Analysis of spin-phase diagrams for $R_xY_{1-x}Co_5$ (R identical to Pr, Tb, Dy and Ho) and $R_xPr_{1-x}Co_5$ (R identical to Sm, Gd, Tb, Dy, Ho and Er)

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Abstract. The spin-phase diagrams for the pseudo-binary compounds of $R_xY_{1-x}Co_5$ (R ≡ Pr, Tb, Dy and Ho) and $R_xPr_{1-x}Co_5$ (R ≡ Sm, Gd, Tb, Dy, Ho and Er) are reproduced well by the calculations which use the fitted R–Co exchange field and CEF parameters evaluated previously by some of the authors of this paper and co-workers by comparing the calculations with other experimental data.

1. Introduction

The values of the exchange field H_{ex} and the crystalline-electric-field (CEF) parameters A_{nm} at the magnetic rare-earth ion sites in RCo_5 (R ≡ Pr, Nd, Sm, Gd, Tb, Dy, Ho and Er) [1], $R_xY_{1-x}Co_5$ (R ≡ Pr [2], Nd [3], Tb [4] and Dy [4]) and $R_xSm_{1-x}Co_5$ (R ≡ Pr [2] and Nd [5]) have been evaluated by some of the authors of this paper and co-workers by comparing the calculations and experimental data. The experimental data, which have been reported by previous workers, include mainly the temperature dependence of the spontaneous magnetization $M_s(T)$ of the compound, the temperature dependence of the magnetic moment $M_R(T)$ of the rare-earth ion, the temperature dependence of the cone angle $\theta(T)$ made by M_s with the c axis, and the magnetization curves $M(H)$ along the crystal axes, all measured on single crystals. In the calculations, the rare-earth ions were assumed to be triply ionized, and the anisotropies of the magnetic moment M_{Co} of the Co sublattice and of the R–Co exchange interaction have been taken into account.

This paper shows that the spin-phase diagrams of the pseudo-binary compounds of $R_xY_{1-x}Co_5$ (R ≡ Pr, Tb, Dy and Ho) and $R_xPr_{1-x}Co_5$ (R ≡ Sm, Gd, Tb, Dy, Ho and Er) which have been reported by several workers [6–12] can be reproduced well by the calculations which use the fitted parameters in the above-mentioned studies. For $Ho_xR_{1-x}Co_{5+0.5x}$ (R ≡ Y and Pr), including $HoCo_{5.5}$, however, the parameters which have been evaluated for $HoCo_{5.5}$ in the previous work [1] are slightly revised for a better fit.

2. Details of the calculation

The RCo_5 (R ≡ rare earths) compounds have a $CaCu_5$-type hexagonal structure with the space group $P6/mmm$ [6–12], in which the rare-earth site has the point symmetry D_{6h}.

Some rare-earth ions are replaced by the Co dumbbells randomly for non-stoichiometric RCo_{5+y} compounds [6, 9–12]. It was assumed that the rare-earth ions are triply ionized. The Hamiltonian of the R ion in the $R_xR'_{1-x}Co_5$ compounds consists of the spin–orbit coupling interaction, the CEF interaction, the R–Co exchange interaction and the Zeeman energy, i.e.

$$\mathcal{H}(\mathrm{R}, x) = \lambda(\mathrm{R})\boldsymbol{S}(\mathrm{R}) \cdot \boldsymbol{L}(\mathrm{R}) + \mathcal{H}_{\mathrm{CEF}}(\mathrm{R}, x) + 2\mu_{\mathrm{B}}\boldsymbol{S}(\mathrm{R}) \cdot \boldsymbol{H}_{\mathrm{ex}}(\mathrm{R}, x, T, \theta_{\mathrm{Co}}) + \mu_{\mathrm{B}}[\boldsymbol{L}(\mathrm{R}) + 2\boldsymbol{S}(\mathrm{R})] \cdot \boldsymbol{H}. \tag{1}$$

Here, $\boldsymbol{S}(\mathrm{R})$ and $\boldsymbol{L}(\mathrm{R})$ are the total spin and orbital angular moments of the R ion, and $\boldsymbol{H}$ is the applied field. The CEF interaction in the $\langle 100\rangle$ coordinate system with the z and x axes along the c and a axes is formulated as

$$\mathcal{H}_{\mathrm{CEF}}(\mathrm{R}, x) = \sum_{\mathrm{R}=2,4,6} A_{n0}(\mathrm{R}, x)C_{n0}(\mathrm{R}) + A_{66}(\mathrm{R}, x)[C_{66}(\mathrm{R}) + C_{6_n,-6}(\mathrm{R})] \tag{2}$$

where A_{nm} are the CEF parameters,

$$C_{nm}(\mathrm{R}) = \sum_j \frac{4\pi}{2n+1} Y_{nm}(\theta_{\mathrm{R}j}, \varphi_{\mathrm{R}j}) \tag{3}$$

$Y_{nm}(\theta_{\mathrm{R}j}, \varphi_{\mathrm{R}j})$ are the spherical harmonics, and $\theta_{\mathrm{R}j}$ and $\varphi_{\mathrm{R}j}$ are the polar and azimuthal angles of the position vector $\boldsymbol{r}$ of the jth 4f electron. The R–R exchange interaction, which is much smaller than the R–Co exchange interaction, was neglected. Both the magnetic moment $\boldsymbol{M}_{\mathrm{Co}}(x, T, \theta_{\mathrm{Co}})$ of the Co sublattice and the exchange field $\boldsymbol{H}_{\mathrm{ex}}(\mathrm{R}, x, T, \theta_{\mathrm{Co}})$ are anisotropic and are represented as

$$\boldsymbol{M}_{\mathrm{Co}}(x, T, \theta_{\mathrm{Co}}) = \boldsymbol{M}_{\mathrm{Co}}(x, T)[1 - p(T)\sin^2\theta_{\mathrm{Co}}] \tag{4}$$

$$\boldsymbol{H}_{\mathrm{ex}}(\mathrm{R}, x, T, \theta_{\mathrm{Co}}) = \boldsymbol{H}_{\mathrm{ex}}(\mathrm{R}, x, T)[1 - p'(T)\sin^2\theta_{\mathrm{Co}}] \tag{5}$$

where θ_{Co} is the cone angle between $\boldsymbol{M}_{\mathrm{Co}}$ and the c axis, $p(0) = 0.037$ and $p'(0) = 0.020$ [13]. $p(T)$ was taken from that of YCo_5 [14] and the relation $p'(T)/p'(0) = p(T)/p(0)$ was assumed. $\boldsymbol{H}_{\mathrm{ex}}(\mathrm{R}, x, T)$ was assumed to be proportional and antiparallel to $\boldsymbol{M}_{\mathrm{Co}}(x, T)$ as

$$\boldsymbol{H}_{\mathrm{ex}}(\mathrm{R}, x, T) = -H_{\mathrm{ex}}(\mathrm{R}, 1, 0)\boldsymbol{M}_{\mathrm{Co}}(x, T)/M_{\mathrm{Co}}(1, 0). \tag{6}$$

The values of $M_{\mathrm{Co}}(x, T)/M_{\mathrm{Co}}(x, 0)$ are treated in the same way as those of YCo_5 after scaling the different Curie temperature T_{C} [14]. $M_{\mathrm{Co}}(x, T = 0)$ is linear to the R concentration x with the value of $M_{\mathrm{Co}}(1, 0)$ given in [1]. For a given applied field $\boldsymbol{H}$ and a direction of $\boldsymbol{H}_{\mathrm{ex}}(\mathrm{R}, x, T, \theta_{\mathrm{Co}})$, the eigenvalues $E_n(\mathrm{R}, x)$ and eigenstates $|n(\mathrm{R}, x)\rangle$ ($n = 1, 2, \ldots, \sum_J (2J+1)$) are obtained by diagonalizing the $\sum_J (2J+1) \times \sum_J (2J+1)$ matrix of equation (1). Mixing of the first excited J multiplet for the Pr ion with $\lambda(\mathrm{Pr}) = 610$ K [15], mixing of the two lowest excited J multiplets for the Sm ion with $\lambda(\mathrm{Sm}) = 410$ K [15], and no mixing for the other heavy rare-earth ions were taken into account.

The free energy is given by

$$F(\boldsymbol{H}, \boldsymbol{H}_{\mathrm{ex}}, T) = -xk_{\mathrm{B}}T\ln[Z(\mathrm{R}, x)] + K_{1\mathrm{Co}}(x, T)\sin^2\theta_{\mathrm{Co}} - \boldsymbol{M}_{\mathrm{Co}}(x, T, \theta_{\mathrm{Co}}) \cdot \boldsymbol{H} \tag{7}$$

for the $R_xY_{1-x}Co_5$ system and

$$F(\boldsymbol{H}, \boldsymbol{H}_{\mathrm{ex}}, T) = -xk_{\mathrm{B}}T\ln[Z(\mathrm{R}, x)] - (1-x)k_{\mathrm{B}}T\ln[Z(\mathrm{Pr}, x)] + K_{1\mathrm{Co}}(x, T)\sin^2\theta_{\mathrm{Co}} - \boldsymbol{M}_{\mathrm{Co}}(x, T, \theta_{\mathrm{Co}})\cdot\boldsymbol{H} \tag{8}$$

for the $R_xPr_{1-x}Co_5$ system. Here

$$Z(\mathrm{R}, x) = \sum_n \exp\left(\frac{-E_n(\mathrm{R}, x)}{k_{\mathrm{B}}T}\right) \tag{9}$$

and $K_{1\mathrm{Co}}(x, T)$ is the magnetocrystalline anisotropy constant of the Co sublattice per formula unit, which is taken from that of YCo_5 after scaling the different Curie temperature $T_{\mathrm{C}}(\mathrm{R}, x)$ [14]. $K_{1\mathrm{Co}}(x, T)$ and $T_{\mathrm{C}}(\mathrm{R}, x)$ are linear to the R concentration x with the values of $K_{1\mathrm{Co}}(1, 0)$ given in [1] and $T_{\mathrm{C}}(\mathrm{R}, 1)$ given in [16]. The equilibrium direction of $\boldsymbol{H}_{\mathrm{ex}}(\mathrm{R}, x, T, \theta_{\mathrm{Co}})$ was determined from minimization of the free energy.

Table 1. The values of $2\mu_{\mathrm{B}}H_{\mathrm{ex}}(0)$ and A_{nm} for the R ions in $R_xY_{1-x}Co_5$ (R ≡ Pr, Tb, Dy and Ho) and $R_xPr_{1-x}Co_5$ (R ≡ Sm, Gd, Tb, Dy, Ho and Er) compounds.

R	x	$2\mu_{\mathrm{B}}H_{\mathrm{ex}}(0)$ (K)	A_{20} (K)	A_{40} (K)	A_{60} (K)	A_{66} (K)	Reference
Pr	1.0–0.0	1300	25	−75	250	−600	[1]
Sm	1.0–0.0	440	−330	−50	0	0	[1]
Gd	1.0–0.0	290					[1]
Tb	1.0	265	−340	−240	0	0	[1,4]
	0.8	261	−350	−230	0	0	[4]
	0.6	256	−375	−225	0	0	[4]
	0.4	249	−390	−220	0	0	[4]
	0.3	246	−400	−215	0	0	This work
	0.2	243	−405	−210	0	0	This work
	0.1	240	−415	−205	0	0	This work
Dy	1.0	235	−425	−140	180	0	[4]
	0.8	232	−455	−175	180	0	This work
	0.6	228	−485	−210	180	0	This work
	0.5	227	−500	−230	180	0	[4]
	0.35	224	−520	−250	180	0	[4]
	0.2	222	−545	−280	180	0	[4]
	0.1	220	−560	−300	180	0	[4]
Ho	1.0–0.0	220	−590	−250	0	70	This work
	1.0	220	−615	−260	−30	0	[1]
Er	1.0–0.0	210	−350	−100	0	0	[1]

The magnetic moments of the R ions are given by

$$M_{\mathrm{R}}(x, T) = \sum_n \frac{\mu_n(\mathrm{R}, x)\exp[-E_n(\mathrm{R}, x)/k_{\mathrm{B}}T]}{Z(\mathrm{R}, x)} \tag{10}$$

where

$$\mu_n(\mathrm{R}, x) = -\mu_{\mathrm{B}}\langle n(\mathrm{R}, x)|\boldsymbol{L}(\mathrm{R}) + 2\boldsymbol{S}(\mathrm{R})|n(\mathrm{R}, x)\rangle \tag{11}$$

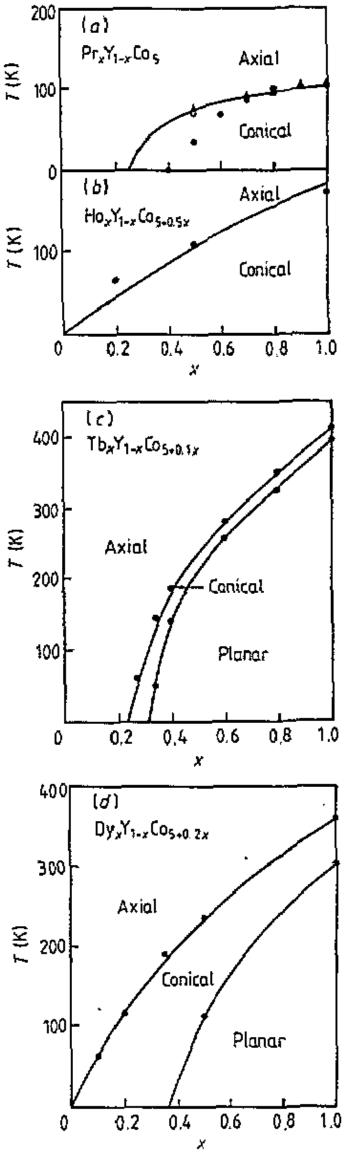

Figure 1. Spin-phase diagrams for $R_xY_{1-x}Co_5$ with (*a*) R ≡ Pr, (*b*) R ≡ Ho, (*c*) R ≡ Tb and (*d*) R ≡ Dy: ●, experimental data from [6] for R ≡ Pr, from [9] for R ≡ Tb, from [10] for R ≡ Dy and from [11] for R ≡ Ho; ○, experimental data from [9] for R ≡ Pr; ▲, experimental data from [8] for R ≡ Pr; ——, calculations.

and the magnetic moments of the $R_xY_{1-x}Co_5$ and $R_xPr_{1-x}Co_5$ systems are given by

$$M(T) = -\partial F/\partial H = xM_R(x,T) + M_{Co}(x,T,\theta_{Co}) \tag{12}$$

$$M(T) = -\partial F/\partial H = xM_R(x,T) + (1-x)M_{Pr}(x,T) + M_{Co}(x,T,\theta_{Co}) \tag{13}$$

respectively.

3. Results and discussion

Table 1 lists the values of the parameters $H_{ex}(T=0)$ and A_{nm} used in this work for the Pr,

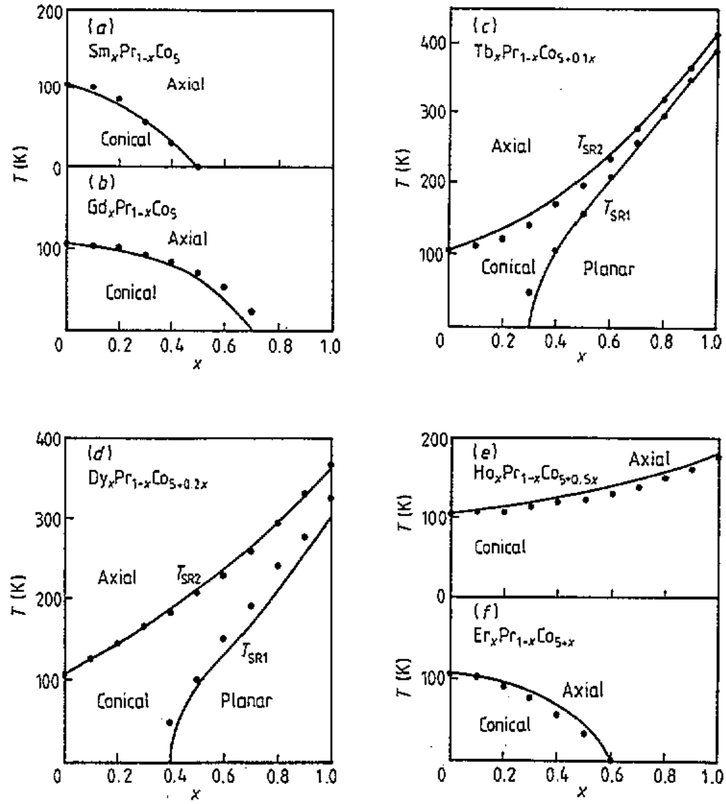

Figure 2. Spin-phase diagrams for $R_xPr_{1-x}Co_5$ with (*a*) R ≡ Sm, (*b*) R ≡ Gd, (*c*) R ≡ Tb, (*d*) R ≡ Dy, (*e*) R ≡ Ho and (*f*) R ≡ Er: ●, experimental data from [6]; ——, calculations.

Sm, Gd, Tb, Dy, Ho and Er ions in $R_xY_{1-x}Co_5$ (R ≡ Pr, Tb, Dy and Ho) and $R_xPr_{1-x}Co_5$ (R ≡ Sm, Gd, Tb, Dy, Ho and Er). The parameters for the Ho ions in $HoCo_{5.5}$ previous evaluated [1] are also listed for reference. The parameters for the Pr, Sm, Gd, Ho and Er ions are invariant with the R concentration x, while those for the Tb and Dy ions vary slightly with x in a linear way. The parameters A_{nm} are invariant with temperature.

Figures 1 and 2 and figures 4 and 5 show comparisons of the calculations with experiments. The full curves represent the calculations, and the symbols the experiments. The agreement between them is satisfactory. Figures 1(*a*)–(*d*) show the spin-phase diagrams for $R_xY_{1-x}Co_5$ with R ≡ Pr, Ho, Tb and Dy, respectively. For lower-x $Pr_xY_{1-x}Co_5$ compounds, three independent experimental data are available [6–8], and our calculation reproduces the results of [7, 8]. Figures 2(*a*)–(*f*) show the spin-phase diagrams for $R_xPr_{1-x}Co_5$ with R ≡ Sm, Gd, Tb, Dy, Ho and Er, respectively. Figures 3(*a*)–(*c*) demonstrate the calculated cone angles of M_{Pr}, M_R, M_{Co} and M_s at 4.2 K for $R_xPr_{1-x}Co_5$ with R ≡ Gd, Dy and Ho, respectively. Figure 4 shows the temperature dependence of the cone angle of M_s for $Ho_xY_{1-x}Co_{5+0.5x}$ (x = 1.0, 0.5 and 0.2) and those of M_{Co} and M_{Ho} for $HoCo_{5.5}$, and figure 5 shows the temperature dependences of M_s, M_{Co} and M_{Ho} for $HoCo_{5.5}$.

Figure 6 shows the ground-state energies for the rare-earth ions in RCo_5 at 0 K as functions of the cone angle of M_{Co}. It can be seen that the Co sublattice, Er and Sm ions have increasingly large axial magnetic anisotropy (MA). The axial MA values for the rare-

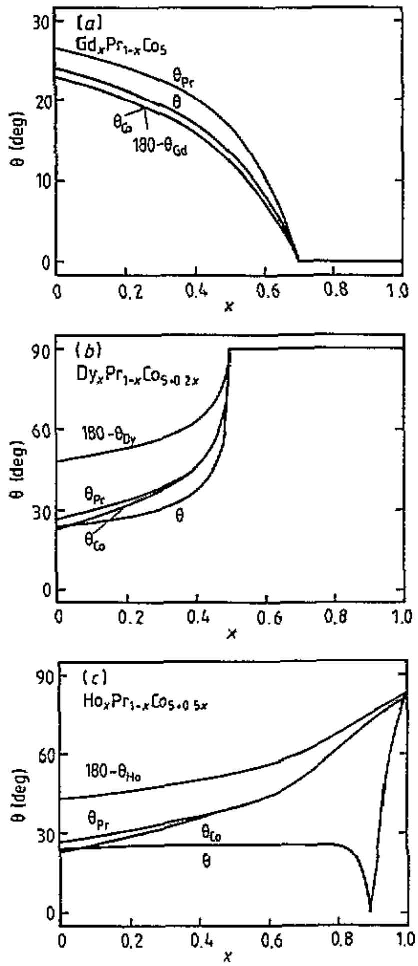

Figure 3. x dependences of the cone angles of M_{Pr}, M_R, M_{Co} and M_s at 4.2 K for $R_xPr_{1-x}Co_5$ with (*a*) R ≡ Gd, (*b*) R ≡ Dy and (*c*) R ≡ Ho.

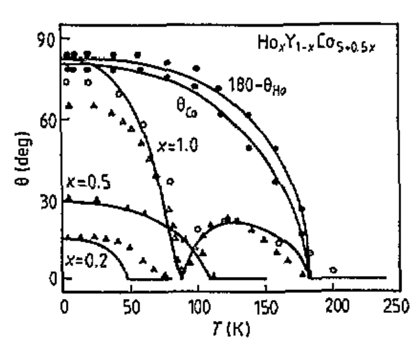

Figure 4. Temperature dependences of the cone angle of M_s for $Ho_xY_{1-x}Co_{5+0.5x}$ ($x = 1.0$, 0.5 and 0.2) and those of M_{Ho} and M_{Co} for $HoCo_{5.5}$: △, ▲, experimental data from [11]; ○, ●, experimental data from [12]; ——, calculations.

earth ions are connected with the positive second-order Stevens coefficients. The Pr ion has an easy cone magnetic structure with small MA, and the Ho, Tb and Dy ions have an easy basal-plane magnetic structure with increasingly large MA from Ho to Dy. The second-order Stevens coefficients are negative for these ions. The competition between the axial MA of the Co sublattice and the cone or planar MA of the rare-earth ions results in the cone magnetic

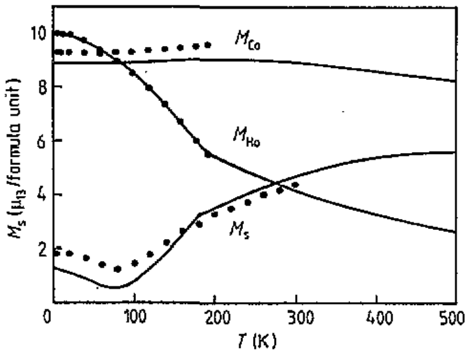

Figure 5. Temperature dependences of the spontaneous magnetization and magnetic moments of the Co sublattice and Ho ion for $HoCo_{5.5}$; ●, experimental data from [12]; ——, calculations.

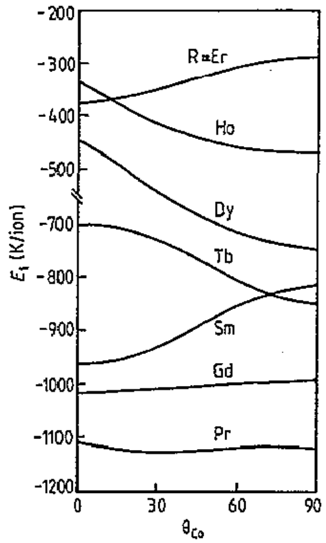

Figure 6. The ground-state energies of the rare-earth ions in RCo_5 at 0 K as functions of the cone angle of M_{Co}.

structure for $PrCo_5$ and $HoCo_{5.5}$ and the basal-plane magnetic structure for $TbCo_{5.1}$ and $DyCo_{5.2}$ at low temperatures. Since the MA of the rare-earth ions decreases more rapidly than the MA of the Co sublattice, the magnetic structure of $R_xY_{1-x}Co_5$ transforms from conical to axial for R ≡ Pr and Ho and from planar to conical and then to axial for R ≡ Tb and Dy with decrease in x and increase in temperature. The spin-phase diagrams for the $R_xPr_{1-x}Co_5$ compounds can be explained in the same way.

It is noticeable that, although there is strong evidence to show that the valence of the Pr ion in $PrCo_5$ is fluctuating [2], the parameters for the ion which have been evaluated on the assumption that the ion is triply ionized reproduce the series of experiments on $R_xPr_{1-x}Co_5$ successfully as shown in this work and [2].

Acknowledgments

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