Thermal expansion and spontaneous magnetostriction in R_2Co_7 intermetallic compounds

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Thermal expansion in R_2Co_7 single crystals (R = Y, Nd, Gd, Tb) is investigated by x-ray dilatometry. The linear and volume magnetostriction deformations are deduced from the thermal expansion anomalies during magnetic ordering and spin-flip transitions. In conjunction with the temperature dependence of the magnitude and direction of the magnetic moment, these deformations can be used to calculate the anisotropic magnetostriction constants in the single ion model for all R_2Co_7 compounds in which the orbital moment of the rare-earth ion is nonzero.

INTRODUCTION

Because intermetallic compounds of the type R_2Co_7 (R denoting either yttrium or a rare-earth metal) form in R–Co alloy systems by a series of complex peritectic reactions, it is difficult to obtain single-phase alloys, let alone single-crystal specimens. These alloys have therefore been studied much less than related compounds such as RCo_5 or R_2Co_{17}. Yet they are of interest, as they have been found[1–6] to possess various types of magnetic anisotropy and to undergo spontaneous and induced spin-flip phase transitions; in addition, the magnetic moment becomes inverted at the temperature where the magnetic moments of the sublattices cancel, and the magnetic properties change radically when hydrogen is reversibly absorbed. Drawing an analogy with compounds of the type RCo_5 (Refs. 7–9), one anticipates that phase transitions (magnetic ordering and spin–flip) in R_2Co_7 should produce anomalies in the thermal expansion. The nature and magnitude of these anomalies can yield information on the magnetoelastic interactions, for which virtually no data is available for these compounds.

In the present work we use x-ray dilatometry to study the thermal expansion for single-crystal intermetallic compounds of the type Y_2Co_7, Nd_2Co_7, Gd_2Co_7, and Tb_2Co_7. The anomalies in the thermal expansion are used to find the linear and volume magnetostriction deformations of the crystal lattice, and the magnetostriction constants are calculated from the magnitude of the deformations and a knowledge of the temperature dependence of the magnitude and direction of the magnetic moments. The results are discussed in the framework developed in Refs. 10 and 11.

EXPERIMENTAL METHOD

The R_2Co_7 alloys, with R and Co pure to 99.9 and 99.99%, respectively, were prepared by alloying the components in an electric induction furnace in a helium atmosphere. The ingots were remelted in a resistance electric furnace to increase the grain size and were homogenized by holding them for 170 h at 1000 °C. The specimens were prepared from alloys containing less than 3% of extraneous phase (determined from x-ray and metallographic data). Single-crystal balls 2–3 mm in diameter were cut out from large grains in the ingots. We verified that specimens with subgrain misorientations less than 3° did not contain any satellite grains whose crystallographic axes deviated significantly from those of the principal grain.

The temperature dependence of the magnitude and direction of the magnetic moments of the compounds was measured by a vibrating magnetometer in static fields <2 MA/m between 4.2 and 800 K, by the induction method between 4.2 and 1000 K using pulsed fields to 8 MA/m, and also in a torque magnetometer between 77 and 320 K in static fields up to 2 MA/m.

The thermal expansion was investigated for $T = 5$–1000 K by analyzing the α_1 or β reflections recorded by the x-ray diffractometer in Fe and Cr K-radiation. For this purpose the specimens were ground perpendicular to the principal crystallographic axes. By using single crystals, we were able to get very strong reflections for all the diffraction angles of interest; in each specific case, the radiation was therefore selected to give reflections of the type $(h\,00)$, $(hh\,0)$, or $(00l)$ for Bragg angles 70–80°. The relative error in measuring the lattice constants was less than 10^{-4}.

We used the formula[12]

$$T_D = \frac{h}{k}\left(\frac{9N}{4\pi V}\right)^{1/3}\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)^{-1/3} \qquad (1)$$

for the Debye constant T_D for R_2Co_7 needed to calculate the phonon contribution to the thermal expansion. Here h and k are the Planck and Boltzmann constants, N is the number of atoms per unit cell, of volume V, and v_l and v_t are the mean propagation velocities for the longitudinal and transverse acoustic waves; v_l and v_t were measured at room temperature at 20 MHz by the pulse-phase technique in Ref. 13. For Y_2Co_7, $T_D = 340$ K, while $T_D = 300$ K for the other compounds.

The linear magnetostriction deformations and the volume magnetostriction were determined to within 10^{-4} and $3\cdot10^{-4}$, respectively. The errors were estimated by extrapolating the temperature dependence of the lattice parameters for paramagnetic Th_2Co_7, with the same structure as the compounds R_2Co_7 studied here, from $T > 600$ K to 0 K. The error in measuring the rhombic distortions of the lattice symmetry was less than 10^{-4}.

MEASUREMENT RESULTS AND DISCUSSION

Structurally, the R_2Co_7 compounds can be regarded as consisting of a combination of hexagonal RCo_5 elements (with the same structure as $CaCu_5$, space group $P6/mm$) and cubic RCo_2 elements ($MgCu_2$ structure, space group $Fd3m$), the elements alternating along a common third-order axis. The repeating structural unit $2RCo_5 + 2RCo_2$ con-

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tains two R_2Co_7 formula units and has unit cell parameters $a \approx 0.5$ nm and $c \approx 1.2$ nm (hexagonal crystal derivation). A double-layer arrangement of the structural units ($c \approx 2.4$ nm) gives rise to the hexagonal modification of R_2Co_7 with the same structure as Ce_2Ni_7 (space group $P6_3/mmc$). A triple-layer packing ($c \approx 3.6$ nm) gives the rhombohedral modification of type Gd_2Co_7 ($R\bar{3}m$). The metals in the cerium subgroup generally give hexagonal compounds R_2Co_7, while a rhombohedral structure is preferred for yttrium. It is found experimentally that the Curie temperature T_c and the molecular magnetic moment μ_m do not depend on whether the crystal lattice is hexagonal or rhombohedral,[2] but that the anisotropy does depend on the symmetry of the R_2Co_7 crystal.[3] Our Nd_2Co_7 and Gd_2Co_7 crystals were hexagonal and rhombohedral, respectively, while both hexagonal and rhombohedral Y_2Cr_7 and Tb_2Co_7 crystals were used. The structure of the unit cell is easily established from the Laue diffraction pattern—if a $1/m$ symmetry plane is present the space group is $P6_3/mmc$, otherwise it is $R\bar{3}m$.

Figure 1 shows $\mu_m(T)$ for the specimens; these curves were used to calculate the magnetostriction constants. Figure 2 shows the temperature dependence of the lattice constants a, c and of the unit cell volume $V = a^2c3^{1/2}/2$ for rhombohedral Y_2Co_7. Since yttrium has no magnetic moment, the results for Y_2Co_7 reflect the magnetostriction of the cobalt subsystem in R_2Co_7. The dashed lines in Fig. 2 show the phonon contribution to the thermal expansion. It was determined by extrapolating the temperature curves for a, c, and V from the paramagnetic to the magnetically ordered regions. The extrapolation was based on the following equations, derived from the Debye theory and Grüneisen's law (see, e.g., Ref. 14):

$$\begin{aligned} a_0(T) &= a_0(0) + A_1 TF(T_D/T), \\ c_0(T) &= c_0(0) + A_2 TF(T_D/T), \\ V_0(T) &= V_0(0) + A_3 TF(T_D/T). \end{aligned} \tag{2}$$

Here $a_0(T)$, $c_0(T)$, and $V_0(T)$ are the extrapolated values, and the A_i are constants. The function F is defined by

$$F(T_D/T) = T^{-1}\int_0^T C_V\, dT,$$

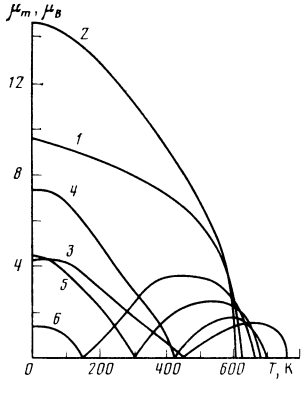

FIG. 1. Temperature behavior of the molecular magnetic moments μ_m (divided by the Bohr magneton μ_B) for Y_2Co_7 (1), Nd_2Co_7 (2), Gd_2Co_7 (3), Tb_2Co_7 (4), $(Tb_{0.8}Y_{0.2})_2Co_7$ (5), $(Tb_{0.6}Y_{0.4})_2Co_7$ (6).

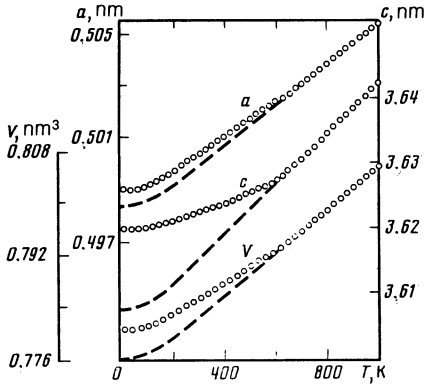

FIG. 2. Temperature dependence of the lattice parameters a, c and unit volume V for rhombohedral Y_2Co_7.

where C_V is the specific heat at constant volume (tabulated, e.g., in Ref. 15).

Figure 2 shows that for $T < T_c$, a, c, and $V(T)$ for Y_2Cr_7 differ from the predictions of the Debye theory. The relative differences $\Delta a/a$, $\Delta c/c$, and $\Delta V/V$ between the measured and extrapolated values are equal to the spontaneous linear (λ_a, λ_c) and volume (λ_V) magnetostriction deformations during the magnetic ordering transition. The thermal expansion for hexagonal Y_2Co_7 is the same as for the rhombohedral modification: λ_a, λ_c, and λ_V are identical, i.e., the crystal lattice symmetry does not affect the spontaneous magnetostriction of the cobalt subsystem in R_2Co_7.

Up to constants of fourth order, the linear magnetostriction for crystals with a distinguished symmetry axis (hexagonal, rhombohedral, and tetragonal crystal classes) is given by the formula[16]

$$\begin{aligned} \lambda = {} & \lambda_1^{\alpha,0}(\beta_x^2+\beta_y^2) + \lambda_2^{\alpha,0}\beta_z^2 + \lambda_1^{\alpha,2}(\beta_x^2+\beta_y^2)(\alpha_z^2-{}^1/_3) \\ & + \lambda_2^{\alpha,2}\beta_z^2(\alpha_z^2-{}^1/_3) + \lambda^{\gamma,2}[{}^1/_2(\beta_x^2-\beta_y^2)(\alpha_x^2-\alpha_y^2) + 2\beta_x\beta_y\alpha_x\alpha_y] \\ & + 2\lambda^{\epsilon,2}(\beta_x\alpha_x+\beta_y\alpha_y)\beta_z\alpha_z + \lambda_1^{\alpha,4}(\beta_x^2-\beta_y^2)(7\alpha_z^4-6\alpha_z^2+{}^3/_5) \\ & + \lambda_2^{\alpha,4}\beta_z^2(7\alpha_z^4-6\alpha_z^2+{}^3/_5) \\ & + \lambda_1^{\gamma,4}[{}^1/_2(\beta_x^2-\beta_y^2)(\alpha_x^2-\alpha_y^2) + 2\beta_x\beta_y\alpha_x\alpha_y](\alpha_z^2-{}^1/_7) \\ & + \lambda_2^{\gamma,4}[(\beta_x^2-\beta_y^2)(6\alpha_x^2\alpha_y^2-\alpha_x^4-\alpha_y^4) + 8\beta_x\beta_y\alpha_x\alpha_y(\alpha_x^2-\alpha_y^2)] \\ & + 2\lambda^{\epsilon,4}(\beta_x\alpha_x+\beta_y\alpha_y)\beta_z\alpha_z(\alpha_z^2-{}^1/_7) + \dots . \end{aligned} \tag{3}$$

Here β_i, α_i are the direction cosines for the magnetostriction and magnetic moment vectors, respectively. The zero-order constants $\lambda_1^{\alpha,0}$, and $\lambda_2^{\alpha,0}$ (in the basal plane and along the x axis, respectively) characterize the "exchange" magnetostriction, which depends on the strength of the magnetic moment. The remaining constants describe the deformations that depend on the direction of the magnetic moment (the anisotropic magnetostriction). The constants $\lambda_i^{\alpha,0}, \lambda_i^{\alpha,2}$, and $\lambda_i^{\alpha,4}$ appear because the lattice parameters can change even though the crystal symmetry remains the same (this is alpha-striction). The constants $\lambda^{\gamma,2}$ and $\lambda_i^{\gamma,4}$ describe the rhombic distortions (gamma-striction), and $\lambda^{\epsilon,2}$ and $\lambda^{\epsilon,4}$ describe monoclinic distortions. In most cases, only constants of zero and second order need be considered (in particular, they suffice to describe alpha-striction in R_2Co_7);

however, we will see below that constants through fourth order are needed to describe the gamma-striction.

In Y_2Co_7 the magnetic moment lies along the c axis for temperatures below T_c. We therefore find from (3) that

$$\lambda_a(T)=\lambda_b(T)=\lambda_1^{\alpha,0}(T)+{}^2/_3\lambda_1^{\alpha,2}(T),$$
$$\lambda_c(T)=\lambda_2^{\alpha,0}(T)+{}^2/_3\lambda_2^{\alpha,2}(T), \quad \lambda_V(T)=2\lambda_a+\lambda_c. \tag{4}$$

Figure 3 compares the temperature curves for the magnetostriction deformations with the temperature dependence of the square of the magnetic moment for Y_2Co_7. The linear deformations as well as λ_V are seen to be proportional to μ_m^2, and λ_a and λ_c are enormous, roughly 10^{-3}. According to present theory,[10,11] such large linear deformations can arise only through exchange magnetostriction or through anisotropic magnetostriction of the single ion type. However, the temperature dependence of the single-ion magnetostriction differs from $\mu_m^2(T)$. The exchange magnetostriction must thus be responsible for the large λ_a and λ_c in Y_2Co_7, and just as in the case of RCo_5 (Ref. 9) we conclude that the anisotropic alpha-striction of the subsystem contributes negligibly to λ_a and λ_c, i.e., $\lambda_a \approx \lambda_1^{\alpha,0}, \lambda_c \approx \lambda_2^{\alpha,0}$. The expression[17]

$$\lambda_V = n_{CoCo}\mu_{Co}^2 + n_{RCo}\mu_{Co}\mu_R + n_{RR}\mu_R^2 \tag{5}$$

for the magnetoelastic coupling coefficient n_{CoCo} gives the value $3.1\cdot10^{-3}\,\mu_B^{-2}$ for Y_2Co_7 (we have used the fact that $\mu_R = 0$ for R = Y), and it follows from Fig. 3 that n_{CoCo} is independent of T. The volume magnetostriction in Y_2Co_7 is less than in YCo_5. This is because the cobalt magnetic moment is considerably smaller (at $T = 0$ K, $\mu_{Co} = 1.37\mu_B$ for Y_2Co_7 as compared with $\mu_{Co} = 1.65\mu_B$ in YCo_5). However, n_{CoCo} is larger than the value $2.5\cdot10^{-3}\mu_B^{-2}$ for YCo_5.

We found previously[18,19] that in RCo_5 compounds with tetravalent Ce and Th, the coefficients n_{CoCo} are also much larger than for YCo_5. These results indicate that the magnetoelastic coupling in the cobalt subsystem in R–Co compounds is enhanced when the d-band is filled by valence electrons from the rare-earth metal, partly because the effective valence of the R ions is increased, and partly because their concentration is higher.

The thermal expansion for Gd_2Co_7 is shown in Fig. 4; like Y_2Co_7, this compound is magnetically uniaxial for all temperatures below T_c. The curves a, c, $V(T)$ are therefore qualitatively the same also.

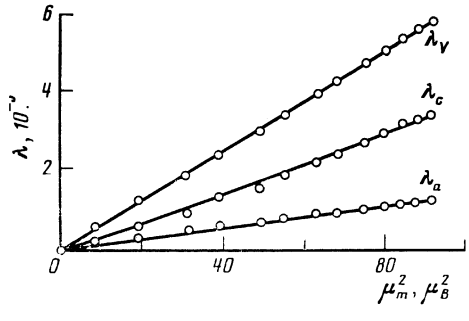

FIG. 3. Spontaneous linear (λ_a,λ_c) and volume (λ_V) magnetostriction deformations in Y_2Co_7 as functions of the square of the molecular magnetic moment μ_m.

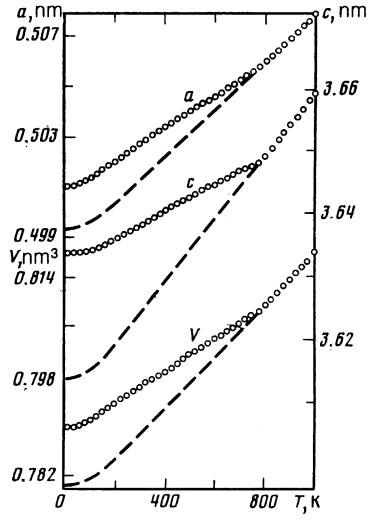

FIG. 4. Temperature dependence of the lattice parameters a, c and unit cell volume V for Gd_2Co_7.

Figures 5 and 6 show how a,c, and V depend on T for Nd_2Co_7 and Tb_2Co_7. In addition to the unusual behavior of the thermal expansion at T_c, two other anomalies not present for Y_2Co_7 are apparent. First, rhombic distortions set in at low temperatures. A third parameter b (identically equal to $a\sqrt{3}$ in the absence of distortions) is needed to describe the unit cell. Table I lists values for λ_a,λ_b,λ_c,λ_V extrapolated to $T = 0$ K, in addition to the volume coefficient of thermal expansion α_V at temperatures for which the material is paramagnetic ($T = 800$ K). Second, the thermal expansion [particularly the curve $c(T)$] is influenced by spin-flip phase transitions. These two effects are both due to the anisotropic magnetostriction and will be discussed below. Let us first consider the volume magnetostriction. Figure 7 shows $\lambda_V(T)$ for the compounds we investigated. We see that in contrast to the case of R_2Fe_{17} (Ref. 20) and $R_2Fe_{14}B$ (Ref. 21), λ_V depends strongly on the rare-earth ion R, indicating that the R–Co interaction plays a significant role in

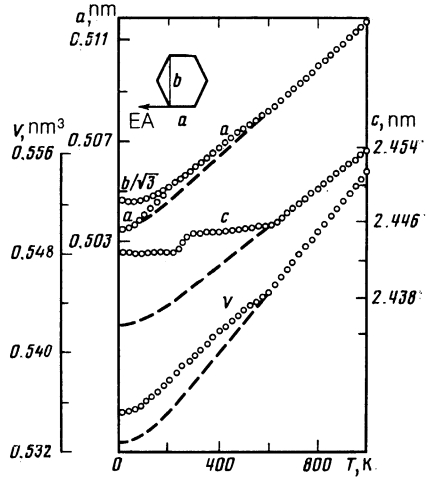

FIG. 5. Temperature dependence of a, c, V, and the rhombic distortions in Nd_2Co_7.

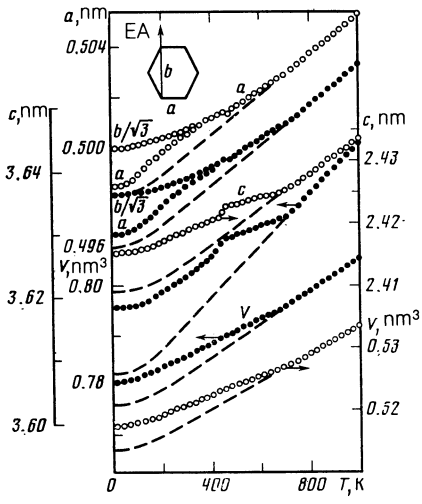

FIG. 6. Temperature dependence of a, c, V, and the rhombic distortions for hexagonal (○) and rhombohedral (●) Tb_2Co_7.

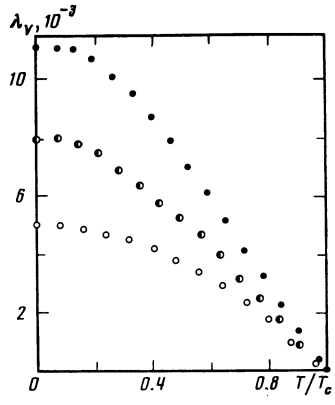

FIG. 7. Temperature dependence of the spontaneous volume magnetostriction λ_V for Nd_2Co_7 (○), Gd_2Co_7 (●), and Tb_2Co_7 (◐).

the exchange magnetostriction in R_2Co_7. The linear magnetostriction deformations differ somewhat for hexagonal and rhombohedral Tb_2Co_7, evidently because the anisotropic magnetostrictions differ, as λ_V is the same in both cases. The lattice symmetry thus does not affect the Co–Co and R–Co magnetoelastic interactions associated with exchange effects.

We made the following assumptions in calculating the coefficients n_{RCo}.

1. $n_{RR} = 0$; this follows from the familiar fact that the R–R magnetoelastic interaction contributes negligibly to the exchange magnetostriction in $4f$–$3d$ compounds.

2. The magnetic moment μ_{Co} in R_2Co_7 is the same as for Y_2Co_7.

3. If differences in the compressibilities are neglected, n_{CoCo} for R_2Co_7 is the same as for Y_2Co_7.

4. The compressibility is proportional to α_V in the paramagnetic region, so that it suffices to consider the ratio of α_V for R_2Co_7 and Y_2Co_7.

The resulting values n_{RCo} and n_{CoCo} are shown in Table I. We see that although n_{RCo} is an order of magnitude less than n_{CoCo}, the contribution from the R–Co exchange interaction is extremely large owing to the large magnetic moment μ_R. The sign of n_{RCo} differs for the various compounds, possibly because the magnetic ordering between the R- and Co-sublattices is different: it is ferromagnetic for light R (Nd) and ferrimagnetic for heavy R (Tb, Gd).

As we have noted above, thermal expansion anomalies and rhombohedral distortions of the lattice are both present for Nd_2Co_7 and Tb_2Co_7; the latter distortions arise because the easy axis of magnetization (EA) for these compounds is not parallel to the c axis at low temperatures. The spin-flip transition in Nd_2Co_7 and Tb_2Co_7 may be attributed to competition between the uniaxial anisotropy of the cobalt sublattice, dominant at high temperatures, and the multiaxial anisotropy of the rare-earth sublattice, which dominates at low temperatures. The spin-flip transition for hexagonal Nd_2Co_7 and Tb_2Co_7 occurs in the intervals 226–290 and 423–450 K, respectively. Figure 8 shows how the angle φ between the c and EA axes depends on T. In the "planar" region the easy axis in Nd_2Co_7 lies in planes of the type ac, while in Tb_2Co_7 they lie in the planes bc, as predicted by the single-ion magnetostriction model.

Unlike the RCo_5 compounds studied previously,[7,8,22] in which the R-ions occupy only a single crystallographic position, the direction of the easy axis in R_2Co_7 is also determined by competition between the magnetic anisotropies of R ions occupying inequivalent sites in the lattice and possessing local environments with different symmetries (cubic for RCo_2, hexagonal for RCo_5). The spin-flip transition in Nd_2Co_7 is thus shifted to lower temperatures than for Nd_2Co_5, even though the rare-earth metal concentration in Nd_2Co_7 is higher. Rhombohedral Tb_2Co_7 exhibits a complex type of triaxial anisotropy; the easy axis lies in the basal plane only in the special case when $T = 330$ K—at all other temperatures below 450 K, the angle φ differs from 90° (Fig. 8).

To determine the constants for the anisotropic alpha-

TABLE I. Spontaneous magnetostriction deformations $\lambda_a, \lambda_b, \lambda_c, \lambda_V$ (all at 0 K), volume thermal expansion coefficient α_V (at 800 K), and magnetoelastic coupling coefficients n_{CoCo}, n_{RCo} for several compounds R_2Co_7.

R	λ_a, 10^{-3}	λ_b, 10^{-3}	λ_c, 10^{-3}	λ_V, 10^{-3}	α_V, 10^{-5} K^{-1}	n_{CoCo}, 10^{-3} μ_B^{-2}	n_{RCo}, 10^{-3} μ_B^{-2}
Y	1.2	1.2	3.4	5.8	4.3	3.1	0
Nd	−0.3	2.1	3.2	5.0	4.4	3.2	−0.2
Gd	2.7	2.7	5.6	11.0	5.2	3.7	0.4
Tb	0.9* / 1.0	4.0* / 3.9	3.1* / 3.0	8.0	4.2	3.0	0.3

*The upper and lower values are for hexagonal and rhombohedral unit cells, respectively.

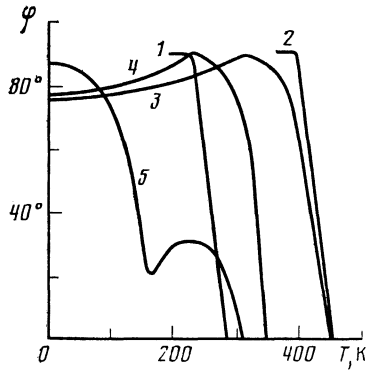

FIG. 8. Temperature dependence of the angle between the easy axis and the [001] axis for hexagonal Nd_2Co_7 (1), Tb_2Co_7 (2), and rhombohedral quasibinary $(Tb_{1-x}Y_x)_2Co_7$ with $x = 0$ (3), 0.2 (4), and 0.4 (5).

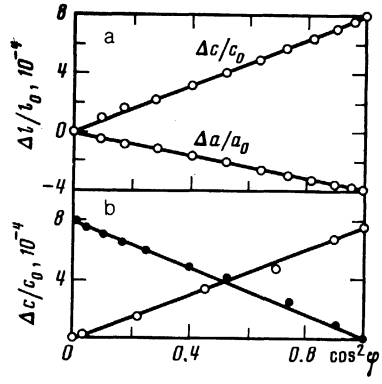

FIG. 9. Linear magnetostriction deformation $\Delta l/l_0$ as a function of the angle φ between the easy axis and the [001] axis for Nd_2Co_7 (a) and Tb_2Co_7 (b); ○, hexagonal unit cell; ●, rhombohedral unit cell. $\Delta l/l_0$ was found by extrapolating the temperature curves for the lattice parameters (from the region of planar anisotropy for the hexagonal crystals, and from the magnetically uniaxial region for rhombohedral Tb_2Co_7, respectively).

striction, one can use the technique we employed previously to study RCo_5 compounds, for which the structure is not appreciably distorted.[7,8] This is because in the present case, the rhombic distortions disappear before the onset of the spin-flip transition in hexagonal Nd_2Co_7 and Tb_2Co_7 crystals, while for rhombohedral Tb_2Co_7 they disappear before one reaches the temperatures at which $\varphi(T)$ changes most strongly (i.e., for which the curves $a(T)$ and $c(T)$ become anomalous), so that $\lambda_a \approx \lambda_b$. One finds that the additional magnetostriction deformations accompanying rotation of the easy axis are proportional to $\cos^2\varphi$ (Fig. 9). According to Eq. (3), this indicates that as in the case of RCo_5, the contribution from the anisotropic alpha-striction to the anomalous thermal expansion can be described by constants of second order: $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$. Since there is no anomaly caused by volume magnetostriction, we have $2\lambda_1^{\alpha,2} = -\lambda_2^{\alpha,2}$. Calculating $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ at the midpoint of the spin-flip interval as described in Refs. 7 and 8, we obtain $\lambda_1^{\alpha,2} = -0.4\cdot10^{-3}$, $\lambda_2^{\alpha,2} = 0.8\cdot10^{-3}$ for Nd_2Co_7 at $T = 250$ K and for hexagonal Tb_2Co_7 at $T = 430$ K. The values for rhombohedral Tb_2Co_7 at $T = 430$ K are essentially the same.

In view of the results of our investigation of the spontaneous magnetostriction for Y_2Co_7, indicating that the anisotropic striction in the cobalt subsystem is negligible, we used the single-ion magnetostriction model to extrapolate the above values of $\lambda_1^{\alpha,2}$ and $\lambda_2^{\alpha,2}$ for Nd_2Co_7 and Tb_2Co_7 to $T = 0$ K, and then calculated $\lambda_1^{\alpha,2}(0)$ and $\lambda_2^{\alpha,2}(0)$ for all the R_2Co_7 compounds with magnetic ions (i.e., ions with nonzero orbital moment), as was done previously for RCo_5 in Ref. 8. The results of the calculation are shown in Table II. These values of the anisotropic alpha-striction constants for Nd_2Co_7 and Tb_2Co_7 were used to analyze the exchange alpha-striction, also shown in Table II.

By comparing the magnetostriction constants for RCo_5 (Ref. 8) and R_2Co_7 we conclude that the exchange magnetostriction constants decrease and the anisotropic magnetostriction constants increase with increasing R-ion concentration. This is yet another indication that in rare-earth metallides containing metals in the iron group, most of the

TABLE II. Magnetostriction constants for R_2Co_7 at $T = 0$ K.

R	$\lambda_1^{\alpha,2}$, 10^{-3}	$\lambda_2^{\alpha,2}$, 10^{-3}	$\lambda_1^{\alpha,0}$, 10^{-3}	$\lambda_2^{\alpha,0}$, 10^{-3}	$\lambda^{\gamma,2}$, 10^{-3}	$\lambda_1^{\gamma,4}$, 10^{-3}	$\lambda_2^{\gamma,4}$, 10^{-3}
Pr	−2.0	4.0	—	—	1.1 * / 1.3	27.8 * / 37.2	0.6 * / 0.8
Nd **	−1.4	2.8	0.6	3.8	0.9 * / 1.0	16.7 * / 22.6	0.5 * / 0.6
Sm	2.3	−4.6	—	—	−1.2 * / −1.5	−4.5 * / −6.1	−0.1 * / −0.1
Tb **	−3.2	6.4	1.6	4.7	1.7 * / 2.1	−16.7 * / −22.0	−0.5 * / −0.6
Dy	−3.0	6.1	—	—	1.6 * / 2.0	20.5 * / 27.4	0.6 * / 0.6
Ho	−1.2	2.3	—	—	0.6 * / 0.8	14.2 * / 19.0	0.4 * / 0.5
Er	1.1	−2.2	—	—	−0.6 * / −0.7	−13.1 * / −17.5	−0.4 * / −0.5
Tm	2.7	−5.4	—	—	−1.4 * / −1.7	−17.4 * / −23.4	−0.5 * / −0.6

*Upper and lower values are for hexagonal and rhombohedral unit cells.

**Experimental. All other values were calculated using the single-ion magnetostriction model.

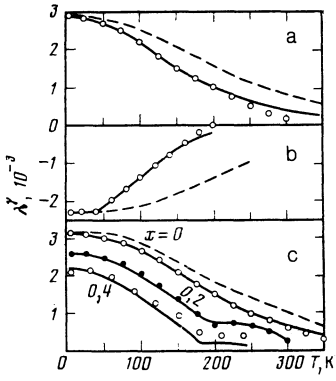

FIG. 10. Temperature curves for gamma-magnetostriction in hexagonal Tb_2Co_7 (a), Nd_2Co_7 (b) and rhombohedral $(Tb_{1-x}Y_x)_2Co_7$ (c). The points and dashed curves give experimental and calculated results, respectively. The calculations were based on the single-ion magnetostriction model and included only the second-order constants $\lambda^{\gamma,2}$; the solid curves include both the second- and fourth-order constants ($\lambda^{\gamma,2}$,$\lambda_1^{\gamma,4}$, and $\lambda_2^{\gamma,4}$).

contribution to the anisotropic magnetostriction is from the single-ion interaction of the 4*f*-shell of the rare-earth metal with the crystal field, while the magnetoelastic interaction among the collectivized 3*d*-electrons gives the dominant contribution to the exchange magnetostriction.

Figure 10 shows the temperature dependence of the gamma-striction for Nd_2Co_7 and Tb_2Co_7 deduced from the rhombic distortions for crystals with a distinguished axis of symmetry using the following formulas:

$$\lambda^\gamma=\lambda_a-\lambda_b=\lambda^{\gamma,2}\sin^2\varphi+\lambda_1^{\gamma,4}\sin^2\varphi\,(^6/_7-\sin^2\varphi)-2\lambda_2^{\gamma,4}\sin^4\varphi, \tag{6a}$$

$$\lambda^\gamma=\lambda_b-\lambda_a=\lambda^{\gamma,2}\sin^2\varphi+\lambda_1^{\gamma,4}\sin^2\varphi\,(^6/_7-\sin^2\varphi)+2\lambda_2^{\gamma,4}\sin^4\varphi, \tag{6b}$$

which follow from (3). The first holds when the easy axis lies in the (100) plane, as in Nd_2Co_7, the second when the easy axis is parallel to (010), as in Tb_2Co_7. The large value of λ^γ testifies to the single-ion nature of the gamma-striction, since we have already pointed out, none of the other magnetostriction mechanisms currently known can lead to anisotropic strictions greater than 10^{-4}. The results of our investigation of rhombic distortions in the quasibinary compounds $(Tb_{1-x}Y_x)_2Co_7$ presented below also point to a dominant single-ion contribution to λ^γ. Since the anisotropic alpha-striction is accurately described by second-order constants, it seems plausible that λ^γ should be describable in terms of the constant $\lambda^{\gamma,2}$. However, the single-ion model predicts that $\lambda^{\gamma,2}$ should have the same sign for Nd_2Co_7 and Tb_2Co_7, whereas one finds experimentally that λ^γ is negative (resp., positive) (Fig. 10). In addition, λ^γ falls off as T increases much faster than predicted by the single-ion model neglecting the contribution from cobalt to λ^γ.

As in the RCo_2 compounds, the cobalt subsystem plays an important role in the anisotropic magnetostriction. Indeed, the R_2Co_7 crystal lattice contains "fragments" of the RCo_2 cubic structure, and it would seem, judging from the available evidence, that these portions of the crystal are responsible for the enormous magnitude of the gamma-striction (under the plausible assumption that the cobalt subsystem gives a large contribution to the gamma-striction in RCo_7 also). However, this cobalt contribution cannot account for the above features of the gamma-striction, because in those compounds for which the cobalt contribution has the same sign as λ^γ for the R-sublattices, this contribution should make the temperature dependence of the gamma-striction less pronounced, not steeper, than the dependence $\lambda^{\gamma,2}(T)$ for the rare-earth sublattice.

Clearly, the fourth-order magnetostriction constants $\lambda_1^{\lambda,4}$ and $\lambda_2^{\gamma,4}$ are also needed to describe the gamma-striction in R_2Co_7 [see Eq. (3)]. According to the single-ion model, these constants have opposite signs for Nd_2Co_7 and Tb_2Co_7 and should decrease in absolute value much faster than $\lambda^{\gamma,2}$ with increasing temperature.

The measurement results for Y_2Co_7 cannot be used to estimate the magnitude of the cobalt contribution to the gamma-striction because T_2Co_7 (as noted above) is uniaxial, so that the rhombic distortion in this compound must vanish in principle even though the gamma-striction constants may be large. We therefore analyzed rhombic distortion in the related quasibinary compounds $(Tb_{1-x}Y_x)_2Co_7$ with a rhombohedral structure ($x = 0$, 0.2, 0.4). All these materials exhibit the same kind of magnetic anisotropy. Dilution of the terbium sublattice by nonmagnetic yttrium ions causes the angle φ at $T = 0$ K to become smaller, and the transition temperature T_2 to the uniaxial state also drops [see the curves $\varphi(T)$ in Fig. 8]. In our analysis we assumed that the dependence of μ_{Co} on the reduced temperature T/T_c for $(Tb_{1-x}Y_x)_2Co_7$ is the same for all x; $\mu_{Tb}(T)$ for compositions with different x is then equal to the difference between μ_m for $x = x$ and $x = 0$ at a fixed reduced temperatur T/T_c. We assumed further that the cobalt contribution to the gamma-striction is independent of x and describable, like the magnetic anisotropy of the cobalt sublattice, using second-order constants. Finally, we postulated that the constants $\lambda_{Tb}^{\gamma,2}$,$\lambda_{1Tb}^{\gamma,4}$, and $\lambda_{2Tb}^{\gamma,4}$ behave as predicted by the single-ion model, i.e., they depend linearly on x and vanish when $x = 1$, and that the temperature dependence is given by the formula[22]

$$\lambda_l(T)/\lambda_l(0)=\mathscr{L}_l^J(\sigma), \tag{7}$$

where l is the order and $\mathscr{L}_1^J(\sigma)$ (tabulated in Ref. 22) is a modified normalized Bessel function involving the total momentum quantum number J.

With the above assumptions, we can substitute our experimental values for $\lambda^\gamma(T)$ and $\varphi(T)$ into (3) and solve for the gamma-striction constants. We find that $\lambda_{Co}^{\gamma,2}$ is less than $2\cdot10^{-4}$, i.e., is at least an order of magnitude less than λ^γ, and may thus be neglected.

For rhombohedral Tb_2Co_7 we obtain $\lambda^{\gamma,2}=2.1\cdot10^{-3}$, $\lambda_1^{\gamma,4}=-22\cdot10^{-3}$, and $\lambda_2^{\gamma,4}=-0.5\cdot10^{-3}$ at $T=0$ K. Figure 10 shows that the curves $\lambda^\gamma(T)$ for the various compositions $(Tb_{1-x}Y_x)_2Co_7$ agree closely with the experimental data. However, if these values are used to calculate λ^γ for hexagonal Tb_2Co_7, we get a value $4.2\cdot10^{-3}$ which is 50% larger than the experimental result. The constants $\lambda^{\gamma,2}$ and $\lambda_i^{\gamma,4}$ thus differ for the hexagonal and rhombohedral modifications. The lattice symmetry therefore significantly influences the gamma-striction constants for R_2Co_7, but not the exchange and anisotropic alpha-magnetostrictions,

which are independent of the symmetry.

Equations (6) simplify greatly for hexagonal Nd_2Co_7 and Tb_2Co_7 at the temperatures for which the rhombic lattice distortions are appreciable, because in this case $\varphi = 90°$. For Nd_2Co_7 (easy axis parallel to [100])

$$\lambda^{\gamma}=\lambda_a-\lambda_b=\lambda^{\gamma,2}-{}^{1}/_{7}\lambda_1^{\gamma,4}-2\lambda_2^{\gamma,4}. \quad (8a)$$

while for Tb_2Co_7 (easy axis parallel to [120])

$$\lambda^{\gamma}=\lambda_b-\lambda_a=\lambda^{\gamma,2}-{}^{1}/_{7}\lambda_1^{\gamma,4}+2\lambda_2^{\gamma,4}. \quad (8b)$$

Substitution of the experimental values into (8) yields $\lambda^{\gamma,2} = 0.9\cdot10^{-3}$ for R = Nd and $1.7\cdot10^{-3}$ for R = Tb at $T = 0$ K. The ratio of $\lambda^{\gamma,2}$ for Nd_2Co_7 and Tb_2Co_7 agrees closely with the ratio of the quantities $\alpha_J J(J-0.5)\langle r_{4f}^2\rangle$ for the ions Nd^{3+} and Tb^{3+}, which is evidence for the validity of the assumptions made in the calculations (α_J is the Elliot-Stevens constant and $\langle r_{4f}^2\rangle$ is the mean square radius of the 4*f*-shell).

Because φ is constant for the temperatures for which rhombic distortions are present, while $\lambda_1^{\gamma,4}$ and $\lambda_2^{\gamma,4}$ depend in the same way on temperature, (8) yields only a linear combination of the fourth-order constants. To find $\lambda_1^{\gamma,4}$ and $\lambda_2^{\gamma,4}$ separately, we exploit the fact that the products $\beta_J J(J-0.5)(J-1)(J-1.5)\langle r_{4f}^2\rangle$ for Nf^{3+} and Tb^{3+} have the same magnitude but opposite sign (β_J is the Elliot-Stevens constant), and these products determine the single-ion fourth-order magnetostriction constants. It follows that

$$\lambda_{1\,\mathrm{Nd}}^{\gamma,4}=-\lambda_{1\,\mathrm{Tb}}^{\gamma,4}, \qquad \lambda_{2\,\mathrm{Nd}}^{\gamma,4}=-\lambda_{2\,\mathrm{Tb}}^{\gamma,4}.$$

We then obtain $\lambda_1^{\gamma,4} = 16.7\cdot10^{-3}$ and $\lambda_2^{\gamma,4} = 0.5\cdot10^{-3}$ for Nd_2Co_7 at $T = 0$ K; the corresponding values for Tb_2Co_7 have the same magnitude but are negative. The curves $\lambda^{\gamma}(T)$ obtained using these values for hexagonal Nd_2Co_7 and Tb_2Co_7 agree closely with the experimental data (Fig. 10). It is evident by comparing the gamma-striction constants for hexagonal and rhombohedral Tb_2Co_7 that the uniaxial magnetoelastic interaction is enhanced at the lower (rhombohedral) symmetry.

Just as we did above for the anisotropic alpha-striction, we can use the values of $\lambda^{\gamma,2}$, $\lambda_1^{\gamma,4}$, and $\lambda_2^{\gamma,4}$ to calculate the gamma-striction constants at $T = 0$ K in the single-ion model for all compounds R_2Co_7 in which the R ions have an anisotropic 4*f*-shell. The results are shown in Table II.

CONCLUSIONS

For compounds with a large magnetic anisotropy the determination of the magnetostriction constants, which are an important characteristic of magnetic materials, poses serious technical difficulties. For one thing, it is not easy to obtain single-crystal specimens large enough to suit the standard methods for investigating magnetoelastic properties. For another, one must work with very strong magnetic fields comparable to the anisotropy fields, which may be as strong as 50–100 T. Furthermore, the external field deforms the starting magnetic structure in highly anisotropic magnets, and because of the strong magnetoelastic interactions, the housing of the sensor recording the change in the sample shape and dimensions may significantly alter the values obtained for the magnetostriction deformations. Finally, there is no practical method for measuring the constants associated with exchange effects. Because of these difficulties, the magnetoelastic properties of the rare-earth intermetallides are much less known that the magnetic moments, the magnetic-ordering transition temperatures, or the anisotropies. Although the sensitivity of the dilatometric technique employed in this paper is quite low ($1\cdot10^{-4}$), it is perfectly adequate for studying magnetostriction in the rare-earth intermetallides, for which the magnetostriction may be as large as 10^{-3}–10^{-2}.

In conjunction with measurements of the magnitude and direction of the magnetic moment, our x-ray studies of thermal expansion in R_2Co_7 single crystals make it possible for the first time to obtain data on all the magnetostriction constants (except epsilon-striction). We may summarize our work as follows.

1. Magnetic ordering in R_2Co_7 is accompanied by a large positive volume magnetostriction due to primarily to the Co–Co magnetoelastic interaction. The magnetoelastic coupling coefficient for the R–Co interaction is an order of magnitude weaker; however, due to the large magnetic moments of the rare-earth ions, the R–Co interaction also contributes significantly to the volume magnetostriction. The crystal symmetry has no effect on volume magnetostriction in R_2Co_7.

2. The magnetostriction for the cobalt subsystem in R_2Co_7 is describable in terms of the constants $\lambda_1^{\alpha,0}$ and $\lambda_2^{\alpha,0}$, which are of exchange origin. The contribution from cobalt to the anisotropic alpha- and gamma-strictions (which leave the crystal symmetry unchanged and reduce it, respectively) is negligible compared to the contribution from the rare earth subsystem.

3. The anisotropic magnetostriction for the rare-earth sublattice in R_2Co_7 is described by the single-ion model. Second-order constants suffice to describe the alpha-striction, but gamma-striction requires constants through fourth order as well. Although the entire rare-earth sublattice contributes to the alpha-striction, the gamma-striction is due almost completely to the rare-earth ions at the quasicubic sites. The gamma-striction constants depend on the symmetry of the R_2Co_7 unit cell and are larger for less symmetric crystals.

4. We used the anomalous characteristics of the thermal expansion near the spin-flip transition, in addition to measurements of the rhombic distortions, to find the anisotropic magnetostriction constants $\lambda_1^{\alpha,2}$, $\lambda_2^{\alpha,2}$, $\lambda^{\gamma,2}$, $\lambda_1^{\gamma,4}$, and $\lambda_2^{\gamma,4}$ for Nd_2Co_7 and Tb_2Co_7. The constants for all the other compounds R_2Co_7 with magnetic ions R were then deduced using the single ion model.

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