Magnetic anisotropy of alloys of terbium with yttrium and gadolinium

S. A. Nikitin and N. P. Arutyunian

Moscow State University
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The nature of the magnetic anisotropy of terbium-yttrium and terbium-gadolinium alloys is investigated. The single-ion magnetic anisotropy constant \( K_1 \) at 4.2 K and the magnetic anisotropy constant in the basal plane \( K_2 \) of these alloys are measured in the temperature interval 78-190 K. Anomalies are observed in the concentration dependence of \( K_1 \) in \( \text{Tb}_x\text{Y}_{1-x} \) alloys in the interval \( x = 0.3-0.5 \), and a nonlinear concentration dependence of \( K_2 \) is observed in the \( \text{Tb}_x\text{Gd}_{1-x} \) alloys. An analysis of the experimental data indicates predominance of the single-ion crystal anisotropy and the presence of a smaller contribution due to anisotropic exchange. It is established that the dependence of \( K_1 \) on the relative magnetization and on the concentration can be described by the single-ion mechanism of the interaction of the orbital angular momentum with the crystal lattice field.

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INTRODUCTION EXPERIMENTAL PROCEDURE

The gigantic magnetic anisotropy of rare-earth metals (REM) is presently attributed to two competing mechanisms: the interaction of the orbital angular momentum with the crystal lattice field (single-ion model), or anisotropic indirect two-ion exchange interaction.\(^{1,2}\) The relative role of these mechanism is not clear to this day, and the published data lead to contradictory conclusions.\(^{3,4}\) Further theoretical and experimental investigations of the magnetic anisotropy of REM alloys are therefore necessary.

The purpose of the present study was to determine the nature of the magnetic anisotropy of alloys of terbium with yttrium and gadolinium, in which the magnetic anisotropies of the components differ greatly. Terbium has a gigantic magnetic anisotropy,\(^{5,6}\) whereas the magnetic anisotropy of gadolinium is smaller by two orders of magnitude.\(^{7}\) This difference is due to the singularity of the electronic structures of terbium and gadolinium. Whereas the trivalent gadolinium ion is in the \( S \) state \((L=0)\) and has a spherical \( g_f \) electron shell, the trivalent terbium ion, which has one more \( f \) electron, has an oblate \( g_f \) electron shell because an additional electron is added to the spherical \( g_f \) subshell of the gadolinium ion, resulting in an orbital angular momentum \( L=3.\)

As for yttrium, it is a Pauli paramagnet and assumes in REM alloys the role of an ideal magnetic solvent\(^{8}\) because the external electron shells of yttrium and the REM are similar, while the crystal-lattice constants of yttrium and heavy REM are quite close. Alloys of heavy REM with each other and with yttrium have hope lattices.\(^{9}\)

Results of studies of the anisotropy of the paramagnetic Curie points in terbium-yttrium and terbium-gadolinium alloys were reported earlier.\(^{10,11}\) These data, however, are insufficient for a final elucidation of the nature of the magnetic anisotropy in alloys, because the magnetic anisotropy can differ greatly in the paramagnetic and magnetically ordered states.

EXPERIMENTAL PROCEDURE

The technology of growing single crystals of the alloys \( \text{Tb}_x\text{Y}_{1-x} \) and \( \text{Tb}_x\text{Gd}_{1-x} \) and of the control of their quality were described in earlier papers.\(^{10-12}\) The uniaxial magnetic anisotropy constants were determined by us from the magnetization curves measured at 4.3 K along the hexagonal \( c \) axis (the difficult magnetization axis) and is the basal plane along the easy-magnetization axis. The magnetization was measured with a vibration magnetometer in a superconducting solenoid in magnetic fields up to 70 kOe, and in the case of some samples in a pulsed magnetic field up to 500 kOe, using a previously described procedure.\(^{13}\) The magnetic-anisotropy constant in the basal plane was measured by the torque method with an anisometer whose design was similar to that proposed by Bryukhatov and Kirenchik.\(^{14}\)

To measure the magnetization in the superconducting solenoid, the samples were cut in the form of rectangular rods measuring 10 x 10 x 2 mm. The samples used in the torque measurements were disks of 4 mm diameter and 1 mm thickness. After cutting, the samples were chemically etched and annealed. The single-crystal samples were oriented along the crystallographic directions by the Laue method using the UR5-90 apparatus. The orientation accuracy was not worse than \( \pm 3° \). The error in the measurement of the magnetization with the vibration magnetometer was \( \pm 5\% \), in pulsed fields \( \pm 2\% \), and in torque determination \( \pm 3\% \).

EXPERIMENTAL RESULTS

Figures 1a and 1b show the magnetization curves of the alloys \( \text{Tb}_x\text{Y}_{1-x} \) and \( \text{Tb}_x\text{Gd}_{1-x} \), measured with a vibration magnetometer at a temperature 4.2 K. The magnetization along the \( b \) axis saturates rapidly, but is relatively small along the \( c \) axis, which is the difficult magnetization axis. A linear growth of the magnetization \( c \) is observed for all the \( \text{Tb}_x\text{Y}_{1-x} \) alloys, and a nonlinear \( c(\theta) \) dependence is obtained for the \( \text{Tb}_x\text{Gd}_{1-x} \) alloys at a high gadolinium concentration (curve 5 of Fig. 1b).
The magnetic moment of a single-domain ferromagnet, with account taken of the magnetic anisotropy, can be written in the case of a hexagonal crystal lattice in the form

$$F_A = K, \cos \theta + K, \sin \theta \sin \phi + K, \sin \phi \cos \phi,$$  

(1)

where $\theta$ is the angle between the vector of the spontaneous magnetization $I$, and the hexagonal c axis, $K, \ldots$ are the magnetic-anisotropy constants, and $\phi$ is the angle between the magnetization projection and the c axis.

From the condition that the free energy $F_A$ be a minimum as a function of $\phi$, we get

$$2K,\cos \phi - H,\sin \phi = 0,$$

(2)

where $I = I, \cos \theta$ is the projection of the magnetic moment on the c axis. If the magnetic data are used to plot $-H,\cos \phi$ against $1/I, \cos \theta$, then the slope of the line yields $-4K, \ldots$, and the intercept on the ordinate axis is equal to $2K,\cos \theta$. The determination of the magnetic-anisotropy constant from the magnetization curves measured along the difficult magnetization axis was used to determine the magnetic-anisotropy constants of REM alloys.\textsuperscript{18} Quantum mechanical calculations have proved the validity of this method.\textsuperscript{18}

This method can be used for the ferromagnetic Tb$_x$Y$_{1-x}$ alloys without restrictions, since these alloys contain magnetic-active ions of only one type—terbium. When magnetized along the c axis, the magnetic moments of the terbium ions in a single-domain sample are parallel to one another and their angle with the c axis is the same as that of the resultant magnetization. The same angle is made by the c axis and the magnetic moments of the terbium ions also in the antiferromagnetic Tb$_x$Y$_{1-x}$ alloys with helicoidal structure, except that the magnetic moments of neighboring basal planes are at some angle with one another.\textsuperscript{17} In the experiment, a linear growth of the magnetization with increasing field is observed in both cases in fields up to 70 kOe. The magnetic-anisotropy constant determined for the antiferromagnetic Tb$_x$Y$_{1-x}$ alloys must be corrected to allow for the change of the energy of the exchange interaction between the layers when the antiferromagnetic helicoidal structure is destroyed. As a result, the magnetic anisotropy constant $K,^{11}$ determined from the magnetization curves contains a contribution that takes into account the "helicoidal energy":

$$K,^{11} = K, + H,c,H,$$

(3)

where $H,c$ is the critical magnetic field at which the helicoidal structure collapses.

A reduction of the magnetization curves in accord with Eq. (2) has shown that $|K,| = |K,|$ and can be disregarded in first-order approximation. This agrees with the results of Ref. 18, where it was shown that in pure terbium $|K,|/|K,| \approx 0.1$. It is seen from Fig. 3, which shows a plot of the constant $K, \ldots$ of the Tb$_x$Y$_{1-x}$ alloys against the terbium concentration, that the magnetic...

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**Figure 1.** Dependence of magnetization on the true magnetic field: 1) for the alloys Tb$_x$Y$_{1-x}$, along the c axis, curves 1) $x=1$, 2) $x=0.91$, 3) $x=0.09$, and along the c axis, 4) $x=1$, 5) $x=0.09$; b) for the alloys Tb$_x$Gd$_{1-x}$, curves 1) $x=0.94$, 2) $x=0.09$, 3) $x=0.835$, 4) $x=0.94$, 5) $x=0.09$, $H/c$, 6) $x=0.94$, $H/c$.

**Figure 2.** Concentration dependence of the absolute-saturation magnetization $\psi_a$ and of the magnetization $\psi$ in a field along the c axis at 4.2 K. For the alloys Tb$_x$Y$_{1-x}$: 1— for $\psi_a$, 2— for $\psi$, 3—magnetization along the c axis at 70 and 50 kOe, respectively. For the alloys Tb$_x$Gd$_{1-x}$: 4— for $\psi_a$, 5—magnetization along the c axis at 50 kOe.
anisotropy constant reaches the gigantic values (3-5) $\times 10^8$ erg/cm$^3$ in alloys with high terbium concentration ($x>0.5$). The value of $K_1$, obtained for terbium by the method described above is quite close to the value $K_1 = -4.95 \times 10^8$ erg/cm$^3$ previously determined by Levitin and Ponomarev.

The Tb$_x$Y$_{1-x}$ alloys with $x < 0.63$ have an antiferromagnetic helicoidal structure, so that the method based on Eq. (2) leads in this case to a determination of $K''_1$ (curve 3 of Fig. 3). The values of $K_1$ (curve 4 of Fig. 3) were calculated for antiferromagnetic alloys with the aid of Eq. (3) and of the previously determined$^{40}$ values of $H_m$. The most noticeable difference between $K_1$ and $K''_1$ takes place in the region $x > 0.5$-$0.8$, where $H_m$ is quite large, 50-$80$ kOe. When the terbium content is decreased the absolute values of $K_1$ and $K''_1$ are greatly reduced.

Antiferromagnetism exists in the Tb$_x$Gd$_{1-x}$ alloys only at $x>0.94$, and in this case $H_m < 10^8$ Oe, as a result of which the anisotropy-constant correction that takes into account the energy lost to the collapse of the antiferromagnetic structure is quite small. The magnetic-anisotropy constants $K'_2 = - K_1$, calculated by the method described below and shown in Fig. 4 are noticeably non-linear functions of the terbium concentration.

The mechanical torques $L$ were measured in fields up to 23 kOe for the alloys Tb$_x$Y$_{1-x}$ and Tb$_x$Gd$_{1-x}$ in the temperature interval 78-190 K on disks whose planes coincided with the basal plane. Measurements of $L$ as functions of the magnetic field have shown that the values $L_x$ obtained by extrapolating $L= L(0) H$ to $H = 0$ differ from the value of $L$ at $H = 22$ kOe by not more than 5% in the most unfavorable case (at 78 K in alloys containing a large amount of terbium). The mechanical

**DISCUSSION OF RESULTS**

The magnetic-anisotropy energy of a ferromagnet with helicoidal crystal lattice can be expressed by an expansion in Legendre polynomials

$$ E = -K_1' P_1(\cos \theta) + K_1'' P_2(\cos \theta), $$

where $K_1'$ is the anisotropy constant, $P_1(\cos \theta)$ is a Legendre polynomial, and $\theta$ is the polar angle between the magnetisation vector and the c axis. The magnetic anisotropy constants $K_1$ [in Eq. (1)] and $K''_1$ [in Eq. (5)] are interrelated.$^{40}$ The use of the constants $K''_1$ is preferable in a theoretical investigation of the magnetic anisotropy and in a comparison of theory with experiment, since the temperature dependences of the constants $K_1$ and of the atomic constants are more complicated than that of $K_1''$. On the other hand, $K_1$ is easier to determine from experiment.

In first-order approximation, which can be used for terbium and its alloys because $[A_1] > [A_2]$, the magnetic-anisotropy constant per ion $K_{1-ion}$ is connected with the

**FIG. 5.** Dependence of the magnetic anisotropy constant in the basal plane $K_{1-ion}$ on the relative magnetization $\sigma/m$ for Tb$_x$Y$_{1-x}$ alloys (the solid curve was calculated on the basis of the theory of Ref. 20): $\Omega = x = 0.38, \Delta = x = 0.835, \phi = 0.63$. Expansion in a Fourier series made it possible to determine $K'_2$ from the $L_x = L'_2(\phi)$ curves are shown in Figs. 5 and 6 as functions of the relative magnetization.
constant $K$, by the relation

$$K_{\text{an}} = \frac{2}{3} \frac{e}{N}$$

where $A$ is the molecular weight, $N$ is Avogadro's number, $\rho$ is the density, and $f$ is expressed in erg.$^{-1}$ $cm^{-3}$. For the alloys Tb$_{x}$Y$_{1-x}$, the values of $K_{\text{an}}$ are calculated by us from Eq. (6) are shown in Fig. 3 (curve 1). It is seen that the plot of $K_{\text{an}}$ against the terbium concentration has a maximum in the region $x=0.4-0.5$. The concentration dependence of the anisotropy constant $K_{\text{an}}$, with account taken for the correction for the helicoidal-structure collapse energy (curve 2 in Fig. 3), has a minimum at $x<0.3$. These results cannot be explained on the basis of the simple single-ion theory, according to which the contributions made to the magnetic anisotropy by the individual ions are additive, as a result of which the constant $K_{\text{an}}$ must be proportional to the terbium-ion concentration, while the magnetic-anisotropy constant per ion $K_{\text{an}}/x$ should be a constant. According to the one-ion theory, the magnetic-anisotropy constant $K_{\text{an}}$ is given by

$$K_{\text{an}} = \frac{\mu_{B} \mu_{T}}{2 \alpha r^{5}} \frac{1}{1 + \frac{r_{0}^{5}}{r^{5}}}$$

(7)

Here $\mu$ is the electron charge, $r$ is the mean squared radius of the $\Psi$ orbit, $\alpha$ is the quantum number, $r$ is the valence of the REM ion, and the factor $g = (1.633 - c/a) a^{0.5}$ takes into account the deviation of the crystal structure from an ideal hexagonal one ($c$ and $a$ are the lattice parameters). Estimates made by us on the basis of measurements of Belovol, Finkel', and Smokov' of the lattice parameters in Tb$_{x}$Y$_{1-x}$ alloys have shown that the factor $g$ changes monotonically from 1.11-10$^{-3}$ for terbium to 1.26-10$^{-3}$ for the alloy Tb$_{0.35}$Y$_{0.65}$, and allowance for this factor does not explain the anomalies on the plot of $K_{\text{an}}$ against the terbium concentration.

When the magnetic anisotropy constant of Tb$_{x}$Gd$_{1-x}$ alloys is determined it must be recognized that an external magnetic field applied along the magnetic moments of the gadolinium ions and the terbium ions, $\delta_{\text{Gd}}$ and $\delta_{\text{Tb}}$ in (6), are determined by the equations

$$f_{\text{Gd}}(\mu_{\text{Gd}}, \mu_{\text{Tb}}) = f_{\text{Tb}}(\delta_{\text{Tb}})$$

(8)

$$f_{\text{Tb}}(\mu_{\text{Gd}}, \mu_{\text{Tb}}) = f(\delta_{\text{Tb}})$$

(9)

where $f(\mu)$ is the integral of the exchange interaction between the terbium and gadolinium ions, $\mu_{\text{Gd}}$ and $\mu_{\text{Tb}}$ are their magnetic moments, and $\mu_{\text{Tb}}$ is the magnetic moment along the $c$ axis per ion. From the experimental data for the paramagnetic Curie point we calculated $f_{\text{Tb}} = 1.23 \times 10^{9}$ $G$.$^{2}$/erg. Assuming in accord with the experimental data that $\mu_{\text{Gd}} = 9.3 \mu_{B}$ and $\mu_{\text{Tb}} = 7.5 \mu_{B}$ and determining $\delta_{\text{Tb}}$ from the $f(\delta)$ curves at $H = 0$, we found by simultaneously solving Eqs. (8) and (9) with a computer that the angles $\delta_{\text{Tb}}$ and $\delta_{\text{Gd}}$ differ greatly in the Tb$_{x}$Gd$_{1-x}$ alloys, as is seen from the results for the alloy Tb$_{0.35}$Gd$_{0.65}$ at 4.2 K:

$$\delta_{\text{Gd}} = 6.10 \quad 8.68 \quad 10.49 \quad 12.98 \quad 14.05 \quad 15.03 \quad 16.02 \quad 17.10 \quad 19.10$$

$m$. deg: 86.0 87.9 90.5 90.8 91.0 91.5 91.9 93.0 94.6

The magnetic anisotropy constants for these alloys were determined by solving an equation that follows from the calculations of the magnetization curves by the molecular-field theory,

$$K = K_{\text{an}} + K' = K_{\text{an}} + K_{\text{an}}$$

(10)

The calculations have shown that $K_{\text{an}} = K_{\text{an}}$. The dependence of $K_{\text{an}}$ on the terbium concentration is non-linear (see Fig. 4).

Using the theory of Itzhik and Karpenko', we express the magnetic-anisotropy constant of the disordered binary alloy Tb$_{x}$Gd$_{1-x}$ in the form

$$K = K_{\text{an}} + K_{\text{an}} + K_{\text{an}}$$

(11)

and for the Tb$_{x}$Y$_{1-x}$ alloys in the form

$$K = K_{\text{an}} + K_{\text{an}}$$

(12)

where $K_{\text{an}}$ is the single-ion anisotropy constant governed by the crystal-field mechanism, and $K_{\text{an}}$ and $K_{\text{an}}$ are the constants of the anisotropic exchange between the terbium ions and between terbium and gadolinium. We have neglected here the quantities $K_{\text{an}}$ and $K_{\text{an}}$. We estimate now the contributions made to the magnetic anisotropy by the different mechanisms. According to our experimental data, the magnetic-anisotropy constant per ion in pure terbium is $K_{\text{an}} = 35$ $cm^{-1}$, while in dilute Tb$_{x}$Y$_{1-x}$ alloys $K_{\text{an}} = 35$ $cm^{-1}$ and in Tb$_{x}$Gd$_{1-x}$ alloys $K_{\text{an}} = 65$ $cm^{-1}$. If the anisotropy were due only to anisotropic exchange, then upon dilution of terbium by yttrium or by gadolinium one should expect in these alloys $K_{\text{an}} = 5$ $cm^{-1}$, which differs by one order of magnitude from the experimental values. This indicates that the predominant contribution to the anisotropy is changed very little when the terbium is diluted by yttrium or gadolinium. This contribution, as follows from (11), is the single-ion anisotropy due to the interaction of the angular momentum of the terbium ion with the crystal field of the lattice, inasmuch as the constant that characterizes this anisotropy per ion, $K_{\text{an}}$, should remain constant in these alloys.

Allowance for the change of the lattice parameters introduces only a small correction [see Eq. (7)], inasmuch as the parameters of the lattices of Tb, Gd, and Y are close to one another (for example, in the alloys Tb$_{0.35}$Gd$_{0.65}$, the factor $g$ in (7) changes from 0.893-10$^{-3}$ to 1.12-10$^{-3}$).

Nonetheless, to explain the bending of the $K_{\text{an}}$ plot of the Tb$_{x}$Gd$_{1-x}$ alloys (see Fig. 4), as well as the difference between the values of $K_{\text{an}}$ in dilute alloys and in pure terbium, we must assume also the presence of anisotropic exchange, which makes a noticeable contribution not only on account of the constant $K_{\text{an}}$ but also near the equiatomic compositions on account of the constant $K_{\text{an}}$. 

965 Sov. Phys. JETP 50(5), Nov. 1979 S. A. Nikitin and N. P. Arutyunyan
In accord with the theoretical investigations that have established the connection between the magnetic ordering in REM and the topology of the Fermi surface, it can be assumed that the anomalous concentration dependence of the magnetic-anisotropy constants in Tb,Gd1−x alloys is due to a realignment of the electronic structure when the terbium is alloyed with the yttrium; this is indicated also by experimental data on the electric, magnetic, and magnetostriiction properties, as well as by the paramagnetic Curie points. In this case one should expect a change of the contribution made to the magnetic anisotropy by the anisotropic exchange (the constant \(K^0\)) in Eq. (12), which depends on the properties of the conduction electrons.

The dependence of the magnetic-anisotropy constant in the basal plane on the relative magnetization (see Fig. 6) for ferromagnetic Tb,Y1−x alloys is satisfactorily described by the theoretical formula that follows from the single-ion model with account taken of the finite spin and of the quantum effects:

\[
\kappa_s(T) = K_s(T) = K_s(0, \theta_0) = \frac{K_s(0, \theta_0)}{\alpha_p},
\]

(13)

where \(K_s(0, \theta_0)\) and \(K_s(T)\) are the anisotropy constants in the basal plane per unit volume and per ion, respectively, \(K_s(0)\) are their values at \(T = 0\) K, \(\alpha_p\) is a function of the spin \(S\) and of the relative magnetization \(\alpha_p(T)\), which is tabulated in Ref. 20. The value \(K_s(0, \theta_0)\) calculated by the theoretical formula (13) at \(T = 0\) K from the experimental data shown in Fig. 6 is equal to 0.52 cm⁻¹ for the Tb,Y1−x alloys.

When comparing the experimental data on \(K_s\) of Tb,Gd1−x alloys with the theory it must be recognized that it is necessary to substitute in (13) the magnetization of the terbium sublattice, and not the total magnetization.

The temperature dependences of the terbium and gadolinium sublattices are described in the molecular-field theory by Brillouin functions. Starting from the values of the exchange integrals obtained by us from the paramagnetic Curie points,

\[
\alpha_p = 1.00 \times 10^{-3} \mathrm{erg/cm}^3, \quad \alpha_p = 5.20 \times 10^{-5} \mathrm{erg/cm}^3, \quad \alpha_p = 2.83 \times 10^{-5} \mathrm{erg/cm}^3,
\]

we calculated the magnetizations of the terbium and gadolinium sublattices with the aid of the equations that follow from the molecular-field theory. The dependence of the relative magnetic-anisotropy constant in the basal plane on the relative magnetization of the terbium sublattice is in good agreement with the theoretical equation (13) (see Fig. 6).

We present below the values of \(K_s\) for the Tb,Gd1−x alloys at 77.8 and 0 K.

\[
\begin{align*}
K_s(0) \text{ erg/cm}^3 & = 0.62 \quad 0.28 \quad 0.32 \quad 0.56 \\
K_s(0) \text{ erg/cm}^3 & = 0.20 \quad 0.18 \quad 0.13 \quad 0.21 \\
K_s(0) \text{ erg/cm}^3 & = 0.20 \quad 0.18 \quad 0.13 \quad 0.21 
\end{align*}
\]

Analysis of the experimental data shows that the constant \(K_s(T)\) measured at the given temperatures and the value of \(K_s(20)\) extrapolated in accord with (13) to 0 K increase in proportion to the terbium concentration, in agreement with the single-ion mechanism of the crystal field. The mean value \(\langle K_s(20)\rangle\) calculated per terbium ion amounts to 0.56 cm⁻¹ in the Tb,Gd1−x alloys.

Thus, the results of the present investigation have shown that the concentration dependence of the uniaxial magnetic-anisotropy constant in alloys of terbium with yttrium and gadolinium is determined mainly by the single-ion mechanism of the interaction of the orbital angular momentum with the crystal field of the lattice, while the anisotropic exchange and the change of the electron structure make an additional contribution to the magnetic anisotropy. The temperature dependence of the magnetic-anisotropy constant \(K_s\) in the basal plane is satisfactorily described by the single-ion theory when account is taken of the finite value of the spin and of quantum effects.

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