

Properties of isotropic and anisotropic magnetoelastic interactions of intermetallic RCo₂ compounds

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X-ray studies of the anisotropic and isotropic magnetoelastic strains of the mixed rare-earth intermetallic compounds (R',R'')Co₂ have shown that the magnetostriction constant λ_{111} is determined mainly by the rare-earth subsystem, whereas the cobalt itinerant subsystem makes the main contribution to λ_{100} . It is shown that the bulk isotropic magnetostriction exhibits metamagnetic behavior of the band subsystems in these compounds.

INTRODUCTION

An intermetallic compound RCo₂ (R stands for a rare earth or yttrium) with cubic crystal structure of the MgCu₂ type (Laves C 15 phase) contains two magnetic subsystems—rare-earth (RE) and cobalt. It was found that in these compounds the magnetic 4*f* electrons of the RE subsystem are localized, and the exchange interaction is effected in this subsystem via the conduction electrons.¹ The magnetism of the cobalt subsystem is treated in the band model.^{2,3} It is assumed that the exchange interaction in the system of collectivized cobalt 3*d* electrons hybridized with the RE 5*d* electrons is small, and they do not meet the Stoner band-ferromagnetism criterion, so that the compounds YCo₂ and LuCo₂ with nonmagnetic RE are exchange-enhanced band paramagnets.⁴ In RCo₂ compounds with magnetic RE, the cobalt subsystem is magnetized by the exchange field of the RE subsystem, so that both subsystems are magnetically ordered in these compounds (the magnetic moments of the two subsystems are parallel in compounds with light RE and antiparallel in those with heavy RE).^{1,5} The principal magnetic properties of RCo₂ are listed in Table I.

Research into RCo₂ has recently attracted interest because these compounds serve as good models for the study of band metamagnetism. It is assumed that cobalt-system band structure is such that its magnetization increases discontinuously when a definite value of the field (external or effective) is reached, and a metamagnetic transition of the band paramagnet into the ferromagnetic state takes place.^{3,4} The assumption that the cobalt system has band metamagnetism is confirmed by calculations^{6,7} of the density of states of YCo₂ and explains peculiarities of RCo₂ magnetic properties such as the metamagnetism of DyCo₂, HoCo₂ and ErCo₂ above the magnetic-ordering temperature,⁸ the first-order phase transition from the paramagnetic to the ferromagnetic state in these compounds and possibly also in TmCo₂ (Refs. 3 and 9), and others. Metamagnetism of the cobalt subsystem was recently observed in experiments on YCo₂ in which part of the cobalt was replaced by nonmagnetic aluminum.

The magnetoelastic properties of RCo₂ are quite interesting. In the magnetically ordered state these compounds have a giant anisotropy, on the order of 10⁻³, of the spontaneous magnetostriction.^{11,12} It is assumed that this magnetostriction is due to the RE system and has a single-ion character. Recently, however, tremendous spontaneous magnetoelastic crystal-structure distortions were observed in GdCo₂. The gadolinium in this compound is trivalent, is in the *S* state, and has no orbital momentum; these distor-

tions can therefore not be explained by the model of single-ion magnetoelastic interaction in the gadolinium subsystem. It has therefore been suggested that they are due to the cobalt subsystem. This suggestion requires additional verification, and it is necessary in particular to ascertain whether the cobalt subsystem contributes to the anisotropic magnetostriction of other RCo₂ compounds. In addition, the data on the anisotropic magnetostriction of RCo₂ compounds are incomplete, since the magnetostriction was measured in most studies with the magnetization along the easy magnetization axis (EMA) (the reason was that the magnetic anisotropy of RCo₂ compounds is very large and the magnetic moment deviates insignificantly from the easy-magnetization direction in the experimentally attainable fields). To understand the nature of the magnetoelasticity of RCo₂ it is important to determine the anisotropic magnetoelastic strains produced when the field is oriented along the difficult magnetization direction.

Magnetically ordered RCo₂ compounds acquire also a large (on the order of 5·10⁻³) bulk spontaneous magnetostriction.^{12,14} This magnetostriction is assumed to be of the exchange type and to be due to the cobalt subsystem. Nonetheless, the connection between this magnetostriction and the cobalt-subsystem magnetization is as yet not completely understood, especially the change of the bulk magnetostriction following a metamagnetic transition.

DETERMINATION OF THE ANISOTROPIC AND BULK MAGNETOSTRICTION OF RCo₂ COMPOUNDS FROM X-RAY MEASUREMENTS

In the present study we determine the anisotropic and isotropic magnetostrictions of RCo₂ with heavy RE by in-

TABLE I. Principal properties of the RE intermetallics RCo₂ (Ref. 1)

Compound	Curie temperature T_C	Order of phase transition	EMA
PrCo ₂	50	II	$\langle 100 \rangle$
NdCo ₂	105	II	$\langle 110 \rangle$
SmCo ₂	220	II	$\langle 111 \rangle$
GdCo ₂	408	II	$\langle 100 \rangle$
TbCo ₂	237	II	$\langle 111 \rangle$
DyCo ₂	138	I	$\langle 100 \rangle$
HoCo ₂	78	I	{ $\langle 100 \rangle$ above 18 K $\langle 110 \rangle$ below 12 K}
ErCo ₂	32	I	$\langle 111 \rangle$
TmCo ₂	5	I?	$\langle 111 \rangle$
YCo ₂		Paramagnet	
LuCo ₂		Paramagnet	

TABLE II. Distortion of cubic unit cell as function of the EMA orientation, and connection between the distortion parameters and the magnetostriction constants (φ is the angle between the magnetization direction and the x axis).

EMA	Bravis-lattice symmetry	Space group	Pseudocubic-lattice symmetry	Character of distortions	Parameters of distortions and their connection with λ_{100} and λ_{111}
[110]	Rhombic	$Immm$	Mono-clinic	$\begin{cases} a = b \neq c \\ \alpha = \beta = \pi/2, \gamma \neq \pi/2 \end{cases}$	$\begin{cases} (a-c)/c = 3/4\lambda_{100}, \Delta\gamma \\ = 3/2\lambda_{111} \end{cases}$
III. (001)	Mono-clinic	$C2/m$	Mono-clinic	$\begin{cases} a \neq b \neq c, \\ \alpha = \beta = \pi/2, \gamma \neq \pi/2 \end{cases}$	$\begin{cases} (a-c)/c = 3/2\lambda_{100} \cos^2 \varphi \\ (b-c)/c = 3/2\lambda_{100} \sin^2 \varphi \\ \Delta\gamma = 3/2\lambda_{111} \sin^2 \varphi \end{cases}$
[100]	Tetra-gonal	$I4/mmm$	Tetra-gonal	$\begin{cases} a \neq b = c \\ \alpha = \beta = \gamma = \pi/2 \end{cases}$	$(a-c)/c = 3/2\lambda_{100}$
pl. (011)	Mono-clinic	$C2/m$	Tri-clinic	$\begin{cases} a \neq b = c \\ \alpha \neq \pi/2 \\ \beta = \gamma \neq \pi/2 \end{cases}$	$\begin{cases} (a-c)/c = 3/2\lambda_{100} (\cos^2 \varphi \\ - 1/2 \sin^2 \varphi), \\ \Delta\alpha = 3/2\lambda_{111} \sin^2 \varphi, \\ \Delta\beta = 3 \cdot 2^{-3/2} \lambda_{111} \sin 2\varphi, \\ \Delta\alpha = \lambda_{111} \end{cases}$
[111]	Rhomboidal	$R\bar{3}m$	Rhomboidal	$\begin{cases} a = b = c \\ \alpha = \beta = \gamma \neq \pi/2 \end{cases}$	

investigating the crystal structure of polycrystals of these compounds and of their solid solutions in one another by an x-ray method as temperatures above and below the magnetic-ordering point. The x-ray measurements yielded the unit-cell volume and the character of the distortions of the cubic crystal structure in the magnetically ordered state.

The spontaneous bulk magnetostriction

$$\omega = (V - V_p) / V_p \quad (1)$$

is given by the difference between the volume V of the unit cell at a given temperature and the "paramagnetic" unit-cell volume V_p obtained by extrapolation from the paramagnetic temperature region in accordance with the Debye law that describes the phonon contribution to the thermal expansion.

The character of the crystal-structure magnetoelastic distortions due to the anisotropic magnetostriction depends on the orientation of the magnetic moment in the crystal (in a vanishing magnetic field it is determined by the direction of the EMA). In the most general case, the resultant distortions can be described by five independent quantities: three angular, $\Delta\alpha = \alpha - \pi/2, \Delta\beta = \beta - \pi/2$ and $\Delta\gamma = \gamma - \pi/2$, the deviations of the angles α, β and γ between neighboring edges of the distorted cube from $\pi/2$, and two linear $(a-c)/c$ and $(b-c)/c$, where a, b , and c are the lengths of the distorted-cube edges.¹⁾ The properties of the crystal structure at different orientations of the EMA are summarized in Table II.

The magnetoelastic strains of the crystal lattice can be expressed in terms of the magnetostriction constant. Retaining in the expansion of the magnetostriction constant. Retaining in the expansion of the magnetoelastic energy the terms of second order in the direction cosines α_i , we get for the magnetostriction of a single-domain cubic crystal, in the direction specified by the direction cosines β_i , the expression

$$\lambda = 3/2\lambda_{100} \sum_i \alpha_i^2 \beta_i^2 + 3\lambda_{111} \sum_{i < j} \alpha_i \alpha_j \beta_i \beta_j \quad (2)$$

The connection between the distortion parameters $\Delta\alpha, \Delta\beta, \Delta\gamma, (a-c)/c$ and $(b-c)/c$ and the magnetostriction constants λ_{100} and λ_{111} for different cases of the EMA orientation is given in Table II.¹⁵ It can be seen from this table that the constants λ_{100} and λ_{111} describe magnetoelas-

tic strains produced when the magnetic moment is oriented along the axis $\langle 100 \rangle$ or $\langle 111 \rangle$.

It must be emphasized that relation (2) is approximate and addition of terms of higher order in the magnetic-moment direction cosines leads to a more complicated dependence of the magnetostriction on the magnetic-moment orientation. The magnetostriction constants λ_{100} and λ_{111} given below for $R\text{Co}_2$ compounds should therefore be regarded as certain effective values that describe the crystal strains when the magnetic moment is oriented along $\langle 100 \rangle$ or $\langle 111 \rangle$.

As already noted, x-ray measurements yield directly the magnetoelastic strains only for a state in which the magnetization is oriented along the EMA (since the measurements are made in zero field). In most $R\text{Co}_2$ compounds, the EMA are the high-symmetry directions $\langle 111 \rangle$ or $\langle 100 \rangle$ (see Table I), so that x-ray investigations can yield only one of the two magnetostriction constants (Table II).

To find the second magnetostriction constant we have investigated the spontaneous anisotropic magnetostriction of mixed compounds $R_x'R_{1-x}\text{Co}_2$. If the rare earths R' and R'' are chosen so that the compounds with only one or the other have different EMA, the EMA orientation of the mixed compound can be made close to that of the predominant rare earth. A theoretical analysis, and also our experimental data (see below), show that in addition to those phases in which the magnetic moments of R' and R'' are collinear, phases in which the moments of R' and R'' make an angle with each other can be produced in an intermediate concentration region (noncollinear or oblique phases).

After obtaining the magnetoelastic distortions for the described concentration region and after determining the corresponding magnetostriction constants, we can extrapolate the results to the compositions with only one of the rare earths, using the fact that in the single-ion model a magnetostriction constant is an additive sum of contributions of individual atoms, and should therefore be linear in the concentration.¹⁶ The magnetostriction constants obtained by such an extrapolation characterize the magnetoelastic strains of $R'\text{Co}_2$ and $R''\text{Co}_2$ along the difficult magnetization axis.

SAMPLES AND EXPERIMENTAL PROCEDURES

Polycrystalline samples of the mixed compounds $(\text{Gd}, \text{R})\text{Co}_2, (\text{Ho}, \text{R})\text{Co}_2$ ($\text{R} = \text{Tb}, \text{Dy}, \text{Er}$);

(Tb,R)Co₂ (R = Dy,Er);(Dy,Er)Co were smelted from the initial components in an electric-arc furnace on a water-cooled copper base in an argon atmosphere. The systems (Tm,R)Co₂ (R = Tb,Dy,Er) were smelted, in view of the high volatility of thulium, in an induction furnace in an argon atmosphere under quasi-levitation conditions. The ingots were remelted two or three times and homogenized at 850–900 °C for 150–200 h in a dynamic vacuum of $\sim 10^{-4}$ Torr. The samples investigated were single-phase (no more than 3% impurities) as monitored by x-ray phase analysis.

The crystal structure of polycrystals of the resultant systems was investigated at temperatures 7.5–300 K using an x-ray diffractometer with a free-flow Oxford Instruments cryostat, and Co K α radiation. The measurements were made on relatively distant reflections that are split in a comparatively simple manner due to distortion of the cubic structure. In the present study the rhombohedral distortion $\Delta\alpha$ in the phase with the EMA along $\langle 111 \rangle$ was calculated from the splitting of the (440) cubic reflection, while in the tetragonal phase (EMA along $\langle 100 \rangle$) the value of $(a - c)/c$ was calculated from the splitting of the (620) reflection. The appropriate relations for the calculations can be easily obtained from the structural radiography equations.¹⁷

Note that the x-ray method of determining the magnetostrictions from crystal-lattice distortions, despite its advantages, is rather insensitive. In our case, using Co K α radiation, we were able to discern λ_{111} and $\lambda_{100} \approx (0.5 \pm 0.2) 10^{-3}$.

The signs of the magnetostriction constants at distortions of order 10^{-3} cannot be determined in all cases from the profiles of the split reflections, since the intensity ratios of these reflections do not agree with those which follow from the structural-radiography equations, owing to magnetostatic effects and also to deformation of the base of the lattice (nonuniform displacements of the RE atoms) in magnetoelastic distortions.¹⁸ We verified the signs of the magnetoelastic distortions that followed from our x-ray measurements against results of measurements of the magnetostriction in a magnetic field.^{11,19} In oblique phases it is impossible to calculate the magnetoelastic distortions from x-ray measurements of polycrystalline samples, owing to the complicated character of the splitting of the x-ray reflections; the type of a particular oblique phase was therefore determined from the theoretical phase diagram for a cubic ferromagnet.²⁰

The magnetic-ordering and spin-reorientation (SR) temperatures of the phase transitions were obtained from the maxima on the temperature dependences of the initial susceptibility, plotted by an induction method in oscillating magnetic fields.

EXPERIMENTAL DATA

Phase diagram

For all the binary R_x'R''_{1-x}Co₂ systems, we used the methods described above to plot the SR phase diagrams and to determine the magnetic-ordering temperatures and the boundaries of various magnetic phases with different EMA directions. By way of example, Fig. 1 shows the phase diagram of the system Ho_xEr_{1-x}Co₂. It can be seen that compositions close to ErCo₂ have a rather wide range in which the EMA is parallel to $\langle 111 \rangle$ (the $\langle 111 \rangle$ phase), i.e., the

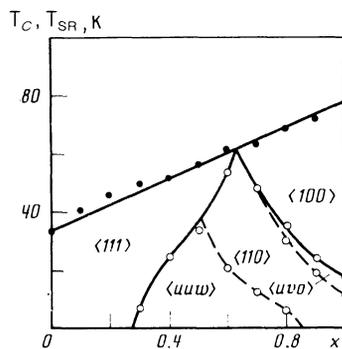


FIG. 1. Magnetic phase diagram of the Ho_xEr_{1-x}Co₂ system: dark circles—Curie temperatures T_C ; light circles—SR transition temperatures T_{SR} . The symbols (hkl) denote the regions where various phases exist.

same as in the initial compound. Similarly, the EMA of compositions close to HoCo₂ have the same directions as in this compound, viz., along $\langle 100 \rangle$ (the $\langle 100 \rangle$ phase) at high temperatures and along $\langle 110 \rangle$ (the $\langle 110 \rangle$ phase) at low ones. Intermediate compositions acquire at low temperatures noncollinear phases of the $\langle uvv \rangle$ type (the EMA lie in $\{100\}$ planes) and of the $\langle uvw \rangle$ type (the EMA lie in $\{110\}$ planes). The phase diagrams of other binary systems in which the individual components have different EMA are qualitatively similar to the one shown in Fig. 1, and only the region in which one magnetic phase or other exists changes. Thus, for example, in systems with gadolinium, the EMA of compositions with large gadolinium content (80–90%) the DMA orientation is that of the second component. The reason is that the magnetic anisotropy of GdCo₂ is negligible compared with the anisotropy of other rare earths.²¹

Anisotropic magnetostriction: temperature dependence

In most mixed systems the anisotropic-magnetostriction constants decrease monotonically as the temperature increases. This is clearly seen in Fig. 2, which shows plots of $\lambda_{111}(T)$ and $\lambda_{100}(T)$ for the mixed compounds (Tb,Ho)Co₂ (Dy,Tm)Co₂ respectively. Noteworthy are the nonmonotonic temperature dependences of the magnetostriction con-

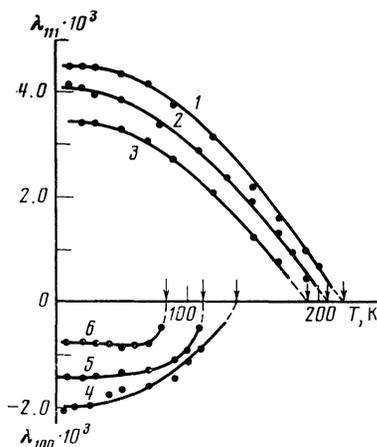


FIG. 2. Typical temperature dependences of the magnetostriction constants λ_{111} and λ_{100} . System Tb_xHo_{1-x}Co₂ (λ_{111}): 1 - $x = 0.9$; 2 - $x = 0.8$; 3 - $x = 0.7$. System Dy_xTm_{1-x}Co₂ (λ_{100}): 4 - $x = 1.0$; 5 - $x = 0.8$; 6 - $x = 0.6$. The arrows indicate T_C .

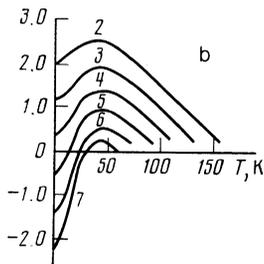
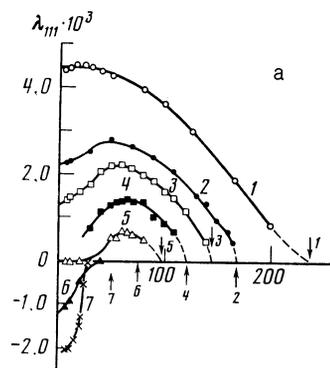


FIG. 3. Temperature dependence of the magnetostriction constant λ_{111} of mixed compounds $Tm_xTb_{1-x}Co_2$: a—experimental data, b—calculated using Eq. (4); 1— $x=0$; 2— $x=0.3$; 3— $x=0.4$; 4— $x=0.5$; 5— $x=0.6$; 6— $x=0.7$; 7— $x=0.8$. The arrows mark T_C .

stant λ_{111} in mixed $Tm_xTb_{1-x}Co_2$ compounds (Fig. 3a). In some compositions this constant increases with temperature and goes through a maximum. The nature of these singularities will be discussed below.

Anisotropic magnetostriction: concentration dependence

Figures 4 and 5 show the concentration dependences of the magnetostriction constants λ_{111} and λ_{100} of mixed $R_xR''_{1-x}Co_2$ compounds (extrapolated to 0 K). Note that in those cases when both initial compounds have the same EMA, or when the given magnetic phase is preserved in a wider range of concentrations, the dependence of the magnetostriction constants on x is linear within the limit of errors, i.e., linear extrapolation of the magnetostriction concentration dependences is justified. The validity of this extrapola-

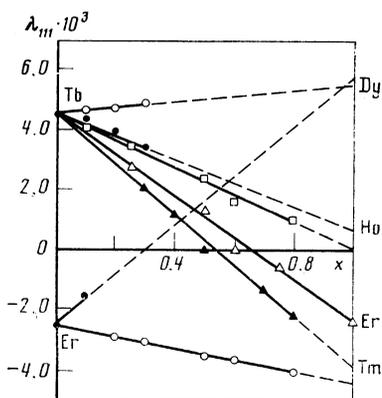


FIG. 4. Magnetostriction constants λ_{111} of the compounds $(R', R'')Co_2$ vs the concentration x . Points—experiment, dashed straight lines—extrapolation (the squares indicate data for Gd).

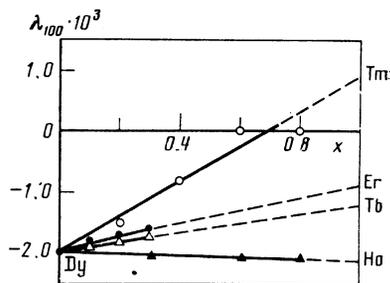


FIG. 5. Magnetostriction constants λ_{100} of the compounds $(R', R'')Co_2$ vs the concentration x . Points—experiment, dashed straight lines—extrapolation.

tion is confirmed also by comparison with direct measurement data e.g., of λ_{111} for $HoCo_2$.

Table III lists the magnetostriction constants λ_{111} and λ_{100} of RCO_2 compounds at 0 K, obtained by us (both by direct measurement and by extrapolation) and by others. The satisfactory agreement among the various data is evident.

Nature of anisotropic magnetostriction of RCO_2 compounds

As already noted, the anisotropic magnetostriction of RCO_2 compounds is explained in terms of the single-ion magnetoelastic interaction model. According to this model, the anisotropic-magnetostriction constants can be represented in the form²³

$$\lambda_i = C\alpha_i J_R (J_R - 1) \langle r_{4f}^2 \rangle, \quad (3)$$

where $J_R = L_R + S_R$ is the total angular momentum of the RE, α_i is a second-order Stevens coefficient, $\langle r_{4f}^2 \rangle$ is the mean squared radius of the 4f shell, and C is a numerical factor and is the same for all RE. We compare our experimental values of the magnetostriction constants of the RCO_2 compounds in Fig. 6 with the theoretical relations calculated from the number of the RE in accordance with Eq. (3) (the normalization is with respect to the magnetostriction of $TbCo_2$). It can be seen that the experimental dependence of the magnetostriction constants agrees quite satisfactorily with the theoretical dependence for the single-ion model. At the same time, Eq. (3) does not describe at all the dependence of the magnetostriction constant λ_{100} on the number of the RE element: for all the investigated compounds (except $TmCo_2$) these constants are close to the constant λ_{100} of $GdCo_2$, whereas the contribution of Gd to the single-ion magnetostriction should be negligible compared with that of the other rare earths. It can therefore be concluded that in RCO_2 compounds with anisotropic RE, just as in $GdCo_2$, the magnetostriction constant is determined mainly by the cobalt subsystem. This conclusion is corroborated also by the fact that in the isostructural compounds GdM_2 ($M = Ni, Fe$) the constant λ_{100} is close to zero.²⁴ In addition, the theoretical calculations show that in the cubic Laves C 15 phases the single-ion magnetostriction along the $\langle 100 \rangle$ axis, which is due to the RE, should be small ($\lambda_{100} \ll \lambda_{111}$).²⁵ A plausible theory of anisotropic magnetostriction in the band-magnetism model, capable of describing the cobalt system in RCO_2 , has not yet been developed. It can be assumed to be determined, in analogy with calculations of

TABLE III. Magnetostriction constants of intermetallic RCo₂ compounds at 0 K.

Compound	$\lambda_{100} \cdot 10^2$	$\lambda_{111} \cdot 10^3$
GdCo ₂	-1.2 [13, 21]	≤ 0.1 * [a]
TbCo ₂	-1.2 * [16, a]	{ 4.5 [12], 4.4 [22], 4.1 [11]
DyCo ₂	{ -2.0 [12], -1.3 [11] -1.2 [19], -1.9 [a]	5.0 * [16, a]
HoCo ₂	{ -2.2 [12], -2.2 * [a], -2.0 [17]	{ 0.3 [12], 0.5 * [a], 0.6 [17]
ErCo ₂	-1.0 * [16, a]	{ -2.5 [12], -2.2 [16], -3.5 [19]
TmCo ₂	0.75 * [a]	-4.1 * [a]

*—Values obtained by extrapolating the concentration dependence; [a]—present data; numbers in brackets—references.

the magnetic anisotropy of other band systems, by subtle singularities from one RCo₂ compound to another can influence the value of λ_{100} . This is confirmed by the data for TmCo₂: the cobalt system of this compound, as will be shown below, is in a state different from that of the other components, and the constant λ_{100} has a different sign. It is possible, however, that some contribution to the constant λ_{100} of RCo₂ compounds is made by the single-ion magnetostriction of the RE subsystem. This question needs further study.

We consider now the temperature dependence of the magnetostriction constants λ_{111} of mixed R_xR'_{1-x}Co₂ compounds (we shall not discuss the temperature dependence of λ_{100} , since there are no theoretical models for the description of the variation of the band anisotropic magnetostriction with temperature). It was shown earlier^{22,26} that the temperature dependence of the magnetostriction constant λ_{111} of TbCo₂ is described by the single-ion model. In this model, the magnetostriction of mixed compounds is given by

$$\lambda(T) = x\lambda_{111}^{R'}(0) I_{5/2}[\mathcal{L}^{-1}(m_{R'}(T))] + (1-x)\lambda_{111}^{R''}(0) I_{5/2}[\mathcal{L}^{-1}(m_{R''}(T))], \quad (4)$$

where $\lambda_{111}^{R'}(0)$ and $\lambda_{111}^{R''}(0)$ are the magnetostriction constants of the compounds R'Co₂ and R''Co₂ at 0 K, $m_{R'}$ and $m_{R''}$ are the relative magnetizations of R' and R'', respectively, $I_{5/2}$ is a modified Bessel function, and \mathcal{L}^{-1} is the inverse Langevin function. Comparison of the experimental

data with the theoretical equation (4) is made difficult by the fact that we do not know $m_{R'}$ and $m_{R''}$. For an approximate comparison we used the data of Ref. 2, in which the parameters A_{RR} , and A_{RC} of RE-RE and RE-cobalt exchange interactions were determined in the molecular-field approximation, and it was shown that these parameters are approximately equal for the heavy rare earths. We have then for $m_{R'}$ and $m_{R''}$, which are described in the model of localized magnetic moments,

$$m_{R'} = \mu_{R'}(T) / \mu_{R'}^0 = B_{J_{R'}}(\mu_{R'}^0 H_{\text{eff}}^{R'} / kT), \quad (5)$$

$$m_{R''} = \mu_{R''}(T) / \mu_{R''}^0 = B_{J_{R''}}(\mu_{R''}^0 H_{\text{eff}}^{R''} / kT),$$

where the effective fields are

$$H_{\text{eff}}^{R'} = n_{R'R'}x\mu_{R'} + n_{R'R''}(1-x)\mu_{R''} + n_{R'Co}\mu_{Co}, \quad (6)$$

$$H_{\text{eff}}^{R''} = n_{R''R''}(1-x)\mu_{R''} + n_{R''R'}x\mu_{R'} + n_{R''Co}\mu_{Co},$$

and

$$n_{ii} = 2A_{RR}(g_i - 1)^2 / g_i^2, \quad n_{iCo} = A_{RCo}(g_i - 1) / g_i, \quad (7)$$

$$n_{ij} = 2A_{RR}(g_i - 1)(g_j - 1) / g_i g_j, \quad (i \neq j) \quad i = R', R'',$$

while μ_i^0 is the magnetic moment of the free trivalent RE ion. The magnetic moment of the band cobalt subsystem was calculated in Ref. 2 in the linear approximation and found to be

$$\mu_{Co} = \chi_{Co} H_{\text{eff}}^{Co}, \quad (8)$$

where the effective field acting on the cobalt system is

$$H_{\text{eff}}^{Co} = n_{R'Co}x\mu_{R'} + n_{R''Co}(1-x)\mu_{R''} = A_{RCo}[x(g_{R'} - 1)J_{R'} + (1-x)(g_{R''} - 1)J_{R''}]. \quad (9)$$

We used the equations above to calculate the temperature dependences of the magnetostriction constants λ_{111} of the system Tm_xTb_{1-x}Co₂. The resulting curves are shown in Fig. 3b. It is seen that $\lambda_{111}(T)$ for the intermediate compositions is nonmonotonic, as are also the experimental curves. This behavior of $\lambda_{111}(T)$ can be qualitatively explained in the following manner. Since, according to (6) and (7), the effective field acting on the thulium is, weaker than the one acting on the terbium (the g factor of terbium, $g_{Tb} = 3/2$, is larger than the thulium g factor $g_{Tm} = 7/6$), it follows that at high temperatures the ordering is greater in the terbium than

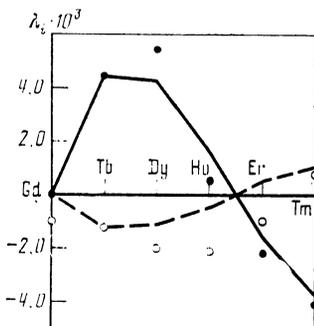


FIG. 6. Dependences of λ_{111} (dark circles) and λ_{100} (light) on the RE atomic number. Solid and dashed lines—calculation of λ_{111} and λ_{100} from Eq. (3) respectively.

in the thulium subsystem. Therefore the magnetostriction of the terbium subsystem predominates in $\text{Tm}_x\text{Tb}_{1-x}\text{Co}_2$ at high temperatures, and as the temperature is lowered an ever increasing contribution is made by the magnetostriction due to thulium. The single-ion magnetostriction constants of these subsystems are approximately equal in magnitude and opposite in sign. It is competition between contributions of opposite sign and with different temperature dependences which produces the observed nonmonotonic dependence of the magnetostriction constant λ_{111} .

Comparison of Figs. 3a and 3b shows that the theoretical calculation describes qualitatively the experimental $\lambda_{111}(T)$ dependences of the system $\text{Tm}_x\text{Tb}_{1-x}\text{Co}_2$. It must be noted that this calculation is very approximate. We have described the temperature dependences of the magnetizations of the different systems in the magnetically ordered state by using exchange parameters obtained from measurements of high-temperature (paramagnetic) susceptibility. In addition, in the calculation we used the simplest linear approximation for the magnetic moment (9) of the cobalt subsystem, an approximation that cannot describe the band metamagnetism of this subsystem. It follows from the calculation, in particular, that the transition to the magnetically ordered state should be a second-order phase transition, whereas the experimental data show it to be (at any rate in compounds with large thulium contents) first order. This gives rise to a quantitative discrepancy between the experimental $\lambda_{111}(T)$ dependences and the theoretical ones, a discrepancy particularly noticeable at high thulium concentrations.

It must be emphasized, in addition, that the foregoing theoretical analysis is valid, strictly speaking, only for compounds in which the energy of the crystal field acting on the RE ion is much lower than the exchange interaction, and this ion can be regarded as almost free. It is just in this approximation that Eqs. (3)–(5) are valid. In RCO_2 compounds the exchange and crystal-field energies are comparable, so that the equations above are suitable only for a semiquantitative description. More accurate relations for the magnetization and magnetostriction can be obtained by diagonalizing the total system Hamiltonian that takes into account, besides the crystal-field and exchange energies, also the magnetoelastic and elastic energies, in analogy with the procedure used in Refs. 27 and 28 for the compounds RAI_2 and RNi_2 . Extension of this method to include RCO_2 compounds, however, is hindered by the fact that the crystal-field parameters of these compounds are at present practically unknown, nor is there an adequate quantitative description of their cobalt systems.

Bulk magnetostriction of RCO_2 compounds

We have already noted that RCO_2 compounds have a large spontaneous bulk anisotropy due to the magnetic ordering of the cobalt subsystem. Figure 7, shows by way of example the temperature dependences of the parameter of the cubic crystal structure of the (Tb,Tm) Co_2 systems (the average lattice parameter $a = (V_{e1})^{1/2}$ is plotted below the magnetic-ordering point, where magnetoelastic distortions of the crystal structure set in). It can be seen that in the magnetically ordered state the dependence of the lattice parameter on the temperature is subject to considerable anom-

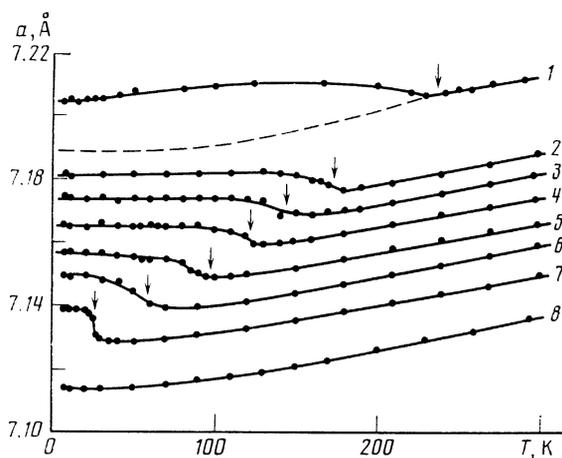


FIG. 7. Temperature dependences of the lattice parameters ($a = (V_{e1})^{1/2}$ in the magnetically ordered region) of the mixed compounds $\text{Tm}_x\text{Tb}_{1-x}\text{Co}_2$: 1 - $x = 0$; 2 - $x = 0.3$; 3 - $x = 0.4$; 4 - $x = 0.5$; 5 - $x = 0.6$; 6 - $x = 0.7$; 7 - $x = 0.8$; 8 - $x = 1.0$ (dashed—Debye dependence). The arrows mark T_C .

alies, deviating substantially from the Debye dependence (shown dashed for curve 1 of Fig. 7). Similar $a(T)$ relations are observed also for other mixed $\text{R}'_x\text{R}''_{1-x}\text{Co}_2$ compounds.

In the band model, the exchange magnetostriction is related not only to the dependence of the exchange integral on the distance, but also to the fact that the volume increase by magnetic ordering balances the average-kinetic-energy increase produced when the subbands with “up” and “down” spins are separated. The theory of band magnetism predicts the following dependence of the bulk magnetostriction on the cobalt-subsystem magnetic moment²⁹:

$$\omega = ck\mu_{\text{Co}}^2, \quad (10)$$

where k is the hydrostatic compressibility and c is a numerical coefficient that relates the volume and the magnetism. Thus, investigations of the bulk spontaneous magnetostriction permit an assessment of the magnetic moment of the

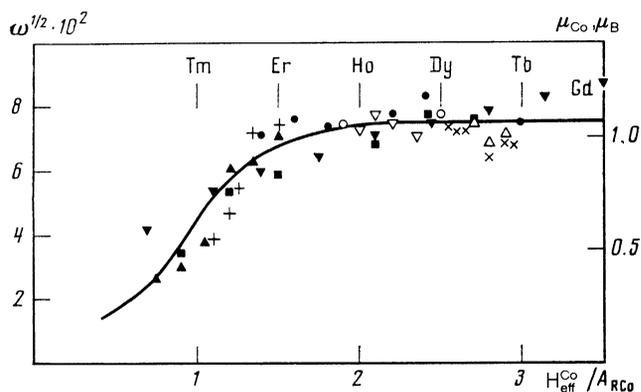


FIG. 8. Dependence of $\omega^{1/2}$ of the compounds $(\text{R}',\text{R}'')\text{Co}_2$ on $H_{\text{eff}}^{\text{Co}}/A_{\text{RCO}} = x(g_{\text{R}'} - 1)J_{\text{R}'} + (1-x)(g_{\text{R}''} - 1)J_{\text{R}''}$. $J_{\text{R}'} = \text{Tm}_x\text{Tb}_{1-x}\text{Co}_2$; $\circ - \text{Tm}_x$. $J_{\text{R}''} = \text{Tm}_x\text{Er}_{1-x}\text{Co}_2$; $\times - \text{Tb}_x$. $\text{Dy}_{1-x}\text{Co}_2$, $\Delta - \text{Ho}_x\text{Tb}_{1-x}\text{Co}_2$, $\blacktriangle - \text{Er}_x\text{Y}_{1-x}\text{Co}_2$ (Ref. 30), $\nabla - \text{Ho}_x\text{Dy}_{1-x}\text{Co}_2$, $\square - \text{Tb}_x\text{Y}_{1-x}\text{Co}_2$, $\blacktriangledown - \text{Gd}_x\text{Y}_{1-x}\text{Co}_2$ (Ref. 31). Solid line—combined data for μ_{Co} (Ref. 33) normalized to the experimental data on $\omega^{1/2}$.

cobalt subsystem. According to (10), the bulk magnetostriction should be proportional to μ_{Co}^2 and should therefore reflect the metamagnetic dependence of the magnetic moment of the cobalt subsystem on the effective field. Figure 8 shows plots of $\omega^{1/2}$ extrapolated to 0 K, for mixed $\text{R}'_x\text{R}_{1-x}\text{Co}_2$ compounds, vs the dimensionless parameter $H_{\text{eff}}^{\text{Co}}/A_{\text{RCo}}$ that characterizes the effective field $H_{\text{eff}}^{\text{Co}}$ acting on the cobalt subsystem [see Eq. (9)]. Both our results and those of others are shown. It is evident that all the data are described satisfactorily by a single curve (the scatter is due to the fact that the measurements were made by different methods and to the appreciable uncertainty in the choice of the Debye temperature). This curve has a metamagnetic form: $\omega^{1/2}$ varies little at large values of the effective field and decreases abruptly when the field drops below the measured value. The $\omega^{1/2}(H_{\text{eff}}^{\text{Co}})$ dependence agrees satisfactorily with the dependence of the magnetic moment of the cobalt subsystem on the effective field (these data are gathered in Refs. 32 and 33) (Fig. 8). It can thus be concluded that the bulk magnetostriction of RCo_2 compounds is of exchange origin and is determined by the cobalt subsystem.

The $\omega^{1/2}(H_{\text{eff}}^{\text{Co}})$ dependence obtained makes it possible to obtain the magnetic moment of the cobalt in TmCo_2 , although the low Curie temperature (our susceptibility measurement gave $T_C \approx 4.5$ K) prevented a direct investigation of the magnetoelastic properties of the cobalt. The large scatter of the data on the magnetic-ordering temperatures in TmCo_2 is noteworthy. Earlier papers^{34,35} cite values of 18 and 33 K. It was shown in Ref. 36 that T_C of this compound depends on its preparation and can range from 3.9 to 6.5 K. This may be due to the existence of a narrow homogeneity region in RCo_2 compounds.

It follows from Fig. 8 that $\mu_{\text{Co}} \approx 5.5\mu_B$ in TmCo_2 . This is intermediate between the values $0.48\mu_B$ (Ref. 36) and $0.8\mu_B$ (Ref. 37) obtained by neutron diffraction. The magnetic moment of the cobalt in TmCo_2 is thus somewhat smaller than in other RCo_2 compounds with heavy RE. Yet a bulk anomaly sets in discontinuously below the magnetic-ordering temperature in all mixed $(\text{Tm,R})\text{Co}_2$ systems having large thulium contents (including systems containing negligible amounts of thulium, in which the magnetic moment varies smoothly, as it should in a second-order transition). This is evidence that the thulium-cobalt exchange field in TmCo_2 exceeds the metamagnetic-transition field of the cobalt transition, and the transition into the magnetically ordered state is a first-order phase transition. The order of the transition deduced in TmCo_2 agrees also with the results of Mössbauer investigations.⁹

CONCLUSION

Systematic investigations of the spontaneous isotropic and anisotropic magnetostriction of intermetallic RCo_2 compounds have thus shown the following:

1) The anisotropic magnetostriction constant λ_{111} has a single-ion character and is due to the interaction of the anisotropic 4f-shell cloud of the RE with the lattice crystal field.

2) The anisotropic magnetostriction constant λ_{100} is governed by the cobalt subsystem.

3) The bulk (isotropic) magnetostriction is of exchange origin and is governed by the cobalt subsystem. The dependence of the bulk magnetostriction on the effective field confirms the metamagnetism of the cobalt system.

¹Strictly speaking, to describe cubic-structure distortions it is necessary to transform to new unit cells. It is more convenient, however, to retain the "pseudocubic" cell and describe it by pseudocubic Miller indices.

²Analysis of magnetic phase diagrams of mixed $\text{R}'_x\text{R}_{1-x}\text{Co}_2$ compounds is of independent interest from the standpoint of explaining the nature of their anisotropy. This question is not discussed in the present paper.

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