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Anisotropy and spin-reorientations in Co-rich rare earth compounds

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Abstract

The effect on the magnetocrystalline anisotropy of substitution of several types of non-magnetic atoms into the various Co sites of R_2Co_{17} compounds has been studied. A substitution scheme is presented taking into account size effects as well as enthalpy effects. The effects of preferential substitution into the various Co sites have been correlated with changes in anisotropy derived from magnetic measurements. Particular attention has been given to various types of spin-reorientation transitions occurring in the temperature dependence of the magnetization. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Magnetocrystalline anisotropy; Spin-reorientation transitions; Co-rich rare earth compounds

1. Introduction

In intermetallic compounds formed by combining rare earths (R) and 3d metals (T), the magnetic anisotropy consists of a contribution due to the 4f and the 3d sublattice. The origin of the former anisotropy is fairly well understood in terms of the crystal-field theory, the latter being frequently attributed to the occurrence of an orbital moment on the 3d atoms. In the present study we will address the magnetic anisotropy in the rhombohedral rare-earth compounds of the type R_2Co_{17}. The Co sublattice in these compounds is composed of four different Co sites: 6c, 9d, 18h and 18f. It has already been known for several years that the so-called Co dumb-bell atoms (6c) in these R_2Co_{17} compounds contribute negatively to the anisotropy [1]. More recently it could be shown that also the more numerous 18h Co atoms contribute negatively to the anisotropy [2]. In the present report, the effect of various types of substitutions on the anisotropy will be discussed.

2. Anisotropy of the 3d sublattice

The main mechanism responsible for the magnetocrystalline anisotropy in solid 3d transition metal (T) systems is frequently assumed as originating from the combined effect of spin–orbit interaction and partial quenching of the orbital angular momentum. Because the spin is coupled to the orbital motion via the spin–orbit coupling, changes in spin direction will be accompanied by directional changes in the orbital motion. The latter motion will, in turn, favour particular crystallographic directions. The latter directions are dictated by electrostatic fields and overlapping wave functions associated with neighbouring atoms in the lattice. Modern electronic-band structure calculations made by Nordström et al. [3] and Daalderop et al. [4,5] have shown, however, that this is an oversimplification. In this report, we will briefly review the experimental material presently available for Co-rich rare-earth compounds. Generally, it is sufficient to describe the 3d sublattice anisotropy by means of the phenomenological expression

$$E_{A,T} = K_{1,T} \sin^2\theta \qquad (1)$$

Experimentally it is found that the sign of the Co-sublattice anisotropy is frequently different from the Fe-sublattice anisotropy for a given crystal structure. A few well-known examples are listed in Table 1.

Table 1
Examples of several ternary Y–Co and Y–Fe compounds and their easy-magnetization direction

Easy-axis	Easy-plane	Structure type
$Y_2Fe_{14}B$	$Y_2Co_{14}B$	$Nd_2Fe_{14}B$
$YFe_{10}V_2$	$YCo_{10}V_2$	$ThMn_{12}$
$YFe_{10}Si_2$	$YCo_{10}Si_2$	$ThMn_{12}$
$Y_2Co_{17}N_X$	Y_2Fe_{17},N_X	Th_2Zn_{17}

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The crystal structure of R_2Co_{17} compounds contains four inequivalent Co positions: 6c, 9d, 18h and 18f. It is well known that the structure of the R_2Co_{17} compounds can be considered as derivative of the more simple $CaCu_5$-type of structure of the corresponding RCo_5 compounds. In the latter compounds, the Co atoms are found in the planes perpendicular to c that they share with the R atoms (2c site) and in planes consisting exclusively of Co atoms (3g site). In the R_2Co_{17} compounds, there are additional Co sites (6c) due to the fact that one third of all R atoms in RCo_5 have to be replaced by a pair of dumbbell Co atoms in order to obtain the R_2Co_{17}, structure. The 18f sites in the R_2Co_{17} compounds correspond to the original 2c sites in RCo_5, whereas the 18h and 9d sites correspond to the original 3g sites.

As discussed in more detail in Ref. [6], for the RCo_5 compounds there is substantial theoretical and experimental evidence that the 2c sites contribute positively ($K_1>0$) to the total Co-sublattice anisotropy while the 3g sites contribute negatively ($K_1<0$). It is reasonable to assume that similar anisotropic properties have to be attributed to the corresponding Co sites in the R_2Co_{17} compounds. There is also experimental evidence that the Co atoms on the 6c sites in the R_2Co_{17} compounds contribute negatively [1]. Based on these considerations, one may expect that the total Co-sublattice anisotropy in the R_2Co_{17} compounds is composed of site-dependent negative and positive contributions, as summarised in Table 2. In this table, also the site relationship with RCo_5 compounds is indicated.

From the fact that the Co-sublattice anisotropy is strongly positive in the RCo_5 compounds it can be derived that the positive contribution of the 2c sites overcompensates the negative contribution of the 3g sites. This means that it is reasonable to assume that the 18f contribution in the R_2Co_{17} compounds also overcompensates the combined contributions of the 18h and 9d sites. However, the additional negative contribution due to the dumb-bell 6c sites in the R_2Co_{17} compounds gives rise to an overall negative anisotropy of the Co-sublattice in these materials. The total Co sublattice anisotropy in the R_2Co_{17} compounds remains nevertheless small, owing to the mutual compensation of the contributions of the various sites. This is probably the reason why relatively small changes can induce a sign reversal of the Co-sublattice anisotropy.

For instance, the anisotropy changes from easy-plane to easy-axis when tetravalent Ce is substituted for the trivalent R atoms in R_2Co_{17} [7]. A possible explanation is that the Ce valence-electron states mix more strongly with the Co 3d states than in the case of trivalent R components, which results in a slightly lower experimentally observed Co-sublattice moment. The moments and anisotropy contribution of the Co atoms at 18h will become most affected because they have comparatively more R neighbours than the Co atoms at the other sites (see Table 2). The relatively stronger reduction in anisotropy of the 18h site then may lead to changing the total Co-sublattice anisotropy from negative to positive.

Table 2
Co sites in R_2Co_{17} compounds and their contribution to the Co-sublattice anisotropy as expected on the basis of their relationship with the 3g and 2c sites in the corresponding RCo_5 compounds[a]

Co site	Contribution to anisotropy		Coordination
6c	easy-plane	$K_1<0$	13 Co; 1R
3g⇒18h	easy-plane	$K_1<0$	9 Co; 3R
2c⇒18f	easy-axis	$K_1>0$	11 Co; 2R
3g⇒9d	easy-plane	$K_1<0$	10 Co; 2R

[a] Also listed are the number and type of atoms in the coordination shell. The sites are arranged in order of decreasing Wigner–Seitz cell volume from top to bottom.

Another example is the temperature dependence of the anisotropy in the compounds Y_2Co_{17} and Gd_2Co_{17} [8]. Although in both compounds only the Co-sublattice contributes to the anisotropy, there is a change from easy-plane to easy-axis with increasing temperature close to the corresponding Curie temperatures. Also this may be associated with the relative vulnerability of the 18h site Co moment, losing its magnitude and anisotropy more rapidly with increasing temperature than the Co atoms at the other sites.

The presence of Co sites with different anisotropy contributions opens the possibility of changing the sign of the anisotropy by preferential subtitutions of non-magnetic atoms into one or more of these sites, Prominent examples are found in the series $R_2Co_{17-x}Ga_x$ where there is a strong preference of the Ga atoms to occupy the 18h site. Results of neutron diffraction [2] are shown in Fig. 1. It can be seen that the Ga atoms completely avoid the 9d site and initially substitute virtually exclusively into the 18h site. For Ga concentrations higher than $x=3$, also the other

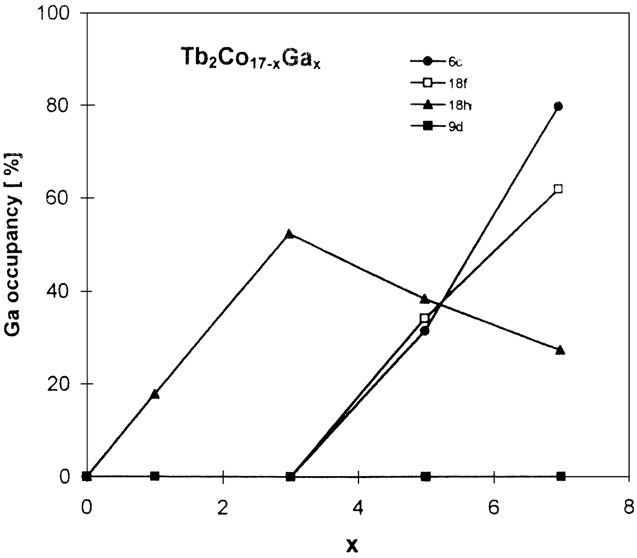

Fig. 1. Results of neutron diffraction showing the preferential site occupancies of Ga atoms in rhombohedral $R_2Co_{17-x}Ga_x$ compounds [2].

sites become occupied by Ga atoms leading to a maximum of the preferred Ga occupancy of the 18h site for this concentration. The results shown in Fig. 1 for $Tb_2Co_{17-x}Ga_x$ can be taken as being representative for other $R_2Co_{17-x}Ga_x$ series, because all Ga-substituted compounds have the same rhombohedral structure for which the lattice constants vary only slightly with the R component. In fact, the $Tb_2Co_{17-x}Ga_x$ series is less suited to obtain information on the Co-sublattice anisotropy because of the strong predominance of the Tb-sublattice anisotropy. The removal of a substantial part of the negative anisotropy contribution by Ga-substitution into the 18h site is clearly illustrated, however, by the behaviour of the concentration dependence of the anisotropy constant in the series $Ce_2Co_{17-x}Ga_x$ and $Gd_2Co_{17-x}Ga_x$ [7,9]. In these compounds, the R-sublattice does not contribute to the anisotropy. It can be seen in Fig. 2 that Ga substitution in Ce_2Co_{17}, a compound that has already easy-axis anisotropy, leads to an initial increase of the anisotropy constant. When interpreting these results one has to bear in mind that magnetic dilution of the Co sublattice by Ga atoms is expected to lead to a decrease of the magnetic anisotropy with increasing Ga concentration. Instead, an initial increase is found. A comparison with the results of Fig. 1 shows that the maximum value of K_1 corresponds to the maximum degree of filling of the 18h site by Ga atoms as found by neutron diffraction [2]. The compound Gd_2Co_{17} is of the easy-plane type and here Ga substitution is seen to lead to a sign reversal of the anisotropy constant. A similar behaviour of the anisotropy constant is also found by substituting Al or Si for Co. Such changes in anisotropy can conveniently be followed in the X-ray diagrams of magnetically aligned powders, as shown for $Gd_2Co_{17-x}Si_x$ compounds in Fig. 3 [8].

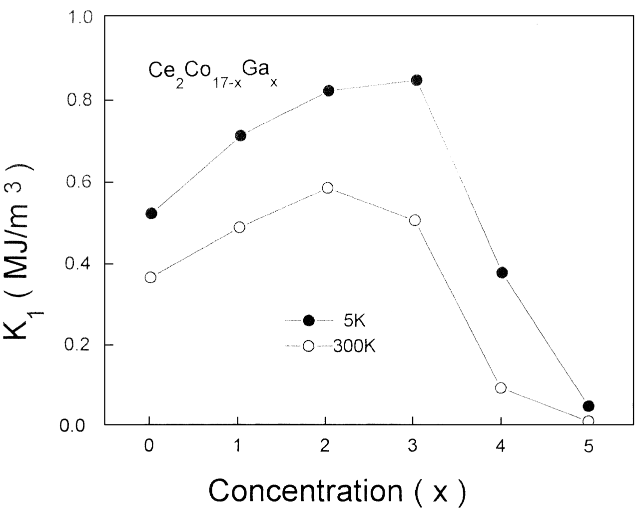

Fig. 2. Concentration dependence of the anisotropy constant, K_1, at 5 and 300 K of several $Ce_2Co_{17-x}Ga_x$ compounds [7].

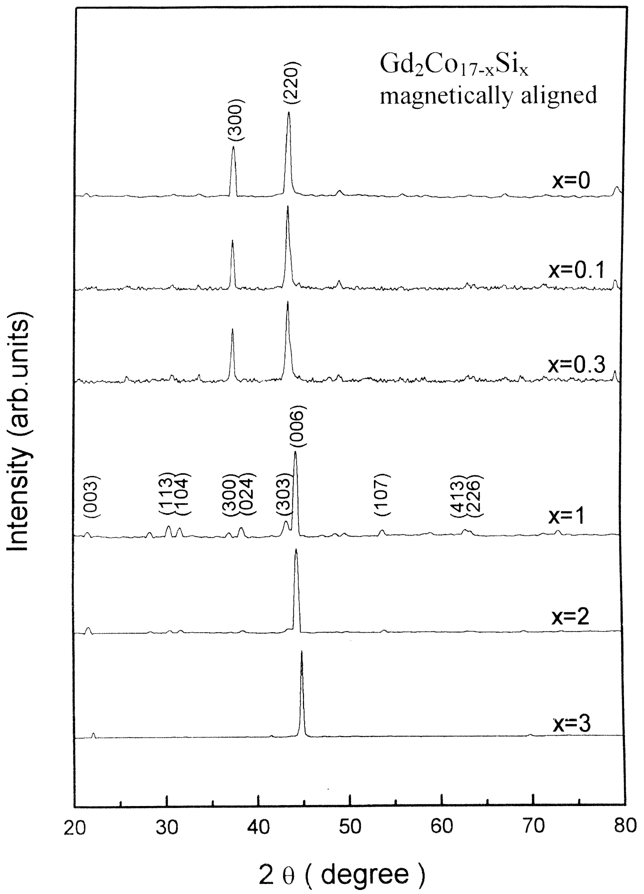

Fig. 3. X-ray diagrams obtained on magnetically aligned powder samples of several $Gd_2Co_{17-x}Si_x$ compounds [8].

Several previous investigations have shown that the substitution of third elements M into the 3d sites of intermetallic compounds of rare earth and 3d elements is governed by size effects and enthalpy effects [10–12]. The M atoms generally have radii different from that of the replaced 3d element. Because the atomic volumes in a given crystal structure are different for the various 3d sites this leads to a natural preference of the substituted element for the most convenient site. However, also enthalpy effects may play an important role. If the interaction of an M atom with R atoms is more attractive ($\Delta H < 0$) than with 3d atoms, the M atoms will preferentially occupy sites in which the number of R neighbours is comparatively large. As an estimate for the mentioned interactions we will use the enthalpies of mixing of equiatomic M–Y and M–Co alloys, respectively. The corresponding ΔH_{MY} and ΔH_{MCo} values, taken from Ref. [13], have been listed in Table 3.

The data listed in Table 2 have been arranged in order of decreasing Wigner–Seitz cell volumes of the corresponding sites (see for instance Ref. [14]). Because the M elements considered here all have larger metallic radii than Co, they prefer occupation of the 6c site if enthalpy effects were comparatively unimportant. The elements Ti and Mo satisfy this condition. Because the ΔH_{MY} values listed in Table 3 are positive, these elements tend to avoid sites with many R neighbours. This enhances the preference of

Table 3
Enthalpy of mixing of MCo and MY alloys (in kJ/mole of atoms)

M element	Y	Co	Ti	Mo	Cu	Al	Ga	Si
ΔH_{MCo}	−22	–	−28	−5	+6	−19	−11	−21
ΔH_{MY}	–	−22	+15	+24	−22	−38	−40	−56

these elements for the 6c site, being the largest site and having the lowest number of R neighbours. By contrast, the elements Al, Ga and Si are seen to have fairly large negative ΔH_{MY} values. The enthalpy effect may predominate in these cases, meaning that these elements will show a preference for the 18h site because it has the largest number of R neighbours. It has already been shown above that these model predictions agree with experimental results obtained for the Ga compounds. Neutron diffraction data obtained on $\mathrm{Nd_2Co_{17-x}Al_x}$ compounds [14] show that also here the 18h site is the most preferred one ($x=4$), although also the 6c and 18f sites become fairly well populated. At present, no neutron diffraction data are available for $\mathrm{R_2Co_{17-x}M_x}$ compounds with M = Ti, Mo and Si. However, magnetic measurements obtained on $\mathrm{R_2Co_{17-x}M_x}$ compounds with Si [8] show that the concentration dependence of the Co-sublattice anisotropy in these materials behaves in the same way as found for the Ga compounds. For the compounds $\mathrm{R_2Co_{17-x}M_x}$ with M = Ti and Mo, we have observed a change from easy-plane anisotropy ($x=0$) to easy-axis anisotropy for $x=1$ [15], which would agree with the preference of these M atoms for the 6c site, all this lending credence to the proposed substitution scheme.

3. Anisotropy of the rare-earth sublattice

The total magnetic anisotropy in compounds of rare earths and 3d transition metals consists of a contribution due to the R sublattice and a contribution due to the Co sublattice. For the Co-sublattice anisotropy, it is sufficient to consider only the lowest-order anisotropy constant. For the R-sublattice anisotropy generally higher-order anisotropy constants have to be taken into account. For the sake of simplicity, we will consider in the present context only the lowest-order constant also for the R sublattice and write:

$$K_1 = K_{1,\mathrm{R}} + K_{\mathrm{l,T}} \tag{2}$$

Microscopically, the rare-earth sublattice anisotropy can be described by the crystal-field theory in terms of the crystal-field parameters B_n^m and the corresponding Stevens operator equivalents O_n^m [16]. The expressions of O_n^m are polynomials in J and J_z, while the crystal-field parameters reflect the intensity of the electrostatic field of the charges surrounding the 4f electrons.

From the transformation properties of the Stevens operator equivalents, the following relations between the anisotropy constant $K_{1,\mathrm{R}}$ and the crystal-field parameters may be obtained [17,18]:

$$K_{1,\mathrm{R}} = -3/2\, B_2^0 \langle O_2^0 \rangle - 5 B_4^0 \langle O_4^0 \rangle \tag{3}$$

Microscopically, it follows from Eq. (3) that the temperature dependence of the rare-earth sublattice anisotropy constants depends on the thermal averages $\langle O_n^m \rangle$. The expressions of O_n^m are polynomials of order n of J and J_z. For instance,

$$O_2^0 = 3J_z^2 - J(J+l) \tag{4}$$

It can be shown that the expectation values of $\langle O_n^m \rangle$ fall off with increasing temperature as $[M_{\mathrm{R}}(T)/M_{\mathrm{R}}(0)]^{n(n+l)/2}$. This means that the higher the order of a given anisotropy constant the lower its contribution at higher temperatures. This is the reason why for the $\mathrm{R_2Co_{17-x}M_x}$ compounds considered here only the the first term of Eq. (3) needs to be taken into consideration at room temperature and higher temperatures

$$K_{1,\mathrm{R}} = -3/2 B_2^0 \langle O_2^0 \rangle = -3/2 \alpha_J \langle r^2 \rangle A_2^0 \langle O_2^0 \rangle \tag{5}$$

where α_J is the second-order Stevens factor and $\langle r^2 \rangle$ the expectation value of the Hartree–Fock 4f radius.

It has been shown in the previous section that the Co-sublattice anisotropy in the $\mathrm{R_2Co_{17-x}M_x}$ compounds depends on the nature of the M component and on its concentration. Examples were presented of regions where $K_{1,\mathrm{Co}}$ in these materials is negative and where it is positive. Depending on the sign of the second-order Stevens factor of the R element, α_J, one may have negative and positive values also for $K_{1,\mathrm{R}}$. Interesting magnetic phenomina are observed in compounds in which these two sublattice anisotropies differ in sign. In these cases, $K_{1,\mathrm{R}}$ may predominate at low temperature, but due to its rapid decay with temperature, $K_{1,\mathrm{Co}}$ can become dominant at high temperatures. This leads to so-called spin-reorientation transitions. An example of such magnetic behaviour will be presented below by means of magnetic measurements made on a single crystal of the compound $\mathrm{Ho_2Co_{15}Si_2}$ [19].

The compound $\mathrm{Ho_2Co_{15}Si_2}$ has a Curie temperature of 830 K. The temperature dependence of the magnetization measured in directions parallel and perpendicular to the c-axis is shown in Fig. 4. These data clearly show that the

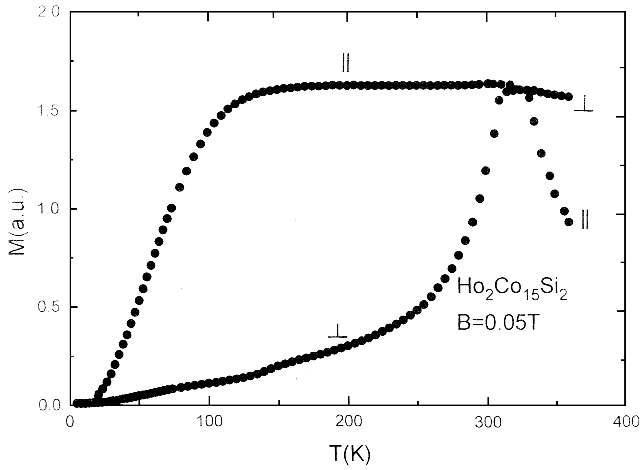

Fig. 4. Temperature dependence of the magnetization measured in a field of 0.05 T parallel and perpendicular to the *c*-direction of a single crystal of $Ho_2Co_{15}Si_2$.

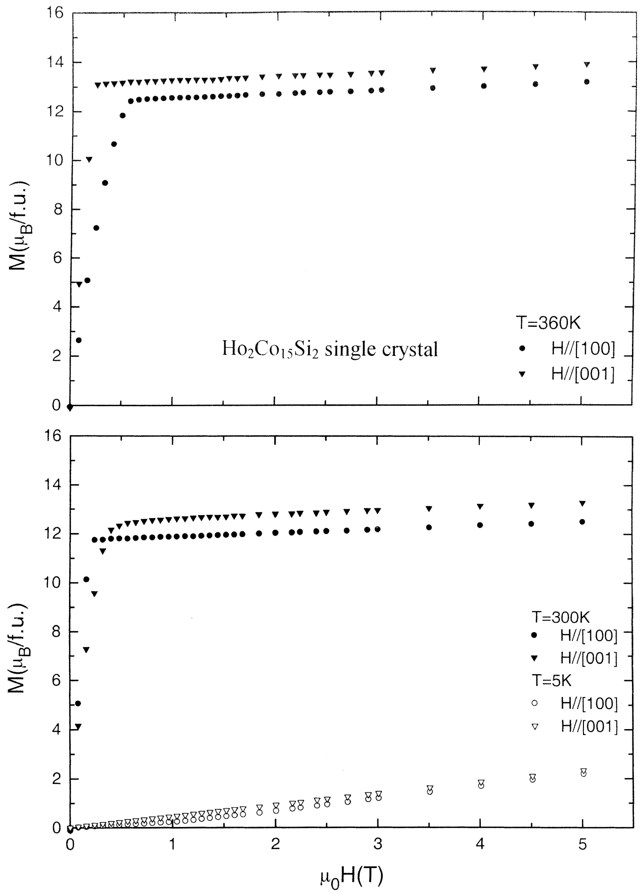

Fig. 5. Field dependence of the magnetization measured at various temperatures with the field applied parallel and perpendicular to the *c*-direction of a single crystal of $Ho_2Co_{17-x}Si_2$.

easy-magnetization direction changes from parallel to the *c*-axis above about $T_{SR} = 320$ K to perpendicular to the *c*-axis below this temperature. This transition has also been confirmed by measurements of the angle dependence of the magnetization for temperatures above and below T_{SR} [19]. The magnetization vanishes in both curves when reaching cryogenic temperatures. This is due to the antiparallel coupling between the Ho and Co moments and the fact that the Ho-sublattice moment is small above room temperature whereas it increases strongly towards lower temperatures. Eventually, the Ho and Co sublattice magnetization have become equal in size and mutually cancel their contribution to the total magnetization. This feature is the reason that the field dependence of the magnetization at 5 K resembles that of an antiferromagnet, as can be seen in the lower part of Fig. 5.

The field dependence of the magnetization at a temperature well above T_{SR} is shown in in the top part of Fig. 5. From the magnetic isotherm measured with the field perpendicular to the *c*-axis (hard-direction) one derives that the anisotropy field at 360 K is fairly small, about 0.3 T. Note that the magnetization values of the isotherm corresponding to the easy-direction are lying above those of the hard-direction. This observation points to the occurrence of a modest magnetization anisotropy.

The magnetic isotherms measured at 300 K in the two directions are shown in the middle part of Fig. 5. This temperature is well below the spin-reorientation transition. The easy-magnetization direction is now perpendicular to the *c*-axis, which is revealed only in the field range below 0.5 T. At sufficiently high field strengths, the isotherm obtained with the field along the *c*-axis is also here located above that obtained with the field perpendicular to the *c*-axis. It means that the magnetization anisotropy has been conserved when passing through the spin-reorientation temperature. This magnetization anisotropy points to a substantial anisotropy of the Co-sublattice orbital moment. The presence of an orbital moment is generally held responsible for the occurrence of magnetocrystalline anisotropy. Experimental results obtained on RCo_5 compounds by Schweizer and Tasset [1] and Streever [20] have shown that there is an unusually large orbital moment associated with the 2c type Co atoms. This site corresponds to the 18f site in the R_2Co_{17} compounds, a site that is left unaffected by the Si substitution according to the substitution scheme presented above.

Spin-reorientation transitions are observed also in the other members of the $Ho_2Co_{17-x}Si_x$ series [21]. This can be seen in the magnetic phase diagram of $Ho_2Co_{17-x}Si_x$ compared with that of $Gd_2Co_{17-x}Si_x$ in Fig. 6. The concentration dependence of T_{SR} in the latter series results from the relative increase of the positive contributions of the Co-sublattice anisotropy. With increasing Si substitution, the area of the phase field where the easy-axis anisotropy prevails is seen to become strongly enlarged. In the magnetic phase diagram of $Ho_2Co_{17-x}Si_x$ this enlargement is considerably reduced because of the negative contribution of the Ho-sublattice anisotropy to the total anisotropy, stabilizing the phase field where the easy-plane

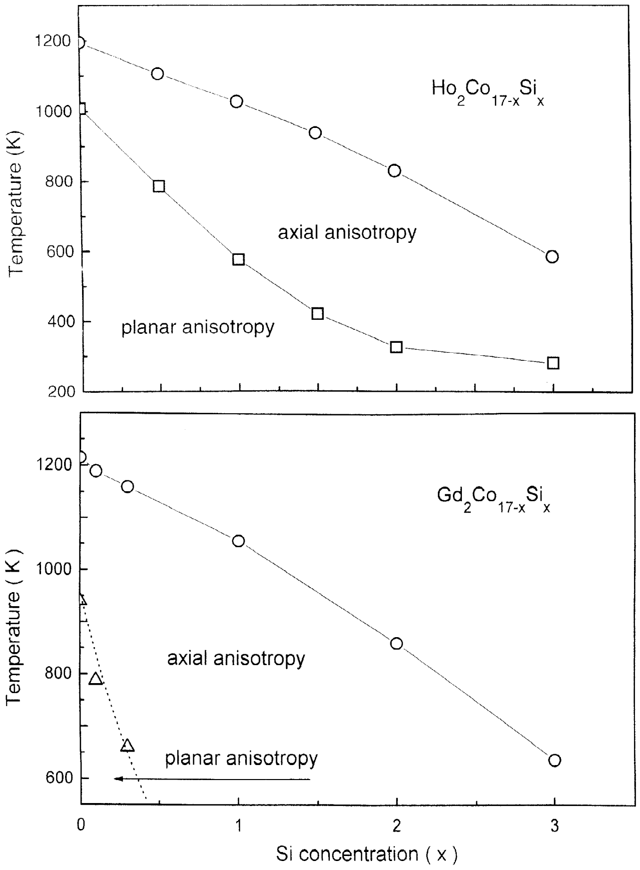

Fig. 6. Magnetic phase diagrams of the systems $Ho_2Co_{17-x}Si_x$ (top, [21]) and $Gd_2Co_{17-x}Si_x$ (bottom, [8]).

anisotropy prevails. Similar concentration dependent spin reorientation transitions have been observed in several other $R_2Co_{17-x}M_x$ systems in which there is a competition between the Co- and R-sublattice anisotropy.

4. Concluding remarks

In this report, a brief survey has been given of the behaviour of the Co-sublattice anisotropy in R_2Co_{17} compounds and the effect of preferential substitutions of non-magnetic atoms into some of the Co sites. Sign and magnitude of the magnetocrystalline anisotropy of the Co-sublattice in R_2Co_{17} compounds can be changed by substitution of several types of non-magnetic atoms into the various Co sites. A scheme for preferential site substitution has been presented, taking into account size effects as well as enthalpy effects. The preferential substitution of nonmagnetic atoms into the various Co sites and the expected anisotropy changes have been shown to agree with changes in the magnetocrystalline anisotropy as derived from magnetic measurements. The scheme for preferential site substitution makes it, therefore, possible to predict changes in anisotropy associated with a given substituent.

From magnetization studies on single crystals, it is derived that there is an anisotropy in the saturation moment of the Co-sublattice only when the easy-magnetization direction of the Co-sublattice is in the *c*-direction. Sign and magnitude of the Co saturation moment anisotropy is not affected when the rare earth sublattice forces the Co moments into their hard-direction.

Various types of spin-reorientation transitions occur in the temperature dependence of the magnetization. These can be due to a competition between the Co- and R-sublattice anisotropies but may also arise exclusively from temperature dependent changes of the Co-sublattice anisotropy.

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