Spin Reorientation Phenomena in $(R_{1-x}R'_x)_2Co_{14}B$ Compounds *

T. Myojin[a], T. Ohno[b], K. Mizuno[c], A. Tsujimura[d], and K. Kojima[e]

[a] Takamatsu National College of Technology, Takamatsu, 761 Japan
[b] Faculty of Engineering, Tokushima University, Tokushima, 770 Japan
[c] Faculty of Integrated Arts and Sciences, Tokushima University, Tokushima, 770 Japan
[d] Faculty of Engineering, Tokushima Bunri University, Kagawa Shido, 769-21 Japan
[e] Faculty of Integrated Arts and Sciences, Hiroshima University, Hiroshima, 734 Japan

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The variation of NMR spectra and magnetization with temperature in $(R_{1-x}R'_x)_2Co_{14}B$ (R = Y or Gd, R′ = Tb, Dy or Ho $0 \le x \le 1$) have been measured. These compounds undergo spin reorientation at a temperature T_{SR} when Y and Gd are substituted by Tb, Dy and Ho, and the temperature T_{SR} increases with the fraction x. Phase diagrams of spin arrangement in these systems have been obtained. The results are discussed from the view point of competition between the crystalline electric field and the Co-R exchange interaction.

Key words: $R_2Co_{14}B$, Spin reorientation, Magnetic anisotropy, NMR, Magnetization.

1. Introduction

$R_2Co_{14}B$ compounds (R = rate earth) exhibit outstanding magnetic properties. Magnetic anisotropies play a very important role in these compounds. Although $Y_2Co_{14}B$ and $Gd_2Co_{14}B$ with S-state R ions show only a planar spin arrangement, $Tb_2Co_{14}B$, which is characterized by a negative Stevens factor, prefers an axial anisotropy at low temperatures. Due to the tendency of the Co sublattice to become planar, $Tb_2Co_{14}B$ undergoes a spin reorientation with increasing temperature. That is, in $Tb_2Co_{14}B$ the spins are ordered parallel to the c-axis at low temperatures, but in the c-plane above the spin reorientation temperature T_{SR} up to the Curie temperature T_C. A wide variety of magnetic properties of $R_2Co_{14}B$ arises from the fact that the R ion is subjected not only to the Co-R exchange field but also to the crystalline electric field [1].

In order to investigate the spin reorientation mechanism microscopically, we have measured the dependence of the spin reorientation temperature T_{SR} on composition by NMR and magnetization measurements. $R_2Co_{14}B$ constitutes an isostructural group of compounds crystallizing tetragonally with space group $P4_2/mnm$ for R = Y, La, Pr, Nd, Gd and Tb. Recently we have reported the phase diagrams of spin arrangements in $(R_{1-x}Tb_x)_2Co_{14}B$ (R = Y and Gd) [2] and $(Y_{1-x}R'_x)_2Co_{14}B$ (R′ = Dy and Ho) [3]. In this paper we extend those works to $(Gd_{1-x}R'_x)_2Co_{14}B$ (R′ = Dy and Ho).

2. Experimental

Samples were prepared from 99.9% pure elements by using an induction furnace, and annealed in vacuum-sealed quartz tubes at 920 °C for 10 days. X-ray diffraction with Cu-K_α radiation at room temperature shows that the compounds $(Gd_{1-x}R'_x)_2Co_{14}B$ (R′ = Dy and Ho) have the same tetragonal structure as $Nd_2Fe_{14}B$ up to $x = 0.7$. Zero field NMR spectra were measured at 4.2, 77 and 300 K with a conventional spin echo spectrometer by plotting the spin-echo intensities with changing the NMR frequency step by step in the range 90 ~ 200 MHz. The magnetizations at 0.5 kOe were measured by a vibrating sample magnetometer from 77 K up to above the Curie temperatures.

3. Results and Discussion

The low field magnetization versus temperature curve for a certain x shows a cusp or step like peak from which one can determine the spin-reorientation temperature T_{SR}. Figure 1 exhibits some typical curves

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Reprint requests to Prof. Takahisa Myojin.

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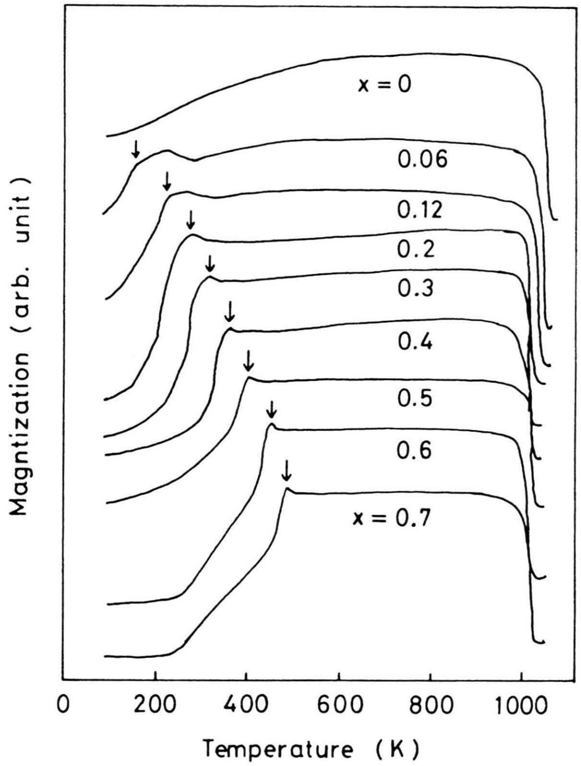

Fig. 1. Magnetization versus temperature curves for $(Gd_{1-x}Dy_x)_2Co_{14}B$. The arrows indicate the spin reorientation temperature T_{SR}.

of $(Gd_{1-x}Dy_x)_2Co_{14}B$ compounds. With increasing temperature from 77 K, the magnetization increases monotonically up to T_{SR}, which implies antiparallel arrangement of the R and Co sublattice moments. After the cusps at T_{SR}, the magnetization again increases slightly and suddenly decreases just below the Curie temperature T_C. T_C's were determined by extraporating the steep decrease to zero magnetization. In the case of $(Gd_{1-x}Dy_x)_2Co_{14}B$ ($x = 0.8$), both the magnetization curve and the X-ray diffraction pattern were quite different from those of the compounds with $x \leqq 0.7$. This means that the tetragonal phase is stable up to $x = 0.7$. For small x ($= 0 \sim 0.1$) the cusps are not clear enough to obtain precise T_{SR} values.

Figures 2 and 3 show the variation of the ^{59}Co NMR spectra at 4.2 K in $(Gd_{1-x}R'_x)_2Co_{14}B$ (R' = Dy and Ho). With increasing x they change from the spectra for the planar spin arrangement ($x \leqq 0.04$ for R' = Dy, $x \leqq 0.08$ for R' = Ho) to those for the mixed state [4] ($0.04 < x < 0.1$ for R' = Dy, $0.08 < x < 0.2$ for R' = Ho) and those for the axial arrangement ($x \geqq 0.1$ for R' = Dy, $x \geqq 0.2$ for R' = Ho). These changes in the NMR spectra correspond to the spin reorientation.

The ^{59}Co NMR spectra at 77 K and 300 K in $(Gd_{1-x}Dy_x)_2Co_{14}B$ and $(Gd_{1-x}Ho_x)_2Co_{14}B$ have also been measured. As seen in Fig. 4, at 300 K the compound $(Gd_{1-x}Dy_x)_2Co_{14}B$ retains the same planar type spectrum for Dy fraction $x \leqq 0.2$ as for $Y_2Co_{14}B$ or $Gd_2Co_{14}B$. It changes to a different type of spectrum for $x \geqq 0.3$. This phenomenon means that at 300 K the compounds $(Gd_{1-x}Dy_x)_2Co_{14}B$ undergo some change of spin-arrangement in the Dy fraction range $0.2 < x < 0.3$. The spectra at 77 K in $(Gd_{1-x}Dy_x)_2Co_{14}B$ change in the same way as at 300 K, and the critical Dy fractions are 0.04 and 0.06. This indicates that at 77 K the compounds $(Gd_{1-x}Dy_x)_2Co_{14}B$ undergo a spin reorientation in the Dy fraction range $0.04 < x < 0.06$.

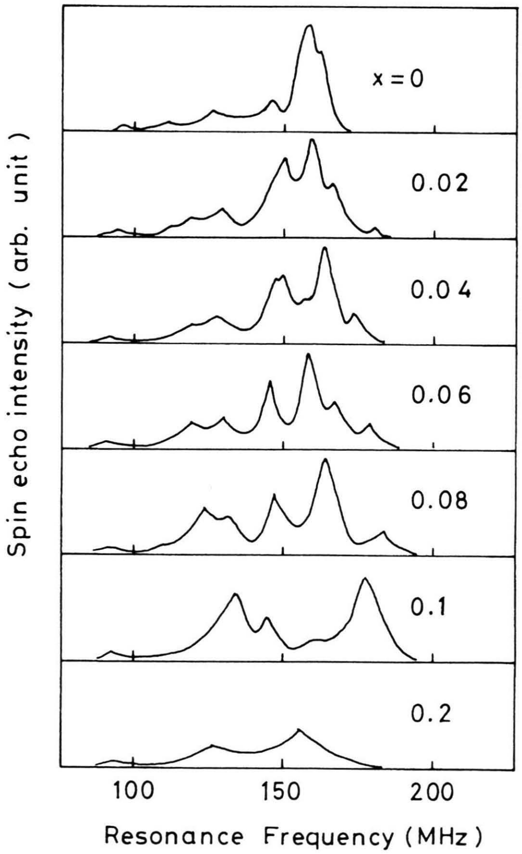

Fig. 2. The ^{59}Co NMR spectra in $(Gd_{1-x}Dy_x)_2Co_{14}B$ at 4.2 K.

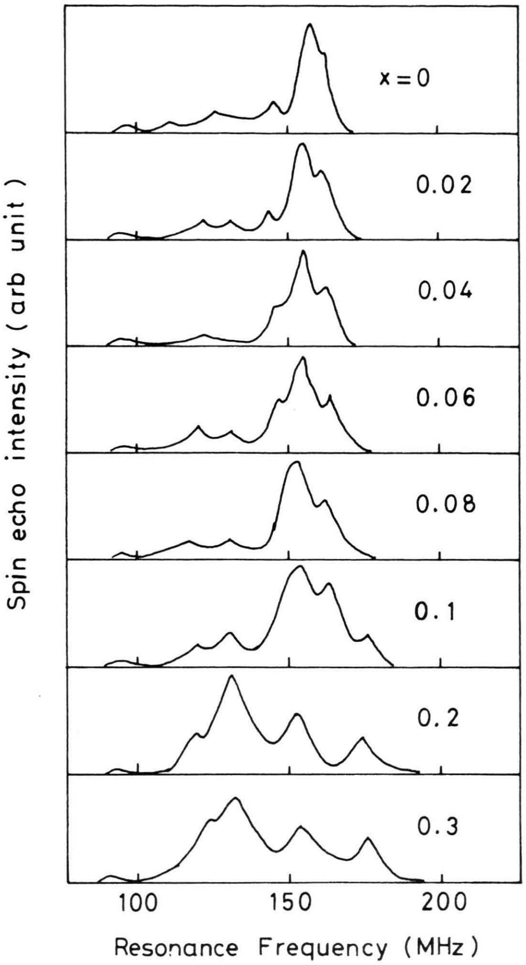

Fig. 3. The ^{59}Co NMR spectra in $(Gd_{1-x}Ho_x)_2Co_{14}B$ at 4.2 K.

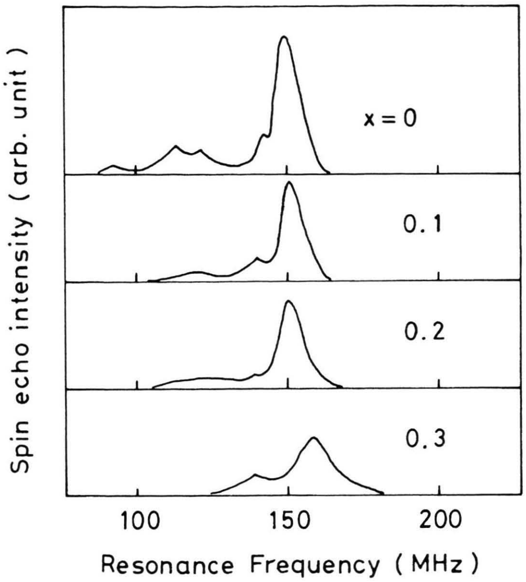

Fig. 4. The ^{59}Co NMR spectra in $(Gd_{1-x}Dy_x)_2Co_{14}B$ at 300 K.

The ^{59}Co NMR spectra at 300 K in $(Gd_{1-x}Ho_x)_2Co_{14}B$ show the same planar type for Ho fractions $x \leqq 0.6$ as for $Gd_2Co_{14}B$. This means that at 300 K the compounds $(Gd_{1-x}Ho_x)_2Co_{14}B$ do not change the spin-arrangement in this fraction range. However, at 77 K it is seen from the change of the ^{59}Co NMR spectra that the compound $(Gd_{1-x}Ho_x)_2Co_{14}B$ alters the spin arrangement in the Ho fraction range $0.1 < x < 0.2$. These changes in spin arrangement observed by the ^{59}Co NMR spectra correspond well to the cusps in the magnetization versus temperature curves. Therefore, we can say that we see the same spin reorientation phenomena in both measurements.

From the cusps in magnetization versus temperature curves and the changes in the NMR spectra we can propose phase diagrams of spin arrangements in $(Gd_{1-x}R'_x)_2Co_{14}B$ for R' = Dy and Ho, respectively. The results are shown in Figure 5. In this figure the bar 1 represents a Dy fraction range $(0.2 < x < 0.3)$ where the change of NMR spectra in $(Gd_{1-x}Dy_x)_2Co_{14}B$ was observed at 300 K. The bars 2 and 3 represent Dy and Ho fraction ranges, respectively, where the changes were observed at 77 K. These phase diagrams of spin arrangements in $(Y_{1-x}R'_x)_2Co_{14}B$ (R' = Dy and Ho) obtained in the previous paper [3] are cited here in Fig. 6 for comparison. It is understood that these phase diagrams are rather similar, because the R ions in both systems are in the S-state.

The phenomenon of the spin reorientation in these systems can be understood by taking into account the Co-R exchange field and the crystalline electric field (CEF). At low temperatures the $(R_{1-x}R'_x)_2Co_{14}B$ compounds (R = Y, Gd and R' = Dy, Ho) show an axial spin arrangement parallel to the *c*-axis like $Tb_2Co_{14}B$, because Dy and Ho are also characterized by a negative Stevens factor. The Co sublattice anisotropy in $(R_{1-x}R'_x)_2Co_{14}B$ favors magnetization in the tetragonal basal plane and overrules the rare-earth 4f anisotropy due to CEF at high temperature.

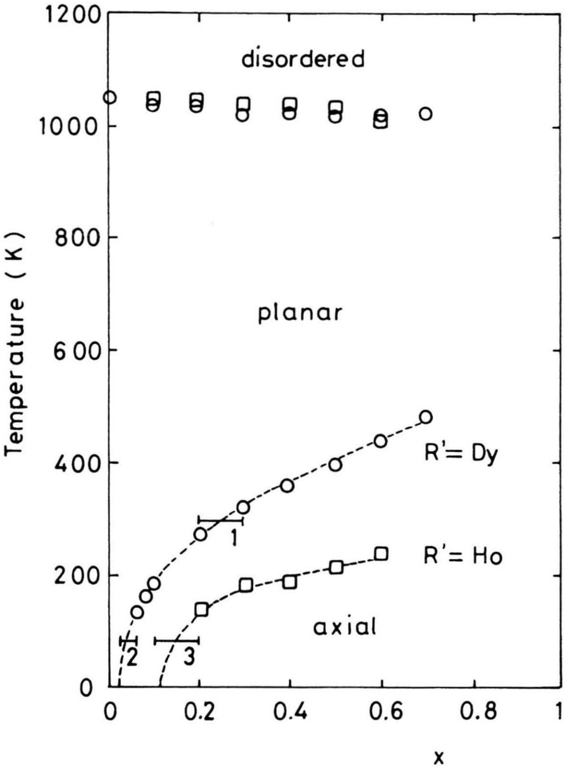

Fig. 5. Magnetic phase diagrams in $(Gd_{1-x}R'_x)_2Co_{14}B$ for R′ = Dy (○) and R′ = Ho (□). Dotted lines are guides to the eye. Bars represent the R′ fraction ranges where changes in NMR spectra are observed at each temperature.

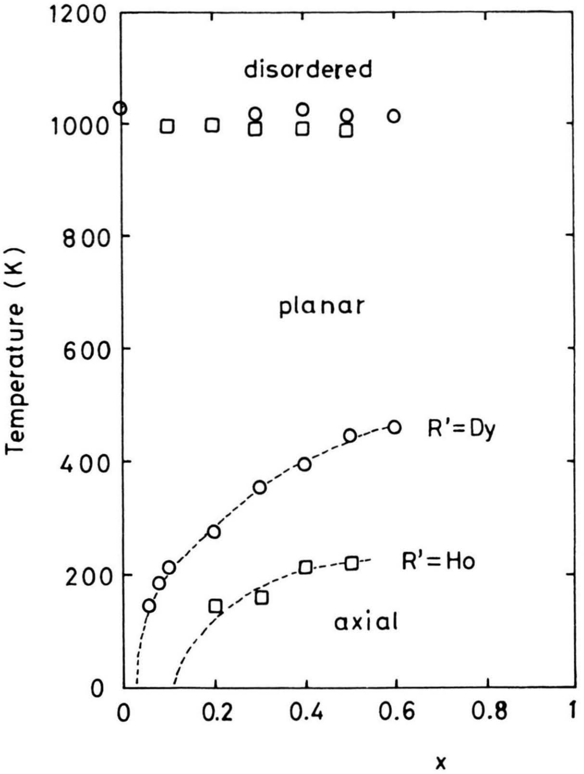

Fig. 6. Magnetic phase diagrams in $(Y_{1-x}R'_x)_2Co_{14}B$ for R′ = Dy (○) and R′ = Ho (□).

They exhibit a change in the easy direction from the *c*-axis to the basal plane at a temperature T_{SR}. $(R_{1-x}R'_x)_2Co_{14}B$ compounds crystallize in the same tetragonal structure with space group $P4_2/mnm$ as $Nd_2Fe_{14}B$. The R and R′ ions lie on the crystallographic f_1, f_2, g_1, and g_2 sites.

The Hamiltonians for an R (*i*) ion and an R′ (*i*) ion at the *i*-th site ($i = 1 \sim 4$ denote f_1, f_2, g_1, and g_2 sites) of the $(R_{1-x}R'_x)_2Co_{14}B$ structure in zero field are expressed by [1] (in units of μ_B)

$$H_R(i) = H_{CEF}(i) + 2(g_J - 1)\boldsymbol{J} \cdot \boldsymbol{H}_m, \tag{1}$$

and

$$H_{R'}(i) = H'_{CEF}(i) + 2(g_{J'} - 1)\boldsymbol{J}' \cdot \boldsymbol{H}_m, \tag{2}$$

where $H_{CEF}(i)$ and $H'_{CEF}(i)$ are the Hamiltonians describing the CEF potential of the R and R′ ions, respectively, $\boldsymbol{H}_m$ is the molecular field due to the R-Co exchange field (antiparallel to the Co magnetic moment) acting on the R ion with $\boldsymbol{J}$ and g_J or R′ ion with $\boldsymbol{J}'$ and $g_{J'}$.

The Hamiltonian for the description of the whole system of this structure in zero field is given by

$$H = \Sigma\,[(1-x)\,H_R(i) + x\,H_{R'}(i)] + 28\,K_{Co}(T)\sin^2\theta, \tag{3}$$

where $K_{Co}(T)$ is the uniaxial anisotropy energy per Co ion, and θ the angle between the magnetic moment of a Co ion and the [001] direction at temperature *T*. The summation is taken over $i = 1 \sim 4$ (f_1, f_2, g_1, and g_2 sites).

The total free energy *F* of $(R_{1-x}R'_x)_2Co_{14}B$ is given by

$$F = -(1-x)\,kT\,\Sigma \ln Z_R(i) - x\,kT\,\Sigma \ln Z_{R'}(i) + 28\,K_{Co}(T)\sin^2\theta, \tag{4}$$

where $Z_R(i)$ and $Z_{R'}(i)$ are the partition functions of the *i*-th ion for R and R′ with the eigenvalues of $H_R(i)$ and $H_{R'}(i)$ ($i = 1 \sim 4$), respectively. At a temperature T the equilibrium direction of the molecular field θ_m makes the free energy minimum. We will get T_{SR} at which θ_m changes from 0° to 90° by plotting θ_m against T.

We are now studying the fine structure of the ^{59}Co NMR spectra, and we are calculating T_{SR} from the free energy of the system in order to understand the behavior of the 4f sublattice magnetization as a function of temperature and rare-earth constitution.

4. Conclusion

The prepared compounds $(Gd_{1-x}R'_x)_2Co_{14}B$ (R′ = Dy and Ho) ($x \leqq 0.7$) have the same tetragonal structure as $Nd_2Fe_{14}B$. Low field magnetization versus temperature curves show cusps due to spin-reorientation. The changes in spin arrangement with R′ fraction x have been also found from the difference of NMR spectra between planar type and axial type at 4.2, 77, and 300 K. Phase diagrams of spin arrangement in these compounds have been obtained.

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