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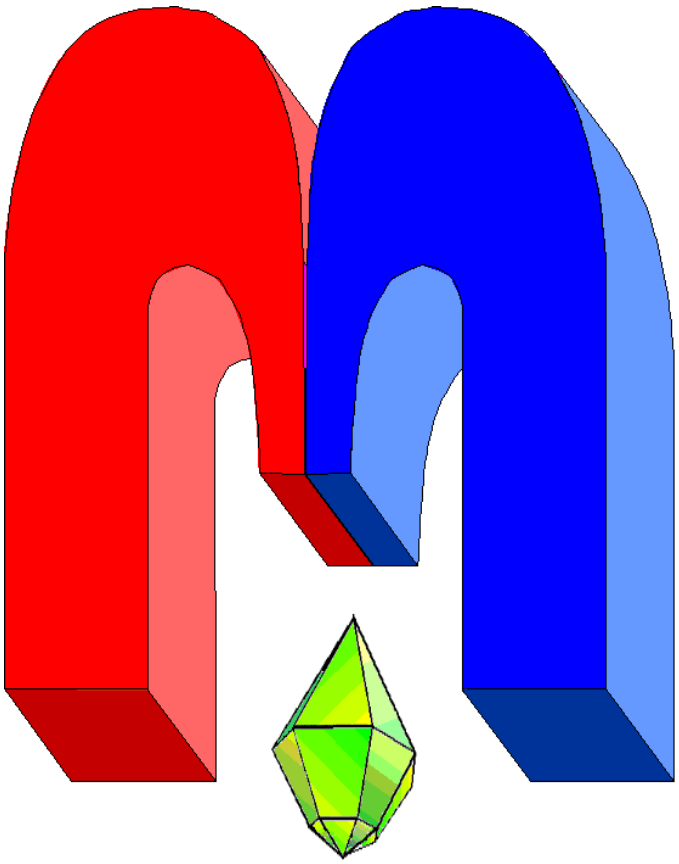

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Study of the crystal field and rare-earth magnetism in $YF_3:Yb^{3+}$

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The electron paramagnetic resonance spectra (X-band, $f \sim 9.42$ GHz) of Yb^{3+} ions have been measured at temperature 15 K in $YF_3:Yb^{3+}$ single crystals. The principal values of the *g*-tensors, $g_b = g_1 = 1.67$, $g_2 = 2.42$, $g_3 = 5.41$, and directions $\mathbf{n}_1 = [0, 1, 0]$, $\mathbf{n}_2 = [\pm\sin(54.8^\circ), 0, \cos(54.8^\circ)]$, $\mathbf{n}_3 = [\mp\sin(35.2^\circ), 0, \cos(35.2^\circ)]$ of the corresponding principal axes for the Yb^{3+} ions which replace Y^{3+} ions at two magnetically nonequivalent sites with the local C_s symmetry in the orthorhombic crystal lattice have been obtained from analysis of the angular dependences of the spectra taken in the static magnetic fields lying in the crystallographic (*bc*) and (*ac*) planes. Experimental data are interpreted in the frameworks of the crystal field theory. Using the obtained set of crystal field parameters for Yb^{3+} ions in the YF_3 host related to the crystallographic system of coordinates, we can reproduce satisfactorily the crystal field energies of Yb^{3+} ions determined earlier from optical measurements.

PACS: 71.70.Ch, 71.70.Ej.

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

1. Introduction

The rare-earth trifluorides RF_3 and rare-earth doped $YF_3:Re^{3+}$ (R is rare-earth ion) yttrium trifluoride have been studied in the past as a model system for testing theories of rare-earth magnetism in insulators (see, for example, Ref. [1-5]) and because of their numerous applications as promising host materials for solid laser and scintillator technology. In recent years interest in the study of rare-earth trifluorides has returned thanks to advances in the fabrication of nanoparticles of pure rare-earth fluorides RF_3 and rare-earth ions doped nanoparticles as well [6-10]. The great interest appeared due to potential applications of the nanosized materials in high resolution displaying, electroluminescent devices and markers for biomolecules.

In present study we report the results of systematic studies of crystal field and low temperature magnetic properties of Yb^{3+} ion in diluted $YF_3:Yb^{3+}$ single crystals. Angular dependences of the electron paramagnetic resonance (EPR) spectrum of Yb^{3+} ion in YF_3 host have been measured in $YF_3:Yb^{3+}$ single crystals which were rotated around the crystallographic *a*- and *b*-axes so that the static magnetic field was applied as $\mathbf{B} \perp \mathbf{a}$, and $\mathbf{B} \perp \mathbf{b}$ respectively. Measured angular dependences of EPR spectrum and known from the literature spectrum of electronic energies of Yb^{3+} ion in YF_3 host [11] have been analyzed in the framework of the crystal field theory. The set of crystal field parameters has been calculated using the semi-phenomenological exchange charge model [12] and then corrected by comparing results of calculations with the experimental data. Obtained set of the crystal field parameters reproduces satisfactorily the angular dependences of Yb^{3+} EPR spectrum, components of *g*-tensor and Stark energies of Yb^{3+} ion in YF_3 host.

2. Experimental details

Two $YF_3:Yb^{3+}$ (0.5%) single crystals were grown from commercial powders of YF_3 (99.99%) and YbF_3 (99.99%) in carbon crucibles in high vacuum (less than 10^{-4} mbar) by temperature gradient technique. All $YF_3:Yb^{3+}$ samples were oriented using the X-ray diffraction pattern with the accuracy of ±3°. The samples were oriented so that angular dependences of EPR spectra were measured in the static magnetic field directed as $\mathbf{B} \perp \mathbf{a}$ and $\mathbf{B} \perp \mathbf{b}$, i.e. perpendicular to the crystallographic axes *a* and *b* of orthorhombic crystal structure of the YF_3.

The EPR spectra of YF_3:Yb^{3+} single crystals were measured with the X-band (~9.42 GHz) Bruker ESP300 spectrometer. The standard ER4102ST rectangular cavity with the TE_{102} mode was used. The studies were performed at 15 K, and the sample temperature was controlled using an Oxford Instruments ESR9 liquid helium flow system.

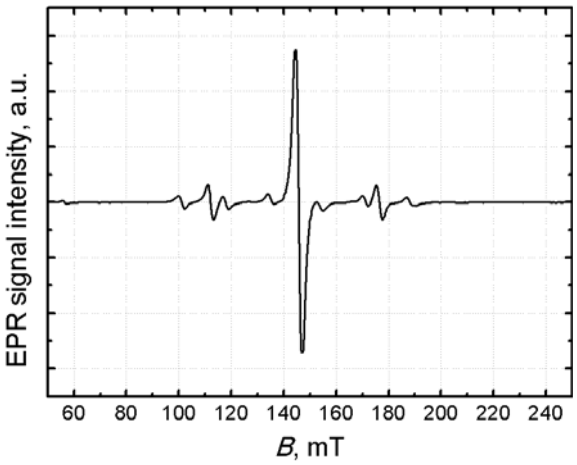

Figure 1. The EPR spectrum in YF_3:Yb^{3+} at the temperature 15 K in the magnetic field $\mathbf{B} \parallel \mathbf{c}$.

In the magnetic field directed along the *c*-axis, the EPR spectrum contains a group of lines (Figure 1) corresponding to Yb^{3+} ions with typical hyperfine structure of three stable isotopes ^{169}Yb, ^{171}Yb and ^{173}Yb. The *g*-factor in this direction is $g_c = 4.635$. Each magnetically nonequivalent Yb^{3+} center in the YF_3 crystal cell gives a resonant line in EPR spectrum due to transitions between sublevels of the ground state doublet of $^2F_{7/2}$ multiplet. Transitions between higher-lying energy levels aren't observed because the distance to the excited levels is too large in comparison with the quantum of the X-band EPR. Also, the excited levels are not populated at $T = 15$ K.

Angular dependences of Yb^{3+} EPR spectra, measured in YF_3:Yb^{3+} single crystals for the magnetic field oriented in the (*bc*) and (*ac*) plane are represented in Figure 2(a) and (b) respectively. The principal values of *g*-tensor $g_1 = 1.67(1)$, $g_2 = 2.42(1)$, $g_3 = 5.41(1)$ and *g*-factors along the crystallographic axes $g_a = 3.68(1)$, $g_b = g_1 = 1.67(1)$, $g_c = 4.63(1)$ have been obtained from the analysis of the angular dependences. Obtained in our experiment the principal values of the *g*-tensor are in a good agreement with the values obtained in Ref. [13]. The principal components g_2 and g_3 are in the crystallographic (*ac*) plane and the principal direction corresponding to g_2 has an angle of 54.8° with the *c*-axis; the principal direction of g_1 coincides with the *b*-axis of YF_3:Yb^{3+} crystal lattice.

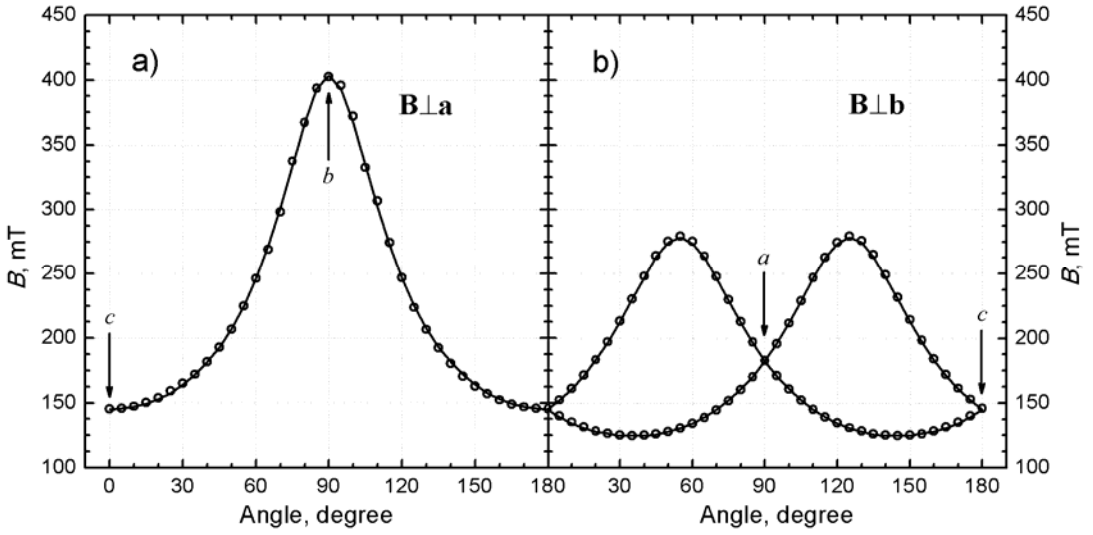

Figure 2. Angular dependences of Yb^{3+} EPR spectra, measured (open circles) in YF_3:Yb^{3+} single crystals for the magnetic field oriented in the a) *bc*- and b) *ac*-plane of YF_3 crystal structure. Calculated angular dependences are shown by solid lines.

3. Discussion

The YF_3:Yb^{3+} samples have an orthorhombic structure with the space group *Pnma* (D_{2h}^{16}) [14]. The parameters of the YF_3 crystal cell are $a = 0.63537(7)$ nm, $b = 0.68545(7)$ nm, $c = 0.43953(5)$ nm [15]. The unit cell contains four formula units. The coordinates of fluorine F1 ions in 4c positions and F2

Table 1. Atomic coordinates of the ions in *Pnma* structure of YF_3 [15].

Y		F1		F2		
u	v	u_1	v_1	u_2	s_2	v_2
0.3673(4)	0.0591(5)	0.5227(5)	0.5910(8)	0.1652(4)	0.0643(3)	0.3755(5)

fluorine 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 rare-earth ions in 4c positions with the point symmetry C_S have the coordinates $\pm(u, 1/4, v)$, $\pm(u-1/2, 1/4, 1/2-v)$. The parameters u_1, v_1, u_2, s_2, v_2, u, v are represented in Table 1 in units of the YF_3 lattice constants [15].

To describe the results of EPR measurements and the electronic energies of Yb^{3+} ion in YF_3 host, we consider the effective Hamiltonian of a single Yb^{3+} ion, operating in the total basis of 14 wave functions of the electronic $4f^{13}$ configuration, in the external magnetic field **B**:

$$H_j = H_0 + H_{\mathrm{CF},j} - H_{\mathrm{Z},j}\,, \tag{1}$$

here H_0 is the free ion Hamiltonian which includes only the spin-orbit interaction for Yb^{3+} ion with parameter $\xi = 2912$ cm^{-1}. The electronic Zeeman energy is $H_{\mathrm{Z},j} = -\boldsymbol{\mu}\mathbf{B}_j$, where $\boldsymbol{\mu} = -\mu_{\mathrm{B}}\sum_n(\mathbf{l}_n + 2\mathbf{s}_n)$ is the electronic magnetic moment of the Yb^{3+} ion. The Yb^{3+} ions in the sublattices j = 1, 2, 3 and 4 are magnetically equivalent in pairs. The crystal field Hamiltonian

$$H_{\mathrm{CF},j} = \sum_{k=2,4,6}\sum_{q=0:k} B_q^k(j)\langle l\,\|\,\alpha_k\,\|\,l\rangle\cdot O_k^q \tag{2}$$

is determined by a single set of 15 crystal field parameters $B_q^k(1)$ (in the Cartesian system of coordinates defined so that $x \| c$, $y \| b$ and $z \| a$), O_k^q are Stevens' equivalent operators, reduced matrix elements $\langle l\,\|\,\alpha_k\,\|\,l\rangle$ are Stevens' coefficients.

At the first approximation the parameters of the electrostatic interaction of open Yb^{3+} electronic 4f-shell with the ion charges in the YF_3:Yb^{3+} crystal lattice can be evaluated corresponding to the point charge model:

$$B_q^{(\mathrm{pc})k} = -\sum_L \frac{e^2 q_L(1-\sigma_k^{nl})\langle r^k\rangle(-1)^q C_{-q}^{(k)}(\theta_L,\varphi_L)}{R_L^{k+1}}, \tag{3}$$

where eq_L is the charge of the ligand, L; θ_L and φ_L are angles in a spherical coordinate system with the origin at the nucleus of the rare-earth ion; R_L is the distance from the rare-earth ion to the ligand L. The values of the moments of the spatial density of the Yb^{3+} 4f-electrons are $\langle r^2\rangle = 0.613$, $\langle r^4\rangle = 0.960$, $\langle r^6\rangle = 3.104$ a.u. [16]; σ_k^{nl} are the shielding factors with values $\sigma_2 = 0.588$, $\sigma_4 = \sigma_6 = 0$ taken for Yb^{3+} ion.

In order to correct the electrostatic interaction for the spatial distribution of the ligand charges, we used the semi phenomenological exchange charge model [12]:

$$B_q^{(\mathrm{ec})k} = \sum_L \frac{2(2k+1)}{2l+1}\cdot\frac{e^2}{R_L}\cdot S_k^{nl}(R_L)(-1)^q C_{-q}^{(k)}(\theta_L,\varphi_L)\,, \tag{4}$$

where S_k^{nl} represents the bilinear forms of overlap integrals for the wave functions of the Yb^{3+} 4f-electrons, and the wave functions of the 2s, 2p-electrons of the ligand ions (F^-):

$$S_k^{nl}(R_L) = G_s\left|S_s^{nl}\right|^2 + G_\sigma\left|S_\sigma^{nl}\right|^2 + G_\pi\gamma_k\left|S_\pi^{nl}\right|^2 \tag{5}$$

Here $S_S^{nl} = \langle nl0\,|\,200\rangle$, $S_\sigma^{nl} = \langle nl0\,|\,210\rangle$, $S_\pi^{nl} = \langle nl1\,|\,211\rangle$ ($n = 4$, $l = 3$ are quantum numbers for

4f-electrons), the coefficients $\gamma_2 = 3/2$, $\gamma_4 = 1/3$, $\gamma_6 = -3/2$ for 4f-electrons. Parameters of the model G_s, G_σ and G_π, were taken for Yb^{3+} ions with values $G_s = G_\sigma = G_\pi = 15.0$.

Thus, the crystal field parameters for Yb^{3+} ions in YF_3 crystal lattice were calculated as a sum:

$$B_q^k = B_q^{(\mathrm{pc})k} + B_q^{(\mathrm{ec})k} \tag{6}$$

Calculated values of the crystal field parameters are shown in Table 2 (column "Calculated"). Final sets of crystal field parameters (see column "Adjusted" in Table 2) was obtained by varying the calculated values of B_q^k to minimize the squared deviation of the theoretically obtained values of *g*-factor (Table 3) from defined in our EPR experiment; squared deviation of calculated values of the energy sublevels of Yb^{3+} ions in YF_3 host from the appropriate measured values [11] (totally four known energies, see Table 4) were also minimized. The errors in the adjusted crystal field parameters (see values given in brackets, column "Adjusted" in Table 2) corresponds to such changes of each B_q^k that give rise to deviation of the minimization result no more than 5% of the best minimized value.

Table 2. The crystal field parameters (in cm^{-1}) of the Yb^{3+} ions in YF_3 crystal lattice.

B_q^k	Calculated	Adjusted
B_0^2	94.7	114.9(1)
B_1^2	749	667.1(1)
B_2^2	–236	–329.8(1)
B_0^4	–1.7	–23.1(1)
B_1^4	–670	–381.8(2)
B_2^4	–12.2	–19.8(1)
B_3^4	275	154.5(4)
B_4^4	90.5	53.7(2)
B_0^6	–0.86	–9.48(4)
B_1^6	–290	–287.5(3)
B_2^6	–284	–171.0(2)
B_3^6	–41.8	–22.2(9)
B_4^6	–73.1	–50.7(3)
B_5^6	–862	–705.1(8)
B_6^6	248	233.3(9)

Table 3. Values of g-factor of Yb^{3+} ion in YF_3 crystal lattice.

g-factor	Measured	Calculated
g_1	1.67(1)	1.670
g_2	2.42(1)	2.423
g_3	5.41(1)	5.409
g_a	3.68(1)	3.690
g_b	1.67(1)	1.670
g_c	4.63(1)	4.638

Table 4. Crystal field energies (in cm^{-1}) of Yb^{3+} ions in YF_3.

Multiplet, $^{2S+1}L_J$	Measured [11]	Calculated
$^2F_{7/2}$	0	0
	116	116
	-	290
	-	390
$^2F_{5/2}$	10230	10231
	10367	10385
	10587	10566

4. Conclusion

The angular dependences of the EPR spectrum of Yb^{3+} ion in YF_3 host have been measured in YF_3:Yb^{3+} single crystals which were rotated around the crystallographic *a*- and *b*-axes so that the static magnetic field was applied respectively in (*bc*) and (*ac*) plane of YF_3:Yb^{3+} crystal structure. The set of crystal field parameters has been calculated using the semi-phenomenological exchange charge model and then corrected by comparing the results of calculations with the experimental data. Using obtained set of the crystal field parameters the angular dependences of Yb^{3+} EPR spectra and values of *g*-factors have been calculated and found in a good agreement with ones measured experimentally. Stark energies of Yb^{3+} ion in YF_3 host have been also reproduced satisfactorily.

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