Magnetocrystalline anisotropy in iron-rich rare-earth intermetallics. A phenomenological approach for the comparison of the overall and Fe sublattice anisotropies in $RE(FeTi)_{12}$, $RE_2(FeTi)_{17}$ and $RE_3(FeTi)_{29}$ related compounds (RE = Y, Sm)

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Abstract. The composition and temperature dependence of the anisotropy field have been measured in $REFe_{12-x}Ti_x$, $RE_2Fe_{17-x}Ti_x$ and $RE(FeTi)_{29}$ compounds with the 3:29 monoclinic cell being formed by the alternate stacking of the tetragonal 1:12 and hexagonal or rhombohedral 2:17 units (RE = Y, Sm). By using a phenomenological approach it has been possible to interpret the magnetic behaviour observed in the 3:29 phase. It has been evidenced that the Fe anisotropy, which mainly originates from itinerant 3d electrons, can be described as the simple addition of the individual contribution of the constituent 1:12 and 2:17 units. On the other hand in spite of the localized nature of the Sm anisotropy, when the overall (Fe and Sm) anisotropy is considered, the simple additivity of the individual unit contributions is only qualitatively fulfilled.

1. Introduction

In the iron-rich rare-earth intermetallic compounds (RE–Fe), 3d and 4f magnetism coexist and the interplay between strongly correlated localized RE 4f states and itinerant Fe 3d states gives rise to the well known outstanding magnetic properties observed in this class of materials [1, 2].

Much of the interest in RE–Fe compounds is related to their large magnetocrystalline anisotropy which is the resultant of the two sublattice contributions. The RE anisotropy is single ion in origin, depending on the action of the non-spherical crystal electric field (CEF) on anisotropic 4f electron states. A large anisotropy contribution is also given by the Fe sublattice for which an electron band picture is more suitable, even if a local site interaction (spin–orbit) is responsible for the anisotropy. Given the localized nature of the 4f magnetism, microscopic CEF calculations are done to treat the RE anisotropy, while a phenomenological approach is usually adopted to treat the more complex 3d contribution. The conflict between itinerant and localized ionic models prevents a unified description of the magnetocrystalline anisotropy of these systems. Therefore a phenomenological approach for the treatment of both 3d and 4f anisotropies is helpful in explaining the anisotropy behaviour of different RE intermetallic compounds. In this frame relevant parameters such as the anisotropy field and the critical field of induced transitions are measured and their behaviour explained in terms of phenomenological anisotropy constants or coefficients [3–6].

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The aim of the present work is to use a phenomenological approach to describe the magnetocrystalline anisotropy of RE and Fe sublattices in the $RE_3(FeTi)_{29}$ compounds (RE = Sm, Y) starting from a precise determination of the anisotropy fields. These investigations can be of relevance in the context of a search for starting materials for the preparation of permanent magnets. In particular there were some expectations after the recent discovery of a new intermetallic phase of composition $RE_3(FeTi)_{29}$ [7]. The study of these compounds has proved to be challenging, given the structural complexity [8] and the puzzling magnetic properties.

The intermetallic compounds $RE_3(FeTi)_{29}$ crystallize in a monoclinic structure pertaining to the $A2/m$ space group [8]. It is formed by an alternated stacking of tetragonal $RE(FeTi)_{12}$ and the hexagonal or rhombohedral $RE_2(FeTi)_{17}$ blocks in a ratio of 1:1 [7]. The solubility of Ti in this structure has not yet been defined but its presence is essential to stabilize the compound $RE_3Fe_{29-x}Ti_x$ which has been usually prepared in the nominal composition range $(1.5 \leqslant x \leqslant 2)$. On the other hand the solubility of Ti was found to be limited in the $RE_2Fe_{17-x}Ti_x$ phase which has a rhombohedral Th_2Zn_{17} or hexagonal Th_2Ni_{17} crystal structure depending on rare earth [9, 10]. In fact a maximum amount of Ti corresponding to $x < 0.8$ can be substituted for Fe [11–13]. In the $REFe_{12-x}Ti_x$ compounds, which crystallize in the tetragonal $ThMn_{12}$ structure [14], the Ti content can be varied in a very narrow range around $x = 1$ [15]. Considering the described structural formation of the 3:29 phase we wanted to explore which kind of relationship exists between its magnetocrystalline anisotropy and that coming from the 1:12 and 2:17 constituent blocks. For such a purpose the temperature and composition dependence of the anisotropy field of the different series of samples was measured and the derived anisotropy constants were analysed taking into account the structural relationship of the different phases.

2. Experiment

Compounds having nominal composition $YFe_{12-x}Ti_x$ and $SmFe_{12-x}Ti_x$ ($x = 0.8, 1.0, 1.2$) were prepared by arc melting pure elements under argon gas atmosphere. In order to compensate the loss of rare earth during melting a 5–8 wt% excess of rare earth relative to the ideal compositions was added. The ingots were remelted three times to insure homogeneity, then wrapped in tantalum foil and annealed under argon atmosphere at 950 °C (4 days) and 900 °C (7 days) for the Y and Sm 1:12 compounds respectively and then quenched in water. The compounds $RE_2Fe_{17-x}Ti_x$ ($x = 0, 0.4, 0.75$) and $RE_3(FeTi)_{29}$ (RE = Y, Sm) were prepared in the same way and the details of the annealing are given in [5] and [16].

Thermomagnetic analysis (TMA) (a measurement of the temperature dependence of the a.c. initial susceptibility in an applied field of about 4 Oe) was used in order to measure the Curie temperature, T_C, and to check for the possible presence of secondary phases. The singular point detection (SPD) technique [17, 18], with high pulsed field up to 300 kOe, was used to measure the temperature dependence of the anisotropy field H_A (i.e. the magnetic field needed to rotate the magnetization M_s from its easy (EMD) to a hard direction) from 78 to 293 K. The SPD allows for a precise determination of the anisotropy fields in polycrystalline materials [5, 6, 19]. In order to enhance the SPD signal, specimens with oriented grains were prepared. The thermomagnetic analysis of the compounds revealed that all the samples were substantially single phase, containing less than 1–2% of α-(FeTi) as secondary phase. It is worth recalling that the presence of secondary phases does not affect the H_A values determined by SPD.
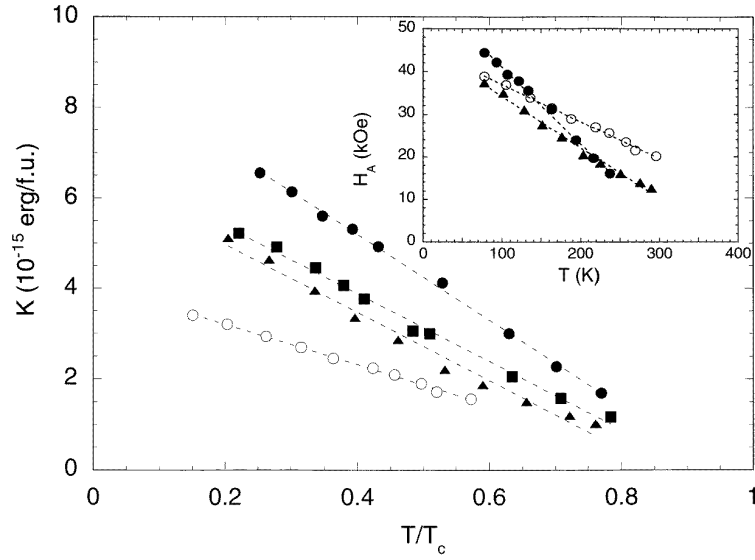
Figure 1. Anisotropy constant $K_1^{1:12}$ for YFe$_{11}$Ti (open symbol) and absolute value of $K_1^{2:17}$ for Y$_2$Fe$_{17-x}$Ti$_x$ (full symbols $x = 0$ (●), $x = 0.4$ (■), $x = 0.75$ (▲)) as a function of the reduced temperature T/T_C. Inset: temperature dependence of the anisotropy field of YFe$_{11}$Ti (open symbol) and of Y$_2$Fe$_{17-x}$Ti$_x$ (full symbols $x = 0$ (●), $x = 0.75$ (▲)). The values have been corrected for demagnetizing field.

3. Results and discussion

3.1. Y–Fe–Ti compounds: the iron sublattice anisotropy

The study of the YFeTi compounds, Y being non-magnetic, allows for the determination of the Fe sublattice anisotropy.

For the compounds YFe$_{12-x}$Ti$_x$, in the considered composition range ($0.8 \leqslant x \leqslant 1.2$), T_C does not change within the experimental error ($T_C = 518 \pm 2$ K). In addition also the anisotropy field is practically constant when varying the Ti content. From these data it is confirmed that the solubility range of Ti has to be very narrow around $x = 1$. The YFe$_{11}$Ti compound is easy axis from 78 K up to T_C. The measured anisotropy field values $H_A = (2K_1 + 4K_2)/M_s$ are reported as a function of the temperature in the inset of figure 1 (the values have been corrected for the demagnetizing field. Henceforth all the lines in the figures are guides for the eye). The measured H_A is the field required to rotate the saturation magnetization M_s from the easy c-axis to a hard direction within the basal plane. Assuming that the higher anisotropy terms are negligible, as usually observed for the 3d anisotropy, the second order anisotropy constant values can be calculated as $K_1^{1:12} = H_A M_s/2$. The deduced values are reported in figure 1 in units of erg fu^{-1} as a function of the reduced temperature T/T_C. The measured $H_A(T)$ values are in very good agreement with those reported in the literature ([1] and references therein).

The EMD of the Y$_2$Fe$_{17-x}$Ti$_x$ compounds lies in the basal plane (easy plane) and the magnetocrystalline anisotropy is significantly affected by the Ti content (inset of figure 1). In this case the measured anisotropy field $H_A = -2K_1^{2:17}/M_s$ is that required to rotate M_s from the easy basal plane to the hard hexagonal c-axis. The measured H_A of Y$_2$Fe$_{17}$ and their temperature dependence are in good agreement with single crystal data [20] and other SPD data
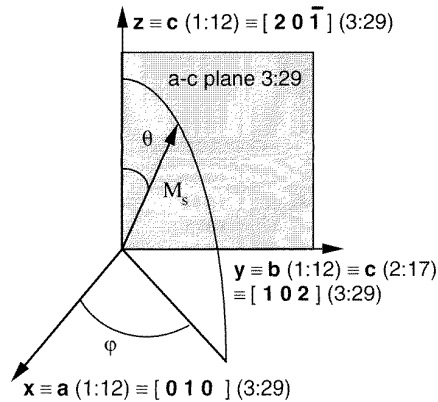
Figure 2. Reference frame used for the description of the anisotropy in $RE_3(FeTi)_{29}$ (RE = Y, Sm). The relationships between the crystallographic directions of the involved structures are indicated along with the a–c-plane of the 3:29 phase (shadowed area).

[21]. To our best knowledge no anisotropy data are reported for Ti substituted compounds. The absolute values of the calculated second order anisotropy constants $K_1^{2:17} = -H_A M_s/2$ are reported in figure 1 as a function of the reduced temperature T/T_C for various Ti concentrations. For $Y_3(FeTi)_{29}$ the $[20\bar{1}]$ direction was indicated to be the easy magnetization direction [16, 22, 23]. The $[20\bar{1}]$ direction lies in the a–c-plane of the 3:29 monoclinic structure and coincides with the c-axis of the constituent 1:12 tetragonal block (figure 2). The [102] is the hardest magnetization direction; it lies in the a–c-plane and coincides with the c-axis of the constituent 2:17 hexagonal block [16]. The [010] is the second hard direction. It corresponds to the unique b-axis of the 3:29 structure and coincides with the a-direction of the 1:12 block (figure 2) [16]. Since the easy and hard directions are mutually orthogonal, the magnetic symmetry of the 3:29 phase can be described in a triaxial (orthorhombic) frame. Assuming the z-axis corresponding to the easy magnetization direction $[20\bar{1}]$ the anisotropy energy of the system, up to the fourth order terms, is given by [16, 24]

$$E_A = \sin^2\theta[K_1 + K_1'\sin^2\phi] + \sin^4\theta[K_2 + K_2'\sin^2\phi + K_2''\sin^4\phi] \qquad (1)$$

where the hard directions [010] and [102] correspond to $\theta = 90°$, $\phi = 0°$ and $\theta = 90°$, $\phi = 90°$ respectively (figure 2); K_1, K_1' and K_2, K_2', K_2'' are respectively second and fourth order anisotropy constants. Starting from equation (1) the expressions for the anisotropy field along the two hard directions are found by minimizing the total energy $E_T = E_A(\theta, \phi) - HM_s\sin\theta$. The two fields along the [102] and [010] are expressed by

$$H_A = \frac{2(K_1 + K_1') + 4(K_2 + K_2' + K_2'')}{M_s} \qquad \text{and} \qquad H_A' = \frac{2K_1 + 4K_2}{M_s} \qquad (2)$$

which correspond to the magnetic fields required to rotate the saturation magnetization M_s from the EMD $[20\bar{1}]$ to the [102] and [010] directions respectively. The temperature dependence of the two anisotropy fields, as measured by SPD, was reported in [16]. Neglecting the fourth order terms, the second order anisotropy constants for the 3:29 phase, relative to the hardest direction [102] and to the hard direction [010], were calculated from the anisotropy field expressions and are given respectively by $K_1 + K_1' = H_A M_s/2$ and $K_1 = H_A' M_s/2$. Their values, expressed in terms of erg fu^{-1}, are reported in figure 3 as a function of the reduced temperature T/T_C. With reference to figure 2 (in the hypothesis of additivity of the anisotropy

contribution of the constituent blocks), taking into account that the 3:29 unit is obtained by the alternate stacking of 1:12 and 2:17 blocks (3:29 = 1:12 + 2:17), the anisotropy per formula unit $(K_1 + K'_1)$ needed to bring M_s from the EMD [20$\bar{1}$] to the hardest [102] direction in the 3:29 phase should be equal to the sum (absolute value) of the anisotropy fu^{-1} of 1:12 and 2:17 blocks. In fact [102] is in the hard plane of the 1:12 and it coincides with the hard c-axis of 2:17. From a comparison of the results reported in figures 1 and 3 it is evident that the anisotropy of 3:29 is indeed the sum of the constituent blocks provided that the composition $x = 0$ is considered for the 2:17 block. On the other hand the rotation of M_s from the EMD to the [010] direction should involve only the anisotropy $K_1^{1:12}$ of the 1:12 block. In fact the [010] direction is in the easy basal plane of the 2:17 and in the hard basal plane of the 1:12. The values of K_1 in the 3:29 phase are indeed in a reasonable agreement with $K_1^{1:12}$ of YFe$_{11}$Ti. The anisotropy constants, at various values of T/T_C, for the different constituent blocks are reported in table 1.

Table 1. Second order anisotropy constants of YFe$_{11}$Ti $(K_1^{1:12})$, Y$_2$Fe$_{17-x}$Ti$_x$ $(|K_1^{2:17}|)$, and Y$_3$(FeTi)$_{29}$ $(K_1^{3:29})$, $(K_1+K'_1)^{3:29}$ in 10^{-15} erg fu^{-1} at various reduced temperature values (T/T_C). The error in the determination of the K values has been evaluated to be ± 0.2 $(10^{-15}$ erg fu$^{-1})$.

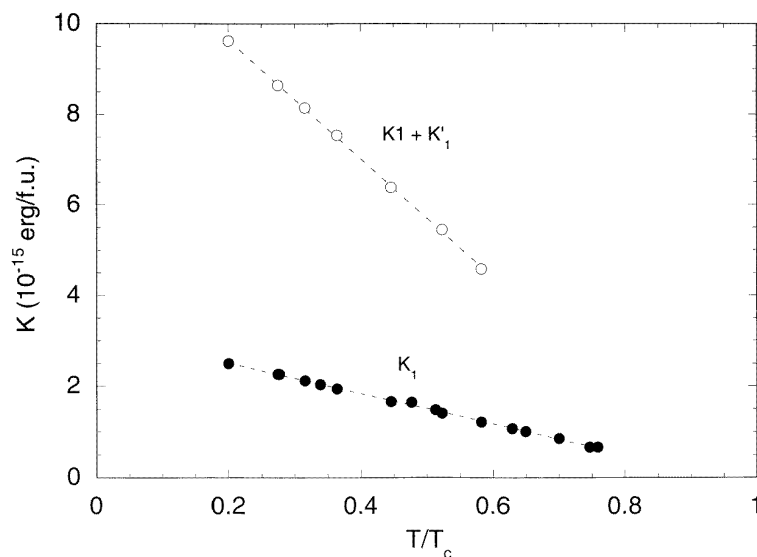| T/T_C | $K_1^{1:12}$ | $|K_1^{2:17}|$ | | | $K_1^{3:29}$ | $(K_1+K'_1)^{3:29}$ |
		$x = 0$	$x = 0.4$	$x = 0.75$		
0.2	3.2	7.1	5.4	5.0	2.5	9.6
0.3	2.8	6.2	4.6	4.2	2.2	8.3
0.4	2.3	5.2	3.9	3.5	1.8	7.0
0.5	1.9	4.3	3.1	2.7	1.5	5.7
0.6	1.4	3.3	2.4	2.0	1.2	4.4
0.7	1.0	2.4	1.6	1.2	0.8	3.1

Figure 3. Temperature dependence of the second order anisotropy constants for Y$_3$(FeTi)$_{29}$.

From the above results we can conclude:

(i) The Fe sublattice anisotropy in the 3:29 phase seems effectively to result from the linear combination of the contribution of the constituent blocks.

(ii) The entrance of Ti into the 3:29 lattice seems to be limited to the solubility in the 1:12 block which in turn is very narrow around $x = 1$. Thus the real composition of the 3:29 compound should actually correspond to $Y_3Fe_{28}Ti$.
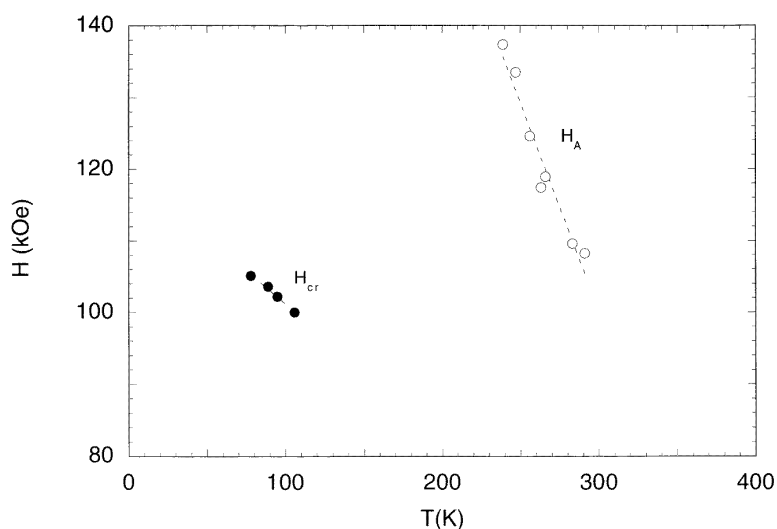

Figure 4. Temperature dependence of the anisotropy field H_A and critical field H_{cr} of the first order magnetization process (FOMP) in $SmFe_{11}Ti$. The values of H_A have been corrected for demagnetizing field.

3.2. Sm–Fe–Ti compounds: the overall (Fe and Sm sublattice) anisotropy

For the compounds $SmFe_{12-x}Ti_x$ a small monotonic decrease of T_C from 581 to 573 K has been found by varying the nominal Ti content from $x = 0.8$ to $x = 1.2$. Also the anisotropy field is slightly affected by Ti content; in fact the H_A value at 293 K decreases from 110 kOe to 106 kOe in the considered composition range. The observed variations (which are indeed very small) of both T_C and H_A with composition can either imply a slightly larger solubility range in Sm than in the $YFe_{12-x}Ti_x$ compound or a larger influence of Ti on the properties of the former. In particular the Sm anisotropy (which is a single ion contribution coming from crystal field interactions) could be sensitive to even small changes in the crystal field which can be caused even by limited variation of Ti content. $SmFe_{12-x}Ti_x$ was found to be easy axis from 78 K to T_C. Thus the expression for the anisotropy field is $H_A = (2K_1 + 4K_2 + \cdots)/M_s$. The H_A value increases rapidly with decreasing temperature and it has been measured down to 220 K (figure 4). Below 150 K a field induced transition has been found, which has been interpreted as a first order magnetization process (FOMP) of type 2 [25], in agreement with [26, 27]. The critical field H_{cr} of the FOMP transition has been measured by SPD from 78 to 120 K and is reported in figure 4. A different interpretation of this transition (as a fast rotation of M_s) was initially given in [19] although later some of the same authors reinterpreted it as a FOMP [28].

In the case of $Sm(FeTi)_{12}$ compounds (also because of the existence of the field induced transition) it is necessary to consider high order terms to describe the magnetocrystalline anisotropy; thus from the measured H_A values, the combination $K \equiv K_1 + 2K_2 + 3K_3 = H_A M_s/2$ is obtained, which represents the anisotropy energy involved in the magnetization process when M_s rotates from the easy c-axis to the hard basal plane. The calculated values of K, expressed in erg fu^{-1}, are reported as a function of the reduced temperature T/T_C in figure 5.
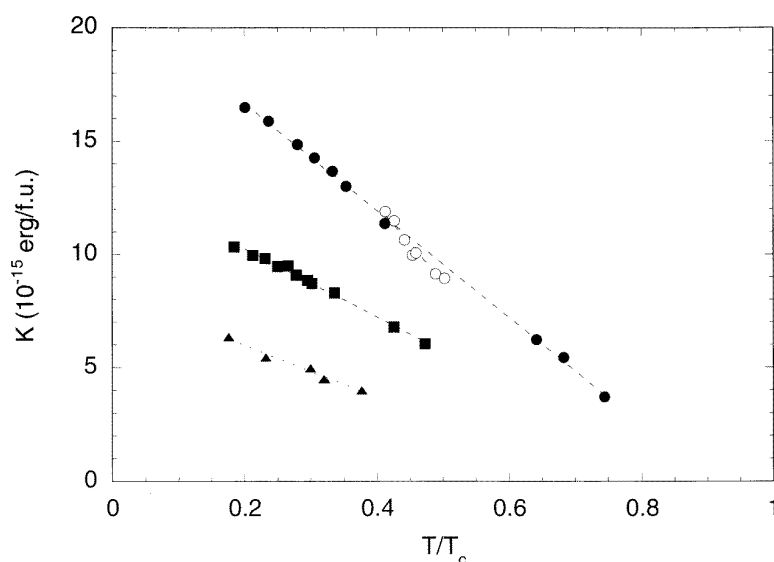

Figure 5. Anisotropy constants $K \equiv K_1 + 2K_2 + 3K_3$ for $SmFe_{11}Ti$ (open symbol) and absolute values of the second order $K_1^{2:17}$ for $Sm_2Fe_{17-x}Ti_x$ (full symbols $x = 0$ (●), $x = 0.4$ (■), $x = 0.75$ (▲)) as a function of the reduced temperature T/T_C.

Concerning the $Sm_2Fe_{17-x}Ti_x$ compounds a dramatic effect of Ti on the Sm anisotropy was evidenced [5]. Being a planar compound its anisotropy field expression is $H_A = -2K_1^{2:17}/M_s$. The second order anisotropy constant $K_1^{2:17} = -H_A M_s/2$, which represents the anisotropy energy involved in the magnetization process from the easy basal plane to the hard rhombo-hedral c-axis, decreases rapidly with increasing Ti content. The absolute values of $K_1^{2:17}$, for various Ti contents, are reported in figure 5 as a function of the reduced temperature T/T_C.

In $Sm_3(FeTi)_{29}$, the easy and hard directions coincide with those of $Y_3(FeTi)_{29}$ [16]. Also for this compound the temperature dependence of the two anisotropy fields H_A and H'_A was successfully measured by SPD and reported in [16]. However, high order anisotropy terms have to be considered for Sm compounds. Thus, from equation (2), the combination of anisotropy constants representing the anisotropy energy involved in the magnetization processes along the [102] and [010] directions respectively are $K_a \equiv (K_1 + K'_1) + 2(K_2 + K'_2 + K''_2) = H_A M_s/2$ and $K_b \equiv K_1 + 2K_2 = H_A M_s/2$. These values are reported in figure 6 as a function of T/T_C. Also in the case of Sm compounds it can be expected that the anisotropy energy for magnetizing along the hardest [102] direction of the 3:29 phase (hard for both 1:12 and 2:17 blocks) would be the addition of the component block contributions. From an analysis of the data in figures 5 and 6 it is deduced that, in the case of Sm, the agreement is only qualitative, unless the maximum entrance of Ti in the 2:17 block is considered. In fact the resultant 3:29
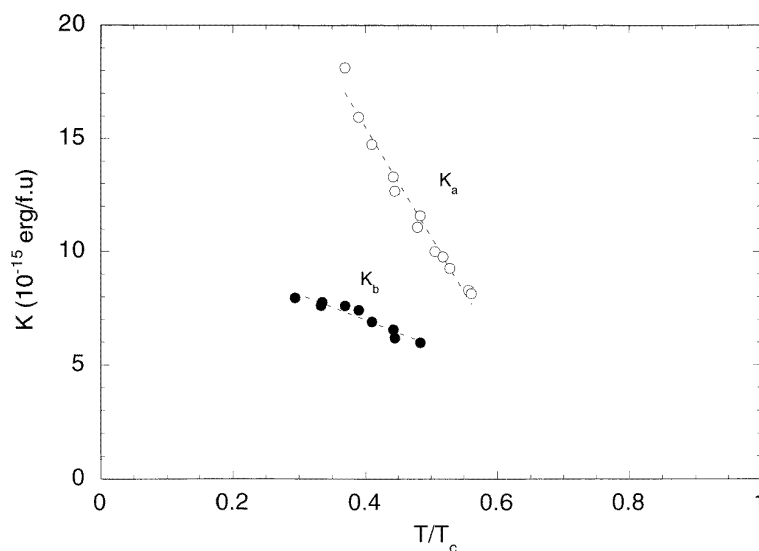
Figure 6. Anisotropy constants $K_a = (K_1 + K_1') + 2(K_2 + K_2' + K_2'')$ (open symbols) and $K_b = K_1 + 2K_2$ (full symbols) for $Sm_3(FeTi)_{29}$ as a function of the reduced temperature T/T_C.

anisotropy can only be obtained provided that the contribution of the 1:12 phase is added to that of the 2:17 one with $x = 0.75$. However the anisotropy of the 1:12 block, which, in the proposed frame, should coincide with that required in the magnetization process along the direction [010] of the 3:29 phase, is instead much larger (by about a factor of 2).

It has to be underlined that a type-2 FOMP occurs in both 1:12 and 3:29 compounds when the magnetization is rotated from the easy c-axis (1:12) to the a-axis (1:12) in both cases (figure 2). However the critical field for the FOMP in $Sm(FeTi)_{12}$ is about 2.5 times larger than that measured in $Sm_3(FeTi)_{29}$, that is 105 kOe as compared to 42 kOe at 78 K.

It can thus be concluded that while the proposed combination scheme of the anisotropy is valid for the Fe contribution (Y compound), the addition of the overall 3d and 4f anisotropies coming from the separated 1:12 and 2:17 blocks is higher than that resulting from the stacking of the two blocks forming the 3:29 sublattice. This is probably due to the much higher sensitivity of the single ion 4f anisotropy of Sm to even small modifications of the environment, which can affect the CEF gradient at the RE site. Small changes of the lattice parameters of the constituent blocks as well as small deformation could indeed take place in the formation of the 3:29 compound.

In summary, by using a phenomenological approach it has been possible to interpret the complex magnetic behaviour observed in the 3:29 compounds. Surprisingly it has been evidenced that the Fe anisotropy, which is mainly originated from the itinerant 3d electrons, can be described in the 3:29 system as the addition of the individual contributions of the constituent 1:12 and 2:17 units. These indications can be useful in the formulations of microscopic models for the 3d anisotropy. On the other hand in spite of the localized nature of the Sm anisotropy, when the overall (Fe and Sm) anisotropy is considered, the simple additivity of the individual unit contributions is only qualitatively fulfilled.

In view of possible applications as permanent magnet materials, given the observed composition scheme for the anisotropy of Y and Sm 3:29 phases, it can be inferred that

an improvement of their magnetocrystalline anisotropy can be obtained by enhancing the axial anisotropy of the 1:12 block and (or) by enhancing the basal plane contribution of the 2:17 block.

On the basis of the present results it can be predicted that the interstitial modification of $Sm_3(FeTi)_{29}$, with nitrogen or carbon, should result in a change of the EMD from the $[20\bar{1}]$ to the $[102]$ direction (figure 2). In fact nitrogenation turns the anisotropy of Sm_2Fe_{17} and $Sm_2(FeTi)_{12}$ from planar to axial and from axial to planar respectively [29–31]. The change of EMD has been indeed observed in the nitrided $Sm_3(FeTi)_{29}$ [32]. For an improvement of the anisotropic characteristics of the $RE_3(FeTi)_{29}$ phase, suitable Fe substitutions or interstitial introductions, which preferentially enter the 1:12 or the 2:17 block, have to be considered.

Acknowledgment

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