Low-temperature anomalies of the elastic properties of terbium titanates

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An experimental investigation was made of the behavior of the Young moduli and acoustic losses in rare-earth titanates such as $Ln_2Ti_2O_7$ and Ln_2TiO_5 (Ln ranging from Sm to Lu, including Y) when the temperature of a sample (1.7–300 K) and the magnetic field applied to it (up to 60 kOe) were varied. All the compounds containing terbium exhibited low-temperature anomalies in the temperature dependences of the elastic moduli and the amplitudes of these anomalies differed for compounds with different crystal structures. The greatest effect was observed for $Tb_2Ti_2O_7$, in which case the fall of the Young modulus amounted to $\sim 25\%$. A theoretical analysis carried out, allowing for the specific system of the energy levels of the Tb^{3+} ion in the crystal fields of the investigated compounds and for the special features associated with the polycrystalline structure, demonstrated that the anomalous behavior of the Young modulus was due to the coupling between the electronic states of the Tb^{3+} ions and lattice deformations resulting from the close spacing of the energy levels, which made it possible to assign terbium titanates to the class of Jahn-Teller compounds.

I. INTRODUCTION

The screening of the $4f$ electrons by the outer electron shells in crystals with rare-earth ions makes these crystals members of a class with a much weaker electron-lattice coupling than the coupling in compounds based on $3d$ elements. However, among rare-earth compounds we can distinguish a group which exhibits a number of interesting and important effects at low temperatures because of the interaction of electrons in a partly filled shell with the crystal lattice, which may be comparable or even exceed the analogous effects in the case of the $3d$ ions. Examples are a giant magnetostriction in the paramagnetic state, anomalous behavior of the elastic moduli, of the thermal expansion, and of the magnetization curves in the paramagnetic region, and structural phase transitions of the Jahn-Teller (JT) type.

A common feature of this group of rare-earth compounds is the existence of certain singularities in the lower part of the energy spectrum of the $4f$ electrons, where the ground multiplet is split by the crystal field producing separations of the order of several hundreds of Kelvin. The main feature is the presence of excited energy levels near the ground state which can be mixed by a magnetic field or by the electron-lattice interaction; the nature of the ground state is also of importance.

These features of the Stark structure of rare-earth ions play the role of an "amplifier" in the manifestation of the electron-lattice coupling in a specific effect. In fact, these effects increase in strength on increase of the change in the energy of the electrostatic interaction of the $4f$ electrons with the lattice ions, because the spatial distribution of the electron density of the $4f$ electrons is charged by external stimuli (magnetic field, deformation, temperature, etc.). In the absence of an external field the spatial distribution of the $4f$-electron density (or the "orientation of an anisotropic electron cloud" in a crystal) is determined by a set of the eigenfunctions of the crystal field operator corresponding to the thermally accessible states. Therefore, an external stimulus may alter the energy of the electrostatic interaction between the $4f$ electrons and the surrounding ions by two mechanisms: mixing of the wave functions corresponding to different energy states (which alters the eigenfunctions themselves) and a redistribution of the populations of the various states (which alters the contribution of a specific wave function to the spatial distribution of the electron density). Since the mixing and population redistribution decrease rapidly in strength on increase in the separation between the energy levels, we can see why the most striking effects due to the electron-lattice coupling can be observed only when there are closely spaced energy levels.

From this point of view an analysis of the structure of the lower energy levels of rare-earth ions provides an opportunity of carrying out a systematic search for new magnetostrictive materials and compounds manifesting other properties typical of the JT systems.

Investigations of rare-earth titanates such as $Ln_2Ti_2O_7$ or Ln_2TiO_5 type (where Ln is a rare earth) have shown that different types of energy levels of the ions are observed in this series. Terbium titanates are the most interesting among them because their magnetostriction reaches giant values at low temperatures, the specific heat exhibits a Schottky anomaly in the same range of temperatures, the susceptibility does not obey the Curie-Weiss law, and the magnetic moment does not reach saturation in fields up to 60 kOe because of the Van Vleck contribution.[1–4] Studies of all these effects in terbium titanates makes it possible to identify the system of energy levels and to demonstrate the presence of closely spaced energy levels of the Tb^{3+} ions in crystal fields of these compounds. According to Refs. 2 and 3, the separations from the ground to the nearest excited levels in $Tb_2Ti_2O_7$ and α-Tb_2TiO_5 are, respectively, $\Delta = 16$ and 20 K.

In the case of systems of this kind we can naturally expect other effects of these closely spaced levels. In particular, on application of an external force (or on excitation of an acoustic wave) the $4f$-electron-lattice coupling should be manifested by a contribution to the elastic moduli.

In fact, the appearance under the influence of an exter-

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nal force of a strain ε in addition to a shift of the ions from their equilibrium positions and also the appearance of an elastic lattice energy $U = c_0\varepsilon^2/2$ alters also the orientation of the $4f$-electron "cloud" in a crystal by the mechanisms described above. If this change in the orientation lowers the free energy by an amount comparable with and partly compensating the increase in the free energy because of the elastic contribution, measurements of the Young modulus can give a value smaller than c_0. The temperature at which both contributions compensate each other exactly represents a point of a structural phase transition of the JT type.[5] Therefore, reduction in any one of the components of the Young modulus to zero as a result of variation of temperature is one of the most striking effects of the existence of the JT effect.

The reduction in the elastic constants of rare-earth compounds was first observed experimentally for intermetallics of the LnSb type and then for some rare-earth vanadates and phosphates. However, only a few rare-earth compounds manifesting these effects are known at present.[5-8] We recently discovered a strong reduction in the Young modulus of $Tb_2Ti_2O_7$ by an amount ~25% due to cooling from 110 to 1.7 K (Ref. 9).

In the present study we determined the temperature dependences of the Young modulus and internal friction for all the terbium compounds and phases observed in the TiO_2-Tb_2O_3 system with different ratios of the initial oxides, including $Tb_2Ti_2O_7$ with the cubic structure of the pyrochlore type, α and β phases of Tb_2TiO_5 with the orthorhombic and hexagonal structures, respectively, a phase F (representing a solid solution of the composition 66 mol.% Tb_2O_3 + 34 mol.% TiO_2), and pure oxide Tb_2O_3, the latter two with the cubic fluorite type structure.[10]

Similar investigations were made for the whole series of rare-earth dititanates, isostructural with the compound $Tb_2Ti_2O_7$, in which the Tb^{3+} ions are replaced with other lanthanides (Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Y).

A study was made of the influence of an external magnetic field on the temperature dependences of the Young modulus of terbium titanates and a detailed theoretical analysis of the anomalous behavior of the Young modulus was carried out allowing for the specific systems of energy levels of the investigated compounds.

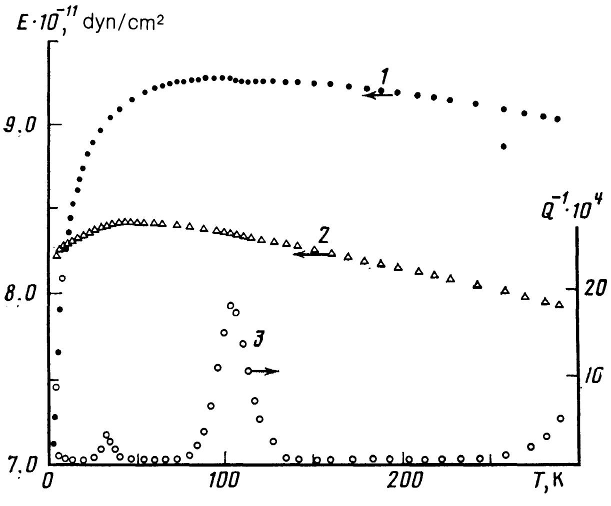

FIG. 1. Temperature dependences of the Young modulus E and of the internal friction Q^{-1}: (1), (3) $Tb_2Ti_2O_7$; (2) $Tb_{0.5}Y_{1.5}Ti_2O_7$.

II. EXPERIMENTAL RESULTS

The main properties of the investigated samples are given in Table I. Polycrystalline ceramics were prepared by chemical coprecipitation followed by compacting under pressure and annealing at temperatures 1200–1400 °C for 3–48 h (Ref. 10).

Measurements of the Young modulus and internal friction were made by the method of a compound "sample-quartz" vibrator with natural vibration frequencies of 130 and 180 kHz at temperatures 1.7–300 K, using magnetic fields up to 60 kOe. The error in the determination of the Young modulus was ≤0.5%, whereas the error in the determination of the temperature of a sample was ≤0.1 K.

Figures 1 and 2 give the temperature dependences of the Young modulus demonstrating an anomalous behavior of this modulus in the case of all the investigated terbium titanates: this behavior occurred at low temperatures and the magnitude and nature of the anomalies differed for compounds with different crystal structures. In the case of $Tb_2Ti_2O_7$ the Young modulus fell by ~25% in the interval

TABLE I

Compound	Rare-earth oxide content	Structure	Local symmetry of rare-earth ion	Separation between lowest energy levels Δ, K	Softening of Young modulus, %	Magnetostriction at $T = 4.2$ K, in $H = 60$ kOe
$Ln_2Ti_2O_7$ (Ln=Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Y)	33 mol.% Ln_2O_3	cubic, pyrochlore type	D_{3d}	>100 K	–	$<10^{-5}$
$Tb_2Ti_2O_7$	33 mol.% Tb_2O_3	cubic, pyrochlore type	D_{3d}	16 K	25	$5\cdot10^{-4}$
α-Tb_2TiO_5	50 mol.% Tb_2O_3	orthorhombic	C_s	~20 K	5	$2.7\cdot10^{-4}$
β-Tb_2TiO_5	50 mol.% Tb_2O_3	hexagonal		~25 K	0.8	$0.7\cdot10^{-4}$
F phase (solid solution)	65 mol.% Tb_2O_3	cubic, fluorite type		–	0.6	$0.6\cdot10^{-4}$
Tb_2O_3	100 mol.% Tb_2O_3	cubic, fluorite type	C_3, C_2	–	0.2	–

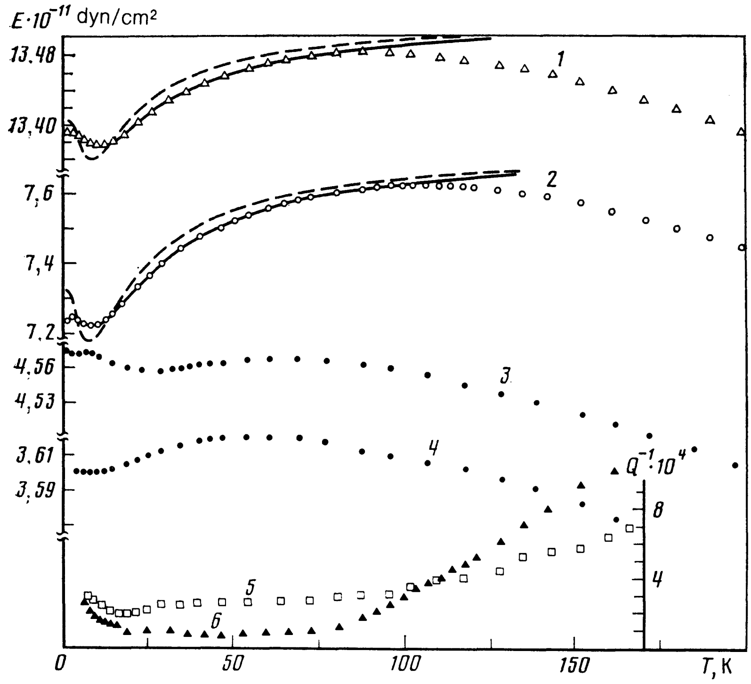

FIG. 2. Temperature dependences of the Young modulus of α-Tb_2TiO_5 (1), β-Tb_2TiO_5 (2), Tb_2O_3 (3), phase F (4), and of the internal friction in β-Tb_2TiO_5 (5) and α-Tb_2TiO_5 (6). The points are the experimental results. The continuous and dashed curves are calculated using Eq. (17) and assuming that $\Delta = 25$ and 16 K, respectively.

1.7–107 K, whereas in the case of other terbium compounds and phases the effect was much smaller: it ranged from 0.2 to 5% and it appeared as a dip or a step.

Measurements on polycrystalline samples prepared under different conditions (so that the porosity ranged from 18 to 30%) demonstrated that, in spite of the fact that the absolute values of the Young modulus differed by a factor of 2–3, the dependences $E(T)$ were the same for these samples. When the Tb^{3+} ion concentration in $Tb_2Ti_2O_7$ (due to substitution with diamagnetic Y^{3+} ions) was reduced from 100 to 5%, the anomalies of the elastic properties decreased in absolute magnitude and disappeared when the terbium ions were replaced completely (curve 2 in Fig. 1).

Measurements of the internal friction in the same temperature and frequency ranges revealed maxima of the acoustic losses for $Tb_2Ti_2O_7$ at 110 and 40 K (Fig. 1), whereas in the case of other terbium compounds and phases the internal friction was slight and it varied with temperature monotonically (curves 5 and 6 in Fig. 2).

Investigations of all other compounds of the $Ln_2Ti_2O_7$ type (where Ln ranged from Sm to Lu) representing a homologous series of rare-earth dititanates with the cubic structure of the pyrochlore type (space group $Fd3m$) showed that the dependences $E(T)$ were typical of insulators and similar to the dependence reported in Ref. 9 for the diamagnetic material $Y_2Ti_2O_7$; at temperatures ~ 110 K there was only a small step corresponding to an increase in the Young modulus at lower temperatures. All the $Ln_2Ti_2O_7$ dititanates, including $Y_2Ti_2O_7$, had internal friction maxima at $T = 40$ and 110 K.

The presence of similar acoustic losses in $Y_2Ti_2O_7$ indicated that this effect was not related to the Stark structure of the $4f$ electrons. Clearly, these maxima were of the same origin as the anomalies of the permittivity and $\tan\delta$ observed earlier[11] at the same temperatures and frequencies, and associated with the existence of relaxation losses in $Ln_2Ti_2O_7$ crystals due to structure defects typical of these crystals. It is clear from Fig. 1 that the contribution of these processes had little effect on the dependence $E(T)$.

Our measurements thus demonstrated that the anomalies of the Young modulus mentioned above occur only in terbium compounds and phases which remain paramagnetic right down to the lowest temperatures ($T_N = 2.6$ K for α-Tb_2TiO_5, $T_N = 2.2$ K for Tb_2O_3, and $T_N < 1$ K for $Tb_2Ti_2O_7$ and β-Tb_2TiO_5), and do not undergo ferroelectric or any other phase transitions.[2–4,11] The application of a magnetic field weakened considerably the anomalous fall of the Young modulus in the case of $Tb_2Ti_2O_7$ (Fig. 3), whereas the general nature of the dependences $E(T)$ obtained for α-Tb_2TiO_5 and β-Tb_2TiO_5 was not greatly affected by the magnetic field, with the exception of the lowest temperatures 1.7–4 K (Fig. 4). It should be pointed out that the fall of the Young modulus of terbium titanates was correlated with the magnetostriction of these compounds and, as dem-

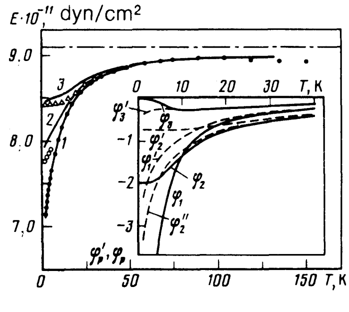

FIG. 3. Temperature dependences of the Young modulus of $Tb_2Ti_2O_7$ in a magnetic field. The points are the experimental results and the continuous curves are calculated using Eqs. (12) and (16) on the assumption that $H = 0$ (●, 1), 30 kOe (○, 2), and 60 kOe (△, 3). The inset shows the temperature dependences of the functions $\varphi_p(H = 0)$, and $\varphi'_p(H = 60\ \text{kOe})$ in the case when $\Delta = 16$ K [φ'_2 and φ''_2 represent components of two doublets which are not miscible and miscible by a magnetic field; see Eqs. (13) and (16)].

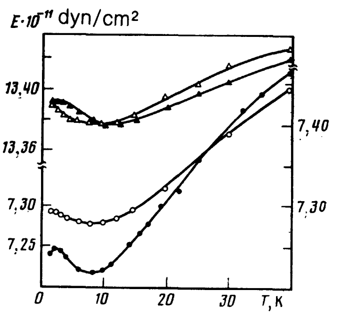

FIG. 4. Temperature dependences of the Young modulus in a magnetic field obtained for α-Tb_2TiO_5 (●, ○) and β-Tb_2TiO_5 (▲,△) in fields $H=0$ (●, ▲) and 60 kOe (○, △).

onstrated in Table I, the effect increased on reduction in the spacing to the nearest excited level.

Our experimental results thus demonstrated that the only reason for the observed anomalies of the temperature dependences of the Young modulus $E(T)$ exhibited by terbium titanates is a feature of the Stark structure of the ground multiplet of the Tb^{3+} ion in the crystal fields of the investigated compounds.

III. THEORY AND ANALYSIS OF EXPERIMENTAL RESULTS

The results obtained can be interpreted following mainly the ideas developed earlier[5,6,8,12] and allowing for the specific nature of polycrystalline samples. We shall write down the free energy of a polycrystalline sample in the form

$$F=\sum_k F_k+{}^1/_2\Omega K_\infty \varepsilon_0{}^2+\Omega\mu_\infty \sum_{q=-2}^{2}\varepsilon^q\varepsilon^{-q}, \tag{1}$$

where F_k is the contribution made to the free energy by the k th crystallite (grain) due to its f electrons; Ω is the volume of the sample; K_∞ and μ_∞ are, respectively, the bulk modulus and the shear modulus considered ignoring the interaction of the f electrons with the lattice; ε_0 and ε^q are irreducible components of the strain tensor $\varepsilon_{\alpha\beta}$

$$\varepsilon_0=\varepsilon_{xx}+\varepsilon_{yy}+\varepsilon_{zz},\quad \varepsilon^0=(\varepsilon_{xx}+\varepsilon_{yy}-2\varepsilon_{zz})/6^{1/2},$$
$$\varepsilon^{\pm1}=\varepsilon_{zx}\pm i\varepsilon_{zy},\quad \varepsilon^{\pm2}=(\varepsilon_{yy}-\varepsilon_{xx}\mp2i\varepsilon_{xy})/2. \tag{2}$$

In the molecular field approximation, we find that

$$F_k=-kT\sum_{i=1}^{N_k}\ln \mathrm{Sp}\{-\beta\mathscr{H}(i)\}+\frac{N_k}{2}\sum_{n,m}\lambda_{n,m}\langle O_n\rangle\langle O_m\rangle, \tag{3}$$

where $\beta=1/kT$; $\langle O_n\rangle$ is the thermal average of the equivalent operator O_n; N_k is the number of ions in a crystal (we shall assume that all the ions in a of a crystal are optically equivalent); λ_{nm} is the constant representing the ion-ion interaction. The Hamiltonian $\mathscr{H}(i)$ of the ith ion consists of two parts:

$$\mathscr{H}(i)=\mathscr{H}^{(1)}(i)+\mathscr{H}^{(2)}(i).$$

The first part corresponds to the interaction of a deformed crystal field with the $4f$ electrons and, in terms of the local symmetry axes of the ith ion, it can be described by

$$\mathscr{H}^{(1)}(i)=\mathscr{H}_0(i)+\sum_n B_{n0}O_n(i)\varepsilon_0+\sum_{nq}B_n{}^qO_n(i)\varepsilon^q(i), \tag{4}$$

where $\mathscr{H}_0(i)=\Sigma_nB_n(i)O_n(i)$ is the Hamiltonian of the crystal field acting on the ith ion in the absence of deformation. It should be pointed out that the Hamiltonian of Eq. (4) has been used earlier[2] to describe the giant magnetostriction of $Tb_2Ti_2O_7$. The Hamiltonian

$$\mathscr{H}^{(2)}=-\sum\lambda_{nm}O_n(i)\langle O_n\rangle$$

allows, in the molecular field approximation, for the direct and indirect (via the phonon field) interactions of the ith ion with other rare-earth ions.[7]

We shall show later that the initial expression for the free energy of a polycrystalline sample given by Eq. (1) automatically separates the "isotropic" parts of the elastic moduli if all the orientations of crystallites (grains) are equally probable. This approach is valid only in the case of a weak anisotropy of the elastic properties of single crystals[13] [in the case of cubic single crystals we should have $2c_{44}/(c_{11}-c_{12})\approx1$].

Expanding the free energy as a series representing the contribution to F quadratic in $\varepsilon_{\alpha\beta}$, we obtain (to within second-order terms)

$$\frac{\delta F}{\Omega}=\frac{1}{2}(K_\infty+\delta K)[\varepsilon_0-\varepsilon_0(T)]^2+(\mu_\infty+\delta\mu)\sum_{q=-2}^{2}\varepsilon^q\varepsilon^{-q}, \tag{5}$$

where $\varepsilon_0(T)$ is the equilibrium value of ε_0 at a temperature T,

$$\delta\mu=-\frac{N\beta}{10\Omega}\sum_{n,m,p}\sum_{q=-2}^{2}B_n{}^qB_m{}^{-q}\chi_{mp}Z_{pn}, \tag{6}$$

$$\delta K=-\frac{N}{\Omega}\beta\sum_{n,m,p}B_{n0}B_{m0}\chi_{mp}Z_{pn}. \tag{7}$$

The following notation is used in Eqs. (6) and (7): N is the number of ions in a polycrystalline sample; $\chi_{nm}=\langle\tilde{O}_nO_m\rangle-\langle O_n\rangle\langle O_m\rangle$ is the generalized susceptibility, where

$$\tilde{O}_n=\int_0^1\exp(\beta\mathscr{H}t)O_n\exp(-\beta\mathscr{H}t)\,dt.$$

Z_{pn} is an element of the matrix $Z=(I-A)^{-1}$, where $A_{mn}=\beta\Sigma_p\lambda_{pm}\chi_{pn}$; I is a unit matrix. It should be pointed out that the expression for the generalized susceptibility χ_{nm} is analogous to an expression given in Ref. 12, but differs from the latter by the term $\langle O_n\rangle\langle O_{nm}\rangle$. The need to include this term arises from the fact that in our case the unit cell contains several rare-earth ions and the local symmetry of these ions (D_{3d}) differs from the symmetry (O_h) of the $Tb_2Ti_2O_7$ crystal. Consequently, even in the case of strains which are not fully symmetric, we find that the thermal average is $\langle O_n\rangle\neq0$. The limitations imposed by the symmetry on the average values $\langle O_n\rangle$ for a crystal with several rare-ions in a unit cell are less rigid than for a crystal with one rare-earth ion in a cell and they can be reduced to the condition $\langle O(\Gamma)\rangle\equiv0$, if Γ is not a unit representation Γ_1 of the local symmetry of the rare-earth ion.

The existence of finite values of $\langle O_n(\Gamma_1)\rangle$ is not in conflict with the requirement of conservation of the unit-cell symmetry at temperatures above the phase transition point and in the absence of external fields. It follows from this requirement that, for example, in the case of a cubic crystal the equilibrium values are $\varepsilon^q = 0$, i.e., we should have

$$\sum_{q'} B_{nq'} \langle O_n \rangle \sum_i \frac{\partial \varepsilon^{q'}(i)}{\partial \varepsilon^q} = 0, \tag{8}$$

where ε^q is expressed in terms of the symmetry axes of the unit cell. In the case of a crystal with one ion per cell the equality given by Eq. (8) is ensured by vanishing of $\langle O_n \rangle$, whereas in the case of a crystal with several rare-ions in a cell characterized by a local symmetry lower than the symmetry of the cell the equality (8) is ensured by vanishing of $\Sigma_i \partial \varepsilon^{q'}(i)/\partial \varepsilon^q$.

In the analysis of the experimental data obtained for terbium titanates we shall use Eqs. (6) and (7), where we shall assume that $\lambda_{nm} = 0$. (This simplification can be justified, as in Ref. 5, by the fact that the electron-deformation coupling is usually the dominant one; moreover, in the present case our aim is to ignore the region where structural cooperative phase transitions take place.) In this approximation, Eqs. (6) and (7) simplify greatly and become

$$\delta K = -\frac{N\beta}{\Omega} \langle \tilde{V}_0 V_0 \rangle, \tag{9}$$

$$\delta\mu = -\frac{N\beta}{10\Omega} \sum_q \langle \tilde{V}^q V^{-q} \rangle$$
$$= -\frac{N\beta}{10\Omega} \sum_{q=2}^{-2} \sum_{n\neq m} \left\{ \rho_n f_{nm} |V_{nm}{}^q| + \frac{1}{2} \rho_n \rho_m (V_{nm}{}^q - V_{mm}{}^q)^2 \right\}, \tag{10}$$

where $V_0 = \Sigma_n B_{n0} O_n$, V^q_{nm} are matrix elements of the operators $V^q = \Sigma B^q_n O_k$ acting on eigenstates $|n\rangle$ and $|m\rangle$ of the crystal field Hamiltonian $\mathscr{H}_0$ ($\mathscr{H}_0 |n\rangle = \mathscr{E}_n |n\rangle$); ρ_n is the population of the state $|n\rangle$;

$$f_{nm} = \{\exp[\beta(\mathscr{E}_n - \mathscr{E}_m)] - 1\} / \beta(\mathscr{E}_n - \mathscr{E}_m).$$

The Young modulus defined as $E = 9K\mu/(3K+\mu)$ when $3K \gg \mu$ (we shall assume that this condition is always satisfied), is given by

$$E = E_\infty + \delta E = 3\mu_\infty + 3\delta\mu, \tag{11}$$

where E_∞ is the Young modulus due to the elastic energy of the lattice without allowance for the interaction of the $4f$ electrons with the deformation field.

Assuming a two-doublet system (a ground doublet with $\mathscr{E}_1 = \mathscr{E}_2 = 0$ and an excited one with $\mathscr{E}_3 = \mathscr{E}_4 = \Delta$), which applies to the Tb^{3+} ions in $Tb_2Ti_2O_7$ (Ref. 2), we find that the temperature dependence of the Young modulus is given by

$$E = E_\infty + \delta E = E_\infty + \Phi(T), \tag{12}$$

where

$$\Phi(T) = \sum_{p=1}^{4} e_p \varphi_p (\Delta/2T),$$

$$e_1 = \frac{3N}{10\Omega k\Delta} \sum_{q=-2}^{2} |V_{12}{}^q|^2, \quad \varphi_1(x) = -x(1+\operatorname{th} x),$$

$$e_2 = \frac{3N}{20\Omega k\Delta} \sum_{q=-2}^{2} [|V_{13}{}^q|^2 + |V_{14}{}^q|^2 + |V_{23}{}^q|^2 + |V_{24}{}^q|^2],$$

$$\varphi_2(x) = -2 \operatorname{th} x,$$

$$e_3 = \frac{3N}{10\Omega k\Delta} \sum_{q=-2}^{2} |V_{34}{}^q|^2, \quad \varphi_3(x) = -x(1-\operatorname{th} x),$$

$$e_4 = \frac{3N}{10\Omega k\Delta} \sum_{q=-2}^{2} (V_{11}{}^q - V_{33}{}^q)^2, \quad \varphi_4(x) = -\frac{x}{2}(1-\operatorname{th}^2 x). \tag{13}$$

We can see from Fig. 3 that the curve calculated using Eqs. (12) and (13) and assuming that $\Delta = 16$ K agrees well with the experimental results. The parameters $e_1 = 0.06 \times 10^{11}$ dyn/cm^2 and $e_2 = 0.7 \times 10^{11}$ dyn/cm^2 are found by least squares; the third and fourth terms in the sum (13) are negligible throughout the investigated temperature range.

The above expressions apply to polycrystalline samples with the zero porosity. However, real terbium titanate samples are characterized by porosities ranging from 18 to 30%. An allowance for the inhomogeneities in the regions between planes can be made by employing a simple model proposed by us earlier[9] postulating that the strain tensor for a single crystallite $\varepsilon^{cr}_{\alpha\beta}$ differs from the strain tensor for the whole sample $\varepsilon^s_{\alpha\beta}$ and that $\varepsilon^{cr}_{\alpha\beta} = \alpha_s \varepsilon^s_{\alpha\beta}$. Consequently, the experimental values of δE obtained for different polycrystalline samples are described satisfactorily by the same temperature dependence $\Phi(T)$, apart from a constant factor.

This theoretical analysis shows that in the case of $Tb_2Ti_2O_7$ at $T > 4$ K the temperature dependence of the Young modulus is dominated by the second term of Eq. (13), which corresponds to mixing—by the electron-deformation interaction—of two doublets separated by $\Delta = 16$ K. The first term proportional to T^{-1} predominates only at the lowest temperatures ($T < 4$ K) and this term corresponds to mixing of the sublevels of the lower doublet in the presence of deformation.

A nonzero term proportional to T^{-1} in the expression for the Young modulus necessarily reduces this modulus to zero at a finite temperature and this corresponds to a cooperative structural JT phase transition.[5] The condition

$$E = E_\infty + \Phi(T_c) = 0 \tag{14}$$

yields an estimate of the critical temperature for $Tb_2Ti_2O_7$: this temperature is $T_c \approx 0.1$ K. An allowance for the exchange between the rare-earth ions via the phonon field has little effect on this value.[5]

Our results thus demonstrate that the anomalous low-temperature behavior of the Young modulus of $Tb_2Ti_2O_7$ is indeed due to the coupling between the electron states of

Tb^{3+} and lattice deformations, which makes it possible to assign terbium dititanate to JT compounds.

The behavior of the Young modulus of $Tb_2Ti_2O_7$ in magnetic fields supports this conclusion. Since in this case the separation to the first excited doublet may be comparable with the Zeeman splitting of the ground doublet, and also because of the strong mixing of states in a magnetic field,[2] the elastic properties of $Tb_2Ti_2O_7$ should be highly sensitive to a magnetic field. Indeed, the curves plotted in Fig. 3 and obtained in fields 30 and 60 kOe demonstrate the reduction in the Young modulus decreases considerably on increase in the magnetic field.

We shall calculate the dependence $E(T,H)$ using the data obtained in Ref. 2 on the wave functions ψ_{12} and ψ_{34} of the ground and first excited doublets, as well as Eqs. (10) and (11) in which now the eigenvalues and the eigenfunctions correspond to the Hamiltonian $\mathscr{H}_0 + \mathscr{H}_z$, which allows for the Zeeman interaction.

Since the energy levels and matrix elements of the electron-deformation interaction depend on the direction of the magnetic field relative to the crystallite axes, in the case of a polycrystalline sample the complete expression for the contribution made to the Young modulus by the $4f$ electrons is governed by the integral

$$\delta E(H)=\frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\delta E\sin\theta\, d\theta\, d\varphi. \tag{15}$$

This procedure in the calculation of the Young modulus of a polycrystalline sample in a magnetic field implies neglect of the magnetostriction effect (in $Tb_2Ti_2O_7$ the relative change in the dimensions in fields of 60 kOe amounts to 5×10^{-4}—see Ref. 2).

In the specific case of two split doublets when we express the new matrix elements $V_{nm}(H)$ in terms of $V_{nm}(H=0)$ and group together the terms with specific values of $V_{nm}(H=0)$, we can describe $\delta E(H)$ by an expression similar to Eq. (13), i.e.,

$$\delta E(H)=\Phi(T,H)=\sum_p e_p\varphi_p'(\Delta,T,H), \tag{16}$$

where e_p represents the same values as in the absence of a magnetic field and the temperature dependences of the functions φ_p' and φ_p'' in a field $H = 60$ kOe are plotted in Fig. 3 ($\Delta = 16$ K), which demonstrates the degree to which they differ from the corresponding functions φ_p obtained in the absence of the field. The specific feature of the polycrystalline structure of the samples is manifested in that the functions φ_1', φ_2', and φ_2'' also fall as a result of cooling, as in the absence of the field, but they do not reach a constant value. This is due to the fact that for a considerable fraction of the Tb^{3+} ions in a polycrystalline sample the splitting of the lower doublet (because of the strong anisotropy of its g factor) does not exceed $\sim kT$. Superposition of the functions φ_p' multiplied by the corresponding values of e_p obtained earlier gives the temperature dependences of the Young modulus in the presence of a magnetic field represented by curves 2 and 3 in Fig. 1 and corresponding to the fields $H = 30$ and 60 kOe. Bearing in mind the above approximations, we can regard the agreement between the theoretical and experimental curves as quite satisfactory.

In discussing the behavior of the Young modulus of other terbium titanates (α- and β-Tb_2TiO_5) we must point out that on the basis of approximate results obtained by magnetic and specific heat measurements[3,4] the lower energy levels of the Tb^{3+} ion in crystal fields of these compounds are weakly split two singlets and the first excited singled is located at ~ 20 K. In the case of such a system of levels Eq. (13) consists of three terms of the $e_p\varphi_p(\Delta/T)$ type:

$$\begin{aligned}
e_1&=\frac{3N}{10\Omega k\Delta}\sum_q |V_{12}{}^q|^2, &\varphi_1&=-\frac{\Delta}{T}\frac{1+e^{\Delta/T}}{1+2e^{\Delta/T}},\\
e_2&=\frac{3N}{10\Omega k\Delta}\sum_q [|V_{13}{}^q|^2+|V_{23}{}^q|^2], &\varphi_2&=-2\frac{e^{\Delta/T}-1}{1+2e^{\Delta/T}},\\
e_3&=\frac{3N}{10\Omega k\Delta}\sum_q (V_{11}{}^q-V_{33}{}^q)^2, &\varphi_3&=-2\frac{\Delta}{T}\frac{e^{\Delta/T}}{(1+2e^{\Delta/T})^2}.
\end{aligned} \tag{17}$$

A comparison of the experimental results shows that the off-diagonal matrix element of the electron-deformation interaction between the two lowest singlets is negligible. The main contribution to $\delta E(T)$ comes from the second and third terms resulting from the mixing (due to the electron-deformation interaction) of an excited singlet with the two lowest states and their relative shift in the presence of deformation. This is why the dependence $E(T)$ observed at low temperatures for α- and β-Tb_2TiO_5 has a dip, in contrast to the case of $Tb_2Ti_2O_7$ discussed above.

It should be pointed out that the $E(T)$ dependences are very sensitive to the parameter Δ. Figure 2 shows curves corresponding to those calculated from Eq. (17) assuming that $\Delta = 16$ and 25 K in the case of α- and β-Tb_2TiO_5. We can see that the experimental points in the region of a dip are described very well by a single curve with $\Delta = 25$ K ($e_2 = 0.5\times10^{11}$ dyn/cm^2, $e_3 = 0.9\times10^{11}$ dyn/cm^2) for α-Tb_2TiO_5 and ($e_2 = 0.14\times10^{11}$ dyn/cm^2, $e_3 = 0.34\times10^{11}$ dyn/cm^2) for β-Tb_2TiO_5.

It therefore follows that the results of an investigation of the temperature dependences of the Young moduli of two structural modifications of the compound Tb_2TiO_5 confirm completely the earlier conclusions[3,4] that the energy spectrum of Tb^{3+} has an adjacent excited state in the crystal fields of these compounds and that quantitative estimates of the value of Δ can be as accurate as those deduced from calorimetric measurements.

It is surprising that there is practically no mixing of the two lower states by the deformation interaction. In a crystal in which the terbium ions have the local symmetry C_s, typical of the orthorhombic structure of α-Tb_2TiO_5, all the energy levels should be split down to singlet states and because of mixing of the states with $|\Delta J_z| = 2$ by the crystal field, only four types of singlet are possible:

$$\begin{aligned}
\psi_a&=a_6\frac{|+6\rangle+|-6\rangle}{\sqrt{2}}+a_4\frac{|4\rangle+|-4\rangle}{\sqrt{2}}+a_2\frac{|2\rangle+|-2\rangle}{\sqrt{2}}+a_0|0\rangle,\\
\psi_b&=b_6\frac{|6\rangle-|-6\rangle}{\sqrt{2}}+b_4\frac{|4\rangle-|-4\rangle}{\sqrt{2}}+b_2\frac{|2\rangle-|-2\rangle}{\sqrt{2}},\\
\psi_c&=c_5\frac{|5\rangle+|-5\rangle}{\sqrt{2}}+c_3\frac{|3\rangle+|-3\rangle}{\sqrt{2}}+c_1\frac{|1\rangle+|-1\rangle}{\sqrt{2}},\\
\psi_d&=d_5\frac{|5\rangle-|5\rangle}{\sqrt{2}}+d_3\frac{|3\rangle-|-3\rangle}{\sqrt{2}}+d_1\frac{|1\rangle-|-1\rangle}{\sqrt{2}}.
\end{aligned} \tag{18}$$

The experimentally observed dependence $E(T)$ (i.e., the absence of mixing in the case of the two lower singlets) may exist only on the assumption of smallness of some of the coefficients a_i, b_i, and c_i depending on which type of singlet is regarded as the ground state. A similar situation clearly occurs also in $LiHoF_4$ (Ref. 8) with a doublet ground state, for which nevertheless the dependence $E(T)$ has a dip at low temperatures.

It is interesting to note one further feature of the $E(T)$ curve of α-Tb_2TiO_5: at $T \approx 2.6$ K there is a small maximum. The temperature of this maximum agrees with the temperatures of similar anomalies of the magnetic susceptibility and specific heat curves.[3] It has been suggested earlier that magnetic ordering of the spin glass type occurs at $T \approx 2.6$ K in this compound. It is clear from Fig. 2 that in a magnetic field of 60 kOe, which exceeds considerably the exchange interaction, the maximum of the $E(T)$ curve disappears for α-Tb_2TiO_5. A small change in the nature of the dependences $E(T)$ observed at higher temperatures for α-Tb_2TiO_5 and throughout the temperature range for β-Tb_2TiO_5 is evidence of a slight change in the separation between the singlets in the presence of a magnetic field.

Measurements of elastic properties of a solid solution F and of the oxide Tb_2O_3 demonstrate a definite similarity in the behavior with α- and β-Tb_2TiO_5, showing that these compounds have excited states of the Tb^{3+} ions separated by slightly more than $\Delta = 25$ K. This is in agreement with the results obtained in a study of the magnetic properties of these compounds,[4] which have provided the basis for establishing the mutual relationship between all the structural phases occurring in the TiO_2-Tb_2O_3 system.

In the case of other rare-earth dititanates, which do not exhibit a fall of the Young modulus at low temperatures, the specific nature of the system of energy levels of the Ln^{3+} ions is such that an isolated ground state is usually the lowest.[2] For example, in the case of $Dy_2Ti_2O_7$, we have $\Delta \gtrsim 150$ K, whereas for $Ho_2Ti_2O_7$ we find that $\Delta \gtrsim 220$ K. In the case of the latter compound ($Ho_2Ti_2O_7$), an additional reason for the absence of the JT behavior is the circumstance that the main contribution to the states of a lower (non-Kramers) doublet comes from the wave functions $|\pm 8\rangle$, which are not mixed by the electrostatic interaction.

It therefore follows from our investigation that the low-temperature elastic properties of terbium titanates are determined entirely, like the magnetic and magnetostriction properties investigated earlier, by the specific structure of the lower energy levels of the rare-earth ions. The observed anomalies of the temperature dependences of the Young modulus are due to closely spaced energy levels and the terbium titanates themselves are convenient materials for the investigation of various effects of the coupling between the electron states of the rare-earth ions and the crystal lattice.

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