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Structure and magnetic properties of $R_2Co_{17-x}Si_x$ ($x = 0$–3) compounds with R = Y and Pr

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Abstract. The influence of Si substitution for Co on the structure and magnetic properties of $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ ($x = 0$–3) compounds were investigated by means of x-ray diffraction and magnetization measurements. X-ray diffraction patterns demonstrate that all samples are single phase with the hexagonal Th_2Ni_{17}-type structure for $Y_2Co_{17-x}Si_x$ and the rhombohedral Th_2Zn_{17}-type structure for $Pr_2Co_{17-x}Si_x$ compounds, except for $Pr_2Co_{14}Si_3$ with a small amount of impurity phases. The unit-cell volume is found to decrease linearly with increasing Si concentration in both series. The Curie temperature decreases monotonically with increasing Si concentration at an approximate rate of 205 and 175 K per Si atom for the $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds, respectively. The saturation magnetic moments of $R_2Co_{17-x}Si_x$ (R = Y, Pr) decrease with increasing Si content and the decline rates are larger than that expected as a simple dilution. For $Y_2Co_{17-x}Si_x$, the substitution of Si has a significant effect on the magnetocrystalline anisotropy of the Co sublattice, and changes the easy magnetization direction from the basal plane to the *c*-axis at room temperature. For $Pr_2Co_{17-x}Si_x$, the Si substitution has not changed the easy magnetization direction at room temperature. However, the spin-reorientation transitions from the basal plane to the *c*-axis for this series with $0.5 \leqslant x \leqslant 2.4$ were observed above room temperature with increasing temperature. The spin-reorientation temperature T_{SR} first decreases with increasing Si content and then increases at higher x values ($x > 2$). The origin of this spin reorientation is interpreted by the competition between the Pr sublattice anisotropy and the Co sublattice anisotropy. This has been confirmed by the magnetocrystalline anisotropy measurements on $Y_2Co_{17-x}Si_x$.

1. Introduction

Rare-earth cobalt intermetallic compounds R_2Co_{17} have attracted much attention since the discovery of Sm_2Co_{17} magnets. It is hard to find practical applications for the R_2Co_{17} series compounds by themselves in the high-energy-product magnets, due to the unfavourable anisotropy, although they have higher saturation magnetization. These compounds have either weak uniaxial (e.g., Sm_2Co_{17}) or planar (e.g., Y_2Co_{17}, Pr_2Co_{17}) anisotropy. In previous studies, the effect of the various elemental substitutions (such as Ga, Al and Si) for Fe in the R_2Fe_{17} compounds on the formation, structure and magnetic properties, especially the magnetocrystalline anisotropy, are investigated [1–8]. The results indicate that these nonmagnetic atoms play an important role in determining the easy magnetization direction (EMD) of these compounds. Recent studies have shown that the substitution of nonmagnetic atoms Ga and Al has also a significant effect on the magnetocrystalline anisotropy in R_2Co_{17}-based compounds, such as the EMD of $Gd_2Co_{17-x}Al_x$ ($x \geqslant 5$) [9] and $Gd_2Co_{17-x}Ga_x$ ($x \geqslant 1$) [10] compounds are uniaxial at room temperature. In addition, the spin-reorientation transitions at higher temperature in $Pr_2Co_{17-x}Al_x$ [11] and $Pr_2Co_{17-x}Ti_x$ [12] compounds were observed. In this paper, the influence of the substitution of Si for Co in $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ ($x = 0$–3) compounds on the structure and magnetic properties is reported. We select R = Y, since yttrium is nonmagnetic and thus has no contribution to the net magnetocrystalline anisotropy as well as no contribution to the overall magnetic moment. Therefore, it is convenient for us to separately investigate the effect of Si substitution on the Co sublattice anisotropy and its magnetic moment.

2. Experiment

The $Y_2Co_{17-x}Si_x$ ($x = 0$, 1, 2 and 3) and $Pr_2Co_{17-x}Si_x$ ($x = 0$, 0.5, 1, 1.5, 1.7, 2, 2.2, 2.4 and 3) alloys were prepared by arc melting in an argon atmosphere of high purity. The raw materials of Y, Pr, Co, Si were at least 99.9% pure. The ingots were melted at least three times to ensure homogeneity. The as-cast ingots were sealed in an evacuated quartz tube and annealed under vacuum at 1273 K for 48 h, then quenched into water. X-ray diffraction using Cu Kα radiation in a Rigaku Rint 1400 was used to determine phase purity, crystal structure and lattice parameters. The saturation magnetic moment μ_s at 1.5 K was deduced from the data collected on free powder samples using an extracting sample magnetometer in a field up to 6.5 T. The Curie temperature T_C and spin-reorientation temperature T_{SR} were determined from the temperature dependence of magnetization measured with a Faraday balance ($T \geqslant 300$ K) or a vibration sample magnetometer in a field of 0.1 T. The aligned samples for the magnetocrystalline anisotropy studies were prepared by mixing the powder with epoxy resin and then aligning in a magnetic field of 1 T. The anisotropy fields were obtained from the magnetization curves measured along and perpendicular to the direction of alignment. The x-ray diffraction procedure was also used to determine the easy magnetization direction at room temperature.

3. Results and discussion

X-ray diffraction patterns indicate that all samples are single phase with the hexagonal Th_2Ni_{17}-type structure for $Y_2Co_{17-x}Si_x$ ($0 \leqslant x \leqslant 3$) and the rhombohedral Th_2Zn_{17}-type structure for $Pr_2Co_{17-x}Si_x$ ($0 \leqslant x \leqslant 3$) compounds, except for $Pr_2Co_{14}Si_3$ with a small amount of impurity phases. Figure 1(a) shows the typical x-ray diffraction pattern of $Y_2Co_{17-x}Si_x$ free powder samples with $x = 1$ and 2. The lattice parameters a, c and the unit-cell volumes v obtained from x-ray data are listed in table 1. The unit-cell volume is found to decrease linearly at a rate of about 1.8 Å^3 per Si atom for both series, as shown in figure 2. In order to compare the volumes of the hexagonal unit cells with the rhombohedral ones, here we multiplied the former by 3/2. Similar variations in lattice parameters were obtained in related systems [8, 13–15].

The saturation magnetizations μ_s of $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds at 1.5 K are presented in table 2 and are shown in figure 3 as a function of Si concentration. It is found that the μ_s decreases linearly with increasing Si content for both the Y and Pr compounds and the slopes of decline are nearly the same in both cases. From figure 3 one

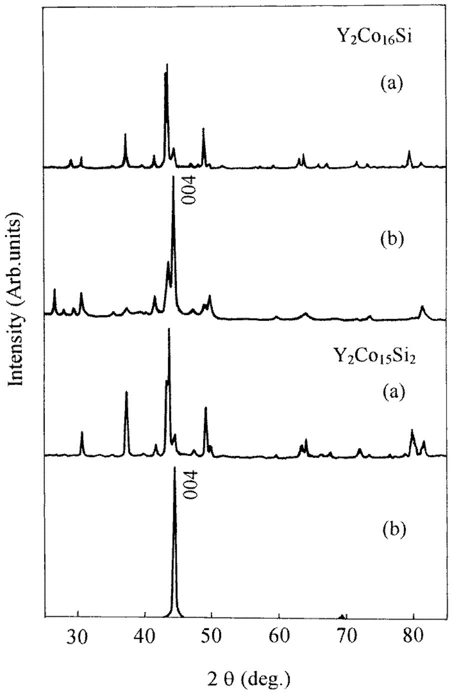

Figure 1. X-ray diffraction patterns at room temperature of unoriented (a) and oriented (b) $Y_2Co_{17-x}Si_x$ powder samples with $x = 1$ and 2.

Table 1. The lattice parameters a, c, c/a and unit-cell volume v of $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds.

Compounds	a (Å)	c (Å)	c/a	v (Å^3)
Y_2Co_{17}	8.347(4)	8.141(1)	1.463	491.2(7)
$Y_2Co_{16}Si_1$	8.334(7)	8.136(9)	1.464	489.5(1)
$Y_2Co_{15}Si_2$	8.321(0)	8.134(2)	1.466	487.7(5)
$Y_2Co_{14}Si_3$	8.324(6)	8.095(1)	1.459	485.8(3)
Pr_2Co_{17}	8.441(5)	12.273(3)	1.454	757.4(1)
$Pr_2Co_{16.5}Si_{0.5}$	8.430(2)	12.249(1)	1.453	753.8(9)
$Pr_2Co_{16}Si_1$	8.425(2)	12.237(4)	1.452	752.2(8)
$Pr_2Co_{15.5}Si_{1.5}$	8.421(5)	12.227(2)	1.452	750.9(9)
$Pr_2Co_{15.3}Si_{1.7}$	8.420(0)	12.236(1)	1.453	751.2(7)
$Pr_2Co_{15}Si_2$	8.419(4)	12.225(8)	1.452	750.5(4)
$Pr_2Co_{14.8}Si_{2.2}$	8.416(5)	12.223(4)	1.452	749.8(7)
$Pr_2Co_{14.6}Si_{2.4}$	8.419(6)	12.212(8)	1.451	749.7(7)
$Pr_2Co_{14}Si_3$	8.414(5)	12.211(9)	1.451	748.8(1)

can also observe that the declines in saturation magnetization are faster than that in the case of a simple magnetic dilution. Similar results have been reported in $R_2T_{17-x}M_x$ (T = Fe or Co; M = Ga, Al or Si) compounds [2, 3, 9, 10]. This phenomenon implies that the decrease in saturation magnetization is not only due to the reduced Co content, but also due to the decrease of the magnetic moment per Co atom.

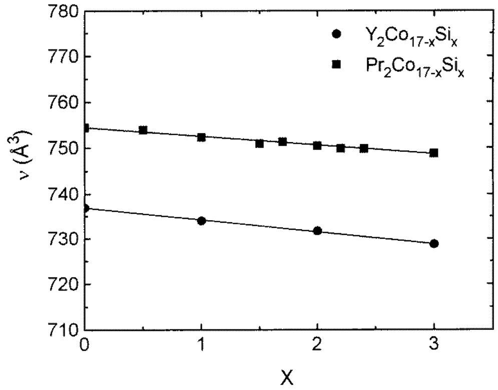

Figure 2. The unit-cell volumes v of $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds as a function of concentration x.

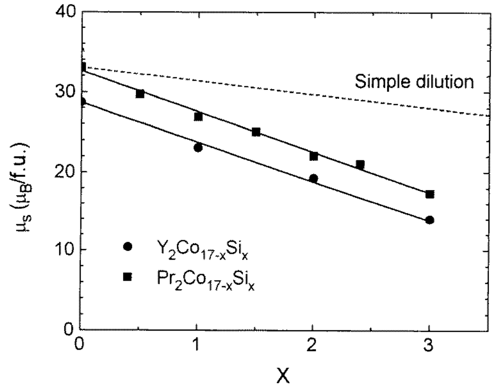

Figure 3. Concentration dependence of the saturation moments at 1.5 K for $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds.

The magnetic moment μ_s of $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds can be described as

$$\mu_s = (17 - x)\mu_{Co} + 2\mu_R. \tag{1}$$

Since the magnetic moment of yttrium $\mu_Y = 0$, we can easily obtain the μ_{Co} values using (1) from the μ_s values listed in table 2. The μ_{Co} values are found to decrease from 1.69 μ_B for $x = 0$ to 1.00 μ_B for $x = 3$. Assuming that the μ_{Co} values in $Pr_2Co_{17-x}Si_x$ compounds are equal to those in $Y_2Co_{17-x}Si_x$ compounds, the values of Pr magnetic moment μ_{Pr} can be derived also by using (1). The μ_{Pr} values are found to be lower than those of the free-ion magnetic moment, as can be seen in table 2, which infers a canted or fanlike spin arrangement.

The Curie temperatures T_C of $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds are also listed in table 2. T_C is found to decrease monotonically with increasing Si concentration for both Y and Pr compounds. This situation is dramatically different from that observed in $R_2Fe_{17-x}M_x$ (M = Ga, Al or Si) compounds where the Curie temperature first strongly increases with x before decreasing at higher x value [2–6]. The relatively low T_C in R_2Fe_{17}

Table 2. Curie temperature T_C (±5 K), magnetic moment μ_s, μ_{Co}, μ_R at 1.5 K (±1%) and easy magnetization direction (EMD) at room temperature of $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds.

Compounds	T_C (K)	μ_s (μ_B fu^{-1})	μ_{Co} (μ_B)	gJ (μ_B)	μ_R (μ_B)	EMD
Y_2Co_{17}	1202	28.7	1.69		0	plane
$Y_2Co_{16}Si_1$	1019	23.0	1.44		0	cone
$Y_2Co_{15}Si_2$	804	19.3	1.28		0	c-axis
$Y_2Co_{14}Si_3$	591	14.0	1.00		0	c-axis
Pr_2Co_{17}	1151	33.1	1.69	3.20	2.17	plane
$Pr_2Co_{16.5}Si_{0.5}$	1083	29.7				plane
$Pr_2Co_{16}Si_1$	986	26.9	1.44	3.20	1.93	plane
$Pr_2Co_{15.5}Si_{1.5}$	896	25.0				plane
$Pr_2Co_{15}Si_2$	770	22.0	1.28	3.20	1.40	plane
$Pr_2Co_{14.6}Si_{2.4}$	723	21.0				plane
$Pr_2Co_{14}Si_3$	665	17.3	1.00	3.20	1.65	plane

compounds may be due to the existence of antiferromagnetic coupling between Fe moments on certain sites: the preferential substitution of Ga, Al or Si on these sites can reduce the antiferromagnetic coupling and consequently enhance the T_C, while the magnetic coupling between Co moments in a metal system is always ferromagnetic, independent of Co moment and structure. It is well known that for the iron- and cobalt-rich rare-earth (R) transition-metal (T) compounds, the T–T interaction is the strongest one and primarily dominates the Curie temperature. Both the decrease of Co–Co exchange interaction and magnetic dilution result in a rapid decrease of T_C with increasing Si concentration. Similar weakening of Co–Co interactions with the replacement of Co by Ga, Al, Mn, Cr etc has been reported in other related systems [9, 10, 16, 17]. The decrease in T_C is estimated as 175 K and 205 K per Co atom replaced by Si in $Y_2Co_{17-x}Si_x$ and $Pr_2Co_{17-x}Si_x$ compounds, respectively.

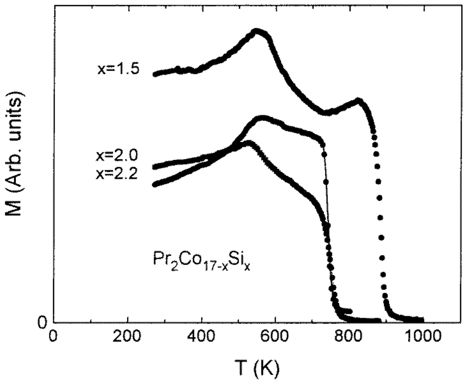

Figure 4. Temperature dependence of the magnetization of $Pr_2Co_{17-x}Si_x$ compounds with $x = 1.5$, 2 and 2.2.

X-ray diffraction measurements on magnetically aligned powder samples show that the EMD of $Y_2Co_{17-x}Si_x$ compounds changes from the basal plane to the cone for $x = 1$ and to the c-axis for $x \geqslant 2$. The x-ray diffraction patterns of oriented samples of $Y_2Co_{17-x}Si_x$ with $x = 1$ and 2 are presented in figure 1(b). For $Pr_2Co_{17-x}Si_x$ ($0 \leqslant x \leqslant 3$), the easy

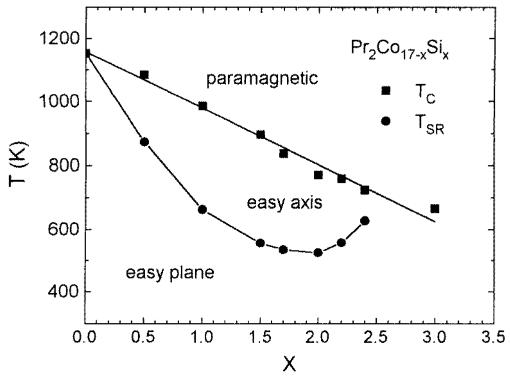

Figure 5. Concentration dependence of the Curie temperature and spin-reorientation temperature of $Pr_2Co_{17-x}Si_x$ compounds.

magnetization direction is all in basal plane at room temperature. At higher temperature $Pr_2Co_{17-x}Si_x$ ($0.5 \leqslant x \leqslant 3$) compounds show an anomaly on M–T curves, which we attribute to a spin-reorientation transition. As an example, the temperature dependence of the magnetization for the compounds with $x = 1.5$, 2 and 2.2 is shown in figure 4. The peak on the M–T curves is assumed to be at the spin-reorientation temperature T_{SR}. The concentration dependence of T_{SR} of $Pr_2Co_{17-x}Si_x$ compounds is shown in figure 5. The T_{SR} first decreases with increasing Si content and then increases at higher x values ($x > 2$), which is not similar to that in $Pr_2Co_{17-x}Al_x$ compounds [11].

It is known that the overall anisotropy of R_2Co_{17} compounds is determined from the sum of the Co sublattice anisotropy and the rare-earth sublattice anisotropy. For $Y_2Co_{17-x}Si_x$, since the nonmagnetic Y atoms have no contributions to the magnetocrystalline anisotropy, the total anisotropy of $Y_2Co_{17-x}Si_x$ arises only from the contribution of the Co sublattice. An increase in Si concentration leads to a decrease of the planar anisotropy and then changes the EMD from basal plane to c-axis for $x \geqslant 2$. A similar change was also observed in $Y_2Co_{17-x}Al_x$ [18], $Gd_2Co_{17-x}Ga_x$ [10] and $Gd_2Co_{17-x}Al_x$ [9] compounds. However, in the case of $Y_2Fe_{17-x}Si_x$ compounds, the EMD does not change until $x = 3$. It is possibly that the anisotropy constant K_1 of Y_2Co_{17} is about one order of magnitude smaller than that of Y_2Fe_{17} (K_1 at 4.2 K is -0.5×10^6 J m^{-3} in Y_2Co_{17} and -3.2×10^6 J m^{-3} in Y_2Fe_{17}, respectively [19]). Thus, the EMD for $Y_2Co_{17-x}Si_x$ is easier to transfer from the basal plane to c-axis than that for $Y_2Fe_{17-x}Si_x$ with increasing Si concentration.

The rare-earth sublattice anisotropy is determined by the product $\alpha_J A_{20}$, which is positive for Pr and leads to basal plane anisotropy. From the results of $Y_2Co_{17-x}Si_x$ studied here, we know that the substitution of Si for Co changes the anisotropy of the Co sublattice to easy c-axis. This is the reason that the spin reorientation occurs at higher temperature for $Pr_2Co_{17-x}Si_x$. The spin reorientation results from the competition between the Pr and Co sublattice anisotropies. At low temperatures the easy plane anisotropy of the Pr sublattice dominates, while at higher temperatures the easy axis anisotropy of Co sublattice takes over. The spin reorientation temperature for $Pr_2Co_{17-x}Si_x$ ($x \leqslant 2$) shifts to lower temperatures, which indicates that the magnitude of the easy axis anisotropy of Co sublattice increases with increasing Si content. It was reported that the change of the easy magnetization direction from the basal plane to the c-axis was attributed to a preferential substitution of the alloying elements (Al, Ti, Mn, Fe) for the plane seeking 6c dumbbell cobalt sites [11, 12, 16].

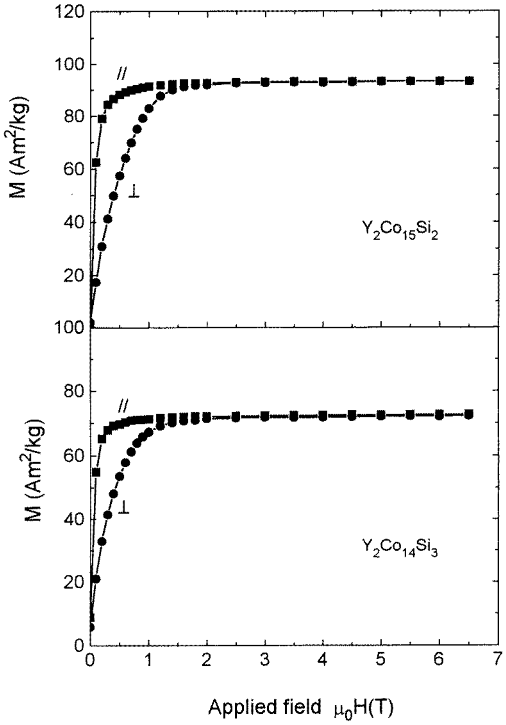

Figure 6. Magnetization curves of the orientated $Y_2Co_{17-x}Si_x$ samples with $x = 2$ and 3 measured along and perpendicular to the aligned directions at 1.5 K.

Inomata [20] has proposed that the 18f site of Co in Y_2Co_{17} makes a positive contribution to the anisotropy (c-axis), while the 18h, 9d and 6c sites make negative contributions (basal plane). In particular, the 6c site has the largest negative contribution. The reason for 6c site preference could explain the behaviours of magnetocrystalline anisotropy of $Y_2Co_{17-x}Al_x$ and $Pr_2Co_{17-x}Al_x$; maybe it can also explain the variation of the T_{SR} for $Pr_2Co_{17-x}Si_x$ compounds with $x \leqslant 2$. However, it cannot be applied to explain the magnetocrystalline anisotropy of $Pr_2Co_{17-x}Si_x$ compounds with $x > 2$. For $Pr_2Co_{17-x}Si_x$ ($x > 2$), the concentration dependence of T_{SR} may be caused by a decrease of the Co anisotropy or an increase of the Pr sublattice anisotropy due to an increase of the absolute value of A_{20} with increasing Si substitution. This problem is not clear until now and needs to be studied in detail. The change in Co sublattice anisotropy could be seen from the anisotropy field of $Y_2Co_{17-x}Si_x$ with $x = 2$ and 3. Figure 6 shows the magnetization curves of the orientated $Y_2Co_{17-x}Si_x$ samples with $x = 2$ and 3 measured along and perpendicular to the aligned direction at 1.5 K. The anisotropy field at 1.5 K, obtained by the extrapolation procedure from the magnetization curves measured along and perpendicular to the aligned direction, is slightly larger for $x = 2$ ($\mu_0 H_A = 1.4$ T) than that for $x = 3$ ($\mu_0 H_A = 1.2$ T). The hard axis magnetization curves were analysed to determine anisotropy constants K_1 and K_2 ($K_1 = 0.2$ MJ m^{-3}, $K_2 = 0.15$ MJ m^{-3} for $Y_2Co_{15}Si_2$ and $K_1 = 0.07$ MJ m^{-3}, $K_2 = 0.1$ MJ m^{-3} for $Y_2Co_{14}Si_3$, respectively) using the method developed for hexagonal single crystals [21]. The influences of polycrystalline particles and misalignment were ignored. The anisotropy field values, calculated as $H_A = 2(K_1 + 2K_2)/M_s$, are 1.4 T for

$x = 2$ and 1.1 T for $x = 3$, respectively, which agree well with those obtained by the extrapolation procedure.

It is interesting to note that the substituent effect on magnetic anisotropy for $Pr_2Co_{17-x}Si_x$ systems studied in the present work is not the same as that for $Pr_2Co_{17-x}M_x$ (M = Ga [22], Al [11], Ti [12], Mn [16]) studied earlier. For example, for $Pr_2Co_{17-x}Al_x$, a spin-reorientation transition was observed above room temperature and the spin-reorientation temperature was found to decrease drastically with Al content [11]. For $Pr_2Co_{17-x}Ga_x$, no spin reorientation was observed in the whole temperature range [21]. The Ga, Si and Al substitutions in Pr_2Co_{17} compounds show an exceptionally different effect on the magnetocrystalline anisotropy. The reasons are possibly not only the different preferential sites, but also the effect of different band structure caused by the Ga, Si and Al substitution on magnetic anisotropy as discussed in [23].

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