

XV INTERNATIONAL
FEOFILOV SYMPOSIUM

Multipole Interactions in a LiTmF_4 Single Crystal

I. V. Romanova, B. Z. Malkin, and M. S. Tagirov

Kazan (Volga Region) Federal University, Kazan, 420008 Tatarstan, Russia

e-mail: Irina.Choustova@kpfu.ru

Received November 18, 2013

Abstract—We have considered magnetic and magnetoelastic characteristics of a van Vleck paramagnet LiTmF_4 taking into account the interaction between thulium ions via the phonon field. We have calculated parameters of the multipole interaction that is caused by the interaction of Tm^{3+} ions with dynamic lattice deformations of the B_g symmetry. We have presented a self-consistent description of previously published results of measurements of temperature dependences of elastic constants and the nonlinear Zeeman effect in the optical spectrum of the LiTmF_4 single crystal, as well as dependences of the magnetostriction on temperature, magnitude, and direction of the external magnetic field.

DOI: 10.1134/S0030400X14060198

INTRODUCTION

Over the last three decades, double lithium–rare-earth fluorides LiLnF_4 (Ln denotes the rare-earth ion) have been studied intensely due to a variety of their magnetic properties [1–5]. Simulation of magnetic-field effects in LiLnF_4 single crystals is an important problem for the development of the theory of magnetoelastic effects in magnetically concentrated crystals that contain rare-earth ions.

LiLnF_4 crystals have a tetragonal structure of scheelite CaWO_4 ; their space-symmetry group is C_{4h}^6 ($I4_1/a$); the unit cell contains two magnetically equivalent Ln^{3+} ions at sites with the S_4 point-symmetry group [6]. LiTmF_4 is a dielectric van Vleck paramagnet [7], a distinctive feature of which is a strong magnetoelastic interaction, which is evidenced by a giant magnetostriction, which was revealed in [8], and characteristic extrema in temperature dependences of elastic constants [9, 10]. The authors of [11, 12], using optical-spectroscopy methods, have observed a substantially nonlinear and anisotropic dependence of the splitting of the first excited doublet of Tm^{3+} ions on the external magnetic field that was oriented in the base plane of the LiTmF_4 crystal, which is caused by the magnetoelastic interaction. Later, the authors of [13, 14] measured the dependences of the magnetization of LiTmF_4 single crystals on the magnitude and direction of the magnetic field at different temperatures. Results of calculations of piezospectroscopic effects [15], magnetostriction [8, 10], and nonlinear Zeeman effect [11, 12], which were done in terms of the model of a linear electron–deformation interaction, agree well with measurement data; however, the values of coupling parameters of thulium ions with lattice deformations that were used in these works differ con-

siderably from the values of corresponding parameters that were found from the analysis of the data of piezospectroscopic investigations of thulium and holmium impurity ions in an isostructural crystal LiYF_4 [16, 17]. It should be noted that the previous analysis of the experimental data was performed taking into account only the magnetic-dipole–dipole interaction between rare-earth ions, which, in the case of the van Vleck paramagnet, plays an insignificant role at low temperatures. The revealed strong interaction of Tm^{3+} ions with static lattice deformations is indicative of the possibility of an efficient multipole interaction between thulium ions that is caused by exchange of phonons. The multipole interaction leads to the renormalization of parameters of an effective one-particle Hamiltonian and, as was noted in [15], can be the reason for the difference between parameters of the electron–phonon interaction in magnetically concentrated and diluted systems. The objective of this work is to calculate the parameters of the Hamiltonian of the interaction between thulium ions using previously found characteristics of the electron–phonon interaction and the lattice dynamics of LiLnF_4 crystals [18–20] and to construct a self-consistent model for the calculation of magnetic and magnetoelastic characteristics of the LiTmF_4 crystal taking into account multipole interactions.

THEORETICAL SUBSTANTIATION OF THE MODEL

The Hamiltonian of the magnetic subsystem, which consists of thulium ions interacting with the crystal lattice with a free surface, will be written as

$$H = \sum_{Ls} H_{L,s} + H_{\text{lat}} + \sum_{Ls} \sum_{\mathbf{q}j} \sum_{pk} \frac{1}{\sqrt{N}} B_p^k(s, \mathbf{q}j) \exp(i\mathbf{q}\mathbf{R}_{Ls}) O_p^k(Ls) Q(\mathbf{q}j). \quad (1)$$

Here, $H_{L,s}$ is the Hamiltonian of the thulium ion with radius vector \mathbf{R}_{Ls} from the s th sublattice ($s = 1, 2$) in the L th unit cell in a static crystal field, H_{lat} is the energy of the crystal lattice in the harmonic approximation with normal coordinates $Q(\mathbf{q}j)$ (\mathbf{q} is the wave vector of a phonon with frequency $\omega_{\mathbf{q}j}$, j is the number of the branch of the vibrational spectrum), the last term in (1) is the energy of the electron–phonon interaction in the linear approximation with respect to displacements of ions from the equilibrium position; N is the number of cells, $O_p^k(Ls)$ are linear combinations of spherical tensor operators [21] that act in the space of electronic states of the thulium ion at the site Ls , and $B_p^k(s, \mathbf{q}j)$ are interaction parameters that are determined by derivatives of corresponding parameters of the crystal field with respect to displacements of ions [1].

Considering corrections to the energy of thulium ions in the second order with respect to the electron–phonon interaction at low temperatures ($k_B T \ll \hbar\omega_0$, where k_B is the Boltzmann constant and ω_0 is the limiting phonon frequency) and taking into account only mixing of electronic states with the energy difference $\Delta \ll \hbar\omega_0$, we can introduce an effective Hamiltonian of interaction between thulium ions [22]

$$\Delta H = -\frac{1}{2} \sum_{LL's's'} (1 - \delta_{LL'} \delta_{ss'}) \times \sum_{pp'kk'} \Phi_{pp'}^{kk'}(ss', \mathbf{R}_{LL'}) O_p^k(Ls) O_{p'}^{k'}(L's'), \quad (2)$$

where $\mathbf{R}_{LL'}^{ss'} = \mathbf{R}_{Ls} - \mathbf{R}_{L's'}$ and

$$\Phi_{pp'}^{kk'}(ss', \mathbf{R}_{LL'}) = \frac{1}{N} \sum_{\mathbf{q}j} \omega_{\mathbf{q}j}^{-2} B_p^k(s, \mathbf{q}j) B_{p'}^{k'}(s', -\mathbf{q}j) \exp(i\mathbf{q}\mathbf{R}_{LL'}^{ss'}). \quad (3)$$

Two-particle interactions will be considered in the self-consistent field approximation, neglecting terms of the second order with respect to deviations of the operators $O_p^k(Ls)$ from their average values $\langle O_p^k(Ls) \rangle = \langle O_p^k \rangle$ (the latter equality is valid if all magnetic ions are equivalent, in particular, Tm^{3+} ions in LiTmF_4).

The free energy of an elastically deformed crystal in external magnetic field \mathbf{B} (per unit cell with the volume v) will be written as

$$F = \frac{v}{2} \left[\mathbf{e}\mathbf{C}\mathbf{e} + 2 \sum_r \mathbf{e}\mathbf{b}(r)\mathbf{w}(r) + \sum_{r,r'} \mathbf{w}(r)\mathbf{a}(r,r')\mathbf{w}(r') \right]$$

$$+ \frac{n}{2} \sum_{pkp'k'} \langle O_p^k \rangle \lambda_{pp'}^{kk'} \langle O_{p'}^{k'} \rangle + \Delta F, \quad (4)$$

$$\Delta F = - \sum_s k_B T \ln \text{Tr} \exp(-H_{\text{ef},s}/k_B T),$$

where \mathbf{C} is the tensor of “seed” elastic constants, \mathbf{e} is the tensor of deformations, $\mathbf{w}(r)$ is the displacement vector of the r th sublattice, $\mathbf{b}(r)$ is the tensor of coupling constants of macro- and microdeformations, $a_{\alpha\beta}(r, r')$ are elements of the dynamic matrix of the lattice at the center of the Brillouin zone, $\lambda_{pp'}^{kk'}$ is the matrix of constants of coupling via the phonon field, n is the number of equivalent magnetic sublattices ($n = 2$ for LiTmF_4 crystals), and $H_{\text{ef},s}$ is the single-ion Hamiltonian. This Hamiltonian is given by

$$H_{\text{ef}} = H^{(0)} + H^{(P)}, \quad (5)$$

$$H^{(0)} = H_0 + H_{\text{cf}} + H_Z, \quad (6)$$

$$H^{(P)} = \sum_{\alpha\beta} V_{\alpha\beta} e_{\alpha\beta} + \sum_{\alpha,r} V_{\alpha}(r) w_{\alpha}(r) - \sum_{pkp'k'} \lambda_{pp'}^{kk'} \langle O_p^k \rangle O_{p'}^{k'}. \quad (7)$$

The first term in (6) is Hamiltonian H_0 of the free ion; the second term is the crystal field energy; and the third term is the electron Zeeman energy $H_Z = \mu_B \mathbf{B}(\mathbf{L} + 2\mathbf{S})$, where μ_B is the Bohr magneton and \mathbf{L} and \mathbf{S} are the orbital and spin moments of the ion, respectively. The first and second terms in (7) determine the linear interaction of the rare-earth ion with homogeneous macro- and microdeformations, respectively. We will represent the electron operators $V_{\alpha\beta}$ and $V_{\alpha}(r)$ by linear combinations of spherical tensor operators,

$$V_{\alpha\beta} = \sum_{pk} B_{p,\alpha\beta}^k O_p^k, \quad V_{\alpha}(r) = \sum_{pk} D_{p,\alpha}^k(r) O_p^k. \quad (8)$$

Taking into account the translational symmetry of the lattice, we can obtain from Eqs. (2) and (3) the following expression for elements of the matrix λ in the last term in (7):

$$\lambda_{pp'}^{kk'} = \frac{1}{n} \sum_{ss'} \left[\sum_{j_o} \frac{B_p^k(s, 0j_o) B_{p'}^{k'}(s', 0j_o)}{\omega_{0j_o}^2} - \frac{\delta_{ss'}}{N} \sum_{\mathbf{q}j} \frac{B_p^k(s, \mathbf{q}j) B_{p'}^{k'}(s', -\mathbf{q}j)}{\omega_{\mathbf{q}j}^2} \right]. \quad (9)$$

In the first term of (9), the summation is performed only over the optical branches of the vibrational spectrum. The one-ion contribution to the free energy (see Eq. (4)) will be written with an accuracy of up to terms of the second order with respect to deformation characteristics of the lattice and deviations of the average values of the operators O_p^k from corresponding equilib-

rium values in a zero magnetic field (to simplify formulas written below, we assume that $\langle O_p^k \rangle_{\mathbf{B}=0} = 0$). Considering operator (7) as a perturbation and writing it as $H^{(P)} = \sum_{pk} A_p^k O_p^k = A : O$, we obtain

$$\Delta F = n \left[F_0(\mathbf{B}) + \langle H^{(P)} \rangle_0 + \frac{1}{2} A : q : A \right], \quad (10)$$

where $F_0(\mathbf{B}) = -k_B T \ln Z$ is the free energy of the ion with Hamiltonian $H^{(0)}$, $Z = \text{Tr}[\exp(-H^{(0)}/k_B T)]$ is the statistical sum, the symbol $\langle \dots \rangle_0$ denotes averaging with the equilibrium density matrix of the ion $\rho = \exp(-H^{(0)}/k_B T)/Z$, and the elements of matrix q are given by

$$\begin{aligned} q_{pp'}^{kk'} &= \frac{1}{k_B T} \left[\langle O_p^k \rangle_0 \langle O_{p'}^{k'} \rangle_0 \right. \\ &\quad \left. - \sum_i \langle \psi_i | \rho O_p^k | \psi_i \rangle \langle \psi_i | O_{p'}^{k'} | \psi_i \rangle \right] \\ &+ \sum_{i,j \neq i} (\varepsilon_i - \varepsilon_j)^{-1} [\langle \psi_i | \rho O_p^k | \psi_j \rangle \langle \psi_j | O_{p'}^{k'} | \psi_i \rangle \\ &\quad + \langle \psi_i | \rho O_{p'}^{k'} | \psi_j \rangle \langle \psi_j | O_p^k | \psi_i \rangle]. \end{aligned} \quad (11)$$

Here, ε_i and ψ_i are the eigenvalues and eigenfunctions of the operator $H^{(0)}$.

Using the conditions of the thermodynamic equilibrium $\partial F / \partial \langle O_p^k \rangle = 0$ and $\partial F / \partial w_{\alpha}(r) = 0$ and the designation of the convolution over the indices p and k introduced above, we obtain the free energy of the crystal in the form

$$\begin{aligned} F &= \frac{V}{2} \mathbf{e} \mathbf{C} \mathbf{e} + n F_0 - \frac{n}{2} \langle O \rangle_0 \\ &: \left[\lambda : (1 + q : \lambda)^{-1} + \frac{n}{V} \sum_{rr'} \hat{\mathbf{D}}(r) \hat{\mathbf{a}}^{-1}(r, r') \hat{\mathbf{D}}(r') \right] : \langle O \rangle_0 \quad (12) \\ &+ n \langle O \rangle_0 : \left[\hat{\mathbf{B}} - \sum_{rr'} \hat{\mathbf{b}}(r) \hat{\mathbf{a}}^{-1}(r, r') \hat{\mathbf{D}}(r') \right] \mathbf{e}, \end{aligned}$$

where $\mathbf{C} = \hat{\mathbf{C}}' - \sum_{rr'} \hat{\mathbf{b}}(r) \hat{\mathbf{a}}^{-1}(r, r') \hat{\mathbf{b}}(r')$ is the tensor of elastic constants, and the following notation for the quantities that are renormalized by the electron–deformation and electron–phonon interactions is introduced:

$$\begin{aligned} \hat{a}_{\alpha\beta}(r, r') &= a_{\alpha\beta}(r, r') \\ &+ \frac{n}{V} D_{\alpha}(r) : q : (1 + \lambda : q)^{-1} : D_{\beta}(r'), \end{aligned} \quad (13)$$

$$\hat{b}_{\alpha\beta\gamma}(r) = b_{\alpha\beta\gamma}(r) + \frac{n}{V} B_{\alpha\beta} : q : (1 + \lambda : q)^{-1} : D_{\gamma}(r), \quad (14)$$

$$\hat{C}'_{\alpha\beta\gamma\delta} = C'_{\alpha\beta\gamma\delta} + \frac{n}{V} B_{\alpha\beta} : q : (1 + \lambda : q)^{-1} : B_{\gamma\delta}, \quad (15)$$

$$\begin{aligned} \hat{D}_{\alpha}(r) &= (1 + \lambda : q)^{-1} : D_{\alpha}(r), \\ \hat{B}_{\alpha\beta} &= (1 + \lambda : q)^{-1} : B_{\alpha\beta}. \end{aligned} \quad (16)$$

It should be noted that, with an accuracy of up to terms of the second order with respect to the parameters of the electron–deformation interaction, the dependence of the elastic constants on temperature and magnetic field can be represented by the expression

$$C_{\alpha\beta\gamma\delta}(T, \mathbf{B}) = C_{\alpha\beta\gamma\delta}^{(0)} + \frac{n}{V} B_{\alpha\beta}^{(d)} : q : (1 + \lambda : q)^{-1} : B_{\gamma\delta}^{(d)}, \quad (17)$$

where the contributions of the magnetic subsystem are determined by the second term and the renormalized constants of coupling with macrodeformations are given by

$$B_{p,\alpha\beta}^{(d)k} = B_{p,\alpha\beta}^k - \sum_{rr'\gamma\delta} b_{\alpha\beta,\gamma}(r) a_{\gamma\delta}^{-1}(r, r') D_{p,\delta}^k(r'). \quad (18)$$

Changes of elastic constants (rates and polarizations of acoustic waves, respectively) in an external magnetic field are determined by corresponding changes of elements of the matrix q (see (11)). It should be noted that, here, we do not consider magnetoelastic effects that are caused by the electron–rotational interaction.

A magnetic field-induced relative change in the dimension of the crystal in the direction that is specified by the unit vector with the direction cosines n_{α} is $\Delta l/l = \sum_{\alpha\beta} n_{\alpha} n_{\beta} e_{\alpha\beta}$, where the components of the deformation tensor are determined from the minimum condition of free energy (12),

$$\mathbf{e}(\mathbf{B}) = -\frac{n}{V} [\mathbf{S} \mathbf{B}_{\text{ef}} : \langle O \rangle_0 |_{\mathbf{B}} - \mathbf{S} \mathbf{B}_{\text{ef}} : \langle O \rangle_0 |_{\mathbf{B}=0}]. \quad (19)$$

Here,

$$B_{\text{ef},p,\alpha\beta}^k = \sum_{p'k'} [(1 + \lambda : q)^{-1}]_{pp'}^{kk'} B_{p',\alpha\beta}^{(d)k'}$$

$\mathbf{S} = \mathbf{C}^{-1}$ is the tensor of elastic compliances.

Energy levels of ions and their magnetic moments in the external magnetic field are determined by above-introduced effective single-particle Hamiltonian H_{ef} in which the perturbation operator takes the form

$$\begin{aligned} H^{(P)} &= \left\{ \mathbf{B}_{\text{ef}} \mathbf{e} - \langle O \rangle_0 : \left[\frac{n}{V} \sum_{rr'} \hat{\mathbf{D}}(r) \hat{\mathbf{a}}^{-1}(r, r') \hat{\mathbf{D}}(r') \right. \right. \\ &\quad \left. \left. + \lambda : (1 + q : \lambda)^{-1} \right] \right\} : O. \end{aligned} \quad (20)$$

In the next section, the expressions that were introduced above for elastic constants, lattice deformations induced by the magnetic field, and the effective Hamiltonian of the paramagnetic ion will be used to calculate corresponding characteristics of the crystal LiTmF₄.

Table 1. Interaction parameters of Tm^{3+} ions with a crystal field and deformations of the B_g symmetry (in cm^{-1})

$p k$	B_p^k	$p k$	$B_p^{(d)k} (B_g^1)$	$B_{\text{ef}, p}^k (B_g^1)^*$	$B_p^{(d)k} (B_g^2)$	$B_{\text{ef}, p}^k (B_g^2)^*$
2 0	184	2 2	1914	1571	4194	3646
4 0	-90	2 -2	1408	1337	-1030	-1169
4 4	-669	4 2	-600	-468	-1615	-1393
4 -4	-638	4 -2	1292	1141	1237	986
6 0	-4.06	6 2	-192	-164	-492	-443
6 4	-328	6 -2	-569	-480	-590	-424
6 -4	-294	6 6	-963	-858	-1375	-795
		6 -6	-1067	-974	-1500	-910

* In a zero magnetic field at a temperature of 4.2 K

ELASTIC CONSTANTS, MAGNETIZATION, AND MAGNETOSTRICTION OF LiTmF_4

The results that are presented below were obtained using the numerical diagonalization of the Hamiltonian of Tm^{3+} ions in the full space of states of the electronic configuration $4f^{12}$ (the number of states is 91). The Hamiltonian of the free ion was written in the standard form taking the parameters of the electrostatic, spin-orbit, and interconfigurational interactions from [23]. In the crystallographic coordinate system, the crystal field that acts on the Tm^{3+} ion in the LiTmF_4 crystal is determined by a set of seven parameters B_p^k

$$H_{cf} = B_2^0 O_2^0 + B_4^0 O_4^0 + B_4^4 O_4^4 + B_4^{-4} O_4^{-4} + B_6^0 O_6^0 + B_6^4 O_6^4 + B_6^{-4} O_6^{-4}. \quad (21)$$

The values of the crystal field parameters that were used in this work are presented in Table 1. The calculated energy levels of the Tm^{3+} ion (see Table 2, where the sublevels of the lowest multiplet 3H_6 are given)

Table 2. Energy levels (in cm^{-1}) of the 3H_6 multiplet of the Tm^{3+} ion in a crystal LiTmF_4

Symmetry	Experiment			Calculation
	[7]	[24]	$\text{LiYF}_4 : \text{Tm}$ [25]	(this work)
$\Gamma_2(1)$	0	0	0	0
$\Gamma_{34}(1)$	32	—	30	31
$\Gamma_1(1)$	57	71	55	62
$\Gamma_2(2)$	—	281	275	282
$\Gamma_2(3)$	—	319	305	313
$\Gamma_1(2)$	—	363	—	362
$\Gamma_{34}(2)$	—	—	—	381
$\Gamma_{34}(3)$	—	—	—	402
$\Gamma_1(3)$	—	—	—	415
$\Gamma_2(4)$	—	—	—	430

agree well with experimental data. The ground state of the Tm^{3+} ions in the crystal field is the singlet $\Gamma_2(1)$, the nearest levels are the doublet $\Gamma_{34}(1)$ and the singlet $\Gamma_1(1)$ (the wave functions of different states of the electron shell $4f^{12}$ of Tm^{3+} ions are transformed according to the irreducible representations Γ_k of the S_4 point group). Comparison of the calculated temperature dependence of the longitudinal magnetic susceptibility with measurement data (Fig. 1a) indicates that the investigated specimens of LiTmF_4 contain paramagnetic impurities, the contribution of which to the magnetization increases considerably at temperatures lower than 10 K.

Calculations are significantly simplified if the symmetry properties of the system are taken into account. Let us introduce linear combinations of components of the deformation tensor $e(A_g^1) = e_{zz}$, $e(A_g^2) = (e_{xx} + e_{yy})/2$, $e(B_g^1) = e_{xx} - e_{yy}$, $e(B_g^2) = e_{xy}$, $e_1(E_g) = e_{xz}$, and $e_2(E_g) = e_{yz}$, which transform according to the irreducible representations $\Gamma = A_g, B_g$, and E_g of the C_{4h} factor group symmetry of the lattice. A magnetic field that is directed along the c axis induces only totally symmetric deformations A_g , whereas field that is directed in the ab plane induces totally symmetric and rhombic deformations (B_g). Corresponding microscopic deformations of the A_g and B_g symmetry are determined by three and five independent linear combinations of displacements of sublattices $w_\eta(\Gamma)$, respectively. In the basis of symmetrized deformations, the operator of the electron-deformation interaction has the form

$$H_{\text{el-def}} = \sum_{\Gamma \cup \eta} \sum_{pk} [B_{p,\eta}^k(\Gamma^\nu) e_\eta(\Gamma^\nu) + D_{p,\eta}^k(\Gamma^\nu) w_\eta(\Gamma^\nu)] O_p^k, \quad (22)$$

where $e_\eta(\Gamma^\nu)$ and $w_\eta(\Gamma^\nu)$ are independent variables, and ν and η are the number and the row of the representation Γ , respectively. Results of calculations of

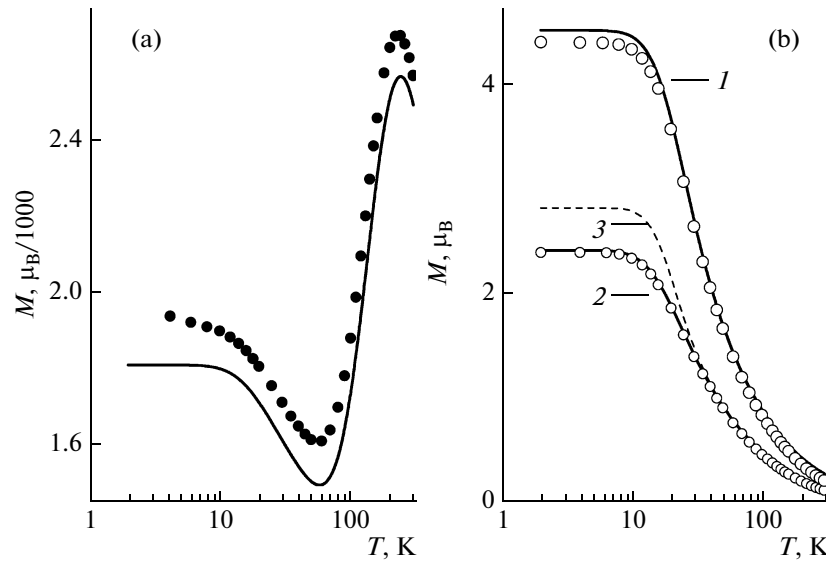


Fig. 1. Temperature dependences of the magnetization of a single crystal LiTmF₄ measured in [14] (symbols) and calculated (solid curves): (a) in a magnetic field $B = 0.1$ T that is parallel to the c axis and (b) in magnetic fields $B = (1)$ 5.5 and $(2, 3)$ 3 T that are perpendicular to the c axis and make an angle of 12.5° with the a axis. Dashed curve 3 represents the magnetization in the field with a strength of 3 T that was calculated without taking into account the multipole interaction between thulium ions.

coupling constants in operator (22) in terms of the model of exchange charges [20] and optical piezospectroscopy of the LiTmF₄ crystal [15] show that the interaction of Tm³⁺ ions with deformations of the B_g symmetry plays a dominant role. As a consequence, we can expect that dynamic deformations of the B_g symmetry make the main contribution to the multipole interaction between Tm³⁺ ions, the interaction with which can be represented by linear combinations of eight electronic operators $O_2^2 = O_1$, $O_2^{-2} = O_2$, $O_4^2 = O_3$, $O_4^{-2} = O_4$, $O_6^2 = O_5$, $O_6^{-2} = O_6$, $O_6^6 = O_7$, and $O_6^{-6} = O_8$. In accordance with (8), neglecting the dispersion of optical branches of the vibrational spectrum, we obtain the following expression for the elements of the matrix λ_{ij} ($i, j = 1 : 8$), which is determined in the space of the operators indicated:

$$\lambda_{ij} = \sum_{\nu=1:5} \frac{B_i(B_g^\nu)B_j(B_g^\nu)}{\omega(B_g^\nu)^2} - \sum_{\nu=1:4} \frac{B_i(A_u^\nu)B_j(A_u^\nu)}{\omega(A_u^\nu)^2} - \frac{1}{N} \sum_{\mathbf{q}j_a} \frac{B_i(\mathbf{l}, \mathbf{q}j_a)B_j(\mathbf{l}, -\mathbf{q}j_a)}{\omega_{\mathbf{q}j_a}^2}. \quad (23)$$

Multipole interaction parameters (23) were estimated using frequencies of gerade ($\omega(B_g^\nu)$) and transverse ungerade ($\omega(A_u^\nu TO)$) optical vibrations of the B_g and A_u symmetry, respectively, of the LiTmF₄ crystal at the center of the Brillouin zone, which were measured in [19], and coupling constants of thulium ions with corresponding vibrations $B_i(B_g^\nu)$ and $B_i(A_u^\nu TO)$, which were found from the analysis of temperature and mag-

netic-field effects in Raman spectra [18, 19] and calculations in terms of the exchange-charge model. The summation over acoustic vibrations in the last term in (23) was performed in terms of the long-wavelength approximation, which made it possible to relate the constants of the electron–phonon interaction $B_i(\mathbf{l}, \mathbf{q}j_a)$ with parameters (18) of the electron–deformation interaction. The corresponding contributions to elements of the matrix λ_{ij} are given by (in units of $10^{-6} (\text{cm}^{-1})^{-1}$)

$$\Delta\lambda_{ij} = -\{4.48B_i^{(d)}(B_g^1)B_j^{(d)}(B_g^1) + 2.29[B_i^{(d)}(B_g^1)B_j^{(d)}(B_g^2) + B_i^{(d)}(B_g^2)B_j^{(d)}(B_g^1)] + 1.89B_i^{(d)}(B_g^2)B_j^{(d)}(B_g^2)\}.$$

The coupling constants with homogeneous deformations of the B_g symmetry are given in Table 2 (see [16, 20]). Table 3 presents parameters of the multipole interaction, which were reduced twofold compared to calculated ones in order to match results of calculations of temperature dependences of the elastic constants C_{11} – C_{12} , C_{16} , and C_{66} , which determine a change in the lattice energy caused by deformations of the B_g symmetry, with data of measurements of [9, 10] (see Fig. 2). We note that contributions to multipole interaction parameters that are caused by the interaction of Tm³⁺ ions with acoustic vibrations (the last term in (23)) and that induce long-range correlations between states of paramagnetic ions play a dominant role. As a consequence, due to renormalization (16), the absolute values of the parameters of the effective electron–deformation interaction $B_{\text{ef}, p}^k(B_g^\nu)$ decrease compared to the parameters $B_p^{(d)k}(B_g^\nu)$ (Table 1).

Table 3. Parameters of the multipole interaction $\lambda_{ij} = \lambda_{ji}$ (in cm^{-1})

$i \backslash j$	1	2	3	4	5	6	7	8
1	-32.41	-24.64	21.82	-24.68	4.581	11.92	10.13	13.48
2		28.34	-7.994	4.897	-3.207	1.582	7.233	-2.955
3			-0.899	2.057	-1.417	-0.217	-6.138	-2.197
4				-12.85	-0.799	2.147	6.34	0.512
5					-0.87	-0.521	-1.866	-0.764
6						-0.869	-2.488	-3.06
7							-2.95	-4.074
8								-2.829

In calculations of magnetic-field effects, magnetic dipole–dipole interactions were taken into account in terms of the self-consistent field approximation. The local magnetic field that acts on Tm^{3+} ions in the s th sublattice was given by

$$\mathbf{B}_{\text{loc}}(s) = \mathbf{B} + \sum_{s'} \left[\mathbf{Q}(s, s') - \frac{4\pi}{3V} N_m \right] \mathbf{M}(s'), \quad (24)$$

where $\mathbf{M}(s)$ is the magnetic moment of the ion in the s th sublattice; $\mathbf{Q}(s, s')$ are the lattice sums, which were calculated by the Ewald method; and N_m is the demagnetization factor. The main attention was concentrated on effects that manifest themselves in magnetic fields that are oriented in the base plane of the lattice and that induce deformations of the B_g symmetry. In the magnetic field $\mathbf{B} \perp c$, which makes angle φ with the

crystallographic a -axis, the relative change in the dimension of the crystal $\Delta l/l$ along the field direction is

$$\Delta l/l = e(A_g^2) + \frac{1}{2} \cos 2\varphi e(B_g^1) + \sin 2\varphi e(B_g^2). \quad (25)$$

Values of $\Delta l/l$ that were obtained upon substitution into (25) of components of the deformation tensor calculated in accordance with Eq. (19) agree satisfactorily with data on the longitudinal magnetostriction of cylindrical specimens of LiTmF_4 with their generatrices along directions [100] and [110] that were measured at a temperature of 4.2 K in fields with a strength of up to 3 T (see Fig. 3a).

The inverse magnetostrictive effect, namely, a change in the crystal field as a consequence of deformations of the crystal lattice, is most clearly pronounced in splittings of non-Kramers doublets in fields that are oriented in directions to which a zero g

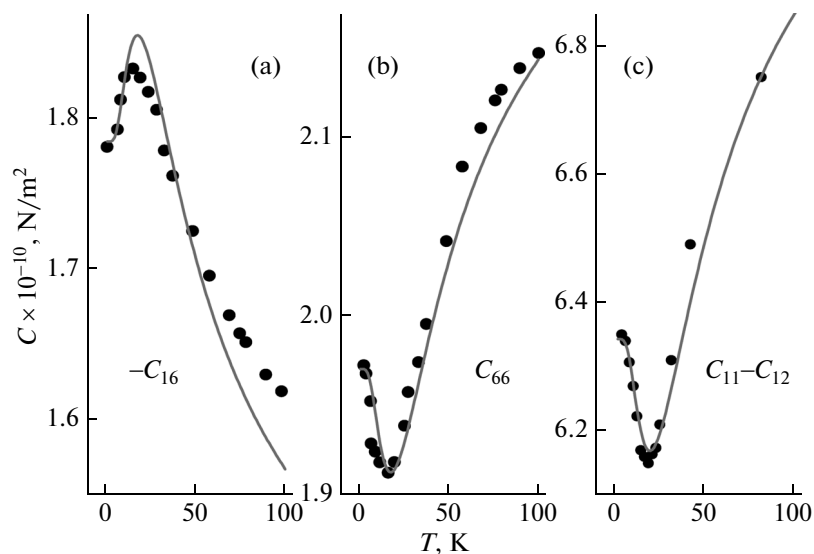


Fig. 2. Measured (symbols) [9, 10] and calculated (curves) temperature dependences of the elastic constants (a) C_{16} , (b) C_{66} , and (c) $C_{11}-C_{12}$ of a single crystal LiTmF_4 .

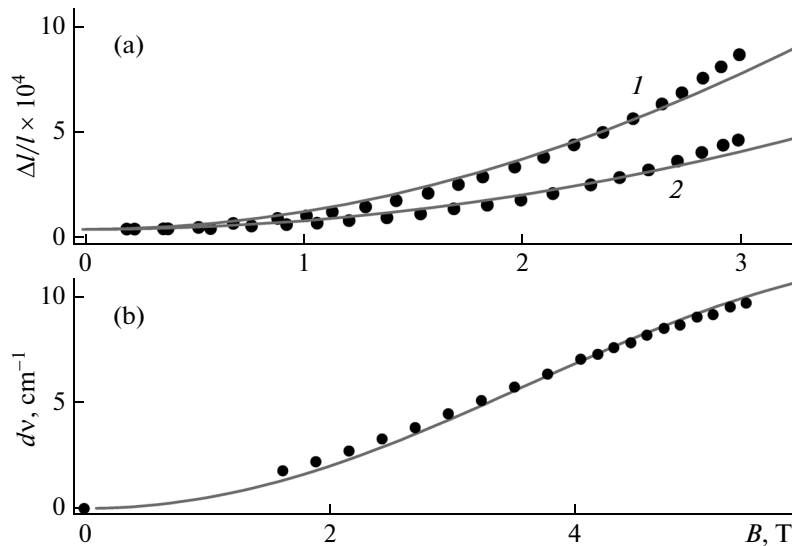


Fig. 3. (a) Field dependences of the longitudinal magnetostriction of a single crystal LiTmF_4 at a temperature of 4.2 K in external magnetic field \mathbf{B} : (1) $\mathbf{B} \parallel [100]$ and (2) $\mathbf{B} \parallel [110]$; (b) field dependence of the splitting of doublet $\Gamma_{34}(1)$ in a magnetic field that oriented in the base plane of a single crystal LiTmF_4 at an angle of $\varphi = 10^\circ$ to the a axis. Results of calculations are shown by solid curves, and symbols correspond to experimental data from [1, 8, 12].

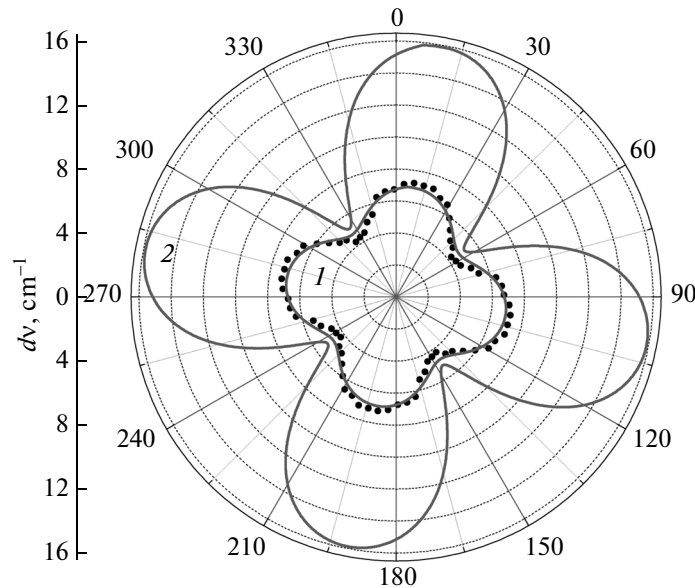


Fig. 4. Measured (symbols) [11, 12] and calculated (curve 1) orientational dependence of the splitting of doublet $\Gamma_{34}(1)$ with an energy of 31 cm^{-1} in external magnetic field $B = 4.05 \text{ T}$ in the base plane of a single crystal LiTmF_4 ; $T = 4.2 \text{ K}$. Curve 2 was obtained without taking into account the multipole interaction.

factor corresponds. In this case, the direct (Zeeman) interaction of a paramagnetic ion with the magnetic field splits the Kramers doublet only in the second order of the perturbation theory. Considerably larger splittings can occur as a consequence of field-incident changes in the lattice structure. In particular, anomalous splittings $d\nu$ of doublet $\Gamma_{34}(1)$ of thulium ions, which significantly change with orientation of the

magnetic field in the base plane of the lattice, were revealed in optical spectra of the crystal LiTmF_4 [11, 12]. As can be seen from Fig. 4, neglect of multipole interactions leads to a strong contradiction between the results of calculations performed with the use of parameters of the electron–deformation interaction that were determined from piezospectroscopic measurements [16] and the experimental data (the calcu-

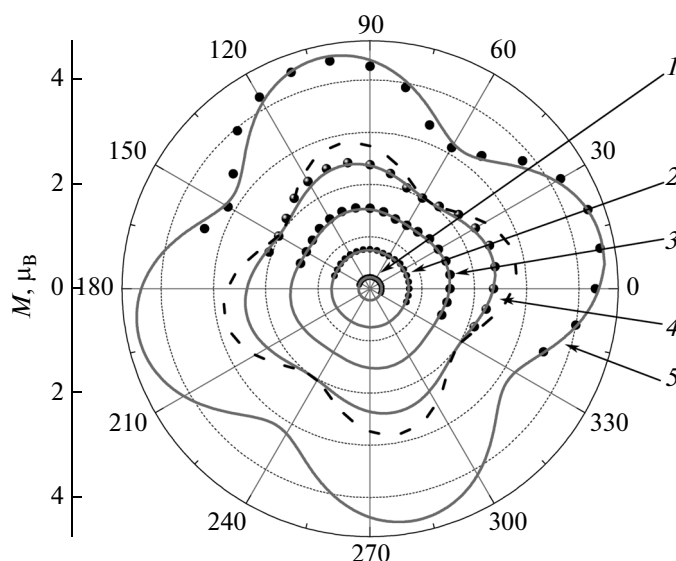


Fig. 5. Measured (symbols) [14] and calculated dependences of the magnetization of a single crystal LiTmF_4 on the orientation of external magnetic field \mathbf{B} ($B = (1) 0.3, (2) 1, (3) 2, (4) 3, \text{ and } (5) 5.5 \text{ T}$) in the base plane of the lattice; $T = 4.2 \text{ K}$. The dashed curve shows results of the calculation ($B = 3 \text{ T}$) that was performed without taking into account the multipole interaction.

lated maximal splitting is more than two times greater than the measured splitting). However, if operator (20) is used, which contains renormalized effective constants of the electron–deformation interaction, the calculated field (Fig. 3b) and orientational (Fig. 4) dependences of splitting $d\nu$ of doublet $\Gamma_{34}(1)$ agree well with the measured dependences.

Changes in the electronic structure of paramagnetic ions that are caused by lattice deformations in a magnetic field give rise to corresponding additional contributions to the field-induced magnetization. As in the case of the splitting of doublet $\Gamma_{34}(1)$ considered above, without taking into account multipole interactions, we obtained overestimated values of magnetic moments of thulium ions in magnetic fields that were perpendicular to the c axis and the strength of which was above 1 T (Figs. 1b and 5). The measured temperature, field, and orientational dependences of the magnetization are reproduced well only in calculations that are performed using parameters of the electron–deformation and multipole interactions that are the same as those that were used in the above-considered calculations of elastic constants, magnetostriction, and spectrum of thulium ions.

CONCLUSIONS

We have calculated elastic, spectral, and magnetic characteristics of a single crystal LiTmF_4 taking into account the electron–deformation and multipole interactions. It has been shown that the entire set of experimental data available at present on the field and temperature dependences of elastic constants, magnetization, magnetostriction, and energy levels can be

reproduced not only qualitatively, but also quantitatively, with a satisfactory accuracy in terms of a self-consistent theory that uses a unified set of parameters of the crystal field and electron–deformation and multipole interactions.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project no. 12-02-00372-a.

REFERENCES

1. L. K. Aminov, B. Z. Malkin, and M. A. Teplov, in *Handbook on the Physics and Chemistry of the Rare-Earths* (North-Holland, Amsterdam, 1996), Vol. 22, p. 295.
2. A. V. Klochkov, V. V. Naletov, I. R. Mukhamedshin, et al., *JETP Lett.* **66** (4), 266 (1997).
3. P. E. Hansen, *Phys. Rev. B* **16**, 146 (1977).
4. V. Vasylyev, E. G. Villora, M. Nakamura, Y. Sugahara, and K. Shimamura, *Opt. Express* **20**, 14460 (2012).
5. K. Kjaer, J. Als-Nielsen, I. Laursen, and F. Larsen, *J. Phys.: Condens. Matter* **1**, 5743 (1989).
6. E. Garcia and R. R. Ryan, *Acta Crystallogr. C* **49**, 2053 (1993).
7. H. P. Christensen, *Phys. Rev. B* **19** (12), 6573 (1979).
8. S. A. Al'tshuler, V. I. Krotov, and B. Z. Malkin, *Pis'ma Zh. Eksp. Teor. Fiz.* **32**, 232 (1980).
9. F. L. Aukhadeev, R. Sh. Zhdanov, M. A. Teplov, and D. N. Terpilovskii, *Fiz. Tverd. Tela* **23**, 2285 (1981).
10. S. A. Al'tshuler, B. Z. Malkin, M. A. Teplov, and D. N. Terpilovskii, *Soviet Scientific Reviews, Section A, Physics Reviews* (Harwood Academic Publishers, New York, 1985), Vol. 6.

11. R. Yu. Abdulsabirov, A. A. Kazantsev, S. L. Korableva, et al., Proc. SPIE—Int. Soc. Opt. Eng. **4766**, 59 (2002).
12. R. Yu. Abdulsabirov, A. A. Kazantsev, S. L. Korableva, et al., J. Lumin. **117** (2), 225 (2006).
13. D. I. Abubakirov, V. V. Kuzmin, H. Suzuki, et al., J. Phys.: Conference Series **51**, 135 (2006).
14. D. I. Abubakirov, K. Matsumoto, H. Suzuki, and M. S. Tagirov, J. Phys.: Condens. Matter **20**, 395223 (2008).
15. A. V. Vinokurov, B. Z. Malkin, A. I. Pominov, and A. L. Stolov, Fiz. Tverd. Tela **30**, 3426 (1988).
16. A. V. Vinokurov, B. Z. Malkin, A. I. Pominov, and A. L. Stolov, Fiz. Tverd. Tela **28**, 381 (1986).
17. S. Bertaina, B. Barbara, R. Giraud, et al., Phys. Rev. B **74** (18), 184421 (2006).
18. A. K. Kupchikov, B. Z. Malkin, A. L. Natadze, and A. I. Ryskin, Fiz. Tverd. Tela **29**, 3335 (1987).
19. A. K. Kupchikov, B. Z. Malkin, A. L. Natadze, and A. I. Ryskin, in *Spectroscopy of Crystals* (Nauka, Leningrad, 1989), pp. 85–109 [in Russian].
20. L. K. Aminov and B. Z. Malkin, *Dynamics and Kinetics of Electronic and Spin Excitations In Paramagnetic Crystals* (Kazanskii Gos. Univ., Kazan, 2008) [in Russian].
21. V. V. Klekovkina, A. R. Zakirov, B. Z. Malkin, and L. A. Kasatkina, J. Phys.: Conf. Ser. **324**, 012036 (2011).
22. R. J. Elliott, R. T. Harley, W. Hayes, and S. R. P. Smith, Proc. Roy. Soc. (London) A **328**, 217 (1972).
23. H. M. Crosswhite and H. Crosswhite, J. Opt. Soc. Am. B **1**, 246 (1984).
24. A. K. Kupchikov, B. Z. Malkin, D. A. Rzaev, and A. I. Ryskin, Fiz. Tverd. Tela **24**, 2373 (1982).
25. S. A. Klimin, D. S. Pytalev, M. N. Popova, et al., Phys. Rev. B **81** (4), 045113 (2010).

Translated by V. Rogovoi