Magnetostriction anisotropy in the rare-earth compounds RCo_5 following spontaneous spin-flip transitions

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The temperature dependences of the crystal-lattice parameters of RCo_5 compounds (R = Pr, Tb, Dy, Ho) are studied with an x-ray diffractometer in the spin-flip region. The results are used to determine the magnetostriction constants $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ for temperatures corresponding to the middle of the spin-flip regions of these compounds (except $PrCo_5$). The values of $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ at $T = 0$ K are calculated on the basis of the one-ion model for all the compounds investigated, as well as for some other intermetallides of the RCo_5 type in which spontaneous spin-flip transitions do not occur.

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INTRODUCTION

It is known (see, e.g., Ref. 1) that in compounds of certain rare-earth metals (R) with cobalt, of the type RCo_5 (R = Pr, Nd, Tb, Dy, Ho), spin-flip phase transitions take place with change of temperature, wherein the magnetic moment is parallel to the basal plane of the hexagonal crystal lattice below a certain temperature T_1 and is directed along the c axis above a temperature T_2, while magnetic anisotropy of the type of "cone of easy-magnetization axes" is realized in the interval from T_1 to T_2. An exception is $PrCo_5$, whose magnetic moment does not deviate away from the c axis by more than 23° when the temperature is lowered down to 4.2 K.[2] We have shown in Ref. 3 that $NdCo_5$ exhibits in the spin-flip region thermal-expansion anomalies that are attributable to magnetostriction deformations of the crystal lattice due to rotation of the magnetic moment. It was assumed that similar anomalies should be observed in other RCo_5 compounds that undergo spin-flip transitions.

We report here an investigation of the effect of spin-flip on the thermal expansion of single-crystal RCo_5 (R = Pr, Tb, Dy, Ho) compounds in the basal plane and along the c axis, and determine from the resultant data the values of certain magnetostriction constants.

EXPERIMENTAL TECHNIQUE

The compounds investigated were obtained by fusing the components (of purity not worse than 99.9%) in an induction furnace in a helium atmosphere. When mixing the alloys, account was taken of the known shift[4] of the stoichiometry in the $PrCo_5$ series with increasing atomic number, so that the compositions of the alloys obtained were $PrCo_5$, $TbCo_{5,1}$, $DyCo_{5,2}$, and $HoCo_{5,5}$. The alloys were homogenized for 100 hr at 1000°C in a helium atmosphere. Metallographic and x-ray analyses have shown that the alloys are single-phase with hexagonal structure of $CaCu_5$ type. The largest grains (several millimeter in size) were cleaved from the ingots, and surfaces parallel to the crystallographic planes (100) and (001) were ground on them. The (400) and (004) reflections obtained with an x-ray diffractometer in Fe-$K\alpha$ radiation were used to investigate the temperature dependences of the crystal-lattice parameters $a(T)$ and $c(T)$, respectively, followed by calculation of the unit-cell volume

$$V=(\sqrt{3}/2)\,a^2c. \tag{1}$$

RESULTS AND DISCUSSION

The spin-flip phase transition is most strongly pronounced on the temperature dependences of $a(T)$ and $c(T)$ of $TbCo_{5.1}$ (Fig. 1), inasmuch as in this compound it takes place in a relatively small temperature interval (13 K). It can be seen from Fig. 1 that when the magnetization vector is rotated away from the basal plane (below $T_1 = 397$ K) towards the c axis (above $T_2 = 410$ K) the parameter c increases whereas the parameter a decreases. The dashed lines in Fig. 1 shows extrapolations of the $a(T)$ and $c(T)$ plots from the regions $T < T_1$ and $T > T_2$ into the spin-flip region. The temperatures T_1 and T_2, defined as the points on the $a(T)$ and $c(T)$ curves at which the latter begin to deviate from the extrapolated ones, agree well with published data obtained from magnetic measurements.

The hexagonal-crystal linear deformation due to magnetostriction can be represented, accurate to second-order constants, in the form[6]

$$\begin{aligned}\lambda=&\lambda_1^{\alpha,0}(\cos^2\beta_1+\cos^2\beta_2)+\lambda_2^{\alpha,0}\cos^2\beta_3\\&+\lambda_1^{\alpha,2}(\cos^2\beta_1+\cos^2\beta_2)(\cos^2\alpha_3-{}^1/_3)\\&+\lambda_2^{\alpha,2}\cos^2\beta_3(\cos^2\alpha_3-{}^1/_3)\\&+\lambda^{\gamma,2}[{}^1/_2(\cos^2\beta_1-\cos^2\beta_2)(\cos^2\alpha_1\\&-\cos^2\alpha_2)+2\cos\beta_1\cos\beta_2\cos\alpha_1\cdot\\&\times\cos\alpha_2]+2\lambda^{\varepsilon,2}(\cos\beta_1\cos\alpha_1\\&+\cos\beta_2\cos\alpha_2)\cos\beta_3\cos\alpha_3+\dots,\end{aligned} \tag{2}$$

where $\lambda_1^{\alpha,0}$, $\lambda_2^{\alpha,0}$, $\lambda_1^{\alpha,2}$, $\lambda_2^{\alpha,2}$, $\lambda^{\gamma,2}$, and $\lambda^{\varepsilon,2}$ are temperature dependent magnetostriction constants, α_i the angles between the magnetic-moment vector and the orthogonal coordinate axes, and β_i the angles between the deformation-measurement direction and the same coordinate axes. The magnetostriction along the c axis, i.e., for $\beta_1 = \beta_2 = 90°$, $\beta_3 = 0°$, is hence

$$\lambda_c=\lambda_2^{\alpha,0}+\lambda_2^{\alpha,2}(\cos^2\alpha_3-{}^1/_3). \tag{3}$$

The additional magnetostriction deformation accom-

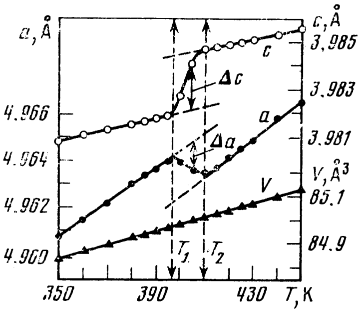

FIG. 1. Temperature dependences of the lattice parameters a and c and of the unit-cell volume V of the compound $TbCo_{5.1}$.

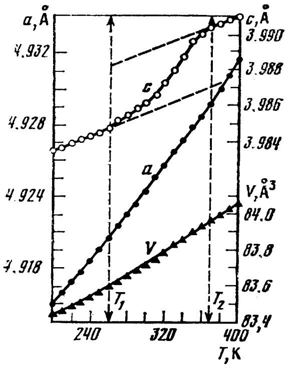

FIG. 2. The same as in Fig. 1, but for $DyCo_{5.2}$.

panying spin flip (see Fig. 1) is equal to the difference between the value of λ_c at a given temperature and the value λ_c' obtained by extrapolating the $c(T)$ curve from the region $T < T_1$ (where $\cos^2\alpha_3 = 0$):

$$\Delta c/c=\lambda_c-\lambda_c'=\lambda_2^{\alpha,0}+\lambda_2^{\alpha,2}(\cos^2\alpha_3-{}^1/_3)-\lambda_2^{\alpha,0}+{}^1/_3\lambda_2^{\alpha,2}=\lambda_2^{\alpha,2}\cos^2\alpha_3. \quad (4)$$

We have shown earlier[3] that in $NdCo_5$ the value of $\Delta c/c$ is indeed proportional to $\cos^2\alpha_3$. At $T > T_2$ we have $\alpha_3 = 0°$. so that $\lambda_2^{\alpha,2}$ in the spin-flip region can be determined from the size of the step on the $c(T)$ plot. The value of $\lambda_2^{\alpha,2}$ obtained by us for $TbCo_{5.1}$ at the temperature $T_{av} = (T_1 + T_2)/2$ is shown in Table I, which lists also the values of the constant $\lambda_1^{\alpha,2}$ calculated from $\Delta a/a$:

$$\Delta a/a=\lambda_1^{\alpha,2}\cos^2\alpha_3. \quad (5)$$

The values of $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ can be similarly calculated by extrapolation from the region $T > T_2$.

Equation (5) is valid if the constant $\lambda^{\gamma,2}$ is small, i.e., there are no rhombic distortions of the crystal lattice. In their presence the (400) x-ray line should split (or at least broaden), but this was not observed in either $TbCo_{5.1}$ or all other investigated compounds when the temperature was lowered to 4.5 K. The upper bound of $\lambda^{\gamma,2}$ is therefore estimated at 1×10^{-4}.

Allowing for the small $\lambda^{\gamma,2}$, the change in the bulk magnetostriction in the spin-flip transition can be expressed in the form

$$\Delta\lambda_V=(2\lambda_1^{\alpha,2}+\lambda_2^{\alpha,2})\cos^2\alpha_3. \quad (6)$$

In the case of $TbCo_{5.1}$ we have $2\lambda_1^{\alpha,2} = -\lambda_2^{\alpha,2}$, so that $\Delta\lambda_v = 0$. In the other RCo_5 compounds the spin flip has likewise no effect on the unit-cell volume (see Figs. 2–4). This may be evidence of conservation of the magnetic moment of a $3d$ metal (in this case, cobalt) under spontaneous spin-flip phase transitions in RCo_5, in contrast, say, to Tm_2Fe_{17}, where such a transition is accompanied[7] by a change of the Fe magnetic moment and by a corresponding change of V.

Figures 2 and 3 show plots of $a(T)$, $c(T)$, and $V(T)$ for $DyCo_{5.2}$ and $HoCo_{5.5}$. The spin-flip transition in these compounds is stretched out in temperature by almost 100 K (270–360 K in $DyCo_{5.2}$ (Ref. 5) and 45–170 K in $HoCo_{5.5}$ (Ref. 8)). This is probably why this transition is weakly discernible against the background of the large thermal expansion along the a axis. On the $c(T)$ curves values of T_2 that agree well with the published data are clearly pronounced, while inflections corresponding to T_1 are weakly discernible. We have therefore taken the value of T_1 for $DyCo_{5.2}$ from Ref. 5 and for $HoCo_{5.5}$ from Ref. 8. Since both the thermal expansion coefficients and the quantity $\lambda_2^{\alpha,2}$ change significantly over a wide range of spin-flip temperatures, we calculated $\lambda_2^{\alpha,2}$ by extrapolating $c(T)$ from high ($T > T_2$) and low ($T < T_1$) temperature and averaging, obtaining thus a value of $\lambda_2^{\alpha,2}$ corresponding to the midpoint of the spin-flip temperature interval. Since the phase transition is not noticeable on the $V(T)$ plots, we have $\Delta\lambda_V = 0$ and $\lambda_1^{\alpha,2} = -0.5\lambda_2^{\alpha,2}$. Our values of $\lambda_1^{\alpha,2}$ (T_{av}) and $\lambda_2^{\alpha,2}$ (T_{av}) for $DyCo_{5.2}$ and $HoCo_{5.5}$ are given in Table I.

Figure 4 shows plots $a(T)$, $c(T)$, and $V(T)$ for $PrCo_5$. As already noted, in $PrCo_5$ the magnetic moment deviates from the c axis by not more 23° ($T_2 = 105$ K). The possible effect is therefore strongly decreased. Along the c axis, for example:

$$\Delta c/c\leqslant\lambda_2^{\alpha,2}(\cos^2 0°-\cos^2 23°)\approx0.16\lambda_2^{\alpha,2}. \quad (7)$$

Thus, if $\lambda_2^{\alpha,2}$ in $PrCo_2$ has approximately the same value as in other RCo_5, the effect should be at the borderline of the measurement error ($\Delta c/c \sim 10^{-4}$). In addition, the $c(T)$ plot has an anomaly of the Invar type (not connected with the spin flip, since it extends to $T\approx400$ K), and this anomaly masks additionally the weak spin-flip effect. For these reasons the spin-flip phase transition did not manifest itself in the thermal expansion.

TABLE I.

	T_1, K	T_2, K	T_{av}, K	$\lambda_1^{\alpha,2}(T_{av})$, 10^{-3}	$\lambda_2^{\alpha,2}(T_{av})$, 10^{-3}	$\lambda_1^{\alpha,2}(0)$, 10^{-3}	$\lambda_2^{\alpha,2}(0)$, 10^{-3}
$NdCo_5$ [3]	235	295	265	−0.4	+0.8	–	–
$TbCo_{5,1}$	397	410	403.5	−0.3	+0.6	−1.8	+3.5
$DyCo_{5,2}$	260	370	315	−0.4	+0.8	−1.9	+3.8
$HoCo_{5,5}$	45	170	107.5	−0.25	+0.5	−0.6	+1.2

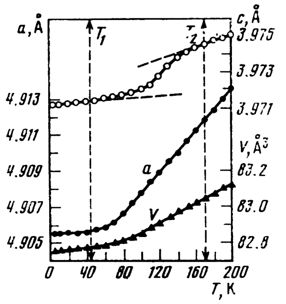

FIG. 3. The same as in Fig. 1, but for $HoCo_{5.5}$.

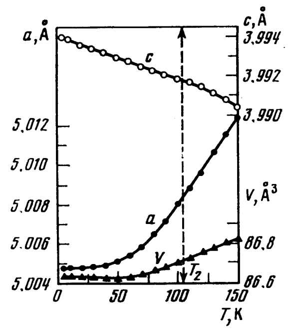

FIG. 4. The same as in Fig. 1, but for $PrCo_5$.

It is difficult to compare the magnetostriction constants $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ obtained by us for different RCo_5 compounds, because they were obtained for different temperatures. As shown repeatedly for other classes of (R-3d) compounds), their anisotropic magnetostriction is determined mainly by the R ions. Its temperature dependence takes within the framework of the one-ion model the form[9]

$$\lambda(T)=\lambda(0)\hat{I}_{5/2}[L^{-1}(\mu_R)], \tag{8}$$

where $\hat{I}_{5/2}$ is a normalized hyperbolic Bessel function, L^{-1} is the inverse of the Langevin function, and μ_R is the relative value of the magnetic moment of the rare-earth ion. The values of μ_R for $TbCo_{5.1}$, $DyCo_{5.2}$, and $HoCo_{5.5}$ were determined from the differences of the molecular magnetic moments μ_m of these compounds and YCo_5. The temperature dependences of μ_m were taken from Refs. 2 and 5. From the values of $\lambda_1^{\alpha,2}(T_{av})$ and $\lambda_2^{\alpha,2}(T_{av})$, using Eq. (8), we calculated the values of $\lambda_2^{\alpha,2}(0)$ and $\lambda_2^{\alpha,2}(0)$ given in the last two columns of Table I. In the case of $NdCo_5$ (as also of other light R) the calculated moment μ_R is subject to a very large error. It is therefore impossible to extrapolate the values of $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ for $NdCo_5$ to $T=0$ K.

Within the framework of the one-ion model of magnetic anisotropy and magnetostriction, the magnetostriction constants $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ should satisfy the relation 10

$$\lambda_{1,2}^{\alpha,2}\propto\alpha J(J-{}^1/_2)\langle r^2\rangle, \tag{9}$$

where α is the Stevens parameter, J is the total mechanical angular momentum of the R ion, and $\langle r^2\rangle$ is the mean squared radius of the $4f$ shell. It is assumed here that the crystal field and the screening remain constant on going from compound to compound, and only the shape and dimension of the $4f$ shell change. Assuming that this holds for all rare-earth metals and that the R ions are in the R^{3+} state, we can calculate the constants $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ for all RCo_5 with magnetoactive R ions at $T=0$ K. Taking the values of $\lambda_1^{\alpha,2}(0)$ and $\lambda_2^{\alpha,2}(0)$ obtained for $TbCo_{5.1}$ from Eq. (8) as the reference point (inasmuch as in $TbCo_{5.1}$ the spin-flip transition is most strongly pronounced and $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ are calculated more accurately than in the other RCo_5), we calculated from Eq. (9), the values of $\lambda_1^{\alpha,2}(0)$ and $\lambda_2^{\alpha,2}(0)$ listed in Table II using the data on α, J, and $\langle r^2\rangle$ from Ref. 11. As seen from a comparison of Tables I and II, the values of $\lambda_1^{\alpha,2}(0)$ and $\lambda_2^{\alpha,2}(0)$ obtained for $DyCo_{5.2}$ and $HoCo_{5.5}$ agree with those calculated by Eq (8) directly from the changes of the lattice parameters in the spin-flip region of these compounds. This confirms the correctness of the predicted values of $\lambda_1^{\alpha,2}(0)$ and $\lambda_2^{\alpha,2}(0)$ for other RCo_5, including those in which there are no spontaneous transitions.

CONCLUSION

An x-ray diffraction study of the spontaneous spin-flip phase transitions in single-crystal RCo_5 compounds has thus shown the following:

1. The influence of the spin flip is more pronounced in thermal expansion along the hexagonal c axis than in the basal plane. The spin-flip transition manifests itself stronger the smaller the spin-flip temperature interval.

2. From the anomalies of the thermal expansion in the spin-flip region one can calculate the anisotropic magnetostriction constants $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$, whose direct measurement is quite difficult because of the large magnetic anisotropy.

3. In spontaneous spin flip inRCo_5, no anomalies are observed in the temperature dependences of the unit-cell volume, and the expansion along the c axis is offset by contraction in the basal plane, i.e., $\lambda_1^{\alpha,2}\approx-0.5\lambda_2^{\alpha,2}$.

4. The relation between the magnetostriction constants of RCo_5 with different R agrees with that calculated in the one-ion model neglecting the magnetostriction of the cobalt sublattice. It follows therefore that the anisotropic magne-

TABLE II.

	$PrCo_5$	$NdCo_5$	$SmCo_5$	$TbCo_{5,1}$	$DyCo_{5,2}$	$HoCo_{5,5}$	$ErCo_{5,9}$	$TmCo_5$
$\lambda_1^{\alpha,2}(0)$, 10^{-3}	−1.1	−0.8	+1.3	−1.8	−1.7	−0.7	+0.6	+1.5
$\lambda_2^{\alpha,2}(0)$, 10^{-3}	+2.2	+1.7	−2.6	+3.5	+3.4	+1.3	−1.2	−3.0

tostriction in RCo_5 is due practically entirely to the contribution of the rare-earth sublattice.

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