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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.
Spectral and magnetic properties of impurity Tm$^{3+}$ ions in YF$_3$

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Stark structure of $^3$H$_6$, $^3$H$_5$, $^3$H$_4$, $^3$F$_4$, $^3$F$_3$, $^3$F$_2$ and $^1$G$_4$ multiplets of impurity non-Kramers Tm$^{3+}$ ions in the orthorhombic YF$_3$ crystal has been determined from luminescence studies. High frequency electron paramagnetic resonance (EPR) spectra ($\sim$ 207 GHz) of Tm$^{3+}$ ions have been measured at temperature 4.2 K in external magnetic field applied perpendicular to the $b$-axis of YF$_3$:Tm$^{3+}$ single crystal. The results of measurements are interpreted in the frameworks of the crystal field theory. The set of crystal field parameters related to the crystallographic system of coordinates of the YF$_3$ lattice has been obtained and used to reproduce satisfactory the crystal field energies and the EPR spectra.

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Keywords: crystal field parameters, exchange charge model, EPR, trifluorides

1. Introduction

The yttrium fluoride YF$_3$ crystals doped with heavy rare-earth ions (Sm, …, Tm and Yb) are investigated rather intensively because they may be suitable as potential solid-state laser materials and scintillators. Optical spectra of YF$_3$:R$^{3+}$ and isostructural RF$_3$ (R = Eu, Tb, Dy, Er, Ho and Yb) crystals have been measured in Refs. [1-5]. Moreover, at present the rare-earth trifluorides attract more and more attention due to synthesis and investigation of magnetic and optical properties of the hollow fullerene-like nanoparticles RF$_3$ (R = La, Pr,…) and nanoparticles of different shapes [6-11] which can have widespread potential for practical applications in high resolution displays, electroluminescent devices and markers for biomolecules.

Fluoride TmF$_3$ and thulium doped YF$_3$ fluoride have been the subject of quite a few studies in the past. As a result, scanty information exists on magnetic properties of non-Kramers Tm$^{3+}$ ions with the ground electronic configuration 4f$^{12}$ in both concentrated, TmF$_3$, and dilute, YF$_3$:Tm$^{3+}$, compounds. Results of dc-magnetometry and NMR $^{19}$F studies in TmF$_3$ powder as well as the high frequency electron paramagnetic resonance (EPR) measurements in YF$_3$:Tm$^{3+}$ single crystal [12] gave unambiguous evidence that TmF$_3$ is a Van Vleck paramagnet with the gap $\Delta \sim 6.5$ cm$^{-1}$ between the ground and the nearest excited energy levels of Tm$^{3+}$ ions.

In present article we report the results of systematic studies of crystal field and magnetic properties of Tm$^{3+}$ ions in YF$_3$:Tm$^{3+}$ single crystal. The angular dependence of the high frequency EPR spectrum of Tm$^{3+}$ ions was measured in the collinear constant ($\mathbf{B}_0$) and alternative ($\mathbf{B}_1$) magnetic fields lying in the crystallographic $ac$-plane ($\mathbf{B}_0 \parallel \mathbf{B}_1 \perp \mathbf{b}$). The Stark structure of electronic multiplets of Tm$^{3+}$ ions was defined by means of the laser-selective spectroscopy. Crystal field parameters (CFP) were estimated in the frameworks of the semi-phenomenological exchange charge model [13] and then corrected by making use of our experimental data. The obtained set of CFP allowed us to reproduce satisfactory the high frequency EPR spectra in YF$_3$:Tm$^{3+}$ single crystal.

2. Experimental data

The YF$_3$ : 0.5 at % Tm$^{3+}$ single crystals for optical and EPR studies were grown by the Bridgman method in carbon crucibles in the atmosphere of the high purity argon at a pulling rate of 1 mm/h.
Spectral and magnetic properties of impurity Tm$^{3+}$ ions in YF$_3$

High purity TmF$_3$ and YF$_3$ powders (99.99% grade) were used as starting materials. Additionally, the growth atmosphere was fluorinated by thermal decomposition of the tetra-fluorine-ethylene.

2.1 Site-selective laser spectroscopy

Fluorescence of YF$_3$:Tm$^{3+}$ crystal was excited with either a pulsed tunable dye laser (Littrow type oscillator and amplifier, linewidth of about 1 Å) pumped by the second or third harmonic of a Nd-YAG laser (LQ129, Solar LS) in the visible spectral range or a Ti:Sapphire tunable laser with the linewidth of about 0.4 Å (LX325, Solar LS) pumped by the second harmonic of a Nd-YAG laser (LQ829, Solar LS) in the near-IR range. The spectra were analyzed with an MDR-23 monochromator. The fluorescence signal was detected by a cooled photomultiplier (PMT-106 or PMT-83) in the photon-counting mode. The studied YF$_3$:Tm$^{3+}$ crystal was kept in the helium vapor at a temperature of 4.2 K. In order to investigate fluorescence spectra at temperatures about 2 K liquid helium bath cryostat with the vapor pumping was used.

We studied the fluorescence of the YF$_3$:Tm$^{3+}$ crystal corresponding to the radiative transitions from the metastable states of the Tm$^{3+}$ ions, namely, from the lowest crystal field sublevels of the $^3G_4$ and $^3F_4$ multiplets, to the low-lying multiplets $^3H_6$, $^3H_5$ and $^3H_4$ ($^3G_4 \rightarrow ^3H_6$, $^3G_4 \rightarrow ^3H_5$, $^3G_4 \rightarrow ^3H_4$ and $^3F_4 \rightarrow ^3H_6$). Energies of the crystal field sublevels of the ground ($^3H_6$) and low lying excited ($^3H_5$ and $^3H_4$) multiplets were determined from the selectively excited luminescence spectra (see luminescence spectra for $^3G_4 \rightarrow ^3H_6$ and $^3F_4 \rightarrow ^3H_6$ in Fig. 1a).

Energies of crystal field sublevels of the $^3F_4$, $^3F_3$, $^3F_2$ and $^1G_4$ multiplets were determined from the excitation spectra of Tm$^{3+}$ ions in YF$_3$ host. The first excited sublevel of the ground multiplet $^3H_6$ (see Table 1) is separated from the ground sublevel by the energy of 6.5 cm$^{-1}$. At temperature $T = 4.2$ K both sublevels are populated. Hence, excitation spectra arise due to transitions from the both lowest

![Figure 1](image)
sublevels of the $^3\text{H}_6$ multiplet to sublevels of the $^3\text{F}_4$, $^3\text{F}_3$, $^3\text{F}_2$ and $^1\text{G}_4$ multiplets. As a result, spectral lines registered at $T = 4.2$ K are split by the energy $6.5 \text{ cm}^{-1}$ (see the transition $^3\text{H}_6 \rightarrow ^1\text{G}_4$ in Fig. 1b). In order to determine the crystal field energies of the $^1\text{G}_4$ and $^3\text{F}_2$ multiplets, the excitation spectra of Tm$^{3+}$ ions corresponding to the transitions from the ground state into the $^1\text{G}_4$ and $^3\text{F}_2$ multiplets at lower temperature $T = 2.3$ K were measured (see inset in Fig. 1b). Crystal field energies for $^3\text{H}_6$, $^3\text{H}_5$, $^3\text{H}_4$, $^3\text{F}_4$, $^3\text{F}_3$, $^3\text{F}_2$ and $^1\text{G}_4$ multiplets of Tm$^{3+}$ ions obtained from the analysis of the experimental data are presented in Tab. 1.

**Table 1. Crystal field energies (cm$^{-1}$) of the Tm$^{3+}$ ions in YF$_3$ host.**

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2.2 High frequency EPR in YF₃:Tm³⁺

The EPR spectra of Tm³⁺ ions in oriented YF₃:Tm³⁺ (0.5% Tm) single crystal were taken with high-frequency tunable EPR spectrometer [14] at frequency of 207 GHz in magnetic fields from 0 to 900 mT at temperature 4.2 K. The microwave magnetic field $B_1$ was applied parallel to static magnetic field $B_0$, i.e. $B_1 \parallel B_0$. The hyperfine structure of the EPR spectra consisting of two resonant lines was observed (Fig. 2a). This observation gives evidence for resonance transitions induced by the microwave field in Tm³⁺ ions ($^{169}$Tm, $I = 1/2$, natural abundance 100%).

High-frequency EPR spectra measured in the YF₃:Tm³⁺ single crystal allowed us to determine the energy gap of 6.5 cm⁻¹ between the two lowest crystal field singlets. The magnetic moments corresponding to this quasi-doublet are determined by the $g$-factor $\sim 13.5$ and lie in the $ac$-plane along the directions declined by the angle $\sim \pm 23°$ from the crystallographic $c$-axis [12]. The angular dependence of the EPR spectrum was measured by rotation of a sample around the crystallographic $b$-axis so that the external magnetic field was applied in the $ac$-plane of the YF₃ crystal lattice, the angular step in the $ac$-plane was 5°. Two magnetically non-equivalent sites of Tm³⁺ ions were found. EPR spectra in the magnetic fields lying in the $ab$-plane were not observed because the resonant field was out of the magnetic field range for our magnet. Some of EPR lines are distorted, split, and have weak satellites. Probable reasons for these effects were discussed in Ref. [12].

![Figure 2. The high frequency EPR (207 GHz) of Tm³⁺ ions measured in YF₃:Tm³⁺ single crystal: (a) a sample spectrum of the Tm³⁺ EPR, measured at $B_0^a = 48°$; (b) the angular dependence measured in external magnetic field applied in the $ac$-plane of YF₃ crystal structure. Open circles and solid lines represent the experimental data and the calculated resonant magnetic fields, respectively.](image)

3. Discussion

The single crystals YF₃:Tm³⁺ studied in this work have an orthorhombic structure with the space group $Pnma$ ($D_{2h}^6$) [15]. The lattice constants are $a = 0.63537(7)$ nm, $b = 0.68545(7)$ nm, $c = 0.43953(5)$ nm [16]. The unit cell contains four formula units. The coordinates of fluorine F1 ions in 4c positions and F2 ions in 8d positions are determined by parameters $u_1$, $u_2$, $s_2$, $v_1$, $v_2$ and equal $\pm (u_1, 1/4, v_1)$, $\pm (u_1 - 1/2, 1/4, 1/2 - v_1)$ for F1, $\pm (u_2, s_2, v_2)$, $\pm (u_2, 1/2 - s_2, v_2)$, $\pm (u_2 - 1/2, s_2, 1/2 - v_2)$, $\pm (u_2 - 1/2, 1/2 - s_2, 1/2 - v_2)$ for F2; the yttrium ions in 4c positions with the point symmetry $C_i$ have the coordinates $\pm (u, 1/4, v)$, $\pm (u - 1/2, 1/4, 1/2 - v)$. The fractional parameters $u_1$, $v_1$, $u_2$, $s_2$, $v_2$, $u$, $v$ (in units of the lattice constants) in YF₃ [16] that is used as a host matrix for Tm³⁺ ions are represented in Tab. 2.

To describe the results of EPR and optical measurements, we consider the effective Hamiltonian of a single Tm³⁺ ion in the $j$-sublattice, operating in the total basis of 182 electron-nuclear states of the electronic 4f¹² configuration, in the external magnetic field $B_0$.
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\[ H_j = H_0 + H_{CF,j} + H_{HF} + H_{Z,j}. \] (1)

Here \( H_0 \) is the free ion Hamiltonian defined by Slater parameters \( F^2 = 102586 \text{ cm}^{-1}, F^4 = 72072 \text{ cm}^{-1}, \) \( F^6 = 51572 \text{ cm}^{-1}; \) two-particle parameters of the configuration interaction, parameters of correlated spin-orbit and spin-spin interactions were taken from Ref. [17]. The term \( H_{HF} \) is the energy of the magnetic hyperfine interaction:

\[ \begin{align*}
H_{HF} &= A \sum_n \left[ l^I \left| \mathbf{I} \right| + \sqrt{3}/2 \left( 2C_{0,n}^{(2)} (3s_{n,z} I_z - s_{n,x} I_y) \right) / \sqrt{6} + \\
&\quad \left( C_{2,n}^{(2)} + C_{2,n}^{(2)} \right) \left( s_{n,x} I_x - s_{n,y} I_y \right) - i \left( C_{2,n}^{(2)} - C_{2,n}^{(2)} \right) \left( s_{n,x} I_y + s_{n,y} I_x \right) - \\
&\quad - \left( C_{1,n}^{(2)} - C_{1,n}^{(2)} \right) \left( s_{n,x} I_x + s_{n,y} I_y \right) + i \left( C_{1,n}^{(2)} + C_{1,n}^{(2)} \right) \left( s_{n,x} I_y + s_{n,y} I_x \right) \right].
\end{align*} \] (2)

Here \( A = 2\mu_B \gamma_{Tm} \hbar \left( r^{-1} \right) / \mu_0 \) is the hyperfine coupling constant, where \( \mu_B \) is the Bohr magneton, \( \gamma_{Tm}/2\pi = 3.52 \text{ MHz/T} \) is the gyromagnetic ratio for \(^{169}\text{Tm} \) nuclei, \( l_n \) and \( s_n \) are the orbital and spin moments, respectively, of 4f-electrons; \( C_{n}^{(i,j)} \) are the electronic spherical tensor operators and \( I \) is the nuclear spin moment. The average value of \( 1/r^3 \) for 4f-electrons defines the effective hyperfine constant that is taken as \( A = -0.016 \text{ cm}^{-1}. \) The sum is taken over all 4f-electrons.

The electronic Zeeman energy is \( H_{Z,j} = -\mu B_{0,j} \), where \( \mu = -\mu_0 \sum_n \left( l_n + 2s_n \right) \) is the electronic magnetic moment of the \( \text{Tm}^{3+} \) ion. The \( \text{Tm}^{3+} \) ions in the sublattices \( j = 1 \) and 2, 3 and 4 are magnetically equivalent in pairs.

The crystal field Hamiltonian

\[ H_{CF,j} = \sum_{k=2,4,6} \sum_n B_k^i (j) \sum_n O_{n,k}^i, \] (3)

in the Cartesian system of coordinates defined so that \( x \parallel c, y \parallel b \) and \( z \parallel a \), is determined by a single set of 15 crystal field parameters (CFP) \( B_k^i (1) \) \( (B_k^i (1) = B_k^i (2) = (-1)^i B_k^i (3) = (-1)^i B_k^i (4)), \) \( O_{n,k}^i \) are linear combinations of spherical tensors defined in Ref. [18].

Initial values of CFP for the \( \text{Tm}^{3+} \) ions in YF\(_3\) (column "Calculated" in Tab. 3) were calculated in the framework of the exchange charge model [13] by making use of the corresponding lattice structure constants and atomic coordinates presented above in Tab. 2:

\[ B_k^i = \sum_L e^i \left[ -Z_L (1 - \sigma_x) (r_L^k) + \frac{2(k+1)}{7} R_L^i s_L (R_L^k) (-1)^i C_{-k}^{(i)} (\theta_L, \varphi_L) / R_L^{k+1} \right]. \] (4)

In the expression (4), the sum is taken over lattice ions \( L \) with charges \( eZ_L \) and spherical coordinates \( (R_L, \theta_L, \varphi_L) \) relative to the rare earth ion at the origin, \( \sigma_k \) are the shielding constants, \( \langle r_L^k \rangle \) are the moments of the 4f-electron charge density, the exchange charges are defined by the overlap integrals between the wave functions of the rare earth ions \( 4f, l_z \) and ligand ions \( l, l_i \) (we take into account only the outer closed 2s\(^2\) and 2p\(^6\) electronic shells of F\(^-\) ions) [13]:

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<th>Y</th>
<th>F1</th>
<th>F2</th>
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<td>( v )</td>
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<tr>
<td>0.3673(4)</td>
<td>0.0591(5)</td>
<td>0.5227(5)</td>
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</table>

**Table 2.** Fractional atomic coordinates of the ions in \( Pnma \) structure of YF\(_3\) [16].
Spectral and magnetic properties of impurity Tm$^{3+}$ ions in YF$_3$

\[ S_\lambda(R_L) = G_{\sigma}^a S_\sigma^a(R_L) + G_{\pi}^a S_\pi^a(R_L) + \gamma \lambda G_{\sigma}^a S_\sigma^a(R_L) , \]

where \( S_\lambda = \langle 4f^0 | 2s^0 \rangle \), \( S_\sigma = \langle 4f^0 | 2p^0 \rangle \), \( S_\pi = \langle 4f^1 | 2p^1 \rangle \), and \( \gamma = -\gamma_\sigma = 3/2, \gamma_\pi = 1/3 \).

Calculations were carried out with \( \sigma_0 = 0.545, \sigma_1 = 0.088, \sigma_6 = -0.043 \) [19], \( \langle r^2 \rangle = 0.646, \langle r^4 \rangle = 1.076, \langle r^6 \rangle = 3.647 \) (atomic units) [20], the dependences of the overlap integrals on the distance \( R \) (in Angstroms) between the ions were approximated by functions \( S_0 \exp(-bR^d) \) with the parameters \( S_0 = 0.33789, 0.19678, 2.93065; b = 1.52924, 1.48051, 0.8624; d = 1.05503, 0.81048, 2.93065 \) for \( s, \sigma \) and \( \pi \) bonds, respectively [21]. The values of the model parameters were assigned as \( G_\sigma = G_\pi = G_\sigma = 11.5 \). Hereafter, the calculated values of CFP (see column "Calculated" in Tab. 3) were corrected to fit the measured electronic energies of Tm$^{3+}$ ions in YF$_3$. The final set of the CFP is represented in Tab. 3 (column "Adjusted").

The calculated crystal field energies of the \( ^3\!H_6, ^3\!H_5, ^3\!H_4, ^3\!F_4, ^3\!F_3, ^3\!F_2, ^1\!G_4 \) multiplets of Tm$^{3+}$ ion in YF$_3$ host are compared with the experimental data in Tab. 1. The total splittings of the excited multiplets and energies of the most sublevels are well reproduced by calculations (see Tab. 1, column "Calculation"). The standard deviation of the calculated values of crystal field energies from those experimentally defined is STD ~ 14 cm$^{-1}$.

The obtained set of CFP allowed us to reproduce satisfactory the angular dependence of the Tm$^{3+}$ EPR spectrum (Fig. 2b). The calculated principal value of the \( g \)-factor for the lowest quasi-doublet equals \( g = 13.59 \), the corresponding principal direction lies in the \( ac \)-plane and has the angle \( \varphi \) of \( \pm 22.0^\circ \) with the \( c \)-axis of YF$_3$ crystal. These calculated values are close to experimental data, \( g = 13.5 \) and \( \varphi = \pm 23.0^\circ \).

### Table 3. The crystal field parameters (in cm$^{-1}$) of the Tm$^{3+}$ ions in YF$_3$ crystal lattice.

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<thead>
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<th>( B_{\lambda} )</th>
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</table>

### 4. Conclusion

The crystal field energies of the impurity Tm$^{3+}$ ions in orthorhombic crystal YF$_3$ have been determined for \( ^3\!H_6, ^3\!H_5, ^3\!H_4, ^3\!F_4, ^3\!F_3, ^3\!F_2, ^1\!G_4 \) multiplets from the optical absorption and luminescence studies. The initial set of crystal field parameters for the Tm$^{3+}$ ions in the YF$_3$ host has been calculated in the framework of the semi-phenomenological exchange charge model and then varied to fit the experimental data. The obtained set of CFPs allowed us to reproduce well the electronic energies and the angular dependence of EPR spectra measured in YF$_3$:Tm$^{3+}$ single crystal in external magnetic fields applied in the \( ac \)-plane. The calculated value and the direction of the magnetic moment of the Tm$^{3+}$ ion in the ground quasi-doublet state agree well with the results of EPR measurements.

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### References