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Anisotropy constants and crystal-field parameters of $Sm_2Fe_{17-x}Ga_x$

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Abstract. The anisotropy constants K_1 and K_2 as well as the Curie temperatures of partially iron substituted $Sm_2Fe_{17-x}Ga_x$ have been studied. The Sm-sublattice contribution to the magnetocrystalline anisotropy has been obtained by subtracting the Fe-sublattice contribution measured in the isostructural compound $Y_2Fe_{17-x}Ga_x$. Using the linear theory of magnetocrystalline anisotropy the crystal-field parameter A_{20} has been calculated from $K_1(T)$ and $K_2(T)$. A_{20} initially decreases towards more negative values than in the parent compound, reaching -270 K a_0^{-2} at $x = 1.5$, though it seems to increase slightly at higher Ga concentrations.

1. Introduction

There is much interest in developing Sm_2Fe_{17} based hard magnetic materials. However, the easy plane anisotropy and the low Curie temperature of Sm_2Fe_{17} make difficult its use as base material for permanent magnets. Several ways to overcome these difficulties have been proposed: the interstitial inclusions of H, N and C increase the Curie temperature and may lead to easy axis materials [1, 2]. Attempts of substituting part of the iron by other elements were also made. It has been found that Ga increases the Curie temperature and changes the magnetocrystalline anisotropy from in-plane to uniaxial. First evidence of this behaviour was obtained from oriented powder x-ray analysis [3–7] which shows that for Ga contents between 2 and 4 atoms fu^{-1} the materials have an easy c-axis. X-ray and magnetic studies on $Y_2Fe_{17-x}Ga_x$ have also shown a change of anisotropy from planar to uniaxial when the Ga contents are higher than 6 atoms fu^{-1} [8].

Analysis of the role of the different sublattices and their interaction can be made from magnetic measurements. For 2:17 compounds, a two-sublattice model is sufficient to describe the magnetic anisotropy [9]. The behaviour of the iron sublattice can be studied using an isostructural compound with a non-magnetic atom on the RE position. K_1 and K_2 from $Y_2Fe_{17-x}Ga_x$ have already been determined at several temperatures [10, 11]. If, as a first approximation, it is assumed that total anisotropy constants are the sum of the two sublattice contributions, the Sm-sublattice value for $Sm_2Fe_{17-x}Ga_x$ can be determined by subtracting the Fe-sublattice contribution measured on $Y_2Fe_{17-x}Ga_x$. As the anisotropy of the rare-earth intermetallic compounds is mainly determined by the RE sublattice, it is interesting to analyse

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how Ga affects the crystal electrical field on the sites occupied by Sm and Fe. Using the linear theory of the magnetocrystalline anisotropy [12–15], the temperature dependence of the sublattice anisotropy constants has been fitted to the experimental values and second order crystal field parameters and exchange coupling parameters have been determined.

2. Experiment

Samples of $Sm_2Fe_{17-x}Ga_x$ (x up to 3.5) were obtained from the Sm_2Fe_{17} ingots, adding the appropriate amounts of Ga and Sm, using excess of Ga and rare earth. Pellets were arc-melted and homogenized in Ar atmosphere for 24 h at 1000 °C. The Curie temperatures were obtained measuring the magnetization versus temperature in 0.1 T field using an Oxford Instruments vibrating sample magnetometer.

The samples obtained were milled down to micrometric size by mechanical grinding in cyclohexane. Part of the powder was mixed with epoxy resin and cured in 1 T field. From the x-ray diffractograms of non-oriented powder the lattice parameters were obtained, while for the field-oriented samples the easy magnetization direction was deduced from the allowed peaks. After this preliminary determination, the rest of the powder, again mixed with resin, was field oriented in a cylindrical container. For the samples with easy axis anisotropy a 1 T field was applied along a cylinder diameter. For the samples with easy plane anisotropy the same field was applied, but the sample was rotated around its axis which ensures that the c-axes are in the same direction. The magnetization curves were measured using a SQUID magnetometer with a 6 T superconducting coil, at temperatures 5, 77 and 300 K with the field applied along the cylinder axis, which coincides with the hard magnetic direction.

3. Results and discussion

The partial substitution of Fe by Ga in the $Sm_2Fe_{17-x}Ga_x$ compound produces an increase of the lattice parameters, see table 1, as has already been observed by different authors [4, 5]. From a magnetic point of view, both the easy magnetization direction as well as the Curie temperature were strongly affected by the Ga substitution. Table 1 shows the obtained results.

Table 1. Cell parameters, Curie temperatures and easy magnetization directions of $Sm_2Fe_{17-x}Ga_x$ alloys.

Ga content (atoms fu^{-1})	a (Å)	c (Å)	V (Å^3)	T_c (K)	EMD
0.5				434	ab-plane
1.0	8.573	12.476	794	477	ab-plane
1.5	8.607	12.522	801	503	ab-plane
2.0	8.618	12.504	806	534	c-axis
3.0	8.640	12.585	813	578	c-axis
3.5				584	c-axis

The first quadrant demagnetization curves were measured perpendicular to the easy magnetization direction. Using the Sucksmith–Thompson method and the procedure described in [10], the first and second anisotropy constants, K_1 and K_2, were determined with an error less than 10%. The results are listed in table 2.

Table 2. Anisotropy constants K_1, K_2 and saturation magnetization of $Sm_2Fe_{17-x}Ga_x$ alloys.

Ga content (atoms fu^{-1})	T (K)	$\mu_0 M_s$ (T)	K_1 (MJ m^{-3})	K_2 (MJ m^{-3})
0.5	5	1.54	−3.71	1.78
	77	1.53	−3.08	1.34
	300	1.34	−1.70	0.69
1	5	1.46	−1.81	0.86
	77	1.42	−1.49	0.65
	300	1.18	−0.63	0.20
1.5	5	1.40	−0.23	0.42
	77	1.36	−0.17	0.32
	300	1.14	−0.08	0.13
2	5	1.28	0.26	0.33
	77	1.25	0.18	0.31
	300	1.08	0.06	0.18
3	5	1.09	1.15	0.04
	77	1.01	0.98	0.06
	300	0.89	0.21	0.09
3.5	5	1.00	1.33	0.4
	77	0.98	1.17	0.5
	300	0.89	0.22	0.5

3.1. Ga effects on the Fe sublattice

The effect of Ga on the Fe-sublattice anisotropy was studied on $Y_2Fe_{17-x}Ga_x$ [10]. As Y is non-magnetic the only contribution to the anisotropy comes from the Fe sublattice. In the Fe sublattice, Ga or Fe can occupy the same crystallographic sites. Although Ga has no magnetic moment, it is expected to change the crystal electric field (CEF) and thus affect the sublattice anisotropy. As first approximation, it can be considered that the total anisotropy constant is the sum of all the site contributions, i.e.

$$K_1^{Fe}(x) = \sum_{j=1}^{m} n_j f_j^{Fe}(x) K_{1,j}^{Fe} + \sum_{j=1}^{m} n_j f_j^{Ga}(x) K_{1,j}^{Ga} \tag{1}$$

where n_j are the number of atoms on crystallographic sites, f_j^{Fe} and f_j^{Ga} are the fractions occupied by Fe and Ga atoms respectively, $K_{1,j}^{Fe}$ and $J_{1,j}^{Ga}$ are the contributions to the sublattice first anisotropy constant from an atom of Fe or Ga on the jth site, respectively. The first term accounts for simple removal of Fe atoms, while the second term is added to describe the influence of Ga on CEF.

Thuy *et al* [16] have calculated the $K_{1,j}^{Fe}$ values for the different crystallographic sites in the 2:17 series. Their reported values are −0.17, +0.35, −1.14 and +0.60 MJ m^{-3} for Fe 18f, 18h, 9d and 6c sites, respectively. Neutron scattering and Mössbauer studies [17–19] indicate that Ga completely avoids the 9d site and occupies the 6c site only at high concentration where the 18f sites are strongly preferred, while at low concentration the 18h sites are preferentially occupied. As Ga is non-magnetic, our first assumption is that it will reduce the contribution of Fe to the sublattice anisotropy constant, i.e. only the first term in (1) is to be taken into account. However, as has already been discussed [10, 11] this assumption results in an enhancement of the planar anisotropy, rather than a weakening as observed in the experiment. We should also take into account that the changes in the electrical field gradient around the Fe positions can be important. The effect of Ga on the crystal electrical field could be quantified using the second term of equation (1), determining the $K_{1,j}^{Ga}$ contribution for the sites 18f, 18h and

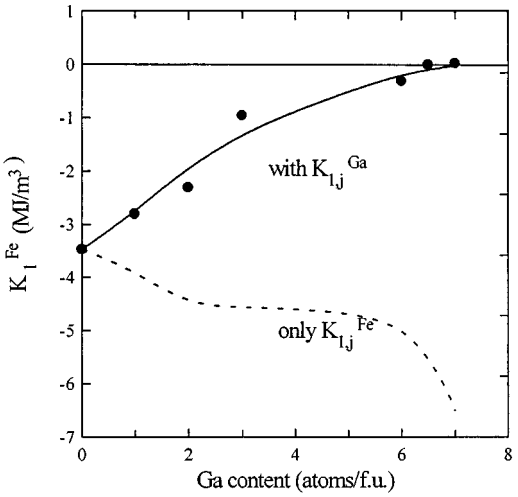

Figure 1. Effect of Ga substitution on the Fe-sublattice first anisotropy constant, K_1^{Fe}, in $R_2Fe_{17-x}Ga_x$. Symbols are the data measured on $Y_2Fe_{17-x}Ga_x$ [10]. The lines correspond to two different assumptions: (a) Ga only removes Fe atoms (dashed line), (b) Ga also contributes to the anisotropy as consequence of the crystal electrical field modifications (solid line).

6c. As the occupancy factors for the different sites are known (we used the data published in [20]), the $K_{1,j}^{Ga}$ values can be determined as fitting parameters using the least-squares method. The result of the fitting, shown in figure 1 as a continuous line, reproduces well the observed behaviour. The values of $K_{1,j}^{Ga}$ used in the fit are -0.02, +0.50 and +0.56 for 16f, 18h and 6c sites, respectively. One should keep in mine that the above values for $K_{1,j}^{Ga}$ result from fitting, while the real picture may be different, involving also changes in the Fe band structure caused by Ga substitution.

3.2. Ga effect on the Sm sublattice

As first approximation, it can be assumed that

$$K_i^{Sm} = K_i^{tot} - K_i^{Fe} \tag{2}$$

where K_i^{Sm}, K_i^{Fe} and K_i^{tot} are the ith order anisotropy constants for the Sm sublattice, the Fe sublattice and the alloy respectively. As the interatomic distances between atoms varies less than 1% between the Y and Sm compounds, K_i^{Sm} can be obtained using the values of K_i determined on $Y_2Fe_{17-x}Ga_x$ and $Sm_2Fe_{17-x}Ga_x$ with the same Ga content. The results are shown in table 3 and in figure 2. It can be seen that for $x = 1$ atom fu^{-1} the Sm sublattice exhibits uniaxial anisotropy ($K_i^{Sm} > 0$). However, its values are lower than the K_i^{Fe}, resulting in a planar anisotropy for the alloy.

From the room temperature dependence of the Sm-sublattice anisotropy constants the CEF parameters can be obtained. The linear model for the magnetocrystalline anisotropy developed by Kuz'min [12] describes this dependence when the main reason for the anisotropy temperature variation is the exchange coupling. According to this model only the second and fourth order parameters are relevant. These two parameters can be related to the two first anisotropy constants as

$$K_1^{Sm} = -3\theta_2 J_2 \langle r_{4f}^2 \rangle A_{20} B_{2,5/2}(x) - 40\theta_4 J_4 \langle r_{4f}^4 \rangle A_{40} B_{4,5/2}(x) \tag{3}$$

$$K_2^{Sm} = 35\theta_4 J_4 \langle r_{4f}^4 \rangle A_{40} B_{4,5/2}(x) \tag{4}$$

Table 3. Sm sublattice anisotropy constants.

Ga content (atoms fu^{-1})	T (K)	K_1^{Sm} (MJ m^{-3})	K_2^{Sm} (MJ m^{-3})
0.5	5	−0.57	0.91
	77	−0.68	0.64
	300	−1.08	0.53
1.0	5	0.99	0.13
	77	0.80	−0.08
	300	−0.01	0.04
1.5	5	2.32	−0.27
	77	1.83	−0.29
	300	0.59	−0.31
2.0	5	2.04	−0.32
	77	1.54	−0.18
	300	0.61	−0.02
3.0	5	2.10	0.25
	77	1.86	0.22
	300	0.65	0.02

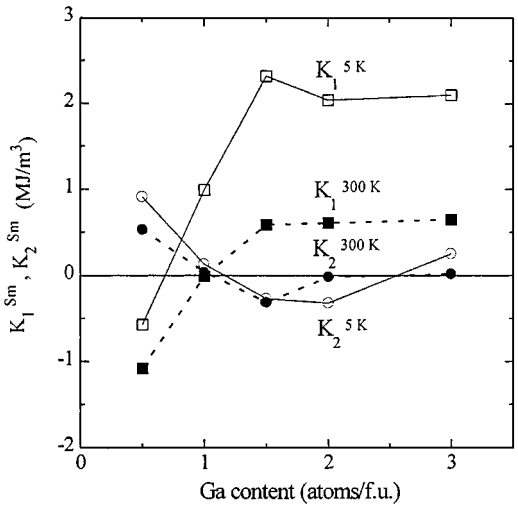

Figure 2. Sm-sublattice first and second anisotropy constants as a function of the Ga content for $Sm_2Fe_{17-x}Ga_x$ alloys. The lines are guides for the eye.

where $B_{n,5/2}(x)$ are the n-order generalized Brillouin functions, with

$$x = 2J|g_j - 1|\frac{\mu_B n_{SmFe}\mu_0 M_s(T)}{3k_B T}. \tag{5}$$

Since K_2^{Sm} is linear with $B_{4,5/2}(x)$, then $B_{2,5/2}(x)$ should be linear with $K_1^{Sm} + (8/7)K_2^{Sm}$ [15]. Plotting this last expression as a function of $B_{2,5/2}(x)$, and using the exchange coupling parameter n_{Sm-Fe} as a free parameter, a linear dependence can be easily achieved. From the slope of the linear plot, A_{20} can be directly obtained. Thus obtained data for A_{20} and n_{Sm-Fe} are presented in figure 3 and listed in table 4 (the value for $x = 0$ is taken from [15]). It can be seen that for small Ga concentration A_{20} decreases quickly towards negative values. The RE-ion anisotropy is usually expressed by the product of electric field gradient, represented by

Table 4. Exchange coupling and second order crystal field parameters obtained from anisotropy constants.

Ga content (atoms fu^{-1})	n_{Sm-Fe} (μ_0)	A_{20} (K a_0^{-2})
1.0	116	−166
1.5	100	−268
2.0	90	−258
3.0	172	−203

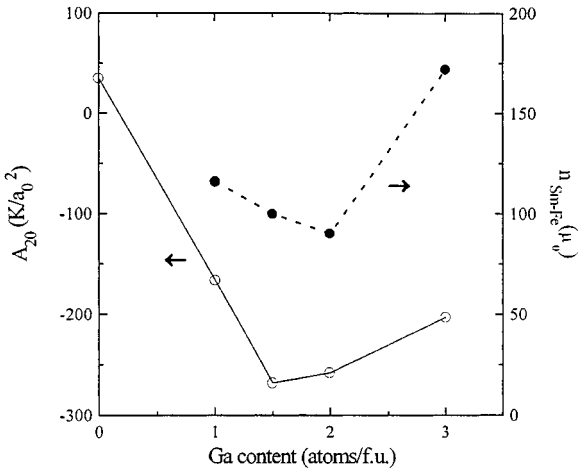

Figure 3. Exchange coupling parameter, n_{Sm-Fe} (●), and second order crystal electrical field parameter, A_{20} (○), on the Sm 6c site as a function of the Ga content. The lines are guides for the eye.

A_{20}, and the second order Steven's coefficient α_j. A negative product of both quantities gives a characteristic uniaxial anisotropy, with $K_1 > 0$. A_{20} depends on the crystal structure and chemical composition. For 2:17 structure A_{20} is generally assumed to be negative and close to zero. Since $\alpha_j > 0$ for the Sm ion, the observed strong decrease of A_{20} towards more negative values at smaller Ga substitution results in an initial strengthening of the uniaxial anisotropy attributed to the Sm sublattice. Although increasing Ga substitution between $x = 1.5$ and $x = 3.5$ has little effect on A_{20} and even an opposite tendency towards less negative values is observed, a change in sign of K_1 takes place due to weakening of the in-plane Fe-sublattice anisotropy [10]. However, it seems that the observed trend towards less negative values, and thus for weakening of the uniaxial anisotropy of the Sm sublattice, becomes faster than the weakening of the Fe-sublattice in-plane anisotropy, so the latter prevails again as observed in [4] for $x > 4$. It is worth mentioning that Mössbauer studies [21] on $Tm_2Fe_{17-x}Si_x$ reveal similar changes in A_{20}.

4. Conclusions

The effect of Ga substitution on the CEF of the Fe-sublattice magnetic anisotropy changes the trend predicted by the reduction of the Fe atoms alone.

Ga substitution affects both the inter-sublattice exchange parameter and the second order crystal field parameter. A_{20} initially decreases with Ga substitution towards more negative values than in the parent compound, though it seems to increase slightly at Ga concentration above $x = 1.5$.

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