19F NMR study of LiTbF4 single crystals

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Abstract. The angular dependences of 19F NMR spectra have been measured in the external magnetic field of 0.5 T oriented in the basis plane of LiTbF4 at the room temperature. We have obtained the constants of transferred hyperfine interaction and the corrected set of crystal field parameters for the Tb3+ ions in LiTbF4. The results of simulations of the magnetization in high pulsed magnetic fields with taking into account magnetoelastic interactions agree satisfactorily with experimental data presented in the literature.

1. Introduction

Double lithium rare-earth fluorides crystallizing in the tetragonal scheelite (CaWO4) structure (C4v) attract much attention as model objects in physics of magnetism [1]. The unit cell of LiRF4 contains two magnetically equivalent lanthanide R3+ ions at sites with the S4 point symmetry. LiTbF4 is a dipolar Ising-like ferromagnet (Tc=2.89 K) [2]. Earlier 19F NMR in this material at 295 K was studied by Hansen et al. [3], and they determined parameters of the transferred hyperfine interactions between the Tb3+ ions and the 19F and 7Li nuclei. The sets of transferred hyperfine interaction constants were obtained from fitting the calculated NMR spectra to the experimental data. The local magnetic fields induced by Tb3+ magnetic moments at 19F nuclei were calculated using bulk magnetic susceptibilities of LiTbF4 measured in [4, 5].

In general case, temperature variations of local magnetic fields in a paramagnetic crystal can be calculated if parameters of the crystal field affecting paramagnetic ions are known. However, different sets of the crystal field parameters have been introduced in the literature to describe magnetic and spectral properties of LiTbF4 [6, 7] and terbium doped isomorphic LiYF4 crystals [8, 9]. Earlier we studied temperature and magnetic field dependences of the magnetization of LiRF4 single crystals (R=Dy, Ho, Tb) [10, 11] taking into account magnetoelastic interactions and found corrected sets of the crystal field parameters for Tb3+, Dy3+ and Ho3+ ions. It should be noted that in theoretical studies of LiTbF4 spectral properties carried out earlier, as well as in our previous work [11], crystal field energies of the Tb3+ ion were calculated by making use of the ion Hamiltonian acting in the truncated space of electronic states belonging to the ground 4f6 configuration. This resulted in remarkable differences between some crystal field parameters obtained for stoichiometric LiTbF4 [6, 7, 11] and for the impurity Tb3+ ions in LiYF4 [8, 9]. To determine unambiguously the total set of seven crystal field parameters (in crystallographic frame) for rare earth ions at the sites with the S4 symmetry, it is necessary to analyze responses of the ions on large enough direction dependent perturbations (in particular, on external magnetic fields). In the present work we use additional information about the local magnetic fields in LiTbF4 obtained from 19F NMR spectra and the results of the magnetization measurements in high pulsed magnetic fields [12], as well as more precise technique of calculations of the terbium magnetic moments, in order to validate different parameters of the microscopic model.
describing static and dynamic magnetic properties of LiTbF₄. Theoretical grounds for simulations of the local magnetic fields are considered in section 2 of the present work, and in section 3 we analyze the results of ¹⁹F NMR measurements.

2. Magnetic moment of the Tb³⁺ ion in LiTbF₄ in external magnetic field

To calculate the angular dependence of the ¹⁹F NMR spectra, we need to know local magnetic fields affecting the ¹⁹F nuclei. Local fields depend on the average values of the Tb³⁺ magnetic moments. The magnetic moments of the Tb³⁺ ions are considered here with taking into account interactions of the Tb³⁺ ion with the static crystal field and lattice deformations and magnetic (dipole-dipole and exchange) interactions between the Tb³⁺ ions.

In the presence of an applied magnetic field \( B \) (below a direction of \( B \) relative to the crystallographic axes is specified by spherical coordinates \( \theta \) (the angle between \( B \) and the \( c \)-axis) and \( \phi \) (the angle between the \( B \) projection onto the \( ab \)-plane and the [100] axis)), we write down the Hamiltonian of a single Tb³⁺ ion in the following form (the nuclear Zeeman energy and the hyperfine interaction are neglected):

\[
H = H₀ + H_{qf} - \mu_B B_{loc}(L + 2S) + \sum_{\alpha\beta} V'_{\alpha\beta} e_{\alpha\beta} + \sum_{\alpha\beta} V''_{\alpha\beta}(s) w_{\alpha\beta}(s).
\]

The Hamiltonian (1) operates in the total space of 3003 states of the electronic ⁴f⁸ configuration, the first term is the free ion Hamiltonian, the second term is the crystal field Hamiltonian:

\[
H_{qf} = B_0^0 O_0^0 + B_0^4 O_4^0 + B_0^4 O_4^4 + B_0^6 O_6^0 + B_0^6 O_6^4 + B_0^6 O_6^4
\]
determined in the crystallographic system of coordinates by the set of seven crystal field parameters \( B_0^k \) and \( \Omega_0^k \) (\( k \) are the linear combinations of spherical tensor operators similar to the corresponding Stevens operators [13]). The third term in (1) is the electronic Zeeman energy (\( \mu_B \) is the Bohr magneton, \( L \) and \( S \) are the electronic orbital and spin moments, respectively, and \( B_{loc} \) is the local magnetic field defined below). The last two terms define linear interactions of rare earth ions with the homogeneous macro- and microdeformations, respectively, where \( e \) is the deformation tensor, and \( w(s) \) is the vector of the \( s \)-sublattice displacement. The electronic operators \( V'_{\alpha\beta} \) and \( V''_{\alpha\beta}(s) \) can be represented, similar to the crystal field energy, through the linear combinations of spherical tensor operators with the parameters which have been calculated earlier in the framework of the exchange charge model [14-16]. Below we consider the electron-deformation interaction (last two terms in (1)) as a perturbation and take into account the corresponding contributions of the first order in deformation parameters \( e \) and \( w(s) \) into the free energy of the magnetic subsystem.

The energy of a deformed crystal lattice (per unit cell with the volume \( v_0 \)) is written as [16]

\[
E_{lat} = \frac{v_0}{2} \sum_s w(s)\tilde{b}(s)e\tilde{b}(s) + \frac{1}{2} \sum_{ss'} \sum_{ss'} w(s)\tilde{a}(s,s')w(s')
\]

where \( \tilde{a} \) is the dynamic matrix of the lattice at the Brillouin zone center, and the tensor of elastic constants is \( \tilde{C} = \tilde{C} - \sum_{ss'} \tilde{b}(s)\tilde{a}^{-1}(s,s')\tilde{b}(s')/v_0 \). Taking into account the equilibrium conditions for the coupled paramagnetic ions and the elastic lattice, we obtain the lattice macrodeformation induced by the magnetic field

\[
\tilde{e}(B) = -\frac{n}{v_0} \tilde{S} \langle V \rangle B - \langle V \rangle_0
\]

and the sublattice displacements

\[
\Delta w(B) = w(B) + \tilde{a}^{-1}\tilde{e}(B) = -n\tilde{a}^{-1}\langle V' \rangle B - \langle V' \rangle_0.
\]

Here \( n = 2 \) is the number of rare earth ions in the unit cell, \( \tilde{S} = \tilde{C}^{-1} \) is the compliance tensor of the lattice, and angular brackets \( \langle...\rangle_B \) and \( \langle...\rangle_0 \) indicate thermal averages over the eigenstates of the
Hamiltonian (1) for \( B \neq 0 \) and \( B = 0 \), respectively. Operators \( V = V' - \hat{b}(s)\hat{a}^{-1}(s,s')V''(s') \) in (4) equal to operators \( V' \) renormalized due to linear coupling between macro- and microdeformations.

**Table 1.** Coupling constants (in cm\(^{-1}\)) of the electron-deformation interaction [16, 17].

| \( A^4_0 \) | \( A^4_2 \) | \( A^4_4 \) | \( A^4_6 \) | \( a^0_2 \) | \( a^0_4 \) | \( a^4_0 \) |
|---|---|---|---|---|---|---|
| 350 | 140 | 2300 | 1550 | 90 | 700 | 300 |
| -900 | 500 | 2400 | 795 | -50 | 1300 | 1100 |

| \( b^2_2 \) | \( b^4_2 \) | \( b^4_4 \) | \( b^4_6 \) | \( b^6_2 \) | \( b^6_4 \) |
|---|---|---|---|---|---|
| 1644 | 1846 | -454 | 1885 | 188 | -543 |
| 3814 | -836 | -1532 | 1424 | -243 | -658 |

To take into account magnetic dipole-dipole and exchange interactions between the rare earth ions, we use the mean field approximation. The local field in the spherical sample equals

\[
B_{\text{loc}} = B + (\hat{Q} + \hat{\chi} - N\hat{I})M
\]

(\( \hat{Q} \) is the tensor of dipole lattice sums, the tensor \( \hat{\chi} \) determines the exchange field, the demagnetizing factor \( N = 4\pi/3, \hat{I} \) is the unit tensor, \( \hat{M} \) is the magnetization). We substitute expressions (4) and (5) for \( e \) and \( w(s) \), respectively, in (1) and thus obtain the effective self-consistent single-ion Hamiltonian \( H_{\text{eff}}(B, \hat{e}(B), w(B), \hat{M}(B)) \) parametrically dependent on the magnetization and renormalized by the electron-deformation interactions. Additional terms, depending on the external magnetic field and the temperature, change the response of rare earth ions on the field \( B \).

**Table 2.** Crystal field parameters \( B_p^k \) (cm\(^{-1}\)) for the \( R^{3+} \) ions in LiRF\(_4\) (R=Ho, Dy, Tb) crystals.

| \( B_p^k \) | LiTbF\(_4\) | LiTbF\(_4\) | LiDyF\(_4\) | LiHoF\(_4\) |
|---|---|---|---|---|
| This work | [8] | [10] | [10] |
| \( B_0^0 \) | 200 | 200 | 170 | 219.7 |
| \( B_2^0 \) | -100.5 | -100 | -85 | -87.3 |
| \( B_6^0 \) | -2 | -3.6 | -4.2 | -3.55 |
| \( B_4^4 \) | -694 | -1103 | -721 | -710 |
| \( B_4^{-4} \) | -829 | 0 | -661 | -612 |
| \( B_6^4 \) | -435 | -529 | -390 | -387 |
| \( B_6^{-4} \) | -283 | 0 | -248 | -253.7 |

Calculations are essentially simplified when making use of symmetry properties of a system. We worked with linear combinations of the deformation tensor \( e(A_g^k) = e_{zz}, e(A_g^k) = (e_{xx} + e_{yy})/2, e(B_g^k) = e_{xx} - e_{yy}, e(B_g^k) = e_{xy}, e_1(E_g) = e_{xx}, e_2(E_g) = e_{yy} \) and the sublattice displacements corresponding to irreducible representations \( \Gamma = A_g, B_g, E_g \) of the lattice factor group \( C_{4h} \). In particular, the magnetic field \( B \) directed along the crystal symmetry c-axis brings about only totally symmetric \( A_g \) deformations, but the field in the \( ab \)-plane induces \( A_g \) and rhombic \( B_g \) deformations. The corresponding internal \( A_g \) and \( B_g \) deformations are described by three and five independent linear combinations of the sublattice displacements, respectively. We can write the electron-deformation interaction in the basis of symmetrical strains as follows

\[
H_{cd} = \sum_{\Gamma \Lambda} \left[ \sum_k V_k(\Gamma \Lambda) e_k(\Gamma \Lambda) + \sum_p V_p(\Gamma \Lambda) \Delta w_p(\Gamma \Lambda) \right],
\]

where \( e_k(\Gamma \Lambda) \) and \( \Delta w_p(\Gamma \Lambda) \) are independent variables. In case of coupling with \( A_g \) and \( B_g \) strains, the electronic operators equal.
The coupling constants $\alpha_{\lambda,\mu}$ and $\beta_{\lambda,\mu}$ determined from piezospectroscopic measurements of the rare earth doped LiYF$_4$ crystals are given in table 1. We used in calculations the compliance constants of LiYF$_4$: $S_{(A\gamma 11)} = 7.78 \cdot 10^{-12}$, $S_{(A\gamma 12)} = -2.33 \cdot 10^{-12}$, $S_{(A\gamma 22)} = 3.36 \cdot 10^{-12}$, $S_{(B\gamma 11)} = 37.1 \cdot 10^{-12}$, $S_{(B\gamma 12)} = 8.0 \cdot 10^{-12}$ (in units of m$^2$/J) [18], components of tensors $\hat{a}$ and $\hat{b}$ were calculated using parameters of a rigid ion model of the LiYF$_4$ lattice dynamics [19].

Components of the magnetic moment of a rare earth ion satisfy to self-consistent equations

$$m_\alpha = \sum_i \mu_B < i | L_\alpha + 2S_\alpha | i > e^{-E_i(M)/kT} \left( \sum_i e^{-E_i(M)/kT} \right)^{-1}, \quad (10)$$

where $E_i(M)$ are the crystal energies (eigenvalues of the Hamiltonian $H_{\text{eff}}$), $T$ – temperature, $k_B$ is the Boltzman constant. To obtain crystal field energies and the magnetization $M=M_0$, $\hat{e}=0$, $\Delta w=0$ is diagonalized, and the macro- ($\hat{e}(\hat{B})$) and microdeformations ($\Delta w(\hat{B})$), and components (10) of the magnetic moment are calculated. At the next step, the obtained values of $M$, $\hat{e}$, $\Delta w$ are substituted into the Hamiltonian $H_{\text{eff}}$, and the procedure is repeated (up to seven times) to get a steady solution.

Figure 1. Differential magnetic susceptibilities of LiTbF$_4$ single crystals in magnetic fields $B||[100]$ and $B||[110]$ (in red and blue, respectively), $T=1.4$ K. Symbols – experimental data digitized from Ref. [12], solid and dashed curves represent the results of calculations carried out with or without taking into account the magnetoelastic interactions, respectively. Inset (a) – calculated energies of the three lower sublevels of the $^7F_6$ multiplet relative to the ground state vs. the magnetic field $B||[110]$. Inset (b) – calculated magnetization components along (induced moment $M_i$) and normal (spontaneous moment $M_s$) to the external field $B||[100]$ vs. the field intensity.
Table 3. Energy levels (cm$^{-1}$) of the Tb$^{3+}$ ion in LiTbF$_4$ and LiYF$_4$.

| Multiplet, symmetry | Experimental energy levels | Calculated energies |
|---------------------|---------------------------|--------------------|
|                     | LiTbF$_4$ [6, 20] | LiYF$_4$:Tb [8,21] |
| $^7$F$_6$            |               |                    |
| $\Gamma_2$          | 1.0           | 0.9                |
| $\Gamma_3$          | 107           | 98                 |
| $\Gamma_4$          | 124           | 114                |
| $\Gamma_5$          | 136           | 128                |
| $\Gamma_6$          | 166           | 169                |
| $\Gamma_7$          | 217           | 220                |
| $\Gamma_8$          | 344           |                    |
| $\Gamma_9$          | 355           |                    |
| $\Gamma_{10}$       | 360           | 363                |
| $^7$F$_5$            |               |                    |
| $\Gamma_2$          | 2110          | 2120               |
| $\Gamma_3$          | 2133          |                    |
| $\Gamma_4$          | 2174          |                    |
| $\Gamma_5$          | 2199          |                    |
| $\Gamma_6$          | 2353          |                    |
| $\Gamma_7$          | 2391          |                    |
| $\Gamma_8$          | 2400          | 2401               |
| $^7$F$_4$            |               |                    |
| $\Gamma_1$          | 3348          |                    |
| $\Gamma_3$          | 3385          |                    |
| $\Gamma_4$          | 3413          |                    |
| $\Gamma_5$          | 3424          |                    |
| $\Gamma_6$          | 3600          |                    |
| $\Gamma_7$          | 3784          |                    |
| $^7$F$_3$            |               |                    |
| $\Gamma_2$          | 4333          | 4337               |
| $\Gamma_3$          | 4406          | 4406               |
| $\Gamma_4$          | 4473          | 4468               |
| $\Gamma_5$          | 4524          | 4509               |
| $\Gamma_6$          | 4532          | 4517               |
| $^7$F$_2$            |               |                    |
| $\Gamma_1$          | 5035          | 5033               |
| $\Gamma_2$          | 5067          | 5071               |
| $\Gamma_3$          | 5285          | 5274               |
| $\Gamma_4$          | 5385          | 5366               |
| $^7$F$_1$            |               |                    |
| $\Gamma_1$          | 5592          | 5592               |
| $\Gamma_3$          | 5690          | 5691               |
| $^7$F$_0$            |               |                    |
| $\Gamma_1$          | 5917          | 5874               |
| $^5$D$_4$            |               |                    |
| $\Gamma_1$          | 20561         | 20553              |
| $\Gamma_2$          | 20571         | 20559              |
| $\Gamma_3$          | 20580         | 20568              |
| $\Gamma_4$          | 20641         | 20627              |
| $\Gamma_5$          | 20654         | 20645              |

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Crystal field parameters (see table 2) were determined by fitting the calculated crystal field energies to the energy levels determined from the optical and EPR spectra [6, 20] of LiTbF₄. As it is seen in table 2, our parameters $B_4^0 = 1081 \, \text{cm}^{-1}$, $B_6^0 = 519 \, \text{cm}^{-1}$ differ only slightly from corresponding parameters determined in [8] for the impurity Tb³⁺ ions in LiYF₄ (note that in [8] instead of the point $S_4$ symmetry, the $D_{2d}$ symmetry was assumed). The $B_2^0$ parameter is fixed by the measured splitting of the $^7F_1$ multiplet. The calculated energies of sublevels of the $^7F_6$, $^7F_3$ and $^7F_2$ multiplets (see table 3) agree satisfactorily with the measured energies, however, large differences remain between the results of calculations and the experimental data for the $^5D_4$ multiplet. In particular, reversed positions of the two lower $^5D_4$ sublevels $\Gamma_3,4$ and $\Gamma_1,2$ are predicted by our set of parameters, as well as by all other published sets [6-9, 11].

To determine ratios of the parameters $B_p^0$ and $B_p^4$ ($p=4$ and 6), we analyzed presented in [12] dependences of the longitudinal magnetization in LiTbF₄ on the external pulsed magnetic fields applied to the oriented samples (rectangular rods with dimensions of 1.5×1.5×2.5 mm³) in the $ab$-plane along the [100] and [110] directions (coinciding with the long edge of a rod) at the temperature 1.4 K. The magnetic field varied from zero up to 50 T during 20 μs, and we calculated the magnetization assuming, similarly to the authors of [12], the adiabatic process. Changes of the temperature $\Delta T$ of the magnetic subsystem induced by the increase of the field with steps $\Delta B$ were calculated using the expression

$$\Delta T = - \frac{1}{T} \left[ < H_{\text{eff}}(B) > m - < H_{\text{eff}}(B) > < m > < H_{\text{eff}}(B)^2 > - < H_{\text{eff}}(B)^2 > \right] \Delta B. \tag{11}$$

There are two terbium ions, Tb1 and Tb2, with coordinates $r(\text{Tb1})=(0, 0, c/2)$, $r(\text{Tb2})=(0, a/2, -c/4)$ in the unit cell. According to neutron scattering data [2] at 100 K, the lattice constants of LiTbF₄ equal $a=0.5181$, $c=1.0873$ nm. In the magnetically ordered state, the local field at the terbium ion $\text{Tb} \eta (\eta=1, 2)$ is written as follows

$$B_{\text{loc,} \alpha} (\text{Tb} \eta) = B_\alpha + \sum_{\beta} \left( \sum_{\eta=1,2} Q_{\text{Tb} \eta, \text{Tb} \eta} (\alpha \beta) + 2 \frac{4\pi}{3V} (\lambda - N_\alpha) \delta_{\text{eff}} \right) m_\beta (\text{Tb}). \tag{12}$$

Here the demagnetizing factors of the rods are $N_\alpha = 0.68$ [22], $N_\gamma = 0$ (for the domains in the system with the dominant dipole-dipole interactions), the lattice sums $Q_{\text{Tb} \eta, \text{Tb} \eta} (\alpha \alpha) = Q_{\text{Tb} \eta, \text{Tb} \eta} (\alpha \beta) = 1.18053$, $Q_{\text{Tb} \eta, \text{Tb} \eta} (\beta \beta) = 1.18053$. 

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Figure 2. $^{19}$F NMR spectrum of LiTbF₄ in the magnetic field $B=0.5 \, \text{T}$ at room temperature ($B_{\perp c}, \varphi=50^\circ$).
\[ Q_{Tb_{1},Tb_{2}}(zz) = 0.63894, \quad Q_{Tb_{1},Tb_{2}}(xx) = Q_{Tb_{1},Tb_{2}}(yy) = 0.41738, \quad Q_{Tb_{1},Tb_{2}}(zz) = 2.16525 \] (in units of \(4\pi/3v\)) have been computed by the Ewald method, the value of the isotropic exchange (antiferromagnetic) field constant \(\lambda = -0.316\) have been determined previously in [11]. To account for the ordering of magnetic moments along the \(c\)-axis, a small initial external field of 0.01 T has been introduced. With the increasing magnetic field normal to the magnetic easy axis [001], the gap between the lower sublevel of the first excited \(\Gamma_{34}\) state and the ground quasi-doublet quickly diminishes (see Inset \((a)\) in figure 1), and the peaks in the differential magnetic susceptibility are observed at the anticlassing point. As an example, evolutions of the spontaneous magnetic moment with the increasing transversal external field and of the induced moment along the field are shown in Inset \((b)\) in figure 1.

As it is seen in figure 1, the differential susceptibilities computed with our set of the crystal field parameters match satisfactorily experimental data. However, the widths of the calculated peaks are much broader than the measured ones. It is evident that more elaborated study of the quantum phase transition in LiTbF\(_4\) in the transversal magnetic fields beyond the mean field approximation is necessary. A comparison of the solid and dashed curves in figure 1 shows that magnetoelastic interactions contribute substantially into the magnetization if magnetic field is strong enough.

3. Experimental results and simulations of the NMR frequencies

The unit cell of LiRF\(_4\) contains eight fluorine ions. Each of the two magnetically non-equivalent subsystems (labeled below by \(s = 1, 2\)) of \(^{19}\text{F}\) nuclei in the external magnetic field lying in the \(ab\)-plane involve four \(F\) sublattices with the following basis vectors \(r_{i}(s)\): \(r_{1}(1) = (ax, ay, cz), r_{2}(1) = (-ax, -ay, cz), r_{3}(1) = (ax, ay - 0.5, c(0.25 - z)), r_{4}(1) = (-ax, ay - 0.5, c(0.25 - z)); r_{1}(2) = (ay, -ax, -cz), r_{2}(2) = (ay, -ax, -cz), r_{3}(2) = (-ay, 0.5, ax - cz), r_{4}(2) = (-ay, 0.5, ax - cz)).\) At 295 K, the lattice structure constants of LiTbF\(_4\) equal \(a = 0.5192, c = 1.0875\) nm, \(x = 0.2802, y = 0.1619, z = 0.0810\) [2].

Single crystal of LiTbF\(_4\) was grown using Bridgman-Stockbarger method. After axes definition by using X-ray diffractometer, it was shaped as a sphere to obtain the homogeneous demagnetizing field. The angular dependence of \(^{19}\text{F}\) NMR spectrum was obtained by using homebuilt CW NMR spectrometer with a frequency sweep. The external magnetic field of 0.5 T was oriented in the basis plane of LiTbF\(_4\). An example of the recorded spectrum is shown in figure 2 where two lines correspond to magnetically non-equivalent fluorine sites. The measured angular dependences of the resonance frequencies are represented in figure 3.

Table 4. Dipole lattice sums (in units of \(4\pi/3v\))

| \(\alpha\beta\) | \(xx\)   | \(xy\)   | \(xz\)   | \(yy\)   | \(yz\)   | \(zz\)   |
|-------------|--------|--------|--------|--------|--------|--------|
| \(Q_{Tb_{1},F_{1}(1)}(\alpha\beta)\) | 0.1971 | 2.8226 | -1.7445 | 3.8486 | -2.3506 | -1.0458 |
| \(Q_{Tb_{1},F_{1}(1)}(\alpha\beta)\) | 0.1925 | -1.3327 | -3.1669 | -0.7825 | 2.4262 | 3.5900 |

According to expression (6), the local magnetic fields at the \(^{19}\text{F}\) nuclei in LiTbF\(_4\) in the paramagnetic phase (in the crystallographic frame)

\[ B_{x}(F_{s}(s)) = B_{loc,x}(ks) = B_{x} + [Q_{Tb_{1},F_{1}(s)}(xx) + Q_{Tb_{2},F_{1}(s)}(xx) + e_{xx}(ks) - \frac{4\pi}{3v} N]m_{x} + \]

\[ [Q_{Tb_{1},F_{1}(s)}(xy) + Q_{Tb_{2},F_{1}(s)}(xy) + e_{xy}(ks)]m_{y}, \]

\[ B_{y}(F_{s}(s)) = B_{loc,y}(ks) = B_{y} + [Q_{Tb_{1},F_{1}(s)}(xy) + Q_{Tb_{2},F_{1}(s)}(xy) + e_{yx}(ks)]m_{x} + \]

\[ [Q_{Tb_{1},F_{1}(s)}(yy) + Q_{Tb_{2},F_{1}(s)}(yy) + e_{yy}(ks) - \frac{4\pi}{3v} N]m_{y}. \]

The independent dipole lattice sums have been calculated by the Ewald method and are given in table 4. Components of transferred hyperfine interaction tensors \(e_{\alpha\beta}(ks)\) have been considered as the fitting
parameters. Note that tensors $\varepsilon_{\alpha\beta}(kS)$ contain contributions due to the transferred hyperfine interactions between a $^{19}\text{F}$ nucleus and a couple of the nearest neighbor terbium ions, Tb1 and Tb2. The dipole sums and tensors $\varepsilon_{\alpha\beta}(kS)$ satisfy the symmetry relations, in particular, $Q_{Tb1,F1(1)}(xy)=Q_{Tb1,F1(1)}(yx)$, $Q_{Tb1,F1(2)}(xy)=Q_{Tb1,F1(1)}(xx)$, $Q_{Tb1,F1(2)}(xy)=-Q_{Tb1,F1(1)}(xy)$, $\varepsilon_{xx}(12)=\varepsilon_{yy}(11)$, $\varepsilon_{xy}(12)=\varepsilon_{yx}(11)$, $\varepsilon_{xy}(12)=-\varepsilon_{yx}(11)$, $Q_{Tb2,F1(1)}(\alpha\beta)=Q_{Tb1,F1(1)}(\alpha\beta)$, $Q_{Tb2,F1(1)}(\alpha\beta)=Q_{Tb1,F1(1)}(\alpha\beta)$ for $\alpha,\beta=x,y$.

Figure 3. The angular dependence of $^{19}\text{F}$ NMR spectra in LiTbF$_4$ in the magnetic field of 0.5 T ($B \perp c$), $T=295$ K. The circles are the experimental points, solid curves represent the results of calculations where the transferred hyperfine interaction parameters obtained in the present work have been used.

Three independent parameters, $\varepsilon_{xx}(11)=-1.743$, $\varepsilon_{xy}(11)=-0.279$ and $\varepsilon_{yy}(11)=-1.481$ (in units of $4\pi/3\nu$) were found from fitting the calculated resonance frequencies of $^{19}\text{F}$ nuclei $\nu(s)=\gamma_F[B_{loc,s}(1s)^2+B_{loc,s}(1s)^2]^{1/2}$ (here $\gamma_F/2\pi=40.07$ MHz/T is the fluorine gyromagnetic ratio) to the results of measurements. The obtained hyperfine interaction constants are compared with the ones presented in [2] in table 5.

Table 5. Transferred hyperfine interaction constants for LiTbF$_4$, g/cm$^3$

|           | This work, accuracy $\pm 1$ g/cm$^3$ | Ref. [2], accuracy $\pm 3$ g/cm$^3$ |
|-----------|-------------------------------------|-------------------------------------|
| $M\varepsilon_{xx}(11)$ | -22.38                             | -18.15                             |
| $M\varepsilon_{xy}(11)$ | -4.35                              | 0.11                               |
| $M\varepsilon_{yy}(11)$ | -17.22                             | -19.49                             |
4. Conclusion

In the present work corrected set of the crystal field parameters for the Tb$^{3+}$ ions in LiTbF$_4$ have been obtained from the analysis of the literature data on the crystal field energies and the differential magnetic susceptibilities in high pulsed magnetic fields. We argue that magnetoelastic interactions contribute remarkably into formation of the magnetization in high magnetic fields. The obtained crystal field parameters correlate with the parameters determined earlier for isomorphic rare earth compounds.

Angular dependence of $^{19}$F NMR spectra in the magnetic field perpendicular to the crystal c-axis has been measured and the corrected set of transferred hyperfine interaction constants for LiTbF$_4$ has been determined. Diagonal components of the transferred hyperfine interaction tensor are similar to, but the nondiagonal component is much larger than corresponding parameters obtained earlier in [2]. The constants of the transferred hyperfine interaction and of the magnetic dipole-dipole interaction between the fluorine nuclei and the terbium ions in LiTbF$_4$ have comparable magnitudes (similar conclusions were obtained in the studies of superhyperfine structures of EPR spectra in dilute paramagnets LiYF$_4$:Yb$^{3+}$ [23], LiYF$_4$:Nd$^{3+}$ [24]), but different signs.

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