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Magnetic properties of $R_2Co_{17-x}Al_x$ compounds (R = Ho, Dy, Y)

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Abstract

The magnetic properties of $Ho_2Co_{17-x}Al_x$ and $Dy_2Co_{17-x}Al_x$ compounds ($x = 2, 3, 4$ and 5) have been investigated by magnetic measurements and X-ray diffraction. The compounds with $x = 5$ do not stabilise in a 2–17 structure. The $Ho_2Co_{17-x}Al_x$ compounds with $x = 2$, 3 and 4 show with increasing temperature, a spin reorientation from the basal plane to the c-axis. The origin of this reorientation is the change in the Co-sublattice anisotropy from planar to easy-axis upon substitution of Al for Co. This has been confirmed by measurements on $Y_2Co_{17-x}Al_x$. The spin reorientation shifts to lower temperatures with increasing Al concentration, indicating that the strength of the easy-axis Co-sublattice anisotropy increases. As the Dy-sublattice anisotropy is significantly larger than the Ho-sublattice anisotropy, the Dy compounds show no spin reorientation. The Curie temperatures of both series decreases linearly but strongly with increasing Al concentration.

Keywords: Magnetic materials; Antiferromagnetism; Spin reorientation transition

1. Introduction

In recent years, much work has been done to improve the hard-magnetic properties of R_2Fe_{17}-based compounds. Yelon et al. [1] have found that in $Nd_2Fe_{17-x}Al_x$ the substitution of Fe by Al not only increases the Curie temperature, but also changes the easy direction of magnetisation to the c-axis. Yan et al. [2] showed that the Fe-sublattice anisotropy is responsible for this. In an earlier investigation, we found evidence for a spin reorientation in $Nd_2Co_{13}Al_4$[3]. The origin was explained in terms of a change in the Co-sublattice anisotropy upon Al substitution as has been reported by Strnat [4]. To study this reorientation in more detail, Al-substituted R_2Co_{17} compounds were made with other rare-earth atoms, having the same sign of the second-order Stevens factor ($\alpha_J > 0$) such as Dy and Ho. The $Y_2Co_{17-x}Al_x$ compounds have been measured to verify our conclusions.

2. Experimental procedure

Samples of $R_2Co_{17-x}Al_x$ with R = Dy, Ho, Y and $x = 2$, 3, 4 and 5 were prepared by arc melting starting materials of at least 99.9% purity. After arc melting, the samples were wrapped into Ta foil, sealed into an evacuated quartz tube and annealed at 900°C for 4 weeks (R = Dy, Ho) or 3 weeks (R = Y). X-ray diffraction diagrams showed that the samples with $x = 2$, 3 and 4 are all ordered in the rhombohedral Th_2Zn_{17} structure, except for $Ho_2Co_{15}Al_2$, which is ordered in the hexagonal Th_2Ni_{17} structure. The annealed samples with $x = 2$ and 3 are single phase, whereas samples with $x = 4$ contain amounts of $R(Co, Al)_5$ and AlCo.

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The amount of second phase decreases slightly after a subsequent anneal treatment at 1000°C for 4 weeks. The samples with $x = 5$ consist solely of R(Co, Al)$_5$ and AlCo, which are ordered in the CaCu$_5$ and CsCl structure, respectively.

Aligned samples for X-ray-diffraction experiments were made by mixing the powdered material with silicon paste. The mixture was aligned for 1 h on a cylindrical permanent magnet producing a field of 0.3 T. The sample holder and magnet were put in an oven to align at elevated temperatures. The magnetic measurements were made on free powder material on a SQUID magnetometer in the temperature range 5–300 K in magnetic fields up to 5.5 T. The high-temperature measurements were made on a home-built magnetometer based on the Faraday principle. In these experiments, polycrystalline bulk samples were used in order to avoid oxidation as far as possible, and to be more sensitive to spin reorientations. The values of the magnetisation of the bulk samples measured on the Faraday balance, were scaled to match with the powder-magnetisation curves measured on the SQUID.

3. Results and discussion

Results of magnetic measurements showing the temperature dependence of the magnetisation for $Ho_2Co_{17-x}Al_x$ and $Dy_2Co_{17-x}Al_x$ compounds are displayed in Figs. 1 and 2, respectively. For the compounds with $x = 3$ and 4, the R-sublattice magnetisation at 5 K is larger than the Co-sublattice magnetisation, resulting in a compensation point. For the Dy compounds, the compensation points are at higher temperatures. This is due to a larger de Gennes factor, resulting in a stronger Dy–Co exchange, and a higher ordering temperature of the Dy-sublattice. The non-zero value at the compensation temperature for $x = 4$, can be ascribed to the impurity phases.

At higher temperatures, all Ho compounds show a large anomaly not present in the parent compound Ho_2Co_{17} [5]. X-ray diffraction measurements on an aligned sample of $Ho_2Co_{13}Al_4$ were made just below and above the anomaly. From the X-ray diffraction patterns in Fig. 3, it is clearly seen that the compound has planar anisotropy at 268 K and axial anisotropy at 368 K. The anomaly is therefore identified as a spin reorientation transition from the basal plane to the c-axis. At low temperatures the easy-plane anisotropy of the Ho-sublattice dominates [6], while at higher temperatures the easy-axis anisotropy of the Co-sublattice takes over.

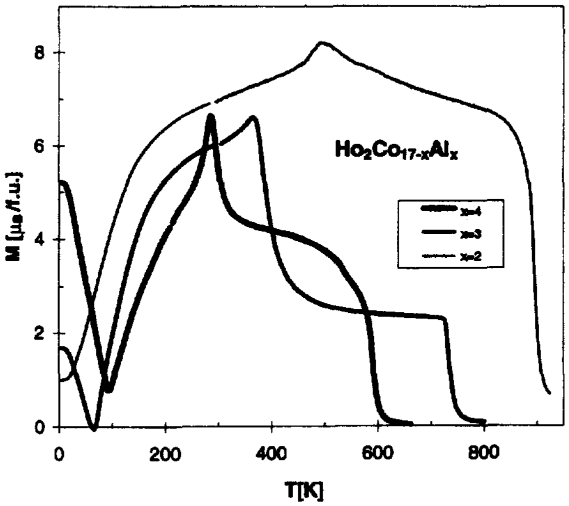

Fig. 1. Temperature dependence of the magnetisation of $Ho_2Co_{17-x}Al_x$ compounds, measured in a field of 0.1 T.

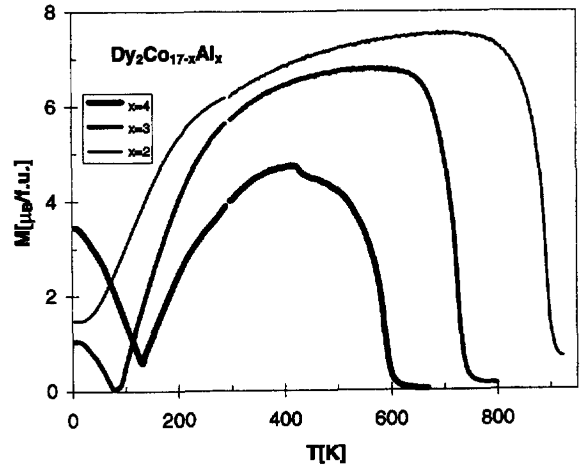

Fig. 2. Temperature dependence of the magnetisation of $Dy_2Co_{17-x}Al_x$ compounds, measured in a field of 0.1 T.

In general, the Co-sublattice has easy-plane anisotropy in R_2Co_{17} compounds, in which case no spin reorientation occurs [7]. However, substitution of Al for Co changes the anisotropy of the Co-sublattice to easy-axis. This has be shown earlier in the compounds $Y_2Co_{17-x}Al_x$, where the Y-sublattice has no anisotropy [4] and is confirmed by our measurements. The spin reorientation for $Ho_2Co_{17-x}Al_x$ shifts to lower temperatures with increasing Al concentration (Fig. 1). This indicates that the magnitude of the easy-axis anisotropy of the Co-sublattice increases with increasing Al concentration. The change in anisotropy is argued to be caused by a preferential filling of the 6c dumbbell site [8, 9]. Our neutron-diffraction measurements on $Nd_2Co_{17-x}Al_x$ show indeed a preferential occupation for the 6c site, in the sense that Al completely avoids the 9d site [3].

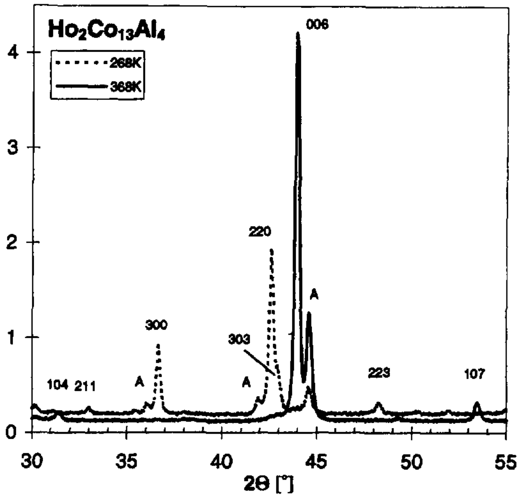

Fig. 3. Room temperature Cu–Kα X-ray diffraction patterns of $Ho_2Co_{13}Al_4$ samples, magnetically aligned at 368 K (solid) and 268 K (dashed). Peaks indexed with 'A' belong to the Ho(Co, Al)$_5$ impurity phase.

The $Dy_2Co_{17-x}Al_x$ compounds with $x = 2$ and 3 show no spin reorientation and have easy-plane anisotropy in the whole temperature range studied. This can be explained by the size of the anisotropy of the rare-earth sublattice. At elevated temperatures, this anisotropy is mainly determined by the second-order crystal field term

$$K(R) = K_1^R = -\tfrac{3}{2}\alpha_J\langle r^2\rangle\langle O_2^0\rangle A_2^0 . \tag{1}$$

The second-order crystal-field parameter A_2^0, the 4f-electron radial expectation value $\langle r^2\rangle$ and the expectation value of the Stevens operator $\langle O_2^0\rangle$ are all of roughly equal size for the Dy and Ho

Table 1

Structural and magnetic properties of $R_2Co_{17-x}Al_x$ compounds. EMD relative to c-axis. T_{co} is the compensation temperature, T_{sr} the spin reorientation temperature and T_c the Curie-temperature. Values between brackets are less reliable.

Compound	a [Å]	c [Å]	Structure	EMD // or ⊥	M_r(5 K) (μ_B/f.u.)	M_{co}(5 K) (μ_B/Co)	T_{co} (K)	T_{sr} (K)	T_c (K)
Ho_2Co_{17}[a]	8.332	12.170	hex.	⊥	8.36	1.67	–	–	1173[b]
$Ho_2Co_{15}Al_2$	8.389	12.258	hex.	⊥ → //	1.2	1.41	–	493	897
$Ho_2Co_{14}Al_3$	8.419	12.281	rho.	⊥ → //	2.1	1.28	66	367	738
$Ho_2Co_{13}Al_4$	8.447	12.293	rho.	⊥ → //	(5.8)	1.09	92	286	606
Dy_2Co_{17}[a]	8.357	12.176	hex.	⊥	7.4	1.61	–	–	1152[b]
$Dy_2Co_{15}Al_2$	8.404	12.257	rho.	⊥	1.8	1.45	–	–	896
$Dy_2Co_{14}Al_3$	8.430	12.281	rho.	⊥	1.3	1.34	Z80	–	727
$Dy_2Co_{13}Al_4$	8.460	12.305	rho.	⊥ → //	(4.8)	1.17	131	(415)	592
Y_2Co_{17}[a]	8.351	12.200	hex.	⊥ → //	27.8	1.64	–	(1000)[c]	1167[b]
$Y_2Co_{15}Al_2$	8.409	12.264	rho.	//	21.0	1.40	–	–	899
$Y_2Co_{14}Al_3$	8.436	12.290	rho.	//	17.1	1.22	–	–	718
$Y_2Co_{13}Al_4$	8.453	12.318	rho.	//	(13.0)	1.00	–	–	635

[a] Lattice parameters and magnetisation of R_2Co_{17} compounds obtained from [11,12,9] for R = Ho, Dy and Y, respectively

[b] Values obtained from Laforest et al. [5].

[c] According to phase diagram of Chen et al. [13].

compounds. Because of the difference in values of the second-order Stevens factors, $\alpha_j = 22.2$ for Ho and 63.5 for Dy [10], the high-temperature anisotropy of the Dy-sublattice is considerably larger. Thus for $Dy_2Co_{15}Al_2$ and $Dy_2Co_{14}Al_3$, the Co-sublattice axial anisotropy is not strong enough to overcompensate the Dy-sublattice planar anisotropy. For $Dy_2Co_{13}Al_4$, the Co-sublattice anisotropy might have become large enough to explain the anomaly at 415 K as a spin reorientation. However, this could not be confirmed by X-ray diffraction and therefore it cannot be excluded that the anomaly is caused by the Dy(Co, $Al)_5$ impurity phase.

An overview of the structural and magnetic properties of the compounds is given in Table 1. Upon Al substitution, the lattice expands monotonously, the expansion in the *ab*-plane being somewhat larger. The remanent magnetisation was determined by extrapolating the magnetisation data measured at low fields to zero field. The values for the compounds with $x = 4$ are less reliable because of the impurity phases present. To calculate the average Co moment, it was assumed that the Dy and Ho moments have their free-ion value. For $x = 3$ and 4, the Co moments derived in this way are considerably larger than for $Y_2Co_{17-x}Al_x$. Either overestimation of the rare-earth moments or non-perfect anti-parallel alignment may be responsible for the discrepancy. Due to the decrease in the value of the Co moment upon Al substitution, the Curie temperature decreases more than is expected on the basis of a simple dilution model. Nevertheless, the decrease in Curie temperature is almost linear.

Acknowledgements

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