Ga_x$ crystallizes to a single phase with a hexagonal structure. However, $Gd_2Fe_{17-x}Ga_x$ was found to be a mixture of the hexagonal and the rhombohedral structures. No impurity such as α-Fe was traced in $Gd_2Fe_{17-x}Ga_x$ or in $Y_2Fe_{17-x}Ga_x$. In order to obtain the magnetically aligned samples for measuring the magnetocrystalline anisotropy field, as-annealed samples were powdered and sieved to particle sizes smaller than 20 μm. The critical point here is that powder particles should be composed of single crystallites. This is important because only single crystals can be magnetically aligned.

The Curie temperatures of all studied samples were determined by measuring the temperature dependence of the magnetization under a low static field (40 kA m^{-1}). The magnetocrystalline anisotropy field was determined by the SPD technique in a pulsed-field magnetometer which can be operated from 4.2 to about 1000 K with a maximum field strength of 24 MA m^{-1} (Grössinger 1992). The quality of the magnetic alignment was checked by x-ray diffraction performed on samples with the surface parallel or perpendicular to the cylindrical axis which is the c-axis.

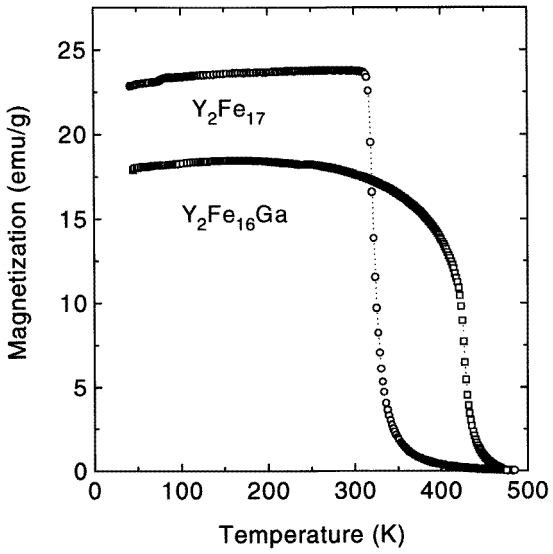

Figure 1. The temperature dependence of the magnetization of Y_2F_{17} and $Y_2Fe_{16}Ga$ measured under a static field of 40 kA m^{-1}. The Curie temperatures of these compounds were obtained from the minimum of the dM/dT versus T curve.

3. Experimental results and discussion

3.1. Curie temperatures and crystallographic structure

Figure 1 shows the temperature dependence of magnetization measured for Y_2Fe_{17} and $Y_2Fe_{16}Ga$ under a low static field (40 kA m^{-1}). The values of the Curie temperatures were determined from the minimum in the dM/dT versus T curve and are listed in table 1. It is evident that $Y_2Fe_{61}Ga$ (415 K) has a higher Curie temperature than Y_2Fe_{17} (310 K). The Curie temperature of $Gd_2Fe_{16}Ga$ (535 K) was found to be higher than that of Gd_2Fe_{17} (479 K). It is worthwhile noting that this seems to be a quite interesting magnetic behaviour concerning the Curie temperature of R_2Fe_{17} compounds. All substituents of Fe in R_2Fe_{17} compounds, independent of whether these substituents carry a magnetic moment or not, for instance Al, Si, Ga, Ni and Co (Rupp *et al* 1988), lead to an increase of Curie temperature. It was proposed that this phenomenon was caused by an expansion of the crystal lattice which results in an increase of the Fe–Fe intermetallic distance. Consequently, the magnetic interaction of Fe–Fe atoms is enhanced, which leads to an increase of the Curie temperature. Concerning the present study, the lattice of $R_2Fe_{16}Ga$ does expand when compared to the corresponding R_2Fe_{17} (see table 1). However, partial Si substitution for Fe in R_2Fe_{17} compounds also causes an increase of the Curie temperature although the lattice is contracted (Long *et al* 1993). Therefore, the actual reason for the enhancement of ordering temperatures of R_2Fe_{17} compounds due to partial substitution of Fe needs to be further explored. In addition, it is of interest to note that the volume expansion in the hexagonal $Gd_2Fe_{16}Ga$ phase is greater than that in the rhombohedral $Gd_2Fe_{16}Ga$ (see table 1).

Table 1. The structural and magnetic properties of $R_2Fe_{17-x}Ga_x$ with R = Y or Gd and $x = 0$ or 1. a and c are the lattice constants, v the volume of the unit cell and $\Delta v/v$ the volume expansion. T_C is the Curie temperature and H_A the magnetocrystalline anisotropy at 4.2 K. * indicates anisotropy field data uncorrected for demagnetizing field.

Compounds	a (nm)	c (nm)	v (nm^3)	$\Delta v/v$ (%)	T_C (K)	H_A (T)
Y_2Fe_{17}	0.846	0.829	0.514		310	4.59
$Y_2Fe_{16}Ga$	0.851	0.833	0.522	1.6	415	4.50*
Gd_2Fe_{17} (r)	0.852	1.248	0.785		479	7.08*
Gd_2Fe_{17} (h)	0.855	0.824	0.522	0.4	479	7.08*
$Gd_2Fe_{16}Ga$ (r)	0.853	1.250	0.788		535	6.90*
$Gd_2Fe_{16}Ga$ (h)	0.856	0.832	0.528	1.2	535	6.90*

3.2. The spinning-sample magnetic alignment method

If single crystallites have an EMD parallel to the c-axis, the c-axis of all single crystallites can be aligned parallel to the direction of an external magnetic field. At the same time, the hard planes (perpendicular to the c-axis) were also aligned parallel to each other. These aligned single crystallites can be fixed by solidifying epoxy resin which is mixed with crystallites before being magnetically aligned. However, if the EMD is not parallel to a specific crystallographic direction, this method is no longer applicable. This is because the anisotropy within the basal plane nearly vanishes at room temperature for most materials having an EMD within the basal plane. This is a consequence of the strong temperature dependence of the higher-order anisotropy constants. Upon applying an external static field to single crystallites that are free to rotate, the basal planes can be aligned parallel to the direction of external fields (left-hand side of figure 2). However, the orientation of magnetically aligned basal planes is still random due to the absence of magnetic anisotropy within the basal planes. In addition, in magnetically aligned samples, thus obtained, the basal planes are not parallel to each other (see the left-hand side of figure 2). The hard directions (perpendicular to the basal planes) are therefore still randomly oriented. The problem here becomes how to fix a basal plane and rotate the other planes parallel to it.

In order to fix a basal plane, a planar field is needed. If a static field is spun around an axis, a quasi-planar field is formed around this axis. This quasi-planar field can be therefore used to rotate the basal planes perpendicular to that axis and keep all basal planes parallel to each other. In the present experiment, the sample (cylindrical shape) instead of the magnetic field is spun. The fine-powdered particles (particle size smaller than 20 μm, being composed of mainly single crystallites) were mixed with epoxy resin and embedded in a Teflon tube of cylindrical shape. The Teflon tube was connected to a motor that enables the tube to be spun in a static field of about 1.2 MA m^{-1} with the cylindrical axis perpendicular to the field direction until the epoxy resin is set (about 6 h). This process ensures the basal planes (perpendicular to the c-axis) to be aligned parallel to each other and the c-axis parallel to the cylindrical axis (see the right-hand side of figure 2). In order to clarify the above statement, we illustrate in figure 2 the magnetic torque force arrangement within the basal plane in static as well as in spinning-sample magnetic alignment.

Figure 3 shows the x-ray diffraction patterns of magnetically aligned $Y_2Fe_{16}Ga$ measured with the sample surface parallel or perpendicular to the cylindrical axis. The measurement on isotropic $Y_2Fe_{16}Ga$ is presented for comparison. From this measurement, it is evident that the intensity of the [004] diffraction is strongly enhanced and that the other peaks are absent when the measurement is performed on the sample surface perpendicular to the

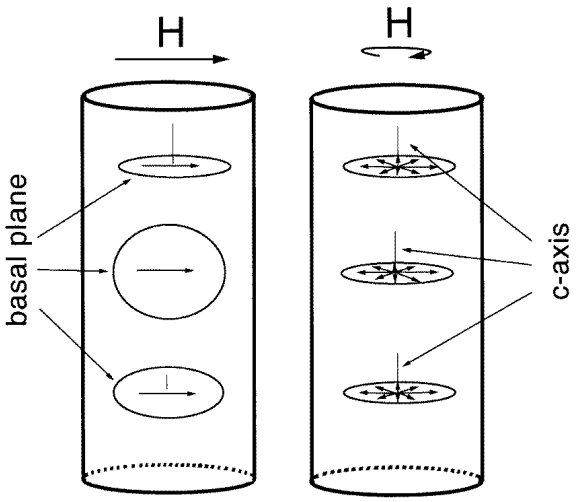

Figure 2. A scheme illustrating the arrangement of magnetic torque force within the basal planes during the magnetic alignment for non-uniaxial fine particles using a static field (left) and a spinning sample (right).

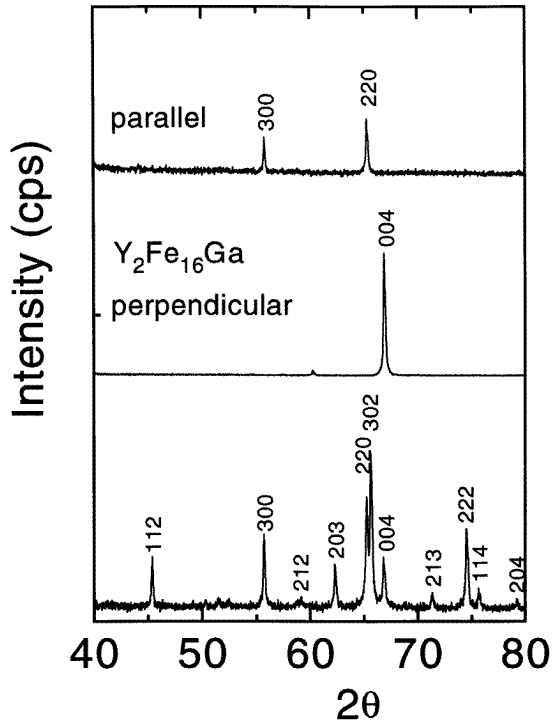

Figure 3. X-ray diffraction patterns using Cr Kα radiation measured on magnetically aligned $Y_2Fe_{16}Ga$ with the sample surface parallel or perpendicular to the cylindrical axis, the *c*-axis. The measured trace for isotropic $Y_2Fe_{16}Ga$ is presented for comparison.

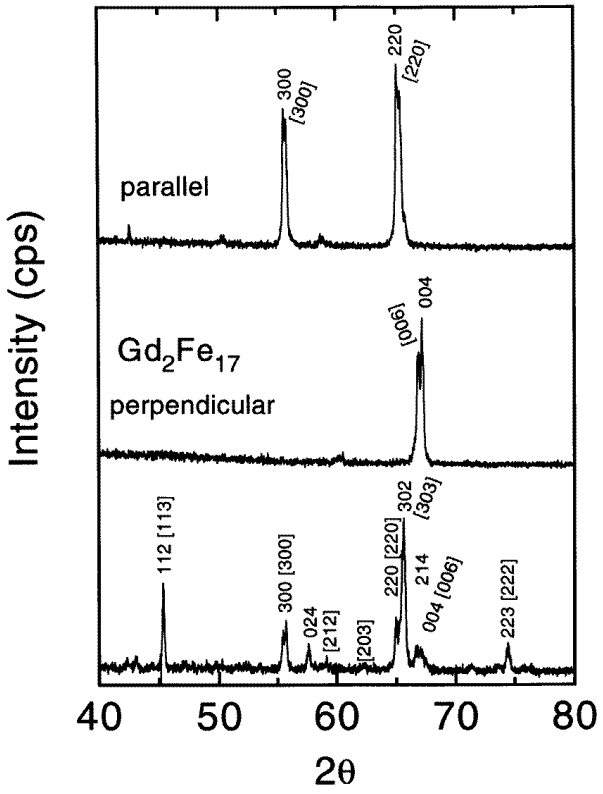

Figure 4. X-ray diffraction patterns using Cr Kα radiation measured on magnetically aligned Gd_2Fe_{17} with the sample surface parallel or perpendicular to the cylindrical axis, the *c*-axis. The measured trace for isotropic Gd_2Fe_{17} is presented for comparison.

cylindrical axis. On the other hand, if the measurement is made on the sample surface parallel to the cylindrical axis, the intensities of the [300] and [220] diffraction peaks are enhanced and other peaks are absent. Two points become evident from these measurements. First, the EMD of $Y_2Fe_{16}Ga$ is within the basal plane. Second, the magnetic alignment is nearly perfect since otherwise all diffraction peaks would appear, although the intensities of some peaks would be reduced or enhanced, depending on the degree of alignment. Similar results were obtained for magnetically aligned Y_2Fe_{17}.

Figure 4 shows the x-ray diffraction patterns of magnetically aligned Gd_2Fe_{17}. As for Y_2Fe_{17} and $Y_2Fe_{16}Ga$, the information on the EMD and the magnetic alignment of Gd_2Fe_{17} can be clearly obtained. Only [00*l*] reflection lines are detectable when the sample surface is perpendicular to the cylindrical axis and only [*h*00] and [*hk*0] reflections appear when the sample surface is placed parallel to the cylindrical axis. In addition, from the x-ray diffraction patterns on magnetically aligned Gd_2Fe_{17}, it is evident that Gd_2Fe_{17} is a mixture of two structures, i.e., the hexagonal Th_2Ni_{17} type and the rhombohedral Th_2Zn_{17} type. However, the coexistence of these two structures is not as clearly identifiable when the x-ray diffraction is performed on the isotropic samples (see the bottom part of figure 4). Both structural types were also detected, but much more clearly in a magnetically aligned $Gd_2Fe_{16}Ga$ sample.

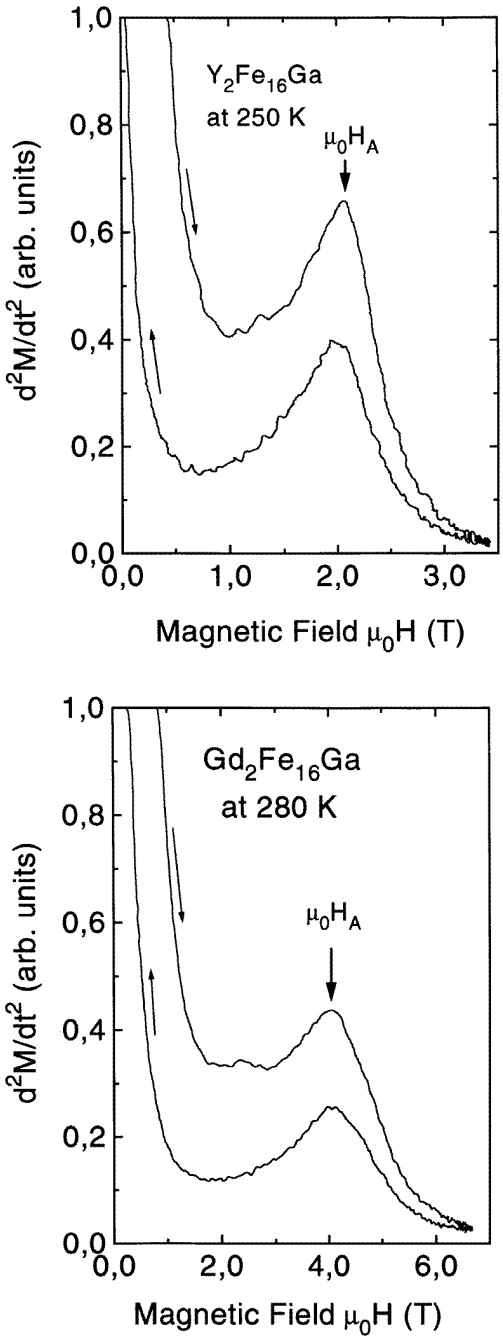

Figure 5. SPD measurements on $Y_2Fe_{16}Ga$ at 250 K and $Gd_2Fe_{16}Ga$ at 280 K using a pulsed-field magnetometer with external fields applied parallel to the cylindrical axis, the *c*-axis. The arrows indicate the measurements made with increasing or decreasing pulsed fields.

3.3. The magnetocrystalline anisotropy field

Since Y is a non-magnetic element and Gd an S-state element, the magnetic anisotropy of $Y_2Fe_{17-x}Ga_x$ and $Gd_2Fe_{17-x}Ga_x$ originates merely from the Fe sublattice. Figure 5 shows

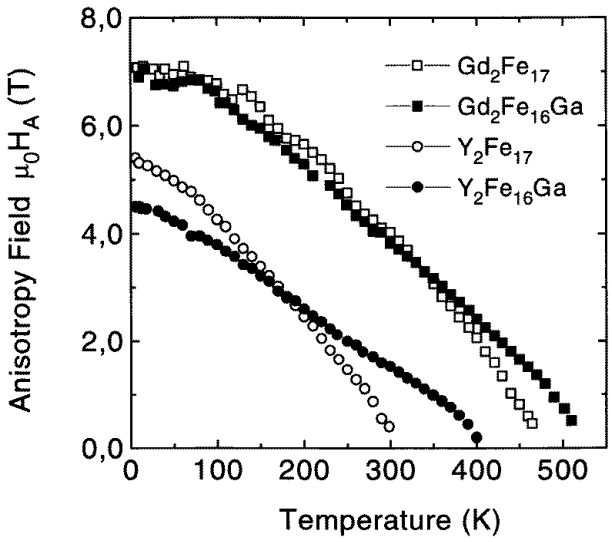

Figure 6. The temperature dependence of the magnetocrystalline anisotropy field of planar $Y_2Fe_{17-x}Ga_x$ and $Gd_2Fe_{17-x}Ga_x$ determined by means of the SPD technique.

curves of d^2M/dt^2 versus H measured on magnetically aligned $Y_2Fe_{16}Ga$ (at 250 K) and $Gd_2Fe_{16}Ga$ (at 280 K) when H is applied parallel to the cylindrical axis, perpendicular to aligned basal planes. Singularities indicating the anisotropy field H_A are clearly detectable. Owing to very good magnetic alignment, singularities were easily distinguishable over all magnetic ordering temperatures. The temperature dependence of H_A for $R_2Fe_{17-x}Ga_x$ (R = Y or Gd; $x = 0$ or 1) has been measured using the SPD technique over all magnetic ordering temperatures and is shown in figure 6. From these measurements it follows that the values of the anisotropy fields of the Ga-containing samples are in general lower than those of the pure compounds at low temperatures. However, due to the higher Curie temperatures of $R_2Fe_{16}Ga$, the anisotropy fields of $R_2Fe_{16}Ga$ are higher at higher temperatures than those of R_2Fe_{17}. At 4.2 K, $\mu_0 H_A(Y_2Fe_{17}) = 4.59$ T (after correcting for the demagnetizing field 0.53 T at 4.2 K), and $\mu_0 H_A(Gd_2Fe_{17}) = 6.71$ T. These data are in good agreement with measured values for single-crystalline Y_2Fe_{17} (García-Landa *et al* 1995) and Gd_2Fe_{17} (Sinnema 1988).

As was detected previously by x-ray diffraction, Gd_2Fe_{17} and $Gd_2Fe_{17}Ga$ are mixtures of the hexagonal and the rhombohedral structures, which would have different anisotropy fields due to the slightly different crystallographic symmetry. Thus two singularities at different fields are expected in the d^2M/dt^2 versus H curves for Gd_2Fe_{17} and $Gd_2Fe_{16}Ga$ when H is applied perpendicular to the aligned basal planes, as was the case for uniaxial $Gd_2(Co_{1-x}Fe_x)_{17}$ with $x < 0.5$ (Grössinger 1982). However, these two singularities predicted were not detectable in the present measurement, suggesting that the compounds with two structures have nearly the same value of anisotropy field consistent with the fact that the two structures differ only slightly (Khan 1973). In addition, it is worthwhile noting the differences in the physical meaning of the uniaxial anisotropy field and of the planar anisotropy field. The former represents the minimum field needed to rotate the magnetic moment from the c-axis to the basal plane and is given by $\mu_0 H_A = 2(K_1 + 2K_2)/M_s$ where K_1 and K_2 are the anisotropy constants and M_s the spontaneous magnetization. However,

the latter represents the minimum field needed to rotate the magnetic moment from the basal plane to the c-axis and is given by $\mu_0 H_A = 2K_1/M_s$ where $K_1 < 0$. Both these formulae can be derived from a more general equation (Kou and Grössinger 1991, Kou 1991):

$$\mu_0 H_A = \left(-1/M_s\right)\left(\partial^2 E_A/\partial\theta^2\right)\big|_{\theta=90.0}$$

where E_A is the anisotropy energy and θ the angle between the spontaneous magnetization and the c-axis and E_A is expressed by $E_A = K_1 \sin^2\theta + K_2 \sin^4\theta + \ldots$.

As was stated previously, the magnetic anisotropy of $Y_2Fe_{17-x}Ga_x$ and $Gd_2Fe_{17-x}Ga_x$ originates only from the Fe sublattice. The anisotropy energy, E_A, of these two types of compound should be the same. However, the values of $\mu_0 H_A$ of $Gd_2Fe_{17-x}Ga_x$ are higher than those of $Y_2Fe_{17-x}Ga_x$. This is because the magnetic anisotropy energy E_A is a product of the anisotropy field $\mu_0 H_A$ and the spontaneous magnetization M_s, i.e., $E_A = -0.5\mu_0 H_A M_s$. The spontaneous magnetization of $Gd_2Fe_{17-x}Ga_x$ is lower than that of $Y_2Fe_{17-x}Ga_x$, which is the consequence of the ferrimagnetic coupling between the magnetic moments of the Gd sublattice and the Fe sublattice in the former.

In conclusion, we have demonstrated in the present paper that the single crystallites of materials having an EMD within the basal plane can be magnetically aligned by a spinning-sample magnetic alignment technique. The magnetocrystalline anisotropy field of these magnetically aligned samples can be then determined by using the well known SPD technique in a pulsed-field magnetometer.

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